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.

(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)Ru-CoMCp(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$_2$C=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.
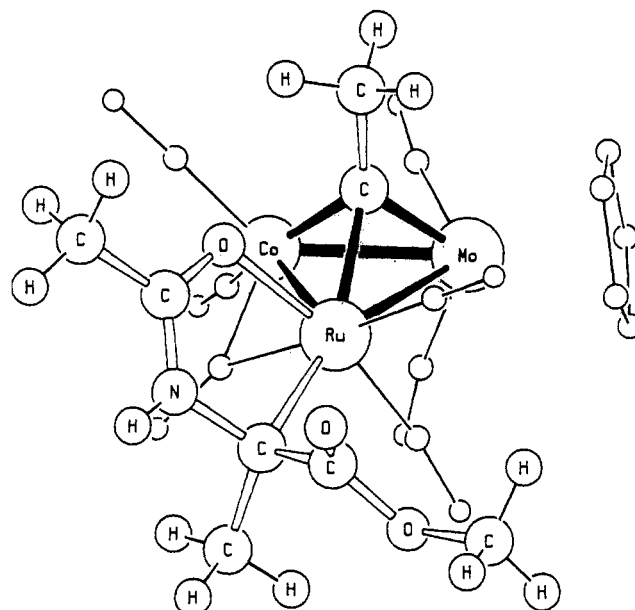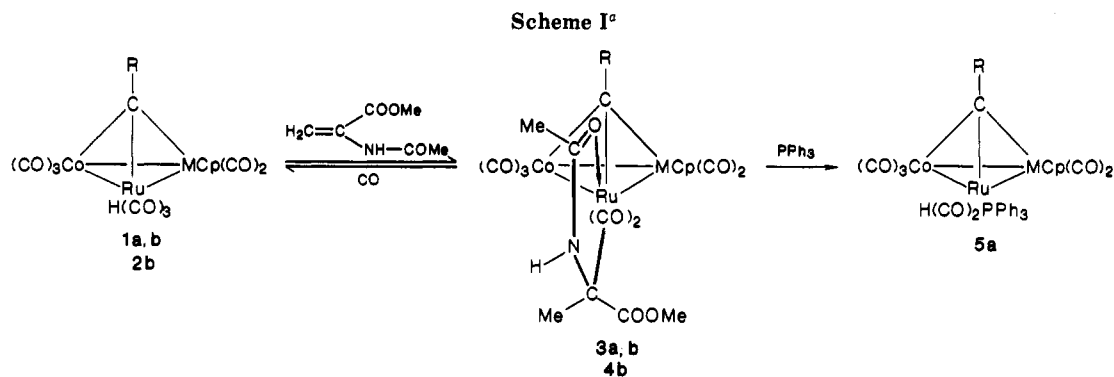

Figure 1. Schematic SCHAKAL plot of the molecular structure of **3a**.

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$_2$Cl$_2$ 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

(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.

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Scheme I[a]

[a] 1 and 3, M = Mo; 2, 4, and 5, M = W; a, R = Me; b, R = Ph.

6 and Figure 1).

Mass spectra and structure determination of **3a** have identified the clusters **3** and **4** as addition (i.e. insertion) products of the enamide substrate to the starting complexes with loss of one cluster CO ligand. The reactions are fully chemoselective (only the olefinic bond is hydrogenated) and regioselective (the terminal CH_2 group of the substrate becomes a CH_3 group and the internal olefinic carbon atom becomes bound to ruthenium) giving the Ru–H addition across the olefinic bond a Markownikow-type stereochemistry. Although Ru–H additions across olefinic bonds are not unusual and similar metallacycles[7] and cluster-bound σ-alkyl ligands[8] have been obtained by using fumaric and maleic acid derivatives, two properties of the clusters **3** and **4** must be considered unusual. These are their high thermal stability and the fact that they contain a σ-bound tertiary carbon atom. σ-Alkyl complexes with transition metals bound to tertiary carbon atoms are extremely rare; in studies related to catalysis they could only be inferred from low-temperature NMR observations.[9] The driving force for the occurrence of this type of complex in **3** and **4** and the explanation of its stability must reside in the formation of the five-membered metallacycle linking the ruthenium atom to the organic substrate. The preference for five-membered metallacycles including those with ruthenium[10] is well-known. Obviously in the present case the alternative six-membered ring resulting from the usual anti-Markownikow addition is significantly less favorable.

The NMR spectra of clusters **3** and **4**, even under conditions of high field and high resolution, give rise to only one resonance for each of the organic units present. This means that of the four possible diastereoisomers only two are formed which are mirror images of one another. The reaction therefore is diastereoselective. This is borne out by the observations that upon addition of the optically active shift reagent (+)-Eu(tfc)$_3$ only doubling occurs for the OMe, C(O)Me, and CMe resonances and that high-performance column chromatography does not lead to any product separation. Chromatography of **3** over a 1-m column with optically active triacetyl cellulose did however lead to partial enantiomer separation, and two fractions with molar rotations (Φ) of $-2400°$ and $+1600°$ at 589 nm could be isolated. Since it has not been possible yet to obtain the optically active starting clusters, this separation after product formation must serve as support for the contention that the reaction is, in principle, enantiospecific. Thereby, to our knowledge for the first time, a model of the key intermediate in enantioselective catalytic hydrogenation[11] has been fully characterized. Without mechanistic information it is difficult to explain the preferred stereochemistry of the products, one possibility being the mutual approach of the two most polar units, the MoCp group and the COOMe group, on the same side of the molecule.

Catalytically, the observed enamide addition reactions are nonproductive. Heating of the products **3** and **4** under hydrogen pressure only led to slow decomposition. Under CO/H_2 or CO alone (benzene, 40 °C, 2 atm, 6 h) **3a** and **3b** were quantitatively reconverted to **1a** and **1b** and the free enamide. Running this reaction with partially resolved **3a** (see above) resulted in almost complete racemization indicating that cluster opening may be involved in the back reaction.[2] The same effect is observed upon treating **4a** with triphenylphosphine in benzene at 40 °C. In a slow reaction, which is accelerated and practically quantitative under 20 atm of hydrogen, only **5a**,[3] the PPh$_3$ substitution product of **2a**, and the free enamide were formed. This reaction also led to racemization of partially resolved **4a**.

Thus the stability of the intermediates **3** and **4**, which is an advantage concerning their isolation, turns into a disadvantage concerning their reactivity. Further efforts will be directed toward clusters that are more rigid in their frameworks and at the same time more labile in their ligand spheres.

(5) Spectra of the new clusters. IR (CH$_2$Cl$_2$, cm^{-1}): **3a,** 2043 m, 2019 vs, 2002 s, 1978 vs, 1960 m, 1932 vw, 1886 m, 1817 m, 1690 w, 1590 m, 1558 w; **3b,** 2071 w, 2039 m, 2019 vs, 2000 s, 1976 vs, 1956 s, 1929 w, 1881 m, 1814 m, 1696 w, 1592 m, 1557 w; **4b,** 2079 vw, 2042 m, 2018 vs, 2000 vs, 1978 s, 1954 s, 1926 w, 1882 m, 1819 m, 1694 w, 1593 m, 1551 m. NMR (C$_6$D$_6$, internal Me$_4$Si): **3a,** δ 5.72 (NH), 4.87 (Cp), 3.67 (Me), 3.52 (Me), 2.07 (Me), 1.20 (Me); **3b,** δ 7.49 (NH), 4.95 (Cp), 3.71 (Me), 3.67 (Me), 2.09 (Me), 1.36 (Me); **4b,** 7.0 (m, Ph), 5.69 (NH), 4.76 (Cp), 3.63 (Me), 2.14 (Me), 1.09 (Me).

(6) Crystal data: monoclinic, $P2_1/c$, a = 981.6 (2) pm, b = 847.0 (2) pm, c = 3586.8 (4) pm, β = 91.77 (2)°, Z = 4; 3682 unique reflections; anisotropic refinement; 308 variables; R(unit weights) = 0.042. Details of the structure determination will be given with the full publication.

(7) Hiraki, K.; Sasada, Y.; Kitamura, T. *Chem. Lett.* **1980**, 449.

(8) Keister, J. B.; Shapley, J. R. *J. Am. Chem. Soc.* **1976**, *98*, 1056. Zuffa, J. L.; Gladfelter, W. L. *J. Am. Chem. Soc.* **1986**, *108*, 4669.

(9) Brown, J. M.; Chaloner, P. A. *J. Chem. Soc., Chem. Commun.* **1980** 344.

(10) Cf. Bennett, M. A.; Bruce, M. I.; Matheson, T. W. *Comprehensive Organometallic* Chemistry; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1982; Vol. 4, Chapters 32.3 and 32.9.

(11) Kagan, H. B. in ref 10, Vol. 8, Chapter 53. Halpern, J. In *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic Press: New York, 1985; Vol. 5, p 41.