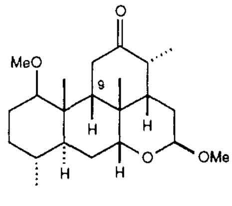

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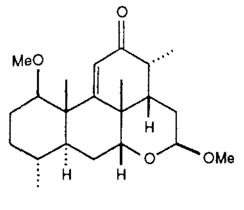

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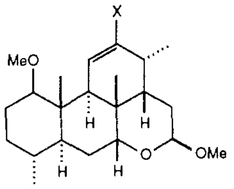
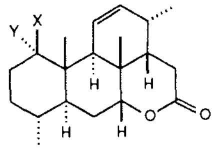


4 X = OPO(OEt)$_2$

5 X = H



6 X = OMe, Y = H

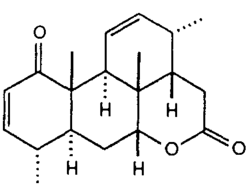
7 X = OH, Y = H

8 X = Y = O

yield. Reductive elimination [Li (100 equiv), $EtNH_2$, t-BuOH (1.0 equiv), THF] of the phosphate group proceeded smoothly affording tetracyclic olefin **5** in 92% yield.

Prior to elaboration of the ring A functionality, the protected lactol in **5** was converted in 77% overall yield into the tetracyclic lactone **6**, mp 174–176 °C, via a two-step sequence (1. 5% HCl, THF, 5 h; 2. Jones oxidation, 0 °C, 30 min). Cleavage of the methyl ether in compound **6** required prolonged exposure (70 h) of **6** to boron trifluoride etherate/ethanedithiol (1.0:1.7) containing a catalytic amount of concentrated hydrochloric acid in order to realize a 70% yield of crystalline tetracyclic alcohol **7**, mp 167.5–169.0 °C. Oxidation [PCC (3.0 equiv), NaOAc (2.5 equiv), $CH_2Cl_2$, 0 °C (30 min) → room temperature (30 min)] of **7** provided in 99% yield ketone **8**, mp 180.5–181.0 °C.

The required ring A functionality was introduced at this stage of the synthesis since all attempts to elaborate ring A in the presence of the C(11), C(12) trans diaxial vicinal diol unit failed. Tetracyclic ketone **8** was converted (82% yield) into enone **9**, mp 206.5–207.5 °C, via a three-step sequence involving enol silyl ether formation [HMDS (7 equiv), $Et_3N$ (7 equiv), TMSI (5 equiv), $ClCH_2CH_2Cl$, −23 °C → room temperature (3 h)], trapping of the enol silyl ether with phenylselenenyl chloride in tetrahydrofuran at 0 °C (20 min), and oxidation ($H_2O_2$, pyridine, 0 °C, 1.5 h) of the corresponding keto selenide which underwent loss of benzene selenenic acid. Elaboration of the ring A functionality required transformation of enone **9** into the corresponding silyl dienol ether.



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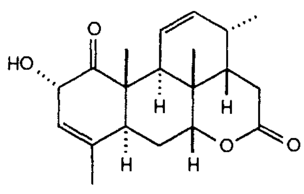
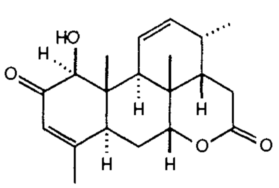


10

Toward this end, enone **9** was treated with 15 equiv of hexamethyldisilazane, 15 equiv of triethylamine, and 10 equiv of trimethylsilyl iodide in 1,2-dichloroethane initially at −23 °C and then at ambient temperature for 13 h. Peracid oxidation[8] [MCPBA (1.2 equiv), $NaHCO_3$ (1.5 equiv), $CH_2Cl_2$, −23 °C, 45 min] of the corresponding silyl dienol ether followed by treatment with 3.0 equiv of a 1.0 M solution of tetrabutylammonium fluoride in tetrahydrofuran for 1 h at −23 °C provided, in 50% overall yield from **9**, tetracyclic $\alpha$-hydroxy ketone **10**. Base-catalyzed tautomerism of **10** into **11**, mp 227–230 °C, was realized in 75% yield by treatment of a 0.02 M solution of **10** in methanol with 1.2 equiv of finely powdered potassium carbonate. Epoxidation [MCPBA, $CH_2Cl_2$, 0 °C (35 min) → room temperature (2.5 h)] of tetracyclic olefin **11** gave rise to crystalline



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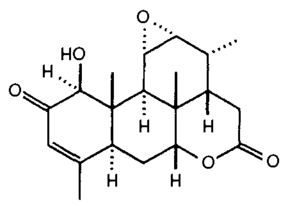

12

epoxide **12**, mp 217.5–219.5 °C, as the sole product in 80% yield. Acid-catalyzed opening of epoxide **12** with 23% perchloric acid in tetrahydrofuran–methylene chloride, 15:1, at ambient temperature (36 h) produced in 76% yield synthetic (±)-klaineanone (**1**), mp 234–239 °C, identical with an authentic sample by 500-MHz $^1H$ NMR, IR, and silica gel TLC analysis in several solvent systems.[9] Completion of the synthesis of **1** confirms the structural assignment put forth by Polonsky and Zylber[7] for klaineanone nearly 25 years ago. Since that time, the structure of **1** has rested upon limited spectroscopic data and its conversion into quassin. The synthesis of racemic klaineanone is noteworthy in that (a) the transformation of tetracyclic ketone **2** into **1** requires no protecting groups, (b) the ring A 1$\beta$-hydroxy-2-oxo-$\Delta^{3,4}$ olefin functionality is surprisingly stable (cf. **12** → **1**) contrary to reports in the literature, and (c) the base-catalyzed tautomerism of $\alpha$-hydroxy ketone **10** into **11** proceeds with remarkable efficiency despite the opportunity for numerous undesired side products.

**Acknowledgment.** Generous support for this work from the National Cancer Institute, National Institutes of Health (Grant CA 28865), is gratefully acknowledged. The 500 MHz NMR instrument (Bruker 500) used in the above studies was purchased in part with funds provided by the National Institutes of Health (RR 02858) and the National Science Foundation (CHE 85-13707). We are grateful to Dr. Zev Lidert (Rohm and Haas) and Dr. Judith Polonsky (Gif-Sur-Yvette) for samples of natural klaineanone.

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(9) All new crystalline compounds have been fully characterized by IR, $^1H$ NMR, and combustion analysis.

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## Spin Echo NMR of Cobalt Zeolite Catalysts: Control of Particle Size and Structure[†]

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Nuclear magnetic resonance (NMR) spectroscopy has recently become a powerful tool in the study of solid zeolite catalysts via magic angle spinning (MAS) procedures.[1] The ordering of $Si^{4+}$ and $Al^{3+}$ in zeolite frameworks and the effects of dealumination

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[†] We thank the Office of Basic Energy Research, Division of Chemical Sciences of the Department of Energy for support of this research.

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[§] Department of Chemical Engineering and Institute of Materials Science.

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**Table I.** SENMR Data for Cobalt Complexes

| sample | treatment | SENMR,[a] frequency |
|---|---|---|
| 1. Co, bulk metal, fcc[b] | *d* | 217.2 |
| 2. Co, bulk metal, hcp[c] | *d* | 228 |
| 3. $Co_2(CO)_8$ | *d* | *e* |
| 4. $Co_2(CO)_8$, NaX | sublimed | *e* |
| 5. $Co_2(CO)_8$, NaX | sublimed, Ar plasma, 3 W | *e* |
| 6. $Co_2(CO)_8$, NaX | sublimed, Ar plasma, 3 W, 120 °C | *e* |
| 7. $Co_2(CO)_8$, NaX | sublimed, Ar plasma, 3 W, >160 °C | 219 ± 1 |
| 8. $Co_2(CO)_8$, NaX | sublimed, 120 °C | 219 ± 1 |
| 9. $Co_2(CO)_8$, NaX | sublimed, Ar plasma, 10 W | 219 ± 1 |
| 10. $(C_5H_5)_2Fe$, $Co_2(CO)_8$, NaX | sublimed, Ar plasma, 3 W | 228 ± 3 |
| 11. $CoFe_9$ | *d* | 275 ± 3 |

[a] Collected at 4.2K, values in MHz. [b] fcc = face-centered cubic. [c] hcp = hexagonal close-packed. [d] No treatment. [e] No signal observed.

have been unraveled with MASNMR. Paramagnetic species in zeolites have been studied with electron spin resonance[2,3] and electron spin echo procedures.[3] We report here the use of spin echo NMR (SENMR) experiments carried out at low radio frequency (RF) power on the $^{59}Co$ ferromagnetic particles with zero external magnetic field. Only nuclei in domain walls[4] are observed for such experiments.

SENMR, a two pulse technique, has been demonstrated to be especially useful in the study of the hyperfine field distributions in magnetically ordered systems.[5] The hyperfine field in transition-metal systems, such as Co, arises from the various exchange couplings between the d electrons and the s electrons (both inner shell and conduction band). As a consequence, the hyperfine field is very sensitive to the electronic structure and near neighbor atomic environment.[6] SENMR, therefore, can be utilized to study the nature of small ferromagnetic particles which are contained in catalyst materials. We note that Murty et al.[7] have used a continuous wave (cw) NMR technique to measure the $^{59}Co$ hyperfine fields which characterize Co/ZSM-5 and $Co/ThO_2$/ZSM-5 catalysts. Their synthetic procedures led to a variety of materials with different structural properties on the surface of the zeolites.

In this work, we shall show that the desired size and structure of cobalt particles in zeolites can be obtained and that coadsorption of organometallics in zeolite pores activated in a microwave discharge[8] can control the structure of the resultant metal particles. In addition, a new alloy of iron and cobalt has been prepared and characterized with SENMR methods.

Cobalt particles were prepared by adsorbing $Co_2(CO)_8$ into the supercages of dehydrated NaX zeolite, then flowing argon over the zeolite, and inducing a microwave plasma at 3 W total power. Samples were transported into a drybox and loaded into polyethylene cells for SENMR experiments. The SENMR spectrometer consisted of a commercially available Matec Model 7700 pulse modulator and receiver (main frame), with a matching Matec Model 765 RF pulsed oscillator plug-in (90–300 MHz at 500 W). In addition, the resonance frequency was calibrated with a Hewlett Packard Model 608F signal generator and Fluke Model 1953A frequency counter, while data acquisition was carried out with a Biomation Model 805 transient recorder and Nicolet Model 1072 time average computer. Operation at liquid helium temperatures was made possible with a conventional glass double Dewar system. Two equal 120° pulses with lengths of 2 μs and a separation of 20 μs were used to obtain the spectra. Additional details concerning the pulsed NMR apparatus, single coil arrangement, data acquisition procedure, and spectra analysis can be found elsewhere.[9]

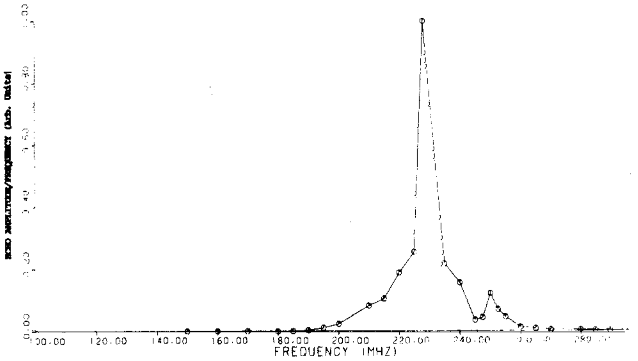

**Figure 1.** $^{59}Co$ spin echo NMR amplitude divided by frequency in arbitrary units versus resonance frequency in MHz obtained at 4.2 K for coadsorbed $Co_2(CO)_8$ and $Fe_2(CO)_9$ in zeolite NaX.

SENMR data for several cobalt standard complexes, cobalt zeolites,[10] cobalt–iron alloys, and mixed cobalt–iron zeolite samples are given in Table I. Note that face-centered cubic (fcc) bulk metallic cobalt, which is the thermodynamically favored form of cobalt, has a signal at 217.2 MHz, whereas the hexagonal close-packed (hcp) cobalt signal occurs at 228 MHz.[11] Different cobalt structures are, therefore, identified by measuring the spin echo signal at various frequencies.

As expected, the $Co_2(CO)_8$ cluster complex shows no SENMR signal due to its molecular nature. The $Co_2(CO)_8$ complex sublimed into NaX zeolite also shows no signal. When $Co_2(CO)_8$ in NaX zeolite is exposed to an argon plasma, there is still no signal observed in the SENMR experiment, even when a signal for cobalt is observed by ferromagnetic resonance (FMR) methods[8,12] for this sample. The FMR signal at $g = 2.18$ is indicative of cobalt in the zero oxidation state, and the temperature dependence of the FMR signal is indicative of superparamagnetic cobalt particles.[8,12,13] The absence of an SENMR signal for this sample is in agreement with a single domain species. Transmission electron microscopy, FMR,[8,12] and chemisorption[12] studies as well as these SENMR studies suggest that the cobalt particles here are on the order of 5 Å.

These same cobalt particles when heated to 120 °C do not show a change in FMR and SENMR characteristics suggesting that the particles are stable to at least 120 °C. On heating to 160 °C a signal at 219 MHz indicative of fcc Co is observed.

When cobalt particles are prepared via *thermal* decomposition of $Co_2(CO)_8$ at 120 °C, the SENMR data show that fcc cobalt and *not* superparamagnetic cobalt particles are being formed. These experiments clearly show that the plasma and thermal routes lead to quite different cobalt particles. Note that FMR experiments only allow the determination of relative particle sizes (larger sizes for thermal than plasma activation).

Treatment of $Co_2(CO)_8$ trapped in NaX with microwave plasmas at higher power (10 W) leads to formation of fcc cobalt as expected. The larger the power used in the plasma treatment the greater the degree of sintering and aggregation.[8,12,13]

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If ferrocene is codeposited with $Co_2(CO)_8$ in NaX and a 3W plasma treatment is applied a broad SENMR signal at 228 MHz indicative of hcp cobalt is observed. Thermal treatment of similar samples yields fcc cobalt particles. These data suggest that not only does the microwave plasma route affect the type of particles produced but that coadsorption procedures also influence the structure of the metal particle that is formed.

Further evidence of the usefulness of coadsorption methods come from studies of coadsorbed $Co_2(CO)_8$ and $Fe_2(CO)_9$. The SENMR spectrum of these two metal carbonyls in zeolite NaX after microwave discharge decomposition of the carbonyls is shown in Figure 1. The signal at 228 MHz is due to hcp Co, and the signal at 250 MHz is assigned to a Co (5 atom% Fe) alloy. The relaxation time of this alloy is markedly different than all other samples we have studied. These data suggest that new alloys can be prepared by coadsorption of metal carbonyls into zeolites followed by microwave discharge decomposition.

The superparamagnetic cobalt, thermally produced fcc cobalt, and coadsorbed hcp cobalt particles show significant differences in their ability to crack, isomerize, and hydrogenate cyclopropane and such will be the focus of another report.[13] Most importantly, we have shown here that the SENMR method is a very sensitive probe of relative metal particle size and of structural parameters which are difficult to determine for cobalt by other methods such as STEM, X-ray diffraction, Mössbauer spectroscopy, and ferromagnetic resonance. In addition, we have realized that synthetic modifications of plasma techniques for catalyst preparation can yield unique metal particles. Alloys and anchored[14] bimetallic complexes are now under investigation in our laboratory[15] as is the use of SENMR in heterogeneous catalysis.

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## Ene Diimidazoles: Ligands for Biomimetic Chemistry

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The preparation of model compounds related to nonheme metalloproteins has attracted much recent attention.[1-8] In an effort to duplicate the juxtapositions of ligands for iron and copper in biomolecules, several types of multidentate ligands have been prepared. The tridentate ligands such as tris(imidazolyl)phosphine,[2] tris(imidazolyl)methane,[1] and tris(pyrazolyl)borate[9] have been used in elegant model compounds for carbonic anhydrase[1,2] and hemerythrin,[3,4,10a] the latter illustrated below. Further reduction in the number of degrees of freedom in these complex ligands has been provided by connecting the two tripod ligands through covalent chain to produce excellent model compounds[5-7] for hemocyanine.[10b,11]

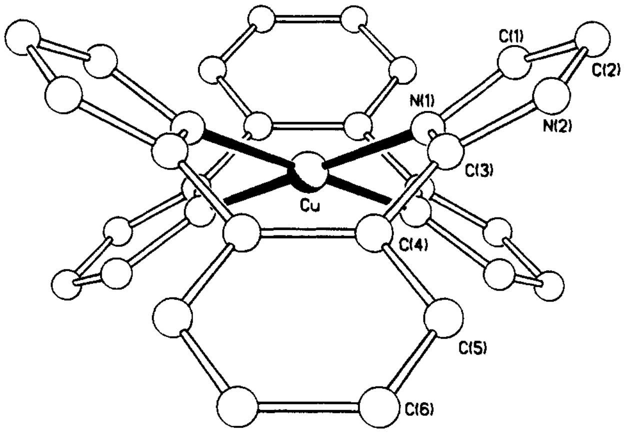
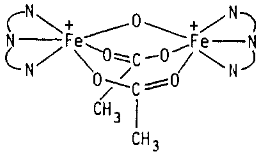
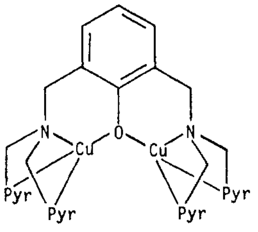


**Figure 1.** Cation structure for **2**: Cu-N(1), 1.996 (4); N(1)-C(1), 1.368 (6); C(1)-C(2), 1.349 (7); C(2)-N(2), 1.372 (7); C(3)-C(4), 1.469 (7) Å; N(1)-Cu-N(1a), 180; N(1)-Cu-N(1b), 90.6 (2); N(1)-Cu-N(1c), 89.4 (2)°. Two of four molecules of $H_2O$ (not shown) form long axial bonds to Cu (Cu-O(4) = 2.624 (3) Å). A different view of the cation drawn with 40% thermal ellipsoids is available as Supplementary Material.





Hemocyanin Model Compound[5]

We present a method for further reducing the degrees of freedom and increasing rigidity of multidentate ligands by in-

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