

ARTICLES

Time-Resolved Infrared Absorption Study of Cyclopentadienyl Manganese Tricarbonyl Derivatives: Chelation of Pendant Sulfides in Acetonitrile

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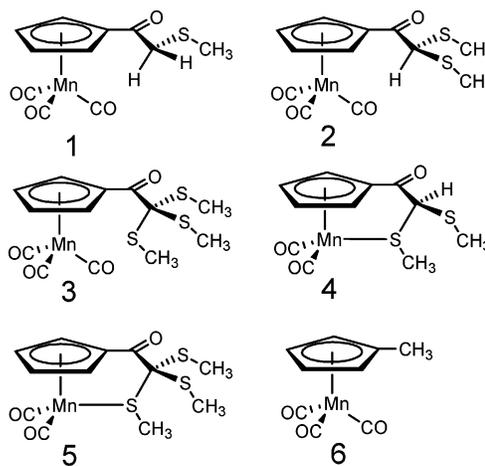
The chelation dynamics of $[\text{Mn}\{\eta^5\text{-C}_5\text{H}_4\text{C}(\text{O})\text{R}\}(\text{CO})_3]$ complexes **1** ($\text{R} = \text{CH}_2(\text{SCH}_3)$), **2** ($\text{R} = \text{CH}(\text{SCH}_3)_2$), and **3** ($\text{R} = \text{C}(\text{SCH}_3)_3$) in room-temperature acetonitrile solution have been investigated on the picosecond time scale by UV-pump IR-probe transient absorption spectroscopy. Similar to the previously observed behavior in *n*-heptane solution, irradiation of **3** in acetonitrile at 289 nm induces CO loss to exclusively yield a Mn–S chelated dicarbonyl product. Unlike the behavior of **1** and **2** in *n*-hexane and *n*-heptane solutions, UV excitation of either **1** or **2** in acetonitrile solution induces CO loss to also exclusively yield the chelated products, with no evidence of a competing solvation pathway. All three complexes exhibit ultrafast chelation in <13 ps. Faster vibrational cooling in acetonitrile vs alkane solutions suggests stronger solute–solvent interaction, perhaps via hydrogen bonding. Ring-opening resulting from continuous irradiation of the pendant sulfide's chelates, $[\text{Mn}\{\eta^5\text{-C}_5\text{H}_4\text{C}(\text{O})\text{CH}(\text{SCH}_3)_2\text{-}\kappa\text{S}\}(\text{CO})_2]$ (**4**) and $[\text{Mn}\{\eta^5\text{-C}_5\text{H}_4\text{C}(\text{O})\text{C}(\text{SCH}_3)_3\text{-}\kappa\text{S}\}(\text{CO})_2]$ (**5**), is also discussed.

Introduction

In the current and previous studies, we have been examining processes that are fundamental to the function of ultrafast photochromic organometallics based on linkage isomerization of complexes with a bifunctional, nonchelating ligand¹ and on intramolecular ligand exchange of organometallic chelates with tethered functional groups.² There is great interest in photochromic materials in photonic devices such as recordable media and reversible optical switches.^{3,4} Fast rates, high quantum yields, and low fatigue are desirable features for optical switches: all of which can be casualties of cage processes such as recombination and solvent coordination. These cage processes are well documented for many coordinatively unsaturated metal centers that are so reactive that they bind even to alkanes and noble gases.⁵ Recombination ultimately slows down a reaction since it lowers the quantum yield and thereby requires additional excitation to complete the reaction. Solvent coordination prolongs the lifetime of transient metal species and provides more opportunities for side reactions.

We have investigated several model compounds capable of chelation to determine how cage processes might be eliminated and recently demonstrated that following irradiation, the pendant sulfide **3**, unlike **1** and **2** (Chart 1), can undergo chelation to the exclusion of ultrafast alkane solvent coordination or cage

CHART 1



recombination of a carbonyl.^{2b,c} A simple analysis might suggest the solvent was excluded because **3** always has sulfur near the metal without an intervening solvent molecule, but this does not preclude the addition of solvent from the opposite side of the metal following CO dissociation. This led us to postulate that encounters with the solvent were unsuccessful during the brief time before the chelation because the available excess thermal excitation far exceeded the weak metal–alkane bond energy.⁶ Thus, addition of a solvent that could form a strong bond with the metal and lead to a stable product might compete

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with the chelation. In this contribution, we investigate the chelation dynamics of **1**, **2**, and **3** in acetonitrile to determine if coordination by this more reactive solvent can compete with ultrafast chelation. Furthermore, studies of the irradiation of the chelates, **4** and **5**, in acetonitrile reveal whether solvent coordination can compete with the ultrafast recombination of a photodissociated, side-chain functional group. These studies serve to model the initial stage of the linkage isomerization of a complex with a bifunctional side chain.^{2a}

Experimental Section

We reported the description of our time-resolved infrared (TRIR) apparatus, experimental procedures, and the synthesis of **2** and **3** in previous publications.^{2b,c} For the present study, a typical UV pulse (289 nm), with 2 to 5 μJ energy, was focused to approximately 100 μm diameter in a 2 mm path length flow cell with CaF_2 windows. To generate a single difference spectrum at a specific time delay, an average of 3000 laser shots was obtained for each of three separate CO-stretch absorption spectral ranges. Up to five of these combined TRIR difference spectra were averaged to obtain the final presented results. Analysis of averaged spectra (typically three) yielded an intensity uncertainty from the baseline of less than ± 0.005 optical density (OD) units ($k = 1$; type B analysis). The apparatus was frequency calibrated with $\text{W}(\text{CO})_6$ in *n*-heptane solution⁷ before or after the apparatus was used to study the manganese complexes. The synthetic procedures to obtain **1** were published elsewhere.⁸ To prepare samples for time-resolved infrared experiments, the Mn complexes (50–71 mg) were dissolved in 100 mL of acetonitrile under argon atmosphere to produce millimolar concentrations (e.g., 1.8×10^{-3} mol/L for 50 mg of **3**). The solution was cannulated to an argon-purged circulation system that included the sample flow cell.

Preparation of $[\text{Mn}\{\eta^5\text{-C}_5\text{H}_4\text{C}(\text{O})\text{CH}(\text{SCH}_3)_2\text{-}\kappa\text{S}\}(\text{CO})_2]$ (4**).** Tetrahydrofuran (25 mL) and **2** (280 mg, 0.85 mmol) were argon purged in a septum-sealed, 25-mL graduated cylinder while irradiated for 90 min in a Rayonet photochemical reactor equipped with eight, 300 nm lamps.⁹ The yellow reaction mixture turned red and was concentrated with a rotary evaporator. The red residue was eluted with ethyl acetate/hexane solution (10 vol %) through an 18×1 cm silica gel column. A red band was collected and concentrated by rotary evaporation, and the residue was dried under vacuum to obtain 150 mg (57% yield) of red solid **4**.¹⁰

Preparation of $[\text{Mn}\{\eta^5\text{-C}_5\text{H}_4\text{C}(\text{O})\text{C}(\text{SCH}_3)_3\text{-}\kappa\text{S}\}(\text{CO})_2]$ (5**).** A yellow solution of hexane (200 mL) and **3** (500 mg, 1.3 mmol) was purged in an immersion well photochemical reactor equipped with a stir bar. As the reactor headspace was purged with argon, a red solid formed during 3 h of irradiation with a 300 nm lamp and stirring. The solvent was decanted, and the residue was dried under vacuum to obtain 350 mg (75% yield) of red-brown solid **5**.¹¹

Acetonitrile (anhydrous) and *n*-heptane (analytical grade) were purchased from Aldrich and Mallinckrodt, respectively, and were used without further purification. Tricarbonyl(η^5 -methylcyclopentadienyl)manganese, $[\text{Mn}\{\eta^5\text{-C}_5\text{H}_4\text{CH}_3\}(\text{CO})_3]$ (**6**), was purchased from Pressure Chemical Company and distilled under vacuum (10.7 Pa or 80 milliTorr) at 327 K.⁹

Results and Discussion

Figure 1 shows transient difference spectra of **1**, **2**, and **3** in acetonitrile recorded at pump–probe delays from –33 to 107 ps (top frame) and static difference Fourier transform infrared (FTIR) spectra of the same compounds in acetonitrile recorded

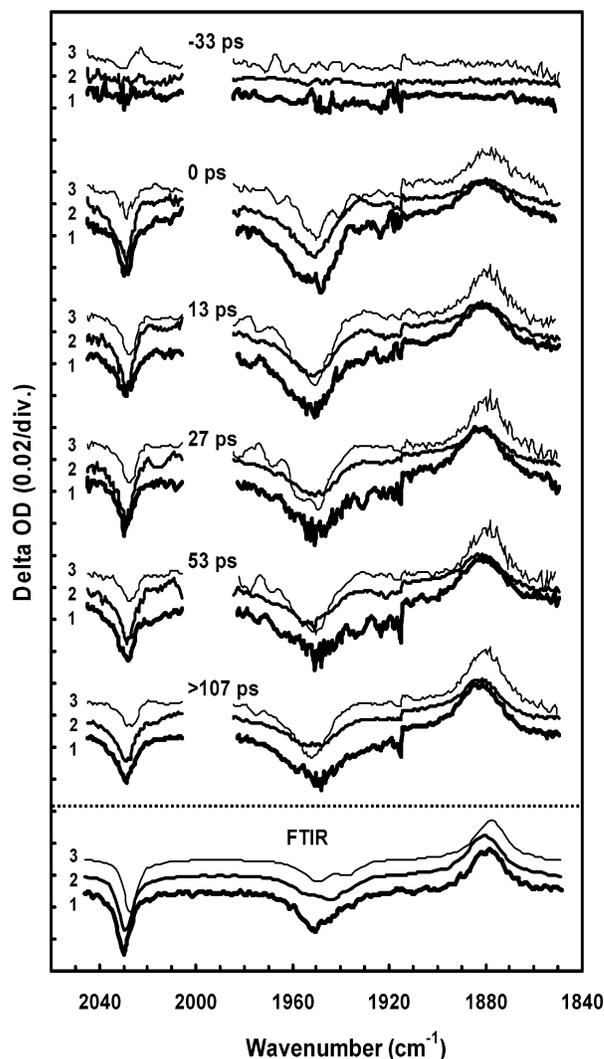


Figure 1. Transient TRIR difference spectra acquired after 289 nm irradiation of **1**, **2**, and **3** in acetonitrile at 298 K. Presented within each labeled time delay, the thickest, medium, and thinnest spectral lines correspond to spectral changes of **1**, **2**, and **3**, respectively, with the corresponding compound number at left (top frame). At each time delay, spectra are offset vertically by 0.01 OD units for clarity. The spectral lines labeled >107 ps are the average of all difference spectra taken at 107, 160, 213, 267, and 533 ps. The spectral coverage of the probe did not extend from 1985 to 2005 cm^{-1} and is not shown. The bottom frame exhibits difference FTIR spectra of **1**, **2**, and **3** in acetonitrile acquired before and after irradiation with either a 300 nm or a xenon arc lamp for approximately 30 s.

before and after irradiation with either a 300 nm lamp or a xenon arc lamp (bottom frame). Upon UV irradiation, spectral results for **1**, **2**, and **3** in acetonitrile are nearly identical. In each case, bleaches of the starting compounds occur near 1950 and 2030 cm^{-1} and a new absorption is observed near 1880 cm^{-1} (Figure 1, top frame). We assign the absorption near 1880 cm^{-1} to one of the metal–CO stretching bands of a manganese dicarbonyl sulfide chelate in agreement with the spectra observed for pure chelate and with the FTIR spectra for continuous irradiation experiments (Figure 1, bottom frame). The second metal–CO stretching band of the chelate near 1940 cm^{-1} cannot be clearly resolved due to the signal-to-noise limitations of the TRIR apparatus and overlap with the bleach near 1950 cm^{-1} . The peak near 1880 cm^{-1} grows to its highest intensity and remains unchanged after 13 ps. At a negative time delay of –33 ps, neither bleaches nor absorptions are observed. Thus, assuming minimal deviation of time zero occurs after calibration with a

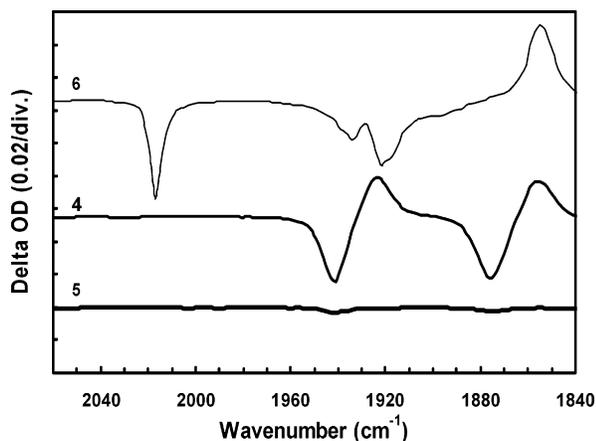


Figure 2. Difference TRIR spectra of **6** and chelates **4** and **5** in acetonitrile solution, presented by (from the top) the thinnest, medium, and thickest spectral lines, respectively, acquired before and after irradiation with a 300 nm lamp for 10 s. The spectra were obtained within 1 min of irradiation.

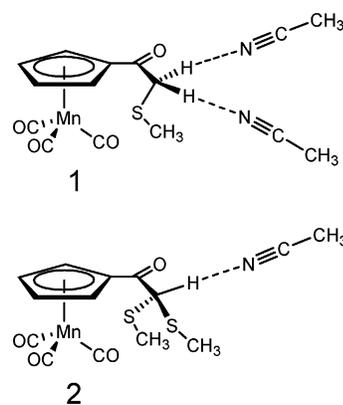
silicon wafer in place of the sample cell (transient reflection); chelation of all three Mn complexes is complete in less than 13 ps.

Following irradiation of **1**, **2**, and **3**, the coordination of acetonitrile prior to the formation of chelates can be ruled out. First, adducts of cyclopentadienyl manganese dicarbonyl with acetonitrile are thermally stable;¹ therefore, it is unlikely that the nitrile first added to the metal center and was subsequently displaced by a pendant sulfide. Second, absorptions near 1855 and 1922 cm^{-1} , indicative of acetonitrile adducts with cyclopentadienyl manganese dicarbonyl (see discussion below), are conspicuously absent in any of the TRIR experiments (within the signal-to-noise limitations, ± 0.005 OD, Figure 1). Third, our results following the irradiation of **4** (Figure 2) demonstrate that the coordinated acetonitrile in **7** (Scheme 2) is not labile in the presence of the pendant sulfides; therefore, if **7** had formed following irradiation of **2**, then **7** should have been observed in the transient or continuous IR experiments with **2**. We therefore conclude that irradiation of **1**, **2**, and **3** in acetonitrile results in CO dissociation and the addition of a pendant sulfide without competition of ultrafast solvent (acetonitrile) coordination.

The results in acetonitrile are strikingly different from those reported previously for UV irradiation of **1**, **2**, and **3** in *n*-heptane.^{2b,c} As in acetonitrile, **3** exclusively forms chelate on the picosecond time scale in heptane, but **1** and **2** form about equal amounts of chelate and Mn-heptane adducts and the adducts later convert to the chelates on the 10 to 100 ns time scale.^{2b,c} It was postulated in the previous studies that picosecond chelation occurred only if the sulfide side chain was in a conformation that provided a sulfide group near the metal during excitation.^{2b,c} Thus, a sulfide group was near the metal half the time for **1** and **2** and all the time for **3**. On first inspection, this and the previous results seem to suggest that heptane is better than acetonitrile at trapping the metal center following irradiation.

Following the same reasoning for results in heptane, the exclusive chelation of **1**, **2**, and **3** following CO dissociation in acetonitrile suggests that favored conformations in acetonitrile always place a reactive sulfide group near the metal center. An examination of the literature suggests two possible explanations for this solvent effect. First, hydrogen bonding between acetonitrile and the CH group α to carbonyl as suggested in Chart 2 might create a steric effect that would make conformations with sulfide near the metal more favorable and promote Mn–S

CHART 2



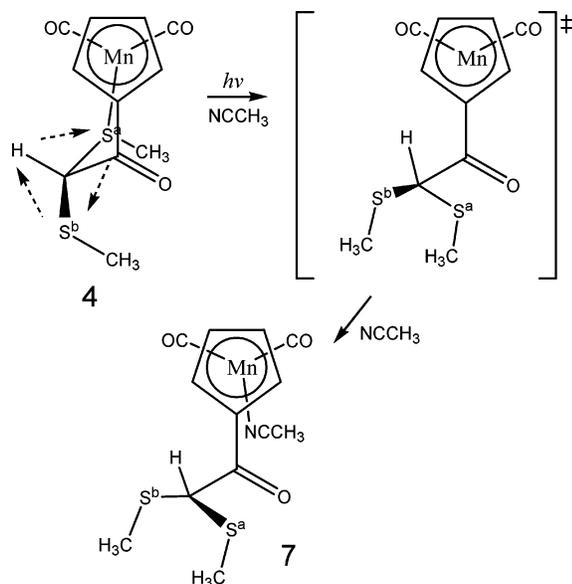
chelation, as we observe. Second, a dative interaction between the sulfur and a metal carbonyl group might also explain the preference for chelation in acetonitrile. Recent studies report a dative interaction for analogous side-chain phosphine and metal carbonyl and a thiolate with a metal carbonyl.¹² If a weak dative interaction between a pendant sulfide and a metal carbonyl were occurring in **1** and **2**, then charge separation caused by the dative interaction would be stabilized more in a polar solvent like acetonitrile than in heptane, and conformers with a dative interaction in acetonitrile would promote chelation upon irradiation by orienting the sulfide near the metal.

While either explanation for exclusive chelation in acetonitrile is speculative at this point it is likely that acetonitrile favors conformations that place the sulfide near the metal. The lack of competing acetonitrile addition during chelation has an important practical implication for a solid-state optical switch based on linkage isomerization. Specifically, a linkage isomerization with two tethered functional groups^{2a} following irradiation should be feasible without the competition of a bimolecular reaction with functional groups from the surrounding matrix.¹³

Our previous report indicated that relatively slow vibrational cooling occurs for the products in *n*-heptane (longer than 50 ps),^{2b,c} but the present study indicates that much faster vibrational cooling takes place in acetonitrile. The spectral changes are clearly resolved and fully completed for probe delays less than 13 ps after excitation. We know of only a few TRIR studies of solute vibrational energy relaxation in acetonitrile, but shorter vibrational cooling times in protic and polar solvents have been demonstrated, especially in solute–solvent systems where energy transfer can proceed mainly through hydrogen bonds.¹⁴ We also note that these metal–carbonyl species exhibit broad CO-stretching absorptions in acetonitrile solution (ca. 20 cm^{-1} full-width at half-maximum (fwhm)) as compared with the same species in alkanes (ca. 3 to 4 cm^{-1} fwhm). The CO-stretching bands are also approximately 30 cm^{-1} red shifted as compared with spectra obtained from *n*-heptane solution. The increased bandwidth implies that the coherence or collisional time with the solute has decreased by about a factor of 6, and the red-shifted CO-stretching bands indicate increased solute–solvent interaction in acetonitrile solution. Despite the increased widths, separation of bleach and absorption features is sufficient (at 4 cm^{-1} fwhm resolution, see above discussion) to identify transient solvates had they occurred. More detailed studies of these effects are clearly required to gain a better picture of these important solute–solvent interactions.

The difference FTIR spectra of chelates **4** and **5** in acetonitrile, acquired before and after UV irradiation, are compared in Figure 2 with that for **6**. The spectra demonstrate that continuous UV irradiation of **4** results in the bleaching of **4** at 1943 and 1878

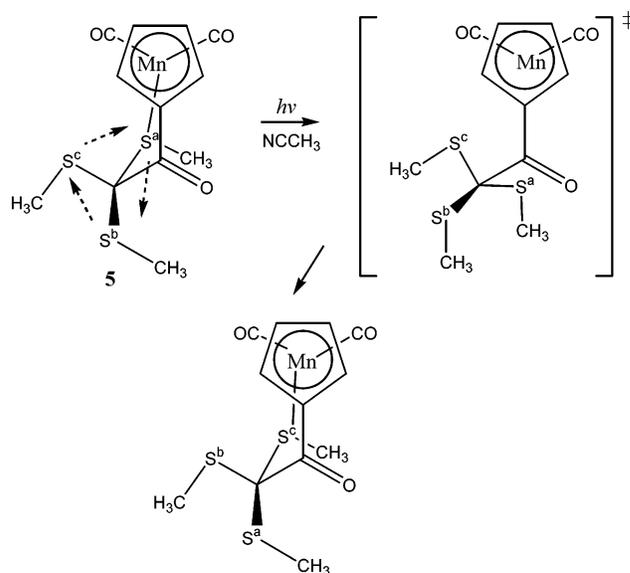
SCHEME 1



cm^{-1} and the formation of two new metal–dicarbonyl stretching bands at 1922 and 1855 cm^{-1} . These new red-shifted absorption bands are assigned to the acetonitrile adduct **7** (Scheme 1) because they are closely matched with the new bands near 1922 and 1855 cm^{-1} for the acetonitrile adduct formed following irradiation of **6**, where only CO can dissociate and be replaced by acetonitrile. There are two CO-stretching bands assigned to **7**, not one, thus **7** must have two metal carbonyls indicating the sulfide and not a carbonyl was replaced by acetonitrile. These results are consistent with the spectra reported previously for Mn–acetonitrile adducts of cyclopentadienyl manganese dicarbonyl derivatives and the fact that only the weakest Mn–ligand bond dissociates following UV irradiation.^{2c,15–17} In contrast, irradiation of **5** under the same conditions for **4** revealed no new bands and only a slight bleaching at 1940 and 1876 cm^{-1} .

The difference spectra in Figure 2 not only show that irradiation of **4** results in the formation of the acetonitrile coordinated adduct but also show that chelate **5** is relatively photoinert. The significant production of acetonitrile adduct demonstrates that dissociation of sulfide is a major pathway for the excited state of **4**. In contrast, irradiation of **5** only leads to a slight loss of bands for **5**, and no new absorption bands are observed. Since there is little difference between the chromophores for **4** and **5**, we likewise anticipate sulfide dissociation to be a major pathway for the excited state of **5**, but this would require recombination with a side-chain sulfide to account for the lack of acetonitrile adduct. In general, there are two possible mechanisms by which this could occur: the original sulfide that dissociated could return (geminate recombination) or one of the other sulfides could add (linkage isomerization). Chemically, the same product is produced in either case; however, the former mechanism would be identical for **4** and **5** and does not account for the difference in product formation. On the other hand, an examination of the structures for **4** and **5** shows that linkage isomerization is fundamentally different for the two compounds (Scheme 2). The linkage isomerization in **5** ultimately leads to a rotation of the trisulfide group and only chelate product. We suspect that the impulse of the sulfide dissociation is “transformed” into a torsion that immediately rotates the adjacent sulfide group toward the metal center before intervention by acetonitrile. On the other hand, sulfide dissociation in **4** can rotate the α -hydrogen toward the metal where the weak interaction could potentially allow subsequent solvent coordina-

SCHEME 2



tion (Scheme 1). If this mechanism is correct, then it would indicate that a linkage isomerization can occur to the exclusion of ultrafast solvent coordination. We have prepared complexes with different functional groups on side chains that would chemically report the linkage isomerization.^{2a}

Summary

Ultrafast chelation dynamics following UV irradiation of manganese complexes **1**, **2**, and **3** reveal the effect of solvent on the fundamental processes occurring during chelation. Irradiation of **1** or **2** in alkane solvent results in competition between direct chelate formation and solvent coordination on the picosecond time scale. The solvent coordinated intermediates form the chelate on the nanosecond time scale. In contrast, irradiation of **3** in alkane solvent leads only to chelation and exclusion of ultrafast solvent coordination. In acetonitrile, however, chelation occurs for all three complexes in less than 13 ps apparently without ultrafast solvent coordination. In general, this study indicates that favorable side-chain conformations can lead to chelation to exclusion of other ultrafast processes such as solvent coordination. Investigations are underway to determine whether similar reaction mechanisms and rates of chelation occur when these prototypical molecules are embedded in nitrile-containing polymeric matrixes.

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(6) Apparently, alkanes can bind to metal centers that have vibrational energy in excess of the metal-alkane bond if the energy is isolated in high-frequency oscillators: see ref 5b. Metal-alkane σ -complexes have been reported to have bond energies on the order of 10–15 kcal/mol. For leading references, see ref 5c.

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(9) Certain commercial equipment, instruments, or materials are identified in this paper to adequately specify the experimental procedure. In no case does such identification imply recommendation or endorsement by NIST, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

(10) Two diastereomers were observed with the relative peak areas of 6 to 1: $^1\text{H-NMR}$ (CDCl_3): δ 1.32 (s, 3H, CH_3), 1.61 (s, 3H, CH_3), 3.29 (m, 1H, Cp), 3.87 (m, 1H, Cp), 4.30 (s, 1H, CH), 4.58 (m, 1H, Cp), 4.72 (m, 1H, Cp) and 1.57 (s, 3H, CH_3), 1.81 (s, 3H, CH_3), 3.17 (m, 1H, Cp), 3.54 (s, 1H, CH), 4.15 (m, 1H, Cp), 4.31 (m, 1H, Cp), 5.06 (m, 1H, Cp). IR (heptane, ν_{CO} cm^{-1}): 1957, 1900, 1719. IR (acetonitrile, ν_{CO} cm^{-1}):

1943(s), 1878(s), 1716(vw). UV-vis (heptane, λ_{max} (ϵ)): 377 nm (770), 490 nm (109).

(11) $^1\text{H-NMR}$ (CDCl_3 at 298 K): δ 2.08 (s, broad, 6H, 2 SCH_3), 2.36 (s, 3H, SCH_3), 4.20 (very broad, 2H, Cp), 5.04 (very broad, 1H, Cp), 5.50 (very broad, 1H, Cp). (248 K): δ 2.01 (s, 3H, SCH_3), 2.13 (s, 3H, SCH_3), 2.34 (s, 3H, $-\text{SCH}_3$), 4.08 (s, 1H, Cp), 4.35 (s, 1H, Cp), 4.94 (s, 1H, Cp), 5.56 (s, 1H, Cp). IR (heptane, ν_{CO} cm^{-1}): 1957, 1898, 1702. IR (acetonitrile, ν_{CO} cm^{-1}): 1940(s), 1876(s), 1693(vw).

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