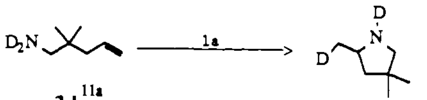
The anaerobic[1a,b] catalytic reaction of $(Cp'_2LaH)_2$ (**1a**)[1b] with a variety of dry, degassed amino olefins (typically in 100–20-fold stoichiometric excess) proceeds to completion in hydrocarbon solvents (toluene, cyclohexane, pentane) as shown in Table I. Reactions are conveniently monitored by NMR spectroscopy, and products are identified by comparison with literature spectral data[9] and/or with those of authentic samples. Several features of this hydroamination reaction are especially noteworthy. These include the formation of a six-membered heterocycle (**5** → **10**), the cyclization of internal amines (**4** → **9**, **6** → **11**), and the rapidity of the *gem*-dimethyl transformation (**3** → **8**). The latter observation strongly suggests that ring formation is turnover-limiting.[10] The present reactions are found to be ≥99% regiospecific by NMR spectroscopy, with the exception of **6** → **11**, where ca. 10% of the product is another species, the identity of which is currently under investigation.

Preliminary mechanistic observations, in addition to the aforementioned *gem*-dimethyl effect, are in accord with the scenario of Scheme I where olefin insertion/cyclization (i, eq 1) is, under all conditions so far investigated, turnover-limiting. Kinetically, we find the hydroaminations in Table I entries 1, 2, and 4 to be first-order in organolanthanide and zero-order in amino olefin within experimental error. That is, the turnover frequency (equiv of olefin transformed/equiv of Ln/time) is independent of olefin concentration over the entire course of the reaction and independent of organolanthanide concentration over a 5-fold range. These observations argue that protonolysis (ii, eq 2) is the rapid step (as expected[4a]). Also in accord with this picture is the relative ordering of catalyst activities for **3** → **8**: $(Cp'_2LaH)_2$ (**1a**) > $[Me_2Si(Me_4C_5)_2LuH]_2$ (**1b**) > $(Cp'_2LuH)_2$ (**1c**) (Table I)—identical with the previously reported ordering for catalytic propylene oligomerization activity.[1b,c] The outcome of the isotopic labeling experiment **3-*d*$_2$**[11a] → **8-*d*$_2$**[11b] (eq 3) further supports the proposed mechanism, revealing the atom transposition pattern expected for Scheme I. The observation that hydroamination/cyclization rates are depressed when THF is the solvent[12] also supports a turnover-limiting k_i process. Such effects are common in Cp'_2Ln-centered olefin transformations[1] and reflect Lewis base competition for the empty coordination site within the Cp'_2LnX coordination sphere, which is a prerequisite for the insertion process.



(3)

3d$_2$[11a]

8d$_2$[11b]

These results demonstrate that organolanthanide centers can facilitate unusual types of olefin insertion processes and that such transformations can be readily incorporated into efficient and novel catalytic cycles. The scope of such chemistry is presently under investigation.

Acknowledgment. We are grateful to NSF for support of this research under Grant CHE8800813. M.R.G. thanks Rhône-Poulenc Corp. for a graduate fellowship. We thank W. R. Grace for gifts of dessicants.

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(8) Solid acids are reported to catalyze the heterogeneous amination of several simple olefins at high temperatures and pressures: (a) Deeba, M.; Ford, M. E. *J. Org. Chem.* **1988**, *53*, 4594–4596. (b) Deeba, M.; Ford, M. E.; Johnson, T. A. *J. Chem. Soc., Chem. Commun.* **1987**, 562–563.

(9) (a) Ambuehl, J.; Pregosin, P. S.; Venanzi, L. M.; Consiglio, C.; Bachech, B.; Zambonelli, L. *J. Organomet. Chem.* **1979**, *181*, 255–269. (b) Ambuehl, J.; Pregosin, P. S.; Vananzi, L. M.; Ughetto, G.; Zambonelli, L. *J. Organomet. Chem.* **1978**, *160*, 329–335.

(10) Kirby, A. J. *Adv. Phys. Org. Chem.* **1980**, *17*, 183–278.

(11) (a) Prepared by exchange of **3** with D_2O. (b) Identified by IR, ^1H, and ^{13}C NMR spectroscopy.

(12) For example, N_t = 17 h^{-1} for **3** → **8** in THF-d_8 at 25 °C using **1a** as the catalyst.

(13) (a) Confirmed with spectroscopic data from an authentic sample. (b) In entry 3, compound **9**[13c] is obtained as a 5:1 trans:cis mixture (8:1 at 0 °C). (c) Harding, K. E.; Burks, S. R. *J. Org. Chem.* **1981**, *46*, 3920–3922.

(14) Prepared by the $BF_3 \cdot Et_2O$-catalyzed rearrangement of *N*-allylaniline (We thank Prof. A. G. M. Barrett for suggesting this procedure).

Interactions between Eight Centers Are Required for Chiral Recognition

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A recent analysis of the interactions of chiral molecules[1] concluded that six-center forces ("chirality forces"[1]) suffice for chiral recognition. We demonstrate[2] that chiral recognition requires at least eight centers.

Salem et al. analyzed the interaction energies of homochiral (*RR'*) and heterochiral (*RS'*) complexes (between tetrahedra having different centers on their vertices) as a sum of *n*-center terms (*n* = 2–8) between these centers; for example, four-center forces involve a pair of points on each monomer. The analysis is performed "in the limit of free relative molecular rotation (high-temperature limit, interactions small relative to kT)".[1] They claim, after rotational sampling of all possible interactions, "six-center forces, occurring simultaneously between triplets of atoms, one triplet on each molecule, are responsible for the discrimination".[1] They state "this is the first phenomenon where six-center forces are found to play an important role",[1] and "chiral discrimination depends on six-center forces alone and is purely a 'face-to-face' phenomenon for the two tetrahedra".[1]

By simply considering that the terms in their analysis correspond to interactions of points, lines, planes, and solids, it follows that, just as with four-centers, six-center interactions must cancel as well. Only eight-center (or higher-order) terms represent interactions between solids and do not cancel. As chirality requires three dimensions, "chirality forces" cannot be represented by the interactions of zero-, one-, or two-dimensional objects.

Figure 1 illustrates such common six-center interactions by conversion of an *RR'* complex (top row) to an *RS'* complex by the interchange of C' and D' of *R'* to give *S'* (center) followed by a 180° rotation of *S'* about the line connecting A' with the midpoint of C'D' (i.e., "flip" the A'C'D' face; bottom), causing the three centers A'C'D' of *S'* and *R'* to coincide. Thus, the corresponding six-center forces will be equal. This was not evident in Salem's analysis where interaction energies of the *RR'* and *RS'* complexes were compared only for rotations which used the same distance (OO') between central atoms (see Tables I and II of ref 1).[3] There, the orientation of S' in the lower portion of Figure 1 corresponds to a different distance between the central atoms. In the high-temperature limit considered by Salem et al., both translations and rotations must be considered.[4] Also, for any arbitrary structure, an analogous analysis can be made with every pair of triplets of centers on *R* and *R'* or *S'*. Because a term-(six-center on *RR'*)by-term (six-center of *RS'*) equivalence can be generated for any arbitrary structure, it follows immediately that sampling all configurations will result in a complete cancellation of terms.

While Salem et al. suggest that the six-center forces model bears "some analogy with the three-center attachment theory of Ogston"[1,5] (or, more generally, the three-contact-point[6] model), the Ogston or three-contact-point model is based on eight-center interactions. Consider the example in Figure 2. While the six-center interactions of ABC with A'B'C' are identical for the *RS'*

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(1) Salem, L.; Chapuisat, X.; Segal, G.; Hiberty, P. C.; Minot, C.; Leforestier, C.; Sautet, P. *J. Am. Chem. Soc.* **1987**, *109*, 2887.

(2) A quantitative demonstration is available as Supplementary Material.

(3) Thus, within the framework of fixed relative origins, six-center forces are discriminatory but, as real molecules do not have fixed origins, eight-center forces are responsible for chiral recognition.

(4) Alternatively, using arguments analogous to those of Salem et al., one could limit the angular sampling space (due to some physically justified constraints) and conclude that two- or four-center forces lead to chiral discrimination.

(5) Ogston, A. G. *Nature* **1948**, *162*, 963.

(6) Topiol, S. *Chirality* **1989**, *1*, 69.

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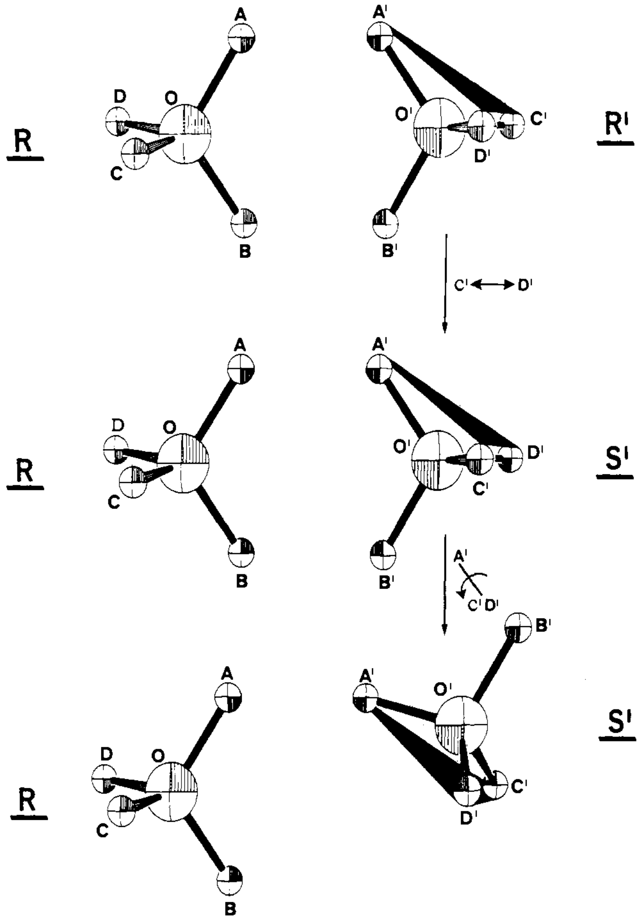

Figure 1. Transformation of *RR′* into *RS′* to show the equal interactions of *R* with the A′C′D′ faces of *R′* and *S′*.

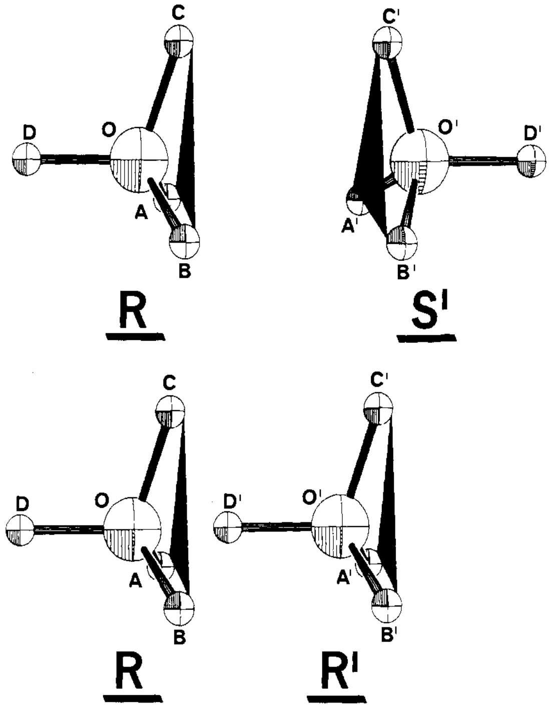

Figure 2. An example of chiral discrimination using the three-contact-point model which is based on eight-center (not six-center) interactions.

and *RR′* complexes shown (shaded triangles), the three-contact-point model excludes this RR′ structure due to the unacceptable steric interactions involving D′, and thereby provides for chiral discrimination. This *RR′* structure is excluded because of eight-center interactions! In a high-temperature limit these eight-center terms will be very different, i.e., chirality effects are due to eight-, not six-, center interactions. Alternatively, when only six centers are considered, the *RR′* and *RS′* structures are energetically equivalent. Again, this cancellation of six-center terms occurs for different OO′ distances in *RR′* and *RS′*. By requiring the same OO′ distances as Salem et al. have done, some of the necessary structures of the complexes would be precluded, which, while physically reasonable, is nevertheless an eight-center effect.

Finally, we have numerically verified the equivalence of the six-center interactions using five different interaction energy expressions, including one which Salem et al. claimed would contribute to chiral recognition.[2]

Supplementary Material Available: Sample results demonstrating the equivalence of six-center interactions using various energy expressions (2 pages). Ordering information is given on any current masthead page.

Magnetic Field Effects in Cobalt(II)-Catalyzed Oxidations: The Role of Electron Spin Angular Momentum

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Magnetic field effects are associated with reaction steps that involve a net change in total angular momentum.[1] We report that an applied magnetic field can influence the rate of a reaction catalyzed by high- and low-spin cobalt(II) complexes in profoundly different ways. The relative rate,[2] k(rel), of the O_2 oxidation of 2,6-dimethylphenol to form 2,6-dimethyl-1,4-benzoquinone catalyzed by high- and low-spin cobalt(II) is shown in Figure 1. The high-spin cobalt complex, cobalt(II) bis(3-(salicylideneamino)-propyl)methylamine, Co^{II}SMDPT ($S = {}^3/_2$), has a maximum *increase* in the initial reaction rate at $\simeq$1000 G, while the low-spin cobalt complex, cobalt(II) *N*,*N′*-bis(salicylidene)ethylenediamine, Co^{II}SALEN ($S = {}^1/_2$), in a 1:10 ratio with pyridine,[3] has a maximum *decrease* in the initial oxidation rate at $\simeq$800 G. Since the electron spin multiplicity of the transition-metal ion results in a different net change in angular momentum in these reactions, it appears high- and low-spin cobalt(II) ions can determine whether an applied magnetic field increases or decreases the initial reaction rate. This could lead to a new approach for the in situ investigation of catalytic reactions.

The leading proposed mechanism[4] for the catalytic oxidation of 2,6-dimethylphenol by cobalt(II) Schiff-base complexes is presented in Figure 2. The magnetic field effect in this reaction has been ascribed[5] to the catalyst regeneration step (f) which

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(1) Atkins, P. W. *Chem. Brit.* **1976**, 214.

(2) The relative rate, k(rel), is the initial rate at magnetic field (H) divided by the initial rate at zero magnetic field approximated by the earth's magnetic field of $\simeq$0.5 G. All values of k(rel) correspond to two standard deviations of the data, ±0.15 for CoSMDPT and ±0.08 for CoSALEN. At zero magnetic field the initial rate of phenol oxidation is 3.30×10^{-2} and 1.19×10^{-1} M^{-1} s^{-1} with CoSMDPT and 1:10 CoSALEN–pyridine, respectively.

(3) Perito, R. P.; Drago, R. S.; Corden, B. B., submitted for publication.

(4) (a) Corden, B. B.; Drago, R. S.; Perito, R. P. *J. Am. Chem. Soc.* **1985**, *107*, 2903. (b) Zombeck, A.; Drago, R. S.; Corden, B. B.; Gaul, J. H. *J. Am. Chem. Soc.* **1981**, *103*, 7580 and references therein; (c) Bedell, S. A.; Martell, A. E. *J. Am. Chem. Soc.* **1985**, *107*, 7909, and references therein.

(5) (a) Perito, R. P.; Corden, B. B. *J. Am. Chem. Soc.* **1987**, *109*, 4418. (b) Perito, R. P.; Corden, B. B. *J. Am. Chem. Soc.* **1988**, *110*, 3472. (c) Perito, R. P.; Corden, B. B. *Inorg. Chem.* **1988**, *27*, 1276. (d) Paquin, J.; Corden, B. B., submitted for publication. The electron spin multiplicity of cobalt(II) can only influence steps (a), (c), and (f). Observation of steric effects by the substituent phenol rules out step (a) as responsible for the observed magnetic field effects [5d]; the initiation step (c) can be ruled out because it exhibits no mass or magnetic kinetic ^2H isotope effect with 2,6-$(tBu)_2$-phenol-OD although a kinetic mass and magnetic isotope effect is observed with 2,6-$(tBu)_2$-phenol-4-d_1-OD [5b].

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