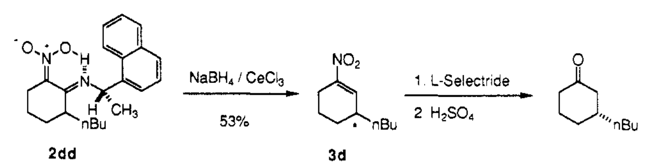
Scheme II



could be easily resolved into major and minor diastereomers. For a direct comparison of diastereoselectivities the purified, but unresolved reaction mixtures were analyzed by HPLC and the results appear in Table III.

To establish the sterochemical course of the alkylation the pure, major diastereomer of α-nitro imine **2dd** was reduced with $NaBH_4/CeCl_3$[2] (Scheme II) to afford nitroalkene **3d** ($[\alpha]^{27}{}_D$ −20.7° (*c* 3.21, $CHCl_3$)) in 53% yield along with recovered (*S*)-1-(1-naphthyl)ethylamine (99.6% e.e.)[7] in 52% yield (distilled). The nitroalkene was converted to 3-*n*-butylcyclohexanone by the method of Kabalka[8] and the absolute configuration of this ketone was established to be *R* (>94% e.e.)[9,10] via the diastereomeric dioxolane ketals prepared from (*R*,*R*)-2,3-butanediol (99.4% e.e[7]). Thus, (*S*)-amine induced attack at the *re* face of the dianion.

It is clear that the amide base is intimately involved with the dianion and is most likely restricting the conformational possibilities of the sterogenic 1-(naphthyl)ethyl unit. The association of lithium amide bases with enolates and metalloenamines has been elegantly demonstrated by X-ray crystallography[11] and isotope labeling experiments.[12] Recent reports of enantioselective reactions of achiral lithium enolates generated by or in the presence of chiral lithium amides must also be interpreted in terms of similar aggregated structures.[13,14] Furthermore, Meyers has demonstrated the special role of LDA for highly selective alkylations of chiral oxazolines.[15] In a control experiment we repeated the alkylation of cyclohexanone using the (*S*)-phenylalaninol methyl ether imine[3c] with LDA and with *s*-BuLi. The enantioselectivities were identical within experimental error (77 ± 0.3%), the base playing no additional role in these reactions. Thus, the α-nitro imine dianions are unique in the lack of stereocontrol from a coordinating auxiliary, while being sensitive to the presence of coordinating bases.

In summary we have demonstrated the diastereoselective alkylation of chiral α-nitro keto imines and their stereospecific conversion to versatile 1-nitrocyclohexenes,[16] in optically active form. Further investigation into the role of the amide base and use of the optically active nitroalkenes in synthesis will be the subject of future reports.

Acknowledgment. We gratefully acknowledge the financial support provided for this project by the National Institutes of Health (PHS RO1 GM 30938) and the Upjohn Company. This work was supported in part by the University of Illinois Mass Spectrometry Laboratory (PHS HHS GM 27029). S.E.D. acknowledges the A. P. Sloan Foundation for a Fellowship (1985–1989).

Supplementary Material Available: Full characterization data for all new compounds (**1a–d**, **2da–2de**) are provided along with a representative procedure for the alkylation of **1d** (11 pages). Ordering information is given on any current masthead page.

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Doubly Charged Gas-Phase Heteronuclear Cluster Ions: Synthesis and Reaction of $LaFe^{2+}$ with Small Hydrocarbons

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Received December 11, 1987

Recently there has been an intense interest in the physical and chemical properties of small transition metal containing ions in the gas phase. The species that have been studied include monatomic positive ions M^+,[1] negative ions M^-,[2] and homonuclear and heteronuclear cluster ions of different sizes.[3] Contrary to a belief that doubly charged transition metal ions might only undergo charge exchange reactions with small hydrocarbons in the gas phase, recent studies have shown that Ti^{2+} and Nb^{2+} undergo a variety of interesting reactions with these compounds.[4] A natural extension of this work is the study of doubly charged cluster ions. Here we report the in situ synthesis of $LaFe^{2+}$ and its reactivity with a few small hydrocarbons in the gas phase. There is only one other report of a verified doubly charged metal dimer in the literature that we are aware of. Tsong recently reported observing $Mo_2{}^{2+}$ using a pulsed-laser field evaporation source in conjunction with a time-of-flight mass spectrometer.[5] However, Jentsch and co-workers[6] successfully observed several doubly charged metal trimer ions and Sattler and co-workers[7] have observed $Pb_n{}^{2+}$ for *n* above a critical number of 30.

The present experiments were performed on a prototype Nicolet FTMS-1000 instrument equipped with a 5.2 cm cubic trapping cell situated between the poles of a Varian 15 in electromagnet maintained at 0.9 T.[8] La^{2+} was generated by focusing the beam of a Quanta Ray Nd:YAG laser (1.06 μm; 10^8–10^9 W/cm^2) onto a La target. Laser desorption forms La^{2+} in varying amounts relative to La^+ depending on the focusing spot on the target, with La^+ being ejected immediately after its formation to avoid any interference.[9,10] The isolated La^{2+} was then reacted with $Fe(CO)_5$, which was pulsed in through a General Valve Corporation Series

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9 pulsed solenoid valve.[11] The reaction of La^{2+} with $Fe(CO)_5$ gives ~80% charge exchange product ions.[12] Carbonyl displacement reactions, however, are also observed (reaction 1). $La^{56}Fe(CO)_2^{2+}$ (~11% of the product ion intensity) was isolated by swept double resonance pulses and subjected to collision-induced

$$La^{2+} + Fe(CO)_5 \rightarrow LaFe(CO)_n^{2+} + (5 - n)CO \quad (n = 1, 2, 3) \qquad (1)$$

dissociation (CID) with background argon at about 4×10^{-6} Torr.[13] As the collision energy is increased, first loss of one and then both carbonyls is observed, resulting in the formation of $La^{56}Fe^{2+}$. This procedure can result in some of the $LaFe^{2+}$ ions being nonthermal. $LaFe^{2+}$ accounts for ~30% of the CID fragment ions at a collision energy of 48 eV. This species was then isolated and its reactions with small hydrocarbons observed at extended trapping times. Reactions of Nb^{2+} and Ta^{2+} with $Fe(CO)_5$ give only charge exchange products.

There are two significant differences between our observation of $LaFe^{2+}$ and the earlier work on Mo_2^{2+}. First, the nominal mass of Mo_2^{2+} is the same as Mo^+, but its presence could be verified by its characteristic isotopic distribution which differs from that of Mo^+. In contrast $LaFe^{2+}$ is heteronuclear and, thus, there are clearly no isobaric interferences from either Fe^+ or La^+. Although, unfortunately, an exact mass measurement could not be obtained for $LaFe^{2+}$, it is generated in a reaction sequence starting with La^{2+} where the nominal masses are verified at each step. Sequential loss of CO from CID of $LaFe(CO)_2^{2+}$ rules out any significant contribution from a possible isobaric interference, $La(CO)_2^{2+}$. In addition, CID of $La(CO)_2^{2+}$ would also be expected to sequentially lose two carbonyls which is not observed when the proposed $LaFe^{2+}$ species undergoes CID, as discussed below. A second difference is that the lifetime of the Mo_2^{2+} species could only be given a lower limit of several times greater than 15 ns, the flight time of the ions in the instrument. Thus, it was not clear whether the ions were stable or metastable. In our system $LaFe^{2+}$ could be stored and observed on the order of seconds.

There are two possible explanations for the bonding in $LaFe^{2+}$. A charge separated species La^+–Fe^+ is possible if the inherent bonding of the species is large enough to overcome the electrostatic repulsion or, more likely, results in a kinetic barrier to the dissociation. Similar explanations have been applied to some nonmetallic polyatomic species.[14,15] Alternatively, the bonding may more closely resemble La^{2+}–Fe where the ion-induced dipole results in a strong attractive interaction. Interestingly, CID on $LaFe^{2+}$ yields La^+ and Fe^+ exclusively over the energy range studied (13–32 eV). Although suggestive, these results do not conclusively distinguish the charge separated model from the La^{2+}–Fe model, since in the latter case, a curve crossing is possible and even likely.

In light of the rich chemistry observed for small transition metal ionic species, the reactions of $LaFe^{2+}$ with a few small hydrocarbons were studied. No reaction is observed with methane,[16] while $LaFe^{2+}$ does react with ethane, predominantly (>75%) by reaction 2. $LaFe(C_2H_4)^{2+}$ from reaction 2 reacts further with

$$LaFe^{2+} + C_2H_6 \rightarrow LaFeC_2H_4^{2+} + H_2 \qquad (2)$$

ethane to form $LaFe(C_2H_4)_2^{2+}$. The observation of $LaFeC_2H_4^{2+}$ and $LaFe(C_2H_4)_2^{2+}$ resembles the reaction of $LaFe^+$ with ethane.[17] However, La^{2+} is not observed to react with either methane or ethane.[16,18]

The reactions of $LaFe^{2+}$ with propane are shown in reactions 3–6. Only the reaction analogous to reaction 4 was observed for

$$\begin{aligned} LaFe^{2+} + C_3H_8 &\rightarrow LaFeC_3H_4^{2+} + 2H_2 \ 11\% && (3)\\ &\rightarrow LaFeC_3H_6^{2+} + H_2 \ 52\% && (4)\\ &\rightarrow FeC_3H_6^{+} + La^{+} + H_2 \ 10\% && (5)\\ &\rightarrow LaC_3H_6^{+} + Fe^{+} + H_2 \ 27\% && (6)\end{aligned}$$

$LaFe^+$ and La^{2+}.[17,18] At longer trapping times, $LaFe(C_6H_{10})^{2+}$ and $LaFe(C_6H_{12})^{2+}$ were observed, arising from the secondary reactions of $LaFeC_3H_4^{2+}$ and/or $LaFeC_3H_6^{2+}$.

Ethylene reacts with $LaFe^{2+}$ predominantly (>65%) by splitting the cluster ion to form $LaC_2H_4^+$ and Fe^+. Some $FeC_2H_4^+$ and La^+, along with minor amounts of $LaFeC_2H_2^{2+}$ and $LaC_2H_2^+$, are also observed. Due to the difficulty of performing a double resonance experiment at this stage, it was not possible to determine whether the $LaC_2H_2^+$ arose from the reaction of the doubly charged cluster or from La^+ reacting with ethylene.

Finally, it is worth mentioning that $LaFe(CO)_2^{2+}$ reacts with ethane slowly, forming $LaFe(CO)_2(C_2H_4)^{2+}$ and $LaFe(CO)_2(C_2H_6)^{2+}$ in roughly a 1:3 ratio, and with propane to yield $LaFe(CO)(C_3H_6)^{2+}$ and $LaFe(CO)(C_3H_8)^{2+}$ in roughly a 3:1 ratio.

The in situ synthesis of a variety of stable doubly charged LaFe species has been demonstrated. Additional studies are underway to try to determine the bond energy and kinetic barrier associated with $LaFe^{2+}$ and its derivatives, as well as to extend these promising preliminary chemical studies. A detailed theoretical calculation on the bonding of this intriguing species is also underway.

Acknowledgment is made to the Division of Chemical Sciences in the Office of Basic Energy Sciences in the United States Department of Energy (DE-FG02-87ER13766) for supporting this research and to the National Science Foundation (CHE-8612234) for continued support of the FTMS. The authors also thank Dr. Charles Bauschlicher at NASA Ames Research Center at Moffet Field, California, and Professor James C. Weisshaar at the University of Wisconsin in Madison for helpful suggestions.

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Studies on the Biosynthesis of the *m*-C_7N Unit in the Antibiotics Manumycin and Asukamycin

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Received January 22, 1988

The manumycin group of antibiotics, represented by manumycin (**1**),[1,2] asukamycin (**2**),[3,4] colabomycin,[5] U-62,162,[6] and U-56,407,[7]

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