the carbon-13 magnetization precesses during the evolution period t_1 in the presence of proton decoupling. A 90° pulse converts transverse coherence into longitudinal magnetization, which is allowed to migrate by spin diffusion for a time τ_m (typically $1-10^2$ s). In this interval, no decoupling is applied. Finally, a 90° pulse reconverts longitudinal polarization into observable transverse coherence, which is detected in the presence of proton decoupling.

An illustration of 2-D spin diffusion spectroscopy is shown in Figure 1, where heterogeneous and homogeneous disordered mixtures of adamantane and 2,2,3,3-tetramethylbutane are compared. The one-dimensional spectra of the two samples cannot be distinguished and show four resonances: A_1 and A_2 correspond to the CH and CH_2 carbons of adamantane, H_1 and H_2 to the quarternary and methyl carbons of 2,2,3,3-tetramethylbutane, respectively.

Figure 1a for a heterogeneous mixture of finely powdered material exhibits besides the four diagonal peaks four cross peaks connecting pairs of signals belonging to the *same* species, suggesting that spin diffusion proceeds exclusively within domains containing either one of the pure species.

Figure 1b shows a similar spectrum of a sample prepared by melting and cooling equal amounts of adamantane and of 2,2,3,3-tetramethylbutane. The spectrum exhibits all 12 possible cross peaks, indicating that spin diffusion proceeds with similar rates between all four carbon sites. This is unambiguous evidence that the two molecules form a mixed crystal.

The elongated shape of the signal peaks, shown in phase-sensitive representation, indicates the absence of spin diffusion between microcrystallites whose resonances are shifted in frequency by susceptibility effects.

Although the presence of cross peaks, as in Figure 1b, is sufficient evidence for the existence of mixed crystals, care must be taken in interpreting the absence of cross peaks as in Figure 1a. In unfavorable systems, spin diffusion rates may be low and indeed undetectable if spin diffusion is much slower than spin lattice relaxation. However, the ratio of the amplitude of cross peaks connecting different species to the amplitude of cross peaks relating signals of the same species provides a quantitative measure of the homogeneity.

The combination of 2-D spin-diffusion spectroscopy with magic angle spinning may greatly enhance resolution. This is particularly useful for rigid solids where the shielding anisotropy is not averaged by molecular motion. Experiments by Szeverenyi[16] and ourselves[17] have indicated that such combined 2-D MAS experiments are straightforward, although spin diffusion rates may be reduced by sample rotation due to averaging of dipolar interactions.[17,23] For the nonspinning samples presented in Figure 1, the efficiency of spin diffusion is enhanced by rotational and translational molecular diffusion,[24,25] which increases the likelihood that pairs of carbon-13 spins interact.

The spin diffusion experiment described here is by no means restricted to carbon-13 NMR. Diffusion between protons is particularly efficient and sensitive to heterogeneity. To achieve better separation of the signals, the proton magnetization may be transferred to the carbon-13 nuclei by selective cross polarization or pulsed coherence transfer.[26]

In conclusion, spin diffusion provides a useful technique for the study of microscopic heterogeneity in a wide variety of materials. The most promising applications appear to be in the field of synthetic and of biological polymers. Applications in mineralogy and in solid state physics are also conceivable.

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Registry No. Adamantane, 281-23-2; 2,2,3,3-tetramethylbutane, 594-82-1.

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Characterization of Novel Rhodium(II) Dimers with *N*-Phenylacetamido Bridging Ligands

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Recently we reported the structure and electrochemical properties of a new dirhodium(II) complex that had trifluoroacetamido in place of carboxylato bridging ligands.[1] This compound, $Rh_2(HNOCCF_3)_4$, undergoes reversible oxidation to yield $[Rh_2(HNOCCF_3)_4]^+$, similar to the rhodium(II) carboxylates[2] but at a much lower potential than $Rh_2(OOCCF_3)_4$. This suggested to us that the synthesis of other rhodium(II) dimers with RNOCR′ ligands could result in a system for which the electronic structure could be "tuned" for redox processes by varying R and R′. This indeed is the case as we report in this communication. Tetrakis(μ-acetato)dirhodium(II) reacts with *N*-phenylacetamide to produce a complex mixture of partially and totally amide-substituted dinuclear rhodium(II) complexes and their isomers. The reaction was carried out by heating a mixture of 1 g of $Rh_2(OOCCH_3)_4$ and 30 g of *N*-phenylacetamide at 150 °C for 48 h. After excess *N*-phenylacetamide was removed by sublimation, the product was a mixture of organic impurities and several different rhodium complexes. The organic impurities were separated from the rhodium complexes by HPLC using a CN-bonded phase column with methanol eluent. As shown in Figure 1 there are four possible isomers of the totally amide-substituted product. Two of the four isomers were isolated and studied. Elemental analysis of one blue isomer complex corresponds to $Rh_2(C_6H_5NOCCH_3)_4(H_2O)$, I (Found: C, 50.61; H, 4.56; N, 7.80; Rh, 26.96. Calcd: C, 50.50; H, 4.58; N, 7.40; Rh, 27.1). Elemental analysis of a second green isomer corresponds to $Rh_2(C_6H_5NOCCH_3)_4$, II (Found: C, 51.69; H, 4.50; N, 7.45; Rh, 27.73. Calcd: C, 51.75; H, 4.31; N, 7.54; Rh, 27.76). The molecular weight of complexes I and II were determined by liquid chromatography/mass spectrometry, operating in the negative ion mode and showed a parent mass of 742. This is the calculated molecular weight of the dinuclear rhodium(II) complex with four bridging *N*-phenylacetamado ions.

The ^1H NMR spectrum of II gives three CH_3 proton resonances at 1.72, 1.77, and 1.92 ppm with an area ratio of 1:2:1 and strongly suggests that II is isomer C in Figure 1. In addition the ^{13}C NMR spectrum shows that the amide group carbon as well as the *o*-, *m*-, and *p*-benzene carbons are split into three bands, also suggesting isomer C. Compound I shows only one ^1H NMR resonance for the CH_3 groups, at 1.75 ppm, and none of the ^{13}C resonances are split. This is the NMR spectra that would be characteristic for either A, B, or D. Cotton and Felthouse[3] have also reported isomers for dinuclear rhodium(II) complexes with 2-oxy-6-methyl-pyridine and 2-oxy-6-chloropyridine bridging anions. The N,O bonding combination of isomers B and C were found for these ligand systems.

As shown in Figure 2, the electrochemical oxidations of I and II proceeds in two steps without destroying the dimeric cage structure. The currents observed by differential pulse polarography and cyclic voltammetry were of equal height, indicating an identical number of electrons transferred in each step. In addition, the $E_{pa} - E_{pc} = 60 \pm 5$ mV from the cyclic voltammograms, indicating that one electron is transferred in each step. Potentials and coulometric data for each process are given in Table I. It is interesting to note that the initial potential for oxidation of $Rh_2(C_6H_5NOCCH_3)_4$ in CH_2Cl_2 is over 400 mV more negative than for any other rhodium(II) dimer of the form $Rh_2(O_2CCR)_4$. More important, however, the second oxidation has never been

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Table I. Electrochemical and Spectral Characterization of $Rh_2(C_6H_5NOCCH_3)_4$ and $[Rh_2(C_6H_5NOCCH_3)_4]^+$

	$E_{1/2}$, V vs. SCE		coulometry, F/mol		λ_{max} of major peaks, nm ($\epsilon \times 10^{-3}$, M^{-1} cm^{-1})	
isomer	1	2	1	2	$Rh_2(C_6H_5NOCCH_3)_4$	$[Rh_2(C_6H_5NOCCH_3)_4]^{+a}$
I	0.55	1.65	0.94 ± 0.05	0.96 ± 0.05	375 (0.38), 420 sh, 470 sh, 655 (0.28)	~350, 420 sh, 513 (2.6)
II	0.53	1.63	0.9 ± 0.1	0.9 ± 0.1	382 (0.46), 410 sh, 460 sh, 575 sh, 699 (0.30)	~360, 420 sh, 522 (2.8)

[a] After electrolysis of $Rh_2(C_6H_5NOCCH_3)_4$ at 0.75 V.

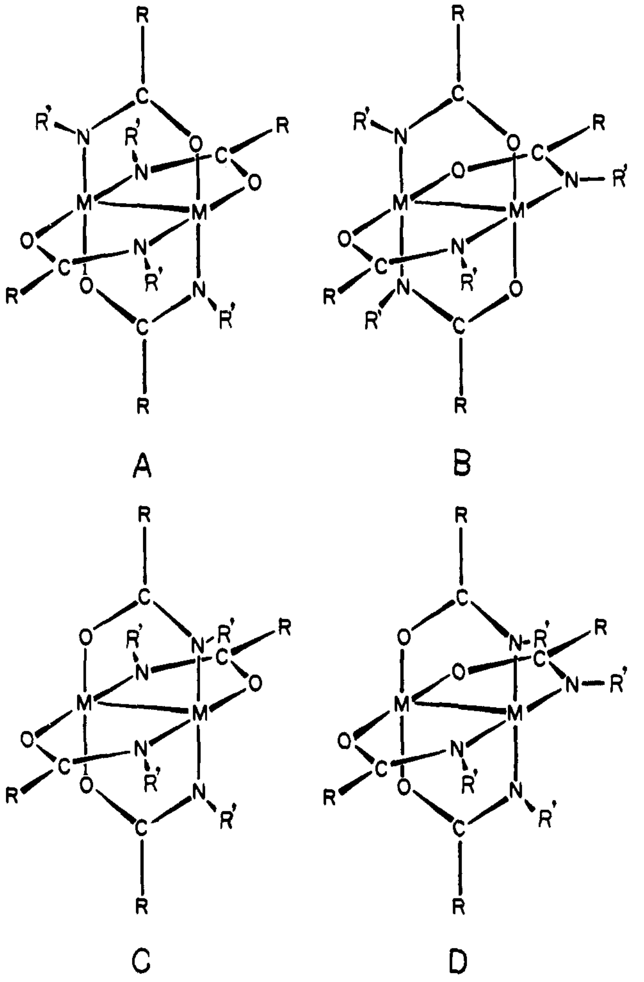

Figure 1. Isomers of $Rh_2(C_6H_5NOCCH_3)_4$ (M = Rh, R = CH_3, R' = C_6H_5).

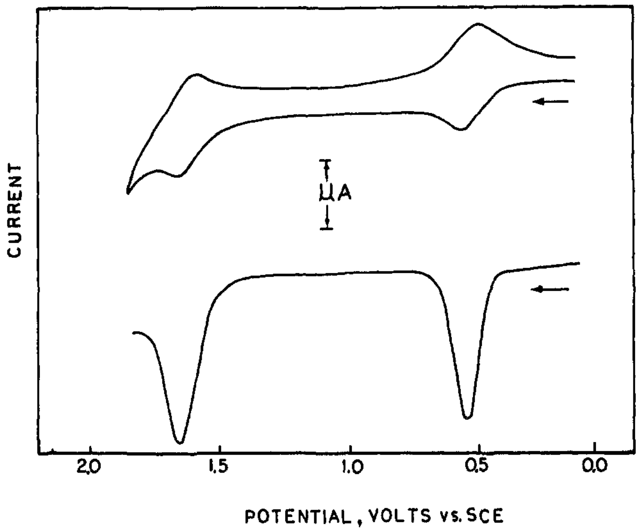

Figure 2. Cyclic voltammogram (top) and differential pulse voltammogram (bottom) for the oxidation (at a Pt electrode) of 1 mM $Rh_2(C_6H_5NOCCH_3)_4$ in 0.1 M TBAP-CH_2Cl_2 solution.

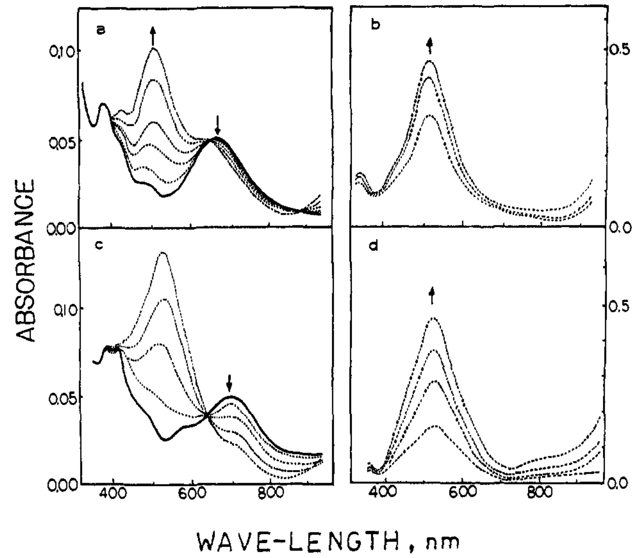

Figure 3. Time-resolved spectra for the oxidation of $Rh_2(C_6H_5NOCCH_3)_4$ in 0.1 M TBAP-CH_2Cl_2 at 0.75 V vs. SCE: (a) isomer I between 0 and 2 min electrolysis time; (b) isomer I between 2 and 20 min electrolysis time; (c) isomer II between 0 and 3 min electrolysis time; (d) isomer II between 3 and 18 min electrolysis time.

observed for any dimeric complex of rhodium(II).

Figure 3, parts a and c, shows the visible spectra of I and II after very short time intervals of oxidation while Figure 3, parts b and d, shows the progressive oxidation to the final product $[Rh_2(C_6H_5NOCCH_3)_4]^+$. Table I gives the visible spectral characterization of the neutral and oxidized complexes. The visible spectra of virtually all dirhodium(II) complexes previously studied are characterized by two bands in the visible region. These bands have been assigned to Rh–Rh $\pi^* \rightarrow$ Rh–Rh σ^* and Rh–Rh $\pi^* \rightarrow$ R–O σ^* transitions by theoretical[4,5] and experimental methods.[6,7] The visible spectrum of $Rh_2(HNOCCF_3)_4$ also shows these two bands but shifted to higher energy than the corresponding carboxylato-bridged complexes.[1] However, a very different spectrum is observed for the *N*-phenylacetamido complexes as seen in Figure 3. The spectrum of II displays five bands in the visible region, and the band at 699 nm is considerably lower in energy than that observed for any other dirhodium(II) system. The visible spectrum of I is similar to that of II with the major difference being a prominent shoulder at 575 nm and a shift in λ_{max} of the lower energy band by ~45 nm. The visible spectra of the cation $[Rh_2(C_6H_5NOCCH_3)_4]^+$ of both I and II are characterized by unusually strong absorbances at 513 and 522 nm, respectively. A similar strong band is observed for the trifluoroacetamido-bridged cation $[Rh_2(HNOCCF_3)_4]^+$ at 449 nm.[1] This transition, with a molar extinction coefficient of ~3.0×10^3 cm^{-1} M^{-1}, is not observed for the carboxylato-bridged cations $[Rh_2(OOCR)_4]^+$, which suggests a transition involving the less electronegative amide nitrogen, possibly a nitrogen to metal charge transfer. It is obvious that the *N*-phenylacetamido bridging ligands cause a considerable alteration of the electronic structure of the rhodium(II) dimer

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compared to carboxylato-bridging ligands.[4,5,8] Further experimental and theoretical studies will be needed to assign the electronic transition for this system.

Attempts were made to spectrally characterize the products of the second oxidation step by controlled-potential electrolysis. Unfortunately, isolation of these compounds in the bulk cell was not possible due to their extremely positive potentials, which were close to the anodic limit of CH_2Cl_2. Further attempts in solvents with a greater anodic potential limit are now underway.

In summary, tetrakis(μ-acetato)dirhodium(II) reacts with *N*-phenylacetamide to produce at least two of four possible geometric isomers of tetrakis(μ-*N*-phenylacetamido)dirhodium(II). Each of these complexes undergoes two reversible one-electron-transfer oxidation steps. The first oxidation occurs at a much lower potential than that found for any other dinuclear rhodium(II) complex of similar structure, and the second oxidation step has never been observed before. The visible spectra of the neutral and cationic complexes are also considerably different from those observed for dinuclear rhodium(II) complexes involving other types of bridging ions. Isolation and characterization of all the substitution products o the exchange reactions and the oxidized complexes is presently underway.

Acknowledgment. The support of the Robert A. Welch Foundation (K.M.K. Grant E680, J.L.B. Grant E918) is gratefully acknowledged.

Registry No. II, 82871-03-2; $Rh_2(O_2CCH_3)_4$, 15956-28-2; Rh, 7440-16-6.

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α-(Phenylthio)-β-vinylbutenolide, a Novel Annulating Reagent for the Synthesis of 4-Oxygenated Perhydro-2-oxo-1-benzofuran Derivatives

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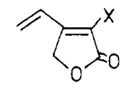
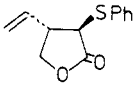
Previously it was reported from this laboratory that β-vinylbutenolide (**1**) and its α-methyl derivative **2** were convenient



1 X = H
2 X = Me
3 X = SPh



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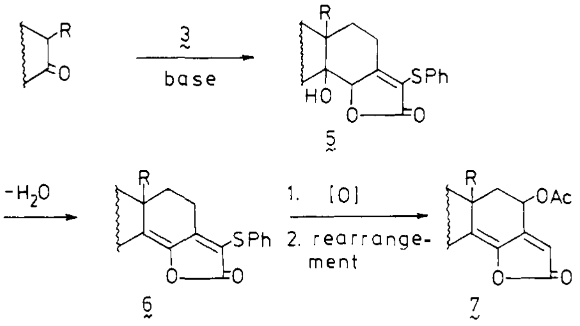
lactone annulating reagents and that the efficacy in natural product chemistry was illustrated by the successful total synthesis of sesquiterpenes such as frullanolide[1] and furoventalene.[2] In this paper we describe α-(phenylthio)-β-vinylbutenolide (**3**) as a novel and intriguing reagent functionalized to annulate carbonyl compounds for the synthesis of 4-oxygenated perhydro-2-oxo-1-benzofuran derivatives; the perhydroxobenzofuran structure has frequently been found in natural products, in particular, sesquiterpene lactones.

The title reagent **3** was readily accessible from α-(phenylthio)-β-vinylbutyrolactone[1] (**4**) by the eliminative Pummerer rearrangement[3,4] as follows: a solution of mCPBA (4.5 mmol) in CH_2Cl_2 (15 mL) was added to a stirred solution of **4** (4.5 mmol) in the same solvent (10 mL) at 0 °C over 15 min. The mixture was stirred at the same temperature for 1 h and then filtered. The filtrate was successively washed with aqueous $NaHCO_3$, water, and brine. The crude sulfoxide thus obtained was dissolved in trifluoroacetic anhydride (1.0 mL) at 0 °C, and then the mixture was stirred at room temperature overnight. The solvent was removed, and the residue, diluted with CH_2Cl_2, was washed with aqueous $NaHCO_3$, water, and brine and dried. Evaporation of the solvent left crystals, which were recrystallized from ether to give pure **3** (694 mg, 71% yield from **4**), mp 70 °C. Unlike **1** and **2**,[1,2] this butenolide is stable and can be stored at ambient temperature in the dark.

The annulation of carbonyl compounds with **3** and the subsequent transformation of the products into the oxygenated perhydroxobenzofurans are shown by the equation: a carbonyl compound adds to **3** under basic conditions in the fashion of exclusive 1,6-conjugate addition followed by consecutive aldol-type cyclization to afford annulated product **5**. Some examples of the annulation are summarized in Table I, which demonstrates that the reaction with this reagent **3** proceeds in much higher yields in comparison with those of **1** and **2**.[1,2]



The product **5** is dehydrated to **6** ($SOCl_2$, py), which is then oxidized to sulfoxide (mCPBA). Under reaction conditions for allylic sulfoxide–sulfenate rearrangement (Ac_2O, py),[4] the sulfoxide yields acetoxyperhydroxobenzofuran **7** as a mixture of epimers with respect to the acetoxyl group (Table II). Judging from limited examples (**13**–**16**), stereoselectivity in the rearrangement appeared to depend on the bulkiness of angular substituents in the tricyclic system.

A sequence of reactions starting with 2-methylcyclohexane-1,3-dione are illustrative of the typical procedure of the annulation and of the subsequent transformation of the annulation product into **7**.

A solution of **3** (0.5 mmol) in DME (0.8 mL) was added dropwise to a stirred solution of the dione (1 mmol) and KF (0.55 mmol) in a mixture of Me_2SO and DME (1 mL of each) at 0 °C over 3–5 min. Stirring was continued at the same temperature for an additional 1 h, and the mixture was then acidified with dilute HCl. The product was extracted with CH_2Cl_2, and the extract was successively washed with water, aqueous $NaHCO_3$, water, and brine and dried. Removal of the solvent left the crude product, which was chromatographed on a silica gel column using 5:1 ether–petroleum ether as solvent to afford **8** (135 mg) sufficiently pure for the next step. An analytically pure sample was obtained by recrystallization from ether.

Thionyl chloride (0.06 mL) was added dropwise to a stirred solution of **8** (0.41 mmol) in dry pyridine (7.5 mL) at 0 °C. After stirring for an additional 30 min at the same temperature, the mixture was diluted with CH_2Cl_2, and the solution was washed with dilute HCl and water and dried. Removal of the solvent gave an oil, which was chromatographed on a silica gel column using CH_2Cl_2 as solvent to give the oily dehydration product (120 mg).

A solution of mCPBA (0.71 mmol) in CH_2Cl_2 (2 mL) was added dropwise to a solution of the above dehydration product (0.68 mmol) in the same solvent at 0 °C. Stirring was continued

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