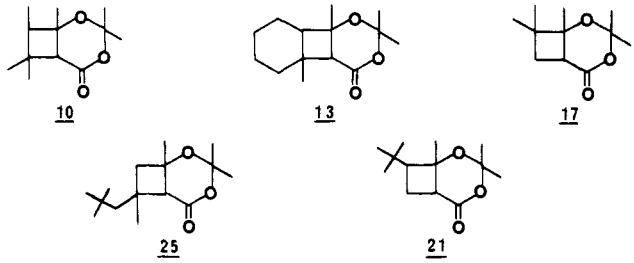
Recent disclosures from these laboratories have shown that formyl acetone (and other acyclic α-formyl ketones) undergo smooth photoaddition to alkenes *exclusively* through that hydrogen-bonded enol tautomer enolized toward the aldehyde carbon.[1a,7] It is of interest that in the present case the keto aldehyde intermediates (e.g., **5**) and thus the final cyclohexenones (e.g., **6**) are the same as would have arisen had the *alternate enol tautomer* of formyl acetone been involved in the initial photocycloaddition. It is also worth noting that the sense of the reaction is to yield differently substituted products from those obtained with other four-carbon cyclohexenone annelation units such as methyl vinyl ketone (Robinson annelation),[8] 1-methoxy-3-trimethylsiloxybutadiene (Diels–Alder),[9] and formylacetone (photoannelation),[1a,7] and as such represents a complementary process.

The results obtained from the reaction of **1** with several unsymmetrical alkenes indicate a remarkable range of regioselectivities in the photoaddition step. For instance trisubstituted alkenes **9** and **12** lead to a preponderence of the head–head regioisomers (**10** and **13** respectively), while 1,1-disubstituted alkenes such as **16** and **24** favor either head–tail (**17**) or head–head (**25**) regiochemistry depending on the degree of steric bulk of the alkene substituents. The single monosubstituted alkene studied, 3,3-dimethylbutene (**20**), favors the head–tail orientation **21**. A rationale for this broad spectrum of regioselectivities is unclear at this time.[10] The complex mixture of steric and electronic factors which governs regiochemical preferences in photocycloadditions seems to be particularly sensitive to substitution at the β position of the unsaturated carbonyl photopartner. Further examination of this rather subtle point is planned.



Although the full scope of this interesting process remains to be established, several further observations are pertinent. Smooth photoaddition has been obtained with oxygenated alkenes such as ethyl vinyl ether and isopropenylacetate as well as with cyclopentenes and cyclobutenes. Moreover, the 6-ethyl homologue of **1**, prepared by γ-alkylation of **1** (LDA, THF–HMPA, CH_3I),[27] is an equally active photopartner.

In summary, it is seen that alkenes can be converted into 5- and 6-substituted cyclohexenones in three laboratory steps with good efficiency and regioselectivity. The sense of the initial photoaddition is to provide photochemical access to that formylacetone enol tautomer which is not available from formylacetone itself (a reactivity "umpolung"), and which thus complements existing methods.

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(4) Typically the alkene and **1** were present in a 3:1 molar ratio, although ratios as low as 1.5:1 have been employed. The [**1**] was generally 0.5–2.0% in hexane, methylene chloride, or acetonitrile, or mixtures thereof, with irradition times of 12–24 h.

(5) Typically the IR spectra of photoproducts showed a strong absorption at ~1740 cm^{-1} in contrast to two strong absorptions at 1715 and 1640 cm^{-1} for the starting material **1**. In addition the NMR resonances for the cyclobutane proton adjacent to the carbonyl appeared in the region δ 2.6–2.9 with expected multiplicities, while remaining cyclobutane resonances appeared at δ 1.9–2.5. The stereochemistry of the cyclobutane–lactone ring fusion was assumed to be cis in all cases by analogy to related literature reports for β-substituted 4-oxaenones. See Margaretha, P. *Helv. Chim. Acta.* **1974,** *57,* 2237.

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(26) The structure of cyclohexenone **26** was assigned on the basis of the following spectral evidence: IR (film) 1680 cm^{-1}; NMR ($CDCl_3$) δ 0.97 (s, 9 H), 1.02 (s, 3 H), 1.16 (s, 2 H), 1.40–2.42 (complex, 4 H), 5.96 (m, 1 H), 6.80 (m, 1 H). In addition conversion of the photoproduct **25** into the symmetrical 5-methyl-5-neopentylcyclohexane-1,3-dione (CH_3OH–H_2O; H_2SO_4, 70 °C) provided ready spectral confirmation of the H–H substitution pattern of **25**: NMR ($CDCl_3$) δ 1.01 (s, 9 H), 1.08 (s, 3 H), (s, 2 H), 2.63 (s, 4 H), 3.33 (s, 2 H).

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NMR of Individual Sites in Protein Crystals. Magnetic Ordering Effects

Sir:

We report a new method for obtaining NMR spectra of individual sites in protein *crystals* which permits direct extraction of static, and in principle dynamic, molecular structural parameters.

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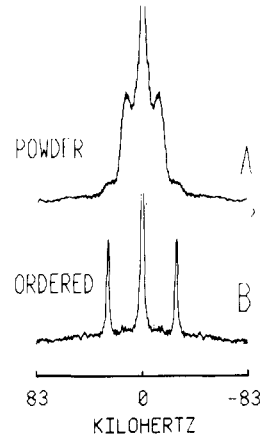

Figure 1. Deuterium Fourier transform NMR spectra obtained using the quadrupole echo pulse method at 55.3 MHz (corresponding to a magnetic field strength of ~8.5 T) of sperm whale (*Physeter catodon*) aquoferrimyoglobin microcrystals labeled as CD_3 at Met-55 and Met-131 at 21 ± 2 °C, pH 6.3. (a) Pelleted microcrystals, recycle time of 61 ms, 4K data points, $\tau_1 = \tau_2 = 61$ μs, 90° pulse widths of 7 μs, 245 839 scans, and a line broadening of 400 Hz due to exponential multiplication. (B) Microcrystals suspended in saturated ammonium sulfate solution (buffered to pH 6.3 with K_2HPO_4) and magnetically ordered at 8.5 T. Spectral conditions as in A except $\tau_1 = \tau_2 = 65$ μs and 176 685 scans.

Our technique involves determination of the electric quadrupole splitting ($\Delta\nu_Q$) of a specifically ^{2}H-labeled group in a *magnetically ordered* paramagnetic protein crystal. From $\Delta\nu_Q$ it is possible to determine the orientation of the appropriate C–D vector (or electric field gradient tensor principal axis) with respect to the magnetic field H_0. Similar information may be deduced from the NMR of any other quadrupolar nucleus (e.g., ^{14}N) or even a spin $I = 1/2$ nucleus, e.g., ^{13}C,[1] and represents a new method for obtaining high-resolution solid-state NMR spectra.

We have synthesized specifically deuterated sperm whale (*Physeter catodon*) myoglobin, labeled as C^2H_3 (50%) at Met-55 and Met-131. The method used was similar to that used previously,[2] except that we used mercaptoethanol as a demethylating agent.[3] A sample of ^{2}H-Met-labeled aquoferrimyoglobin (Fe^{III}–H_2O) was crystallized in the space group $P2_1$ from saturated ammonium sulfate weakly buffered to pH 6.3 with dipotassium hydrogen orthophosphate. The crystals were filtered free of excess medium, and ^{2}H NMR spectra at 8.5 T were recorded, using an 800-μL sample volume and a quadrupole-echo[4] pulse sequence with a 90° pulse width of 7 μs.

We show in Figure 1A a "powder" spectrum of aquoferrimyoglobin microcrystals. The microcrystals form a solid disordered mass after removal of saturated ammonium sulphate solution by filtration. The spectrum of Figure 1A may be attributed to two overlapping spin $I = 1$, $\eta \sim 0.15$ powder patterns having a quadrupole splitting ($\Delta\nu_Q$) of 31 kHz. We have not been able to obtain good spectral simulations of Figure 1A when using $\eta = 0$ asymmetry parameters, even when two overlapping absorptions having different $\Delta\nu_Q$ values are used. It thus appears that in the crystal the motions of the two methionine groups are similar and involve, in addition to fast methyl C_3 rotation, restricted torsional oscillations of the main C^α–C^γ chain resulting in nonzero asymmetry parameters. At low temperatures ($\lesssim -30$ °C), $\eta = 0.08$ spectra having $\Delta\nu_Q \sim 36$ kHz are obtained (unpublished results; see also ref 5). The narrow central component in Figure 1A arises from residual HO^2H.

By contrast to the "powder" spectrum of Figure 1A, a very narrow-line spectrum having $\Delta\nu_Q = 54$ kHz is obtained when the microcrystals of Figure 1A are resuspended in ^{2}H-depleted saturated ammonium sulfate (pH 6.3), Figure 1B. This spectrum has a $\Delta\nu_Q$ much greater than the 38 kHz expected[5] for methyl group rotation, and in fact must originate from a *magnetically ordered* sample of protein microcrystals. This is an unexpected result. Nevertheless, this interpretation is strongly supported by the results of Figure 2. Shown in Figure 2A is the 9.3-GHz continuous-wave electron spin resonance spectrum (at 12 K) of the powder sample of specifically deuterated metmyoglobin, and in Figure 2B the same sample after being magnetically ordered at 0.9 T for 15 min at 20 °C and then cooled to 6 K. The spectrum of Figure 2A obviously corresponds to a normal high-spin ferric iron powder pattern signal having $g_\perp = 5.95 \pm 0.05$ and $g_\parallel = 2.00 \pm 0.01$. It is assumed that the lowest doublet is $S_z = \pm 1/2$ with a zero-field splitting to the other spin doublets much greater than that of the microwave quanta.[6] The spectrum of Figure 2A is essentially identical with that of Hori.[7] In contrast, the spectrum of Figure 2B shows a very symmetric derivative absorption centered at a g value of 5.95, with only a very small component at a g value of 2.00. The spectrum of Figure 2B corresponds therefore to ferrimyoglobin molecules oriented with their maximum g value (~6) along the field direction, together with a very small contribution from less well-ordered material (at a g of 2). This $g = 2.00$ component is even smaller in a sample which has been oriented at 8.5 T and then frozen for ESR (data not shown). Although similar magnetic orientation of highly paramagnetic low molecular weight species has been observed previously[8] in ESR spectroscopy, it may at first seem surprising that the protein crystals are so well ordered. However, the couple on a particle is proportional to its mass, m. Thus, although M for metmyoglobin is ~18 000 Daltons, m is also very large (as is H_0^2 in the NMR experiment). Freezing experiments rule out motional narrowing of the quadrupole interaction by particle oscillation since sharp spectra of the same $\Delta\nu_Q$ are obtained on sample freezing, and in any case calculations indicate that such oscillations are far too slow to affect $\Delta\nu_Q$.

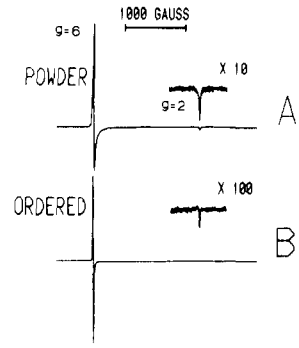

Figure 2. Electron spin resonance spectra of samples similar to those used in Figure 1. Spectra were recorded on a Varian E-4 instrument at 9.29 GHz. (A) Powder sample of aquoferrimyoglobin microcrystals, 12 K, 1.25-G modulation amplitude, 1-mW power level. (B) Sample as in Figure 1B, except magnetically ordered at 0.9 T at 20 °C and then frozen, sample temperature 6 K, 0.32-G modulation amplitude, 0.2-mW power level. The results of additional experiments (data not shown) indicate little saturation of these absorption spectra. The inset in A has a ×10 vertical expansion while that in B has a ×100 expansion.

The spectra of Figure 1 thus indicate that "pseudo-single-crystal" NMR spectra of paramagnetic molecules may be readily obtained by means of the magnetic ordering effect. From the results of Figure 1 it follows that θ for at least one methionine S^δ–C^ϵ vector is 17 ± 2°. The results of sample freezing and additional pH dependence experiments in which orientation is changed by means of a spin-state transition (unpublished results) indicates that a second methionine resonance lies under the HO^2H resonance. Thus θ for this group is 54.7 ± 2°. These results are in excellent agreement with values determined using the crystallographic coordinates[9] and optical microscopy, since we have shown that the microcrystals

are ordered *along the crystallographic C* axis*.[1] These results thus represent the first direct determination by NMR spectroscopy of structural parameters in protein crystals.

The results presented in this communication open a new area for NMR of protein crystals, since the difficulties of preparing large single crystals are eliminated. Observation of "sharp" resonances in magnetically ordered samples (Figure 1B) permits rapid data acquisition due to increased signal-to-noise ratios and naturally permits resolution of signals from numerous sites which would normally all overlap. Dynamic studies of individual resolved sites may now be carried out, and results compared with those obtained from crystallography.[10] The method should also be applicable for investigating the structures of a wide variety of paramagnetic organometallic compounds.

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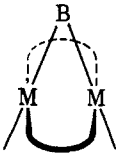
Molecular A Frames. Synthesis from Binuclear Rh(0) Precursors and Catalytic Activity in the Water Gas Shift Reaction and Alkyne Hydrogenation

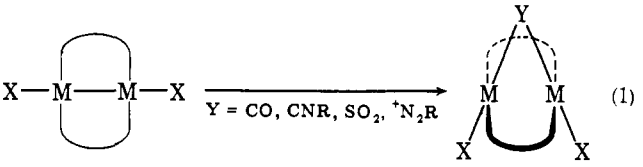
Sir:

The first binuclear complexes of the "A-frame" type geometry, I, were reported in 1977,[1,2] and, since then, other



I

complexes of this structure type have been described including several which bind a small molecule (e.g., CO) on the endo side of the A frame in the so-called "pocket".[3] One approach to the synthesis of A-frame complexes has been through the insertion of small molecules into the metal–metal bond of the bis(diphosphine)-bridged system $[M_2X_2(dpm)_2]$ [M = Pd, Pt; dpm = bis(diphenylphosphino)methane] (eq 1), as evidenced in the



(1)

reports of Balch, Puddephatt, and others.[2,4-7] We report herein our ability to use this approach with the highly reactive and hitherto unknown Rh(0) system $[Rh_2(CO)_2(dpm)_2]$, leading to the synthesis of new Rh A-frame systems including an acetylene species active as a hydrogenation catalyst and a bridging carbonyl hydride formed by the successive addition of H^+ and CO in either order. This latter complex is characterized by a single-crystal X-ray study as well as by spectroscopic methods, and shows itself to be a highly active water gas shift catalyst.

The purple, highly reactive Rh(0) species $[Rh_2(CO)_2(dpm)_2]$, **1**, is synthesized by treatment of $[Rh_2Cl_2(CO)_2(dpm)_2]$[8] with $NaBH_4$ in ethanol. Complex **1**, which precipitates from solution, shows only a single ν_{CO} at 1915 cm^{-1} and the absence of any hydride resonance in the range of 0 to −25 ppm relative to Me_4Si. No change in the IR spectrum is observed when $NaBD_4$ is used as the reducing agent. The extreme chemical reactivity of **1** has made definitive characterization more difficult, but the nature of **1** as a metal–metal bonded Rh(0) dimer is strongly supported by its reaction chemistry (vide infra) and by the preparation of an apparent isomer of **1** starting with $RhH(CO)(PPh_3)_3$ in which stoichiometric evolution of H_2 is observed.[9] There is no spectroscopic or chemical evidence to support a hydride formulation of **1**.

Complex **1** reacts with both H^+ and CO. Protonation of **1** with 1 equiv of a noncoordinating acid, HA (A^- = *p*-$CH_3C_6H_4SO_3^-$ or PF_6^-), leads to brown $[Rh_2(H)(CO)_2(dpm)_2]^+A^-$, **2**. Only a trace of H_2 is observed in the course of the reaction. The ^1H NMR and IR spectra of **2** reveals a featureless hydride resonance at −10.1 ppm and two ν_{CO} at 1962 and 1945 cm^{-1}. The reaction of **1** with CO is accompanied by a rapid solution color change to red-orange after which $[Rh_2(\mu\text{-}CO)(CO)_2(dpm)_2]$, **3**, may be isolated in analytically pure form. The IR spectrum of **3** shows a bridging carbonyl stretch at 1835 cm^{-1} in addition to terminal stretches at 1920 and 1940 cm^{-1}. The controlled addition of CO to **1** shows that 1 equiv of CO is consumed; no H_2 is produced. The ^1H NMR spectrum of **3** displays no resonance attributable to a Rh hydride formulation, while the $^{31}P\{^1H\}$ NMR spectrum shows a complicated mirror symmetry pattern centered at δ 15.72 (relative to trimethyl phosphate) with two major lines separated by 144 Hz.

The identities of **1**, **2**, and **3** are further supported by reactions which lead to the formation of a μ-hydride-μ-carbonyl complex, **4**. Protonation of complex **3** with HA produces the deep purple complex $[Rh_2(\mu\text{-}H)(\mu\text{-}CO)(CO)_2(dpm)_2]^+A^-$, **4**, which is also obtained by the addition of CO to **2**. These reactions are reversible. Heating **4** at 60 °C in THF under N_2 regenerates **2**, while the addition of 1 equiv of $NaHB(OMe)_3$ to **4** yields **3** and 1 equiv of H_2. **4** exhibits ν_{CO} of 1972, 1957, and 1870 cm^{-1} and a broad hydride resonance at −9.71 ppm. The $^{31}P\{^1H\}$ NMR spectrum of **4** is complicated but symmetric. Suitable single crystals of **4** were obtained from THF solution as the *p*-toluenesulfonate salt and used in a definitive X-ray structural study of the complex.

$[Rh_2(\mu\text{-}H)(\mu\text{-}CO)(CO)_2(dpm)_2](p\text{-}CH_3C_6H_4SO_3)\cdot 2THF$ crystallizes in space group $C2/m$ in a cell of dimensions a = 24.391 (11), b = 18.863 (9), c = 14.440 (6) Å; β = 107.81 (2)° (Z = 4; ρ_{calcd} = 1.44, ρ_{obsd} = 1.42 (2) g/cm^2). Intensity data

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