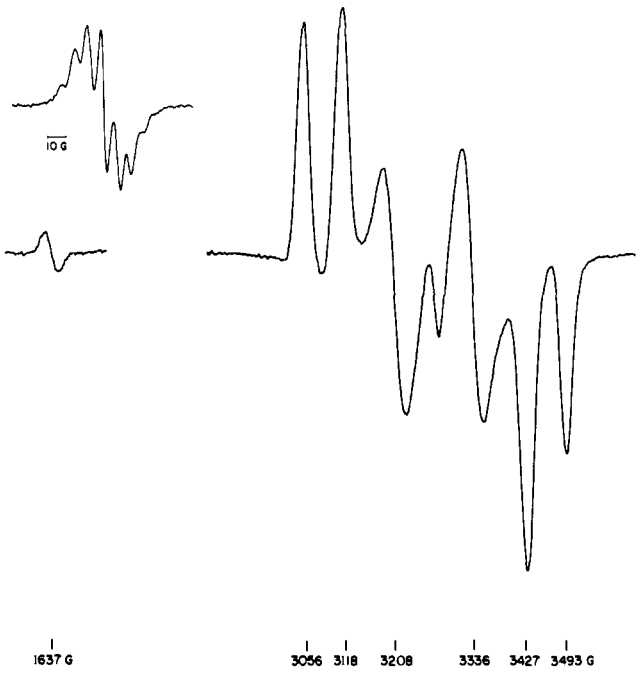

Figure 1. ESR spectrum of **1** observed after sensitized photolysis (λ 315–415 nm) of **3** in MTHF containing 0.27 M Ph_2CO at 10 K. The weak central line near 3270 G is assigned to a double-quantum transition based on its microwave power dependence.[18] Inset: hyperfine structure of the $\Delta m_s = 2$ transition (1637 G).

nickel peroxide[14] at −78 °C in CH_2Cl_2 afforded **3** as an unstable white solid.[15]

The ^1H NMR (CD_2Cl_2) spectrum of **3** at −75 °C exhibited singlets at δ 5.48 and 4.75 in a 1:2 ratio. These decreased with a 1 h half-life at —60 °C, with an accompanying increase in numerous signals associated with as yet uncharacterized products.[16] The ^{13}C NMR (CD_2Cl_2, −75 °C) signals of **3** at δ 157.7, 97.0, and 82.9 and the UV transition at 334 nm (MTHF) were also found to decay in this temperature range.

When a frozen solution of diazene **3** in 2-methyltetrahydrofuran (MTHF) is irradiated (λ 315–415 nm)[17] in the presence or absence of benzophenone at 10 or 77 K, the ESR spectrum of Figure 1 is obtained. The spectrum displays zero-field splitting parameters $|D/(hc)| = 0.0205$ cm^{-1} and $|E/(hc)| = 0.0028$ cm^{-1}. This D value is completely consistent with structure **1** on the basis of the spectra of a variety of other delocalized biradicals[2b] and a calculated value $|D/(hc)| = 0.026$ cm^{-1}, obtained by using a previously described semiempirical method.[2b] The half-field transition (1637 G, Figure 1) shows a seven-line hyperfine splitting of 6–7 G,[19] indicating that the two sets of nonequivalent protons in **1** have similar hyperfine coupling constants. Although triplet **1** decomposes slowly at temperatures near 77 K, a preliminary Curie plot was linear, consistent with a triplet ground state.

Sensitized photolysis (λ 315–415 nm) of **3** in MTHF at 77 K produces a faint orange color. In addition, irradiation of triplet **1** (10 K) at λ 500 ± 15 nm causes irreversible destruction of the ESR signal within seconds, indicating that triplet **1** has a strong electronic transition in this region.

Identification of the thermal and photochemical products from **3** and trapping and spectroscopic studies of **1** are in progress.

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Two-Dimensional ^1H–^{113}Cd Chemical-Shift Correlation Maps by ^1H-Detected Multiple-Quantum NMR in Metal Complexes and Metalloproteins

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The ^{113}Cd nucleus has received increasing attention as a spin $^1/_2$ NMR probe for the study of the structural and/or functional role of metal(s) in metalloproteins.[4-6] This is so in spite of the difficulties of low sensitivity, 1/100 that of protons when fully enriched, and comparatively long T_1's, due to the absence of directly bonded protons, which limit the rate of data accumulation. Furthermore, in certain motional regimes the negative gyromagnetic ratio of ^{113}Cd can also lead to nulling of signals under conditions of partial NOE. If spin coupling exists to a proton, then magnetization transfer experiments, such as INEPT or DEPT, where the shorter T_1 of the coupled proton determines acquisition rate, theoretically offer enhancements of (γ_H/γ_{Cd}) over direct Cd detection.[7,8] If, however, several protons are coupled to the nucleus one wishes to observe with comparable coupling constants, or if these protons are coupled to other protons, this enhancement is significantly reduced.[9]

Recently it has been shown that through proton indirect detection of ^{15}N via heteronuclear multiquantum coherences (HMQC's), enhancements on the order of $(\gamma_H/\gamma_N)^3$, 10^3-fold, can be achieved as theoretically predicted.[10] This approach has been applied to the enhancement of rare and low γ nuclei using direct one-bond ^1H–^{15}N (or ^{13}C) couplings (90 Hz or greater).[10-15] It can, in principle, be used with longer range couplings. This is of importance where no directly bonded proton is present, which is generally the situation for metal nuclei in organometallic complexes and metalloproteins. A pulse scheme related to that

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(15) The compound decomposed explosively on one occasion but with insufficient force to break the flask.
(16) Photolysis of these products does not produce a triplet ESR signal.
(17) Light from a 1000-W Xe arc lamp was filtered through water, Pyrex, and Corning CS 1-75 and 7-54 filters ($315 \le \lambda \le 415$ nm; $\lambda \ge 670$ nm). Sensitized photolysis for 1 min produces a nearly photostationary concentration of biradical **1** (Figure 1), which is about 10 times that obtained upon direct photolysis.
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(2) Yale University.
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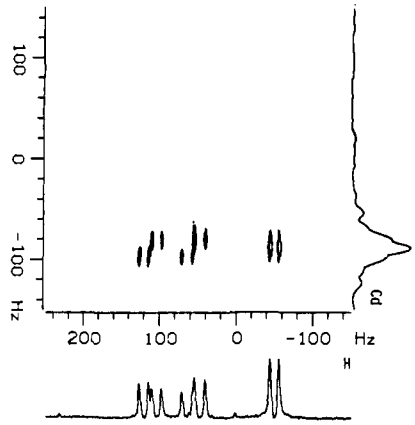

Figure 1. ^{1}H–^{113}Cd 2D shift correlation map with proton and ^{113}Cd projections. Complete data set was acquired in ~3 min by using ^{1}H-detected HMQC's with a 0.4-mL sample of 5 mM ^{113}CdEDTA in D_2O pD 9. Zero frequencies correspond to rf carrier frequencies at 2.89 ppm for ^{1}H and 84.7 ppm relative to $CdClO_4$ for ^{113}Cd. The preparation delay in the first pulse sequence in the text was optimized for a 12-Hz coupling.

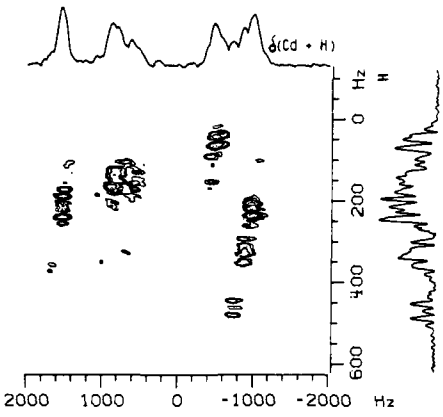

Figure 2. ^{1}H zero-quantum coherence (^{113}Cd + ^{1}H) 2D correlation diagram with projections for $^{113}Cd_6$–metallothionein from *Scylla serrata*. The total accumulation time was 10 h on 0.4 mL of a 3 mM sample. Zero positions correspond to rf carrier frequencies set at 2.47 ppm for protons and 640.2 ppm from $CdClO_4$ for the zero-quantum axis. Cd chemical shift can readily be deduced since (^{113}Cd + ^{1}H) and ^{1}H can be determined from the projections for a given cross peak. Offsets used in this calculation are relative to rf frequencies. The preparation delay was optimized for a 50-Hz coupling in the second pulse sequence in the text.

used in this study has been successfully employed for the indirect detection of ^{199}Hg in complexes with very large long-range couplings, $^{3}J_{H\text{-}Hg} \approx 250$–$350$ Hz.[16] Generally, however, there will be multiple, comparable heteronuclear couplings with, in addition, extensive homonuclear couplings of these protons. Such is the case for the Cd complexes in this study and this situation is very susceptible to the generation of multispin coherences of higher order than desired, a phenomenon that results in the reduction of signal enhancement with magnetization transfer pulse methods.[9] However, in the proton-detected HMQC experiment, even if there are effective losses in the multispin coherence period, the benefits from the detection of a nucleus at higher frequency and with a larger magnetic moment more than compensate for such losses.

In this communication we demonstrate the application and advantages of using the ^{1}H-detected HMQC for metals with multiple long-range couplings to protons in two different complexes. The first is the ^{113}Cd EDTA complex and the second is a macromolecular system, Cd_6–metallothionein. Figure 1 shows the 2D correlation map of the ^{1}H-detected ^{1}H–^{113}Cd MQC experiment for 5 mM ^{113}Cd EDTA in D_2O at pD 9. The total time for 2D data accumulation was about 3 min using 0.4 mL of solution in a 5-mm tube.[17] The pulse sequence used,

$$[90_x°(^{1}H)\text{-}1/4J\text{-}180_x°(^{1}H,^{113}Cd)\text{-}1/4J\text{-}90_{-x}°(^{1}H)90_{\varphi}°$$
$$(^{113}Cd)\text{-}t_1/2\text{-}180_x°(^{1}H)\text{-}t_1/2\text{-}90_x°(^{113}Cd)\text{-}1/2J\text{-}Acq_{\varphi}(^{1}H)]$$

has been previously reported[11] and employs refocusing pulses so that a direct chemical shift correlation is produced. The sensitivity for the detection of the Cd resonance in this experiment is at least100-fold greater than what we achieved via direct detection of Cd. An important factor in the ultimate enhancement is the shorter ^{1}H T_1, <0.5 s, compared to the ^{113}Cd T_1, ~20 s.[18] The multiplicity of cross peaks in the 2D map can be rationalized by analyzing the possible multiple-quantum transitions in a ^{1}H–^{113}Cd energy level diagram. The factors contributing to the enhancement in this case would be equally applicable to other spin $^1/_2$ metal nuclei such as Se, Si, Rh, Ag, Sn, Pt, Hg, and Pb, making metal NMR studies of complexes of these nuclei much more accessible.

Having demonstrated the applicability of the HMQC method in a small Cd complex, we wish to report on the first application of this method for the indirect detection of ^{113}Cd in a complex macromolecular system, metallothionein, under extensive study in one of our laboratories.[4,6] The protein complex, $^{113}Cd_6$–metallothionein (MW ~6000) was isolated from ^{113}Cd-injected mud crabs (*Scylla serrata*).[19] Previous studies using ^{113}Cd NMR have examined and elucidated the unusual structures for the Cd–thiolate sites in this protein[19] and indicated extensive coupling between Cd and the cysteine β protons in the protein. The objective of these studies is to completely elucidate the solution structure of this protein and others in its class. In addition to providing significant enhancement in sensitivity, the proton-detected HMQC method enables one to uniquely identify all of the ^{113}Cd-coupled cysteine β protons in each of the multiple Cd–Cys_4 sites in the primary structure of this protein. The assignment of these cysteine protons to specific residues in the protein sequence can then be achieved by conventional homonuclear 2D ^{1}H NMR methods.[20,21] Figure 2 shows the 2D map using the ^{1}H–^{113}Cd HMQC experiment which directly confirms this coupling. The pulse sequence used in this experiment

$$[90_x°(^{1}H)\text{-}1/2J\text{-}90_{\varphi}°(^{113}Cd)\text{-}t_1\text{-}90_x°(^{113}Cd)\text{-}Acq_{\varphi}(^{1}H)]^{12,15}$$

omits the refocusing pulses used in the previous example to reduce loss of signal intensity arising from multiple couplings between protons and ^{113}Cd's. As a result, the correlation is ^{1}H vs. (^{113}Cd + ^{1}H). Since the proton range is much smaller than the Cd range, the maps have similar appearance to a direct correlation experiment. The 2D plot clearly elucidates the relationships between specific cysteine β-proton resonances and specific Cd sites.[22] Further, since in this experiment all ^{1}H resonances not coupled to Cd have their signals canceled, the results allow us to easily identify all the cysteine β-CH_2's protons some of which are not resolved in the normal 1D or even completely in the 2D proton spectrum, e.g., the resonances between 450 and 500 Hz in the ^{1}H dimension. These data took 10 h to acquire on 0.4-mL samples at ~3 mM, giving excellent signal to noise. To obtain these results with more conventional Cd detected 2D correlation spectroscopy would, in practice, not be feasible. These data are currently being

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(17) Spectra were obtained on a modified NT-300WB spectrometer (66 MHz, ^{113}Cd) using a 5-mm proton probe fit with an additional coil and insert for radiation from 20 to 80 MHz and a separate X nucleus rf channel controlled by the spectrometer pulse programmer. (Live, D. H.; Cowburn, D., unpublished results). The ^{1}H 90° pulse was 8 μs and the ^{113}Cd 90° pulse 140 μs.

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(22) These data can be converted to a direct ^{1}H–^{113}Cd chemical shift correlation map by alternate computational manipulations.[15] For greater accuracy in determining the ^{113}Cd resonance positions, it is advantageous to examine individual slices in the 2D plot.

integrated with results from the ongoing 2D ^1H NMR studies.

In conclusion, it is clear that the ^1H-detected HMQC method provides a valuable approach to exploring the NMR of spin $^1/_2$ metals where resolvable coupling to proton is present. In complex cases the dispersion in two dimensions helps in resolving both ^1H and metal spectra, and by appropriately adjusting the preparation delay in the pulse sequence, sites interacting with different couplings can be selected providing a further means of editing the spectrum.

Acknowledgment. This research was supported by grants from the National Institutes of Health AM 18778 (I.M.A.) and AM 20357 (D.C.) and by AHA (82-1099). We thank Dr. Donald G. Davis for valuable discussions.

Registry No. ^{113}Cd, 14336-66-4; Cd-EDTA, 16950-14-4.

Total Synthesis of (−)-Tirandamycin A[1]

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The unusual skeletal array contained in the antibiotic tirandamycin A (**1**)[3] has stimulated considerable effort toward its construction. Thus far, these synthetic endeavors have focused on the preparation of tirandamycic acid,[4] a degradation product of **1**.[5] We now wish to describe a synthesis of the antibiotic itself which utilizes the simple concept that the unsaturated lactone **2** should afford the bicyclic ketal **3** upon addition of methyllithium followed by acid treatment. A threo- and "Cram"-selective aldol condensation involving the vinylogous urethane **4** expedites the formulation of this lactone.[6]

Vinylogous urethane **4**[7] (2.0 equiv) was deprotonated (LDA/THF) and treated with the aldehyde **5**[8] (1.0 equiv) to afford the lactone **6**,[9] mp 150 °C, in 75% yield after chromatography and crystallization (Scheme I). The thiomethyl group, having played its pivotal role as the agency of threo and "Cram" stereoselection,[9] was then desulfurized (Bu_3SnH/AIBN)[10] to give the lactone **7**, mp 93 °C, after chromatography and crystallization in 90% yield. Compound **7** was then converted into lactone **2** in the following manner. Reductive methylation of **7** (1.0 equiv) was accomplished by its addition to a solution of lithium (5.0 equiv) in NH_3 until the blue color was discharged.[11] THF was then added to the mixture to give a 0.25 M suspension based on **7**. The ammonia was then removed (0.2 torr) and the resulting mixture treated with methyl iodide (6.0 equiv). Filtration of this mixture through silica gel gave an oil. Elimination of the pyrrolidine residue was carried out by the addition of *m*-CPBA (1.1 equiv) to a mixture of this oil (1.0 equiv) and $NaHCO_3$ (1.5 equiv), in CH_2Cl_2, followed after 2 h by DBU (1.2 equiv). The lactone **2**, mp 38 °C, was isolated by chromatography in 70% yield from **7**.

We were gratified at this stage to discover that reaction of **2** (1.0 equiv) with CH_3Li (1.0 equiv) followed by standard workup and treatment of the resultant oil (0.05 M in THF) with hydrochloric acid (1.5 equiv, 0.7 M) gave the bicyclic ketal **3**, mp 54 °C, in 93% yield.[12] As luck would have it, however, our plan to oxidize **3** directly into the aldehyde enone **8** by using chromium trioxide 3,5-dimethylpyrazole,[13] while successful in terms of chemical yield, caused some stereochemical corruption of the product.[14] Hence, we took a somewhat longer route to a similar end.

Epoxidation of **3** (1.0 equiv) with *m*-CPBA (1.05 equiv) in CH_2Cl_2 gave a single epoxide **9**, mp 137 °C. Ring opening of **9** (1.0 equiv) with PhSeNa (10.0 equiv) in ethanol followed by chromatography gave the selenide **10**, mp 104 °C.[15] Finally, elimination of the selenide residue of **10** (1.0 equiv) by oxidation with *m*-CPBA (1.05 equiv) in CH_2Cl_2 containing $NaHCO_3$ (2.0 equiv) followed by chromatography and crystallization gave the diol olefin **11**, mp 124 °C. In this manner, a 95% overall yield for the transformation of **3** into **11** was realized.

At this juncture we commenced elongation of the side chain of **11** into the unsaturated ester enone **12**. Thus, **11** (1.0 equiv) in CH_2Cl_2 (0.5 M) was reacted with PCC (7.0 equiv) to afford the aldehyde enone **8** contaminated with approximately 20% of the corresponding aldehyde containing the unrearranged tertiary allylic alcohol residue. Under these reaction conditions, complete conversion of **11** into **8** was not possible without epimerization of the methyl group adjacent to the aldehyde moiety.[16] As a result, the mixture containing **8** (1.0 equiv) was reacted with (carbethoxyethylidene)triphenylphosphorane (5.0 equiv) in benzene (0.4 M) to yield the corresponding unsaturated ester **12**, together with its unrearranged tertiary allylic alcohol analogue.[17] These esters were readily separable by chromatography, and, thus, that ester containing the tertiary allylic alcohol residue was subsequently treated with PCC in CH_2Cl_2 to afford **12**. In this fashion, **12** (oil), as a single compound, was obtained from **11** in 89% yield.

The epoxide residue was then introduced by treatment of the enone portion of **12** (1.0 equiv) with *t*-BuO_2H (3.0 equiv) and DBU (3.0 equiv) in THF solution at 22 °C to give compound **13**, mp 130–131 °C, in 95% yield.[18] Both the ester and ketone residues of **13** (1.0 equiv) were then reduced with DiBAL-H (3.0 equiv) to afford, in 90% yield, the diol epoxide **14**, oil.[19] PCC (5.0 equiv) oxidation of **14** (1.0 equiv) gave the unsaturated

(1) We dedicate this manuscript to the memory of Professor R. V. Stevens.
(2) Merck and Co. postdoctorate fellow.
(3) See: Reusser, F. In "Antibiotics: Mechanism of Action of Antibacterial Agents"; Hahn, F. E., Ed.; Springer-Verlag: New York, 1979; Vol. V, Part I, p 361 and references cited therein.
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(7) The vinylogous urethane **4** was prepared by thiomethylation of methyl acetoacetate followed by reaction with pyrrolidine. Compound **4**, bp 125–130 °C (3×10^{-6} torr) as well as all other new compounds cited in this manuscript gave satisfactory ^1H NMR (300 and 400 MHz), ^{13}C NMR, IR, and mass spectra. Those intermediates that were stable (e.g., **4**, **2**, **3**, **11**, **13**, and **21**) gave correct elemental analyses.
(8) This aldehyde was first described by Nagaoka et al. (Nagaoka, H.; Kishi, Y. *Tetrahedron* **1981**, *37*, 3873) who obtained this material by oxidation of its corresponding alcohol $[\alpha]_D$ −22.8° (*c* 3.73, $CHCl_3$) under Swern conditions. The aldehyde **5**, $[\alpha]_D$ −60.5° (*c* 1.46, CH_2Cl_2), in these laboratories, was also obtained by Swern oxidation of the same alcohol $[\alpha]_D$ −23.2° (*c* 1.28, $CHCl_3$). The latter substance, however, was obtained by a somewhat shorter route than that previously described.
(9) The mechanism of this interesting threo- and "Cram"-selective aldol condensation reaction has now been studied in some detail and will be published in the near future.
(10) For a leading reference, see: McIntosh, J. M.; Schram C. K. *Can. J. Chem.* **1977**, *55*, 3755.
(11) Under these reaction conditions, between 80% and 90% of 1 equiv of **7** could be added before the reaction color was discharged.
(12) These conditions are similar to those given, for a different rearrangement, in ref 4b.
(13) Salmond, W. G.; Barta, M. A.; Havens, J. L. *J. Org. Chem.* **1978**, *43*, 2057.
(14) This oxidation caused epimerization of the methyl group adjacent to the aldehyde residue under a variety of reaction conditions.
(15) Sharpless, K. B.; Lauer, R. F. *J. Am. Chem. Soc.* **1973**, *95*, 2697.
(16) Dauben W. G.; Michno, D. M. *J. Org. Chem.* **1977**, *42*, 682. Buffered PCC (NaOAc) produces a mixture of methyl group epimers and other products.
(17) These homologation conditions are those employed by Ireland (ref 4a).
(18) The usual epoxidation conditions, as described by Yang et al. (Yang, N. C.; Finnegan, R. A. *J. Am. Chem. Soc.* **1958**, *80*, 5845), which use Triton B as the base, were not effective for this epoxidation.
(19) This reduction yields a single compound with the assigned stereochemistry based on its ^1H NMR spectrum.

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