$$1.0(C_5Me_5)_2Eu^{II}\cdot OEt_2 + 2.0RX \rightarrow 1.0EuX_2 + 2.0C_5Me_5R + 1.0Et_2O \quad (3)$$

These results and the decreasing rates of oxidative addition $Sm^{II} \gg U^{III} > Yb^{II} \ggg Eu^{II}$, which mirror their decreasing reduction potentials,[16,17] $\simeq -2.0$,[17a] -1.3,[17c] $\simeq -1.4$,[17a,d] and $\simeq -0.8$[17a] (V vs. SCE), respectively, must be reconciled with any intimate mechanism proposed for these "atom-abstraction" oxidative additions. The presence of a single electron transfer component in these "atom abstractions" as well as in others[18] is strongly implied.[19]

Acknowledgment. Support from NSF (Grant CHE-8313459) and donors of Petroleum Research Fund, administered by the American Chemical Society (in part) and from Dreyfus Teacher-Scholar (1982–1987) and Guggenheim (1984–1986) Fellowships to R.G.F. is gratefully acknowledged.

Registry No. $(C_5Me_5)_2Sm^{II}\cdot OEt_2$, 85962-90-9; $(C_5Me_5)_2Eu^{II}\cdot OEt_2$, 84254-55-7; $SmBr_2$, 50801-97-3; KC_5Me_5, 94348-92-2; $PhCH_2Cl$, 100-44-7; $C_5Me_5CH_2Ph$, 100692-30-6; $(C_5Me_5)Sm^{II}(Cl)(OEt_2)$, 107846-38-8; $CHCl_3$, 67-66-3; $SmCl_3$, 10361-82-7; *t*-BuCl, 507-20-0; $Eu^{II}Cl_2\cdot 0.5\ Et_2O$, 107799-45-1.

Supplementary Material Available: Summary of products and stoichiometries for 15 RX and ArX; details of GLC studies and NMR studies; summary of attempted independent syntheses of $(C_5Me_5)_2Sm^{III}R$ complexes; details of the preliminary kinetic studies; a table of Sm(II), U(III), and Yb(II) absolute rate constants for *n*-octyl fluoride and phenyl chloride reactions (7 pages). Ordering information is given on any current masthead page.

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(16) (a) Kagan, N. B.; Namy, J. L. *Handbook on the Physics and Chemistry of the Rare Earths*; Gschneidner, K. A., Jr., Eyring, L., Eds.; Elsevier: 1984; Chapter 50. (b) Schumann, H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 474.

(17) (a) Values from ref 1a (footnote 5) converted from the $FeCp_2/FeCp_2^+$ to the SCE reference electrode by adding +0.4 V. (b) For reduction potential determinations under other conditions see: Varlashkin, P. G.; Peterson, J. R. *J. Less-Common Met.* **1983**, *94*, 333. Mikheev, N. B. *Inorg. Chim. Acta* **1984**, *94*, 241. Morss, L. R. *Chem. Rev.* **1976**, *76*, 827. Johnson, D. A. *J. Chem. Soc., Dalton Trans.* **1974**, 1671. Bratsch, S. G.; Lagowski, J. J. *J. Phys. Chem.* **1985**, *89*, 3317. (c) Finke, R. G.; Gaughan, G.; Voegeli, R. *J. Organomet. Chem.* **1982**, *229*, 179. (d) Measured for $(C_5Me_5)_2Yb^{II}(DME)$ in acetonitrile, Gaughan, G. T. Ph.D. Dissertation, University of Oregon, 1983.

(18) (a) Tamblyn, W. H.; Vogler, E. A.; Kochi, J. K. *J. Org. Chem.* **1980**, *45*, 3912. (b) Blackburn, E. V.; Tanner, D. D. *J. Am. Chem. Soc.* **1980**, *102*, 692. (c) Chatgilialoglu, C.; Ingold, K. U.; Scaiano, J. C. *Ibid.* **1982**, *104*, 5123. See also: Perrin, C. L. *J. Phys. Chem.* **1984**, *88*, 3611 for comments on this type of mechanism.

(19) Collman, J. P.; Hegedus, L. S.; Norton, J.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987.

Spectroscopic Identification of the Nickel Acylate Complex

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Summary: NMR and IR spectral data of the pentanoyl nickelate complex are presented and are consistent with a mononuclear nickel complex. This nickel acylate complex is thermally stable in THF at ambient temperature (+20 °C) for prolonged periods (24 h) but decomposes rapidly in air.

The nickel acylate complex formed from the reaction of nickel tetracarbonyl with an organolithium reagent has not been structurally well-characterized.[1] This lack of characterization may be due, in part, to the instability of this complex in the presence of oxygen.[2] In addition, temperatures greater than 0 °C have been reported[1] to cause decomposition of the nickel acylate complex in ether, while temperatures greater than −20 °C and prolonged reaction times have been reported[3] to produce undesirable side reactions in tetrahydrofuran (THF).

Scheme I

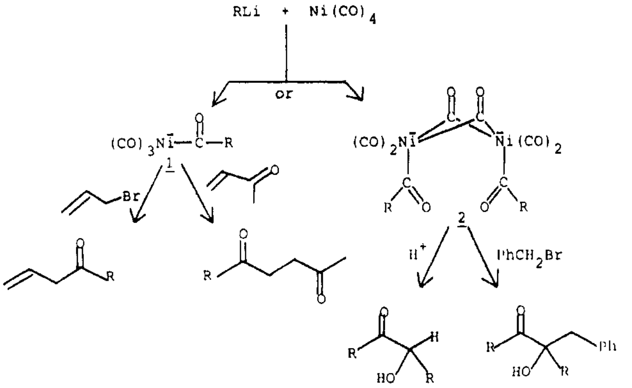
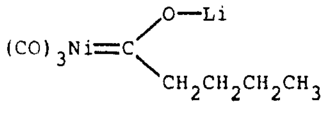


Table I. Spectral Data for the Pentanoyl Nickelate Complex



Carbon Number 2 1 3 4 5 6

^1H NMR δ[a,b]	^{13}C NMR δ[c,d]	IR $\nu(CO)$,[e,f] cm^{-1}
2.555 (t, *J* = 7.50, 2 H, H_{C_3})	317.018 (C1)	1980 (w)
1.625 (m, *J* = 7.50, 2 H, H_{C_4})	205.296 (C2)	1935 (s)
1.356 (m, *J* = 7.35, 2 H, H_{C_5})	66.476 (C3)	1535 (m)
0.973 (t, *J* = 7.20, 3 H, H_{C_6})	27.752 (C4)	
	24.012 (C5)	
	15.013 (C6)	

[a] Solvent: THF-d_8. Reference: residual proton on α-carbon of THF at +3.700 ppm. *J* values in Hz. [b] ^1H chemical shifts of 10.6 M BuLi in THF are +1.576, +1.362, +0.975, and −0.891 ppm. [c] Solvent: THF. Reference: α-carbon of THF at +68.600 ppm. [d] Chemical shift of $Ni(CO)_4$ in THF is +192.964 ppm; chemical shifts of 10.6 M BuLi in THF are +159.367, 82.201, 26.032, and 14.405 ppm. [e] Solvent: THF. Range of scan: 2500–1500 cm^{-1}. [f] CO stretch for $Ni(CO)_4$ in THF is 2050 cm^{-1}; in this spectrum, there is a weak peak at 2025 cm^{-1} which corresponds to $Ni(CO)_4$ in THF with added LiOTf.

Attempts to determine the structure of the nickel acylate complex based on the products isolated from the reaction of the complex with an electrophile have resulted in controversy. As shown in Scheme I, when the nickel acylate complex is allowed to react, in ether, with an allylic halide or a conjugated enone,[3,4] *one* acyl group is transferred to the final product, thus suggesting a monomeric structure, such as 1, for this complex. Similar results have also been observed from the reaction of the nickel acylate with quinone ketals in THF.[2] However, when the nickel acylate complex is allowed to react with a proton source, such as

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(1) Collman, J. P.; Hegedus, L. S. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1980; p 488.

(2) (a) Semmelhack, M. F.; Keller, L.; Sato, T.; Spiess, E. J.; Wulff, W. *J. Org. Chem.* **1985**, *50*, 5566–5574. (b) Semmelhack, M. F.; Keller, L.; Sato, T., Spiess, E. J. *Ibid.* **1982**, *47*, 4382–4384.

(3) Hegedus, L. S. Ph.D. Thesis, Harvard University, Cambridge, MA, 1970, pp 85–92.

(4) Corey, E. J.; Hegedus, L. S. *J. Am. Chem. Soc.* **1969**, *91*, 1233–1234,

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Table II. ^{13}C NMR Spectral Data[a] for the Pentanoyl Nickelate Complex:[b] Thermal Stability Evaluations (Probe Temperatures in Parentheses)

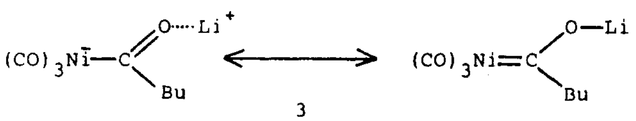
	spectrum					
	I (−100 °C)	II (−60 °C)	III (−20 °C)	IV (+20 °C)	V (−20 °C)	VI (−60 °C)
C1	312.884	314.389	315.617	316.715	315.658	314.401
C2	205.548	205.498	205.507	205.405	205.486	205.498
C3	67.286	66.881	66.667	66.476	66.662	66.881
C4	27.853	27.752	27.733	27.752	27.728	27.752
C5	24.157	24.015	24.058	24.012	24.090	24.012
C6	15.660	15.357	15.212	15.034	15.186	15.384

[a] In δ. Solvent: THF. Reference: α-carbon of THF at +68.600 ppm. [b] See Table I for carbon numbering scheme.

HCl, or with benzyl bromide,[5] in ether, *two* acyl groups are transferred to generate an acyloin derivative. To explain these results, 2 has been proposed as the structure of the acylate complex.[5] Surprisingly, alkyl halides, such as methyl iodide, and aryl iodides do *not* react with the anionic nickel acylate.[1,3]

Before it will be possible to understand the diverse reactivity of this anionic nickel complex, its structure in solution must be known. The purpose of this communication is to report, for the first time, the nuclear magnetic resonance and infrared spectra of the nickel acylate complex. Although more reactions of the nickel acylate have been reported in ether[3-5] than in THF,[2] our initial spectroscopic studies were conducted in THF due to the greater solubility of this complex.

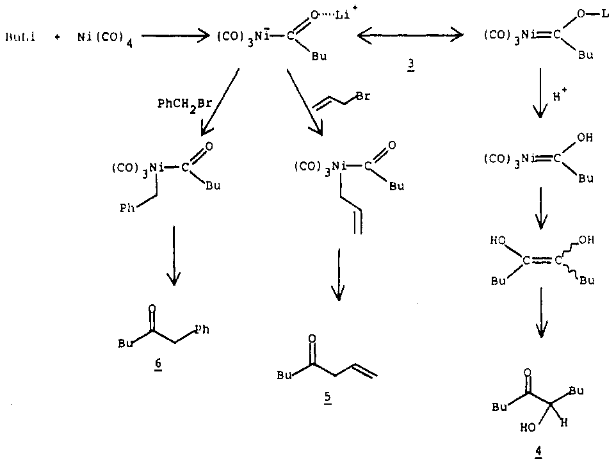
A 0.33 M solution of pentanoyl nickelate complex was prepared under argon for analysis by NMR and IR spectroscopies by allowing nickel tetracarbonyl to react with 10.6 M butyllithium[6] in THF at −78 °C for approximately 10 min. One milliliter of the reaction mixture (red-orange solution with fine particulate[7]) was withdrawn, transferred to an argon-filled NMR tube (the nickelate complex is very air-sensitive), and warmed to ambient temperature. A proton-decoupled carbon NMR spectrum was obtained in 1.5 h. The contents of the tube were then analyzed by IR spectroscopy (Table I), and the spectrum shows CO stretches consistent with terminal carbonyl ligands (1980, 1935 cm^{-1}) and an acyl carbonyl ligand (1535 cm^{-1}). In the ^{13}C NMR spectrum, chemical shifts of 317.018 and 205.296 ppm are characteristic of a metal carbene carbon and terminal carbonyl ligands,[8] respectively. On the basis of NMR and IR spectral data of the nickel acylate complex in THF, the mononuclear nickel carbene complex 3 is



3

proposed. We are currently evaluating the possibility that oxygen–lithium bridging may exist between two or more nickel carbene units.[9] There is no evidence of the bridging carbonyls[5] which would be present in the pentanoyl analogue of structure 2.

Scheme II



Although the pentanoyl nickelate complex appears stable from the NMR and IR spectroscopic analyses described above, reports of thermal decomposition of the complex in THF at temperatures greater than +25 °C[2] and reports of reactions between the nickel acylate complex and the solvent at temperatures as low as −20 °C[3] were of concern. Therefore, examination of the thermal stability of the nickel acylate complex in THF was initiated.

To evaluate the thermal stability of the nickel acylate complex, a 0.33 M solution of pentanoyl nickelate complex was evaluated by variable-temperature ^{13}C NMR spectroscopy.[10] Comparison of the results at −100 and +20 °C indicate that the anion is stable over this temperature range (Table II). In addition, warming and cooling of the sample over prolonged reaction times do not affect the nickel acylate complex as evident by the almost superposition of spectrum II and spectrum VI (−60 °C before and after warming to +20 °C), which were started almost 8 h apart.

Since the nickel acylate was reported to attack THF at prolonged reaction times,[3] the stability of the pentanoyl nickelate was monitored at ambient temperature (18–20 °C) by ^{1}H NMR, ^{13}C NMR, and IR spectroscopies. Spectra obtained after 8 and 24 h are identical with the 1-h results presented in Table I. We find that the nickel

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(5) Sawa, Y.; Ryang, M.; Tsutsumi, S. *J. Org. Chem.* **1970**, *35*, 4183–4188.

(6) Butyllithium (10.6 M) (purchased from Alfa Products) was used, rather than the typical 1.5–2.0 M butyllithium in hexane, to avoid contamination of our NMR spectra by solvent peaks.

(7) The particulate observed is expected to have the same structure as the complex in solution since upon dilution the particulate disappears. However, the concentration was kept at 0.33 M because the particulate did not affect the peak widths and because of the greater signal to noise in the more concentrated solution. Characterization of the solid is in progress.

(8) Mann, B. E.; Taylor, B. F. *^{13}C NMR Data for Organometallic Compounds*; Academic: Orlando, FL, 1981; p 180.

(9) For additional information on oxygen–lithium bridging, see: (a) Laube, T.; Dunitz, J. D.; Seebach, D. *Helv. Chim. Acta* **1985**, *68*, 1373–1393. (b) Amstutz, R.; Schweizer, W. B.; Seebach, D.; Dunitz, J. D. *Ibid.* 1981, *64*, 2617–2621. (c) Seebach, D.; Amstutz, R.; Dunitz, J. D. *Ibid.* 1981, *64*, 2622–2626.

(10) A 0.33 M solution of pentanoyl nickelate complex was prepared in THF at −78 °C by adding 10.6 M butyllithium to nickel tetracarbonyl. Immediately at the end of the butyllithium addition, 1.0 mL of the reaction mixture was transferred to a chilled, argon-filled NMR tube. The tube was sealed and maintained at −78 °C until placed in the NMR spectrometer probe at −100 °C. A proton-decoupled carbon spectrum was obtained in 1.5 h. The probe temperature was then increased by 40 °C and a second spectrum obtained. This procedure was repeated two more times until +20 °C was reached. The probe temperature was then decreased in two 40 °C intervals to return to −60 °C. Proton-decoupled carbon spectra were obtained at each of these temperatures.

carbene complex **3** is thermally stable in THF at ambient temperature (+20 °C) for prolonged periods (24 h).

The products from the reaction of the nickel acylate complex with an allylic halide or a conjugated enone, in ether,[3,4] or from the reaction of a quinone ketal, in THF,[2] are consistent with a mononuclear nickel acylate complex. Carbene coupling[11] of two nickel carbene complexes explains the observation of acyloin derivatives, **4**, when the nickel acylate is allowed to react with a proton source[5] (Scheme II). However, formation of the acyloin derivative from the reaction of the nickel acylate complex with benzyl bromide, in ether,[5] contradicts the one acyl transfer expected for this reaction. Indeed, when the pentanoyl nickelate complex is allowed to react with benzyl bromide, in THF,[12] the major product is 1-phenyl-2-hexanone, **6**.[13] Work with other alkyllithium reagents, electrophiles, and solvents is in progress.

Acknowledgment. We wish to thank the Research Corp. and the Lalor Foundation for financial support of this work. We wish to thank the University Research Council of the University of Cincinnati for a Summer Faculty Fellowship to A.R.P. The NMR spectrometer used in this study was purchased with the aid of an NSF instrumentation grant (CHE-8102974). Finally, we would especially like to thank Dr. Elwood Brooks for his help in obtaining the low temperature NMR spectra.

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(11) For additional information on carbene coupling, see: (a) Casey, C. P. *Transition Metal Organometallics in Organic Synthesis*; Academic: Orlando, FL, 1976; Vol. 1, pp 214–217. (b) Brown, F. J. *Prog. Inorg. Chem.* **1980**, *27*, 1–122 (see specifically, pp 84–86).

(12) A 0.33 M solution of pentanoyl nickelate is prepared by allowing 1.2 mL (10 mmol) of nickel tetracarbonyl to react under argon with 1.6 M butyllithium (6.2 mL, 10 mmol) in 30 mL of THF for 15 min at −78 °C followed by 1 h at ambient temperature. Benzyl bromide (1.2 mL, 10 mmol) is added dropwise to the anion at −78 °C. The reaction is warmed slowly and allowed to react for 5 h. Excess nickel carbonyl is quenched by pouring the reaction mixture into a flask containing 2.5 g (10 mmol) of solid iodine and stirring for 15 min. The mixture is washed with aqueous sodium bisulfite until the aqueous layer is colorless. The combined aqueous layers are then washed with 50 mL of ether. The ether layer is added to the THF solution and dried with potassium carbonate.

(13) This product tentatively has been identified by GC/MS (*m/e*): 176 (33%), 91 (63%), 85 (100%), 57 (64%). Product yields based on benzyl bromide: 1-phenyl-2-hexanone (**6**), 36%; benzyl halide, 39%; 1,2-diphenyl-3-heptanone, 12%; benzyl acyloin, less than 3% (3% is our detection limit for an authentic sample).

Reversible and Diastereospecific Olefin Insertion into a Cluster Ru–H Unit. Formation of Metallacycles with Tertiary Carbon–Ruthenium σ Bonds

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Summary: The chiral hydrido metal clusters (μ_3-RC)RuCoMCp(CO)$_8$H with R = Me or Ph and M = Mo or W react reversibly with the prochiral alanine precursor acetamido acrylic acid methyl ester according to a Markownikow-type insertion of the $X_2C{=}CH_2$ substrate into a Ru–H bond. The cluster products formed consist of only one pair of the possible diastereoisomers rendering the reaction diastereospecific. The resulting σ-alkyl cluster complexes contain a Ru–C–N–C–O metallacycle with a tertiary carbon atom bound to ruthenium.

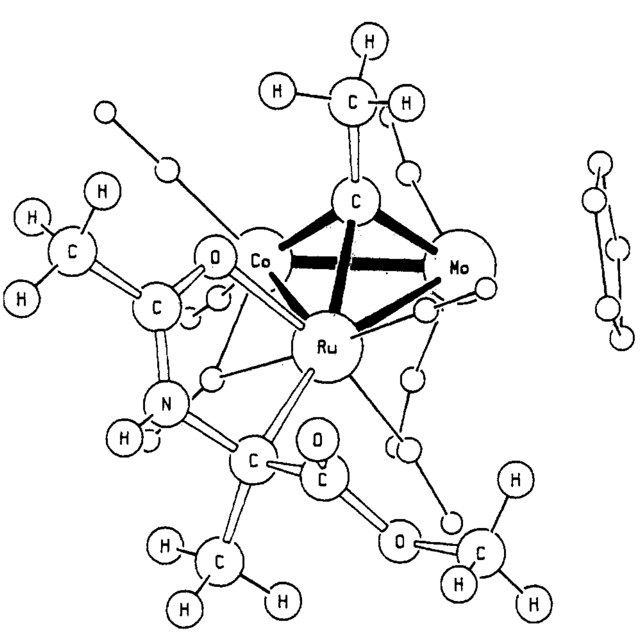

Figure 1. Schematic SCHAKAL plot of the molecular structure of **3a**.

If clusters are to bring new dimensions into homogeneous catalysis, these are most likely to rest on the multifunctionality of the metal assembly or on the stereochemical conditions brought about by the cluster framework.[1] We are investigating both alternatives, emphasizing the possible effects of cluster chirality. After observing that optically active clusters can be racemized under catalysis conditions due to framework opening,[2] we have developed methods of incorporating the typical catalysis elements ruthenium and rhodium in chiral clusters.[3] We hoped to thereby find catalytically active systems which react under milder conditions. One of the compounds obtained this way is the RuCoMo cluster **1a** which has already shown its usefulness in a reversible alkylidyne–vinylidene rearrangement.[4] We have now found that **1a** and the related clusters **1b** and **2b**[3] undergo an olefin insertion which yields organometallic compounds that can be called model intermediates of cluster-generated optical induction.

In an attempt to observe optical induction in a cluster-catalyzed hydrogenation the prochiral alanine precursor acetamidoacrylic acid methyl ester was treated with **1a** in benzene under a hydrogen atmosphere. On a millimolar scale at 40 °C the 1:1 reaction was complete within about 5 h leading to a single product identified as **3a** (cf. Scheme I) and isolated in 70–80% yield via chromatography with CH_2Cl_2 over silica gel. **1b** and **2b** reacted analogously producing **3b** and **4b** in about 75% yield. Hydrogen is not consumed in these reactions, but runs in the absence of hydrogen gave lower yields. It seems that the main function of the hydrogen atmosphere is to suppress the thermal decomposition of the starting clusters **1** and **2**. The reaction products **3** and **4** have been fully characterized[5] including a crystal structure determination of **3a** (ref

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(1) Cf. Gates, B. C.; Guczi, L.; Knözinger, H., Eds. *Metal Clusters in Catalysis*; Elsevier: Amsterdam, 1986. Moskovits, M., Ed. *Metal Clusters*; Wiley: New York, 1986.

(2) Planalp, R. P.; Vahrenkamp, H. *Organometallics* **1987**, *6*, 492.

(3) Mani, D.; Vahrenkamp, H. *Chem. Ber.* **1986**, *119*, 3639, 3649.

(4) Bernhardt, W.; von Schnering, C.; Vahrenkamp, H. *Angew. Chem.* **1986**, *98*, 285; *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 279.