Bistable Photochromic Organometallics Based on Linkage Isomerization: Photochemistry of Dicarbonyl(η^5-methylcyclopentadienyl)manganese(I) Derivatives with a Bifunctional, Nonchelating Ligand

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Cyclopentadienylmanganese complexes of the general formula (η^5-$C_5H_4CH_3$)$Mn(CO)_2L$, where L is a nonchelatable, bifunctional ligand, were found to be photochromic. Irradiation of (η^5-$C_5H_4CH_3$)$Mn(CO)_2L$(3-cyanomethylpyridine) with alternating visible and UV light produced alternating yellow and red solutions, and fatigue of this response was inhibited when free 3-(cyanomethyl)pyridine was present during irradiation. Similar results were observed when L is pyridine in the presence of dispersed acetonitrile. Irradiation of (η^5-$C_5H_4CH_3$)$Mn(CO)_3$ and a pyridine derivative RC_5H_4N (R = 3-CH_2CN, 2-CH_2CN, 4-CHCHPh, 4-$CHCH_2$) generated (η^5-$C_5H_4CH_3$)$Mn(CO)_2L$ in situ, which likewise showed a photochromic response. The results demonstrate that the linkage isomerization occurs by unimolecular and bimolecular processes and that linkage isomerization is an effective photochromic mechanism for organometallics.

Introduction

The potential applications of photochromic materials have inspired several recent studies,[1] and many organic and a few inorganic photochromic compounds have been reported.[2] Since color change is commonly observed during ligand substitution of organometallic complexes, it is surprising that bistable, photochromic, organometallic compounds have not been reported.[3,4] Several years ago Wrighton suggested that a blue solution containing (η^6-benzene)dicarbonyl(4-(2-phenylethenyl)-pyridine)chromium and pyridine would be photochromic because visible irradiation bleaches the solution at long wavelengths, the color changes from blue to red-orange, and the product was known to undergo photosubstitution as well.[5] No results were subsequently reported, and it turns out that 4-(2-phenylethenyl)pyridine is a poor choice as a ligand, since its cis−trans photoisomerization tends to quench the photochromic response and generate side products. In this work, we demonstrate that Cp′Mn complexes (Cp′ = methylcyclopentadienyl) with nonchelatable, bifunctional ligands can be photochromic and bistable. Tricarbonylcyclopentadienylmanganese derivatives were chosen for their thermal stability and high quantum yields for photosubstitution.[6] We find that many of the Cp′$Mn(CO)_3$ derivatives such as **3** and **4** (Scheme 1) undergo linkage isomerization and that most are photochromic.

Experimental Section

General Comments. Except where noted, all procedures were carried out under an argon or nitrogen (Air Products) atmosphere using a glovebox or standard Schlenk techniques. Ethanol (200 proof, ACS grade) was obtained from Aaper Alcohol and Chemical Co. **1** (Pressure Chemical Co.) was distilled under vacuum (80 milliTorr) at 54 °C. Tetrahydrofuran (THF, Fisher) and heptane were distilled over NaK alloy and sodium, respectively. Benzene (Aldrich) was used as received. Pyridine (Mallinckrodt) was distilled from calcium hydride. Published procedures were used to prepare **3b** and *trans*-**2e**.[7,8] All remaining reagents were obtained from Aldrich. Elemental analysis was obtained at Huffman Laboratories (Boulder, CO). For synthesis, samples were irradiated with a RPR-100 Rayonet photochemical reactor (RPR 300 nm lamps). For spectroscopic analysis, samples were routinely irradiated with a Commercial Electric L-38 tungsten−halogen lamp or a single 300 nm lamp. Otherwise, a PRA LN1000 nitrogen laser (337 nm, 2 μJ/pulse, 800 ps fwhi) was used. During sample irradiation in a sealed cuvette the temperature changed less than 2 °C, and the spectra were constant for at least 15

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(1) For recent review articles see: (a) *Chem. Rev.* **2000**, *100* (Irie, M., Ed.). (b) Durr, H.; Bouas-Laurent, H. *Photochromism, Molecules and Systems*; Elsevier: Amsterdam, 1990. (c) *Organic Photochromic and Thermochromic Compounds*; Crano, J. C., Guglielmetti, R. J., Eds.; Plenum: New York, 1999; Vol. 2 (Physicochemical Studies, Biological Applications, and Thermochromism). (d) *Organic Photochromic and Thermochromic Compounds*; Crano, J. C.; Guglielmetti, R. J., Eds.; Plenum: New York, 1999; Vol. 1 (Main Photochromic Families).

(2) Geosling, C.; Adamson, A. W.; Gutierrez, A. R. *Inorg. Chim. Acta* **1978**, *29*, 279−287.

(3) For recent examples of thermally unstable photochromic organometallics, see the following: (a) Rack, J. J.; Winkler, J. R.; Gray, H. B. *J. Am. Chem. Soc.* **2001**, *123*, 2432−2433. (b) Mitchell, R. H.; Brkic, Z. S.; Vittorio, A.; Berg, D. J. *J. Am. Chem. Soc.* **2003**, *25*, 7581−7585.

(4) We include only photochromic compounds that undergo chemical change at a metal.

(5) Wrighton, M. *Chem. Rev.* **1972**, *74*, 401−430.

(6) Geoffroy, G. L.; Wrighton, M. S. *Organometallic Photochemistry*; Academic Press: New York, 1979; Chapter 2.

(7) Crocock, B.; Long, C.; Hoie, R. A. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1992**, *C48*, 1004−1007.

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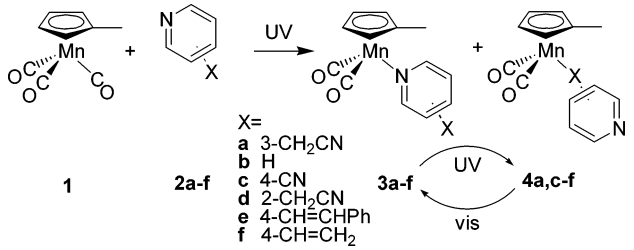
Scheme 1



min following irradiation. Residual solvent NMR peaks were used to determine chemical shifts relative to TMS.

Tricarbonyl(3-(cyanomethyl)pyridine)(methylcyclopentadienyl)manganese(I) (3a). A septum-sealed glass tube containing **1** (2 mL, 12.7 mmol) and **2a** (4 mL, 36.7 mmol) was irradiated for 26 h in the Rayonet reactor equipped with eight lamps while purging with argon. The resulting red solution plus ethanol (15 mL) and water (5 mL) were cannulated to a 50 mL Schlenk flask. Red crystals were Schlenk filtered, washed with cold ethanol, and dried under vacuum to obtain 0.65 g (17%) of product. ^{1}H NMR (270 MHz, C_6D_6): δ 1.25 (s, 3H, CH_3), 1.97 (s, 2H, CH_2), 3.96 (m, 2H, 2,5-Cp′), 4.14 (m, 2H, 3,4-Cp′), 5.84 (m, 1H, 5-py), 6.42 (m, 1H, 4-py), 8.22 (m, 2H, 2,6-py). ^{13}C NMR (67.9 MHz, C_6D_6): δ 12.56 (CH_3), 19.37 (CH_2), 80.55 (2,5-Cp′), 81.82 (3,4-Cp′), 102.73 (1-Cp′) 115.89 (CN), 122.63 (5-py); 126.38 (3-py), 134.00 (4-py) 156.57 (2-py) 156.82 (6-py). IR (NaCl, 0.1 mm, THF, 6.23 $\times$ 10^{-3} M): ν_{CO} 1921 cm^{-1} (s), 1851 cm^{-1} (s), ν_{CN} 2255 (w) cm^{-1}. Anal. Found: C, 57.81; H, 4.35. Calcd: C, 58.45; H, 4.25.

Irradiation Experiments. (a) NMR Analysis. 3a and 2a. An NMR tube containing **3a** (2 mg, 7 μmol), **2a** (4 μL, 37 μmol), and 0.5 mL of benzene-d_6 was irradiated with the tungsten−halogen lamp for 8 min and one 300 nm lamp for 10 min.

1 and 2a. An NMR tube containing **1** (1 μL, 6.3 μmol), **2a** (6 μL, 27 μmol), and 1.0 mL of benzene-d_6 was irradiated alternately with the Rayonet reactor (10 lamps) and the tungsten−halogen lamp for 20 (UV), 4 (vis), 15 (UV), 3 (vis), and 20 min (UV). For comparison with acetonitrile/benzonitrile experiments below, an NMR tube containing **1** (4 μL, 25 μmol), **2a** (27 μL, 250 μmol), and 1.0 mL of benzene-d_6 was irradiated with one 300 nm lamp for 1 min.

3b and 2b and Acetonitrile. An NMR tube containing **3b** (8 mg, 30 μmol), pyridine (12 μL, 150 μmol), acetonitrile (8 μL, 160 μmol), and 1.0 mL of benzene-d_6 was irradiated with the tungsten−halogen lamp for 10 min, one 300 nm lamp for 25 min, and then the tungsten−halogen lamp for 10 min.

1 and 2b and Acetonitrile or Benzonitrile. An NMR tube containing **1** (4 μL, 25 μmol), pyridine (20 μL, 250 μmol), and acetonitrile (13 μL, 250 μmol) or benzonitrile (29 μL, 250 μmol) with 1.0 mL of benzene-d_6 was irradiated with one 300 nm lamp for 1 min.

1 and 2c. An NMR tube containing **1** (1 μL, 6 μmol), **2c** (9 mg, 90 μmol), and 1.0 mL of cyclohexane-d_{12} was purged with argon through a glass capillary during 30 min of nitrogen laser irradiation (4 pulses s^{-1}). The solution was further irradiated for 2 min with the tungsten−halogen lamp.

1 and 2d. An NMR tube containing **1** (4 μL, 25 μmol), **2d** (29 mg, 250 μmol), and 1.0 mL of C_6D_6 was irradiated alternately with a single 300 nm lamp and the tungsten−halogen lamp for 60 (UV), 5 (vis), 120 (UV), 30 (vis), and 40 min (UV).

***trans*-2e.** An NMR tube containing *trans*-**2e** (0.01 g, 55 μmol) and 1.0 mL of C_2D_5OD was irradiated for 5 h with a 300 nm lamp. In addition to those for *trans*-**2e**, new proton peaks were observed at δ 6.65 (d, 1H, J = 12.4 Hz, vinyl), 7.02−7.11 (m, 6H, vinyl and phenyl), 7.60 (d, 2H, J = 6.7 Hz, 3,5-py), and 8.46 (d, 2H, J = 6.7 Hz, 2,6-py).

1 and *trans*-2e. A colorless solution of **1** (2 mL, 13 mmol), *trans*-**2e** (3.34 g, 18 mmol), and ethanol (90 mL) was purged in a septum-sealed 100 mL graduated glass cylinder and irradiated 4 h with the Rayonet reactor (eight lamps). One drop of the irradiated (red) solution and argon-purged ethanol (1.5 mL) were cannulated to an argon-filled, septum-sealed NMR tube and irradiated overnight with a 75 W, incandescent lamp.

1 and 2f. An NMR tube containing **1** (4 μL, 25 μmol), **2f** (6 μL, 56 μmol), and 1.0 mL of cyclohexane-d_{12} was argon-purged with a glass capillary during irradiation. The tube was irradiated alternately with one 300 nm lamp and the tungsten−halogen lamp for 2 (UV), 4 (vis), 2 (UV) and 4 h (vis). Similar experiments were carried out with **1** (4 μL, 25 μmol) and **2f** (6 μL, 56 μmol) in 1 mL of benzene-d_6 with UV light for 20 min and then visible light for 20 min.

(b) UV−Vis Analysis. 3a and 2a. A stock solution was prepared by diluting **3a** (6 mg, 19 μmol) to 10 mL in benzene. A second stock solution contained **2a** (10 μL, 90 μmol) diluted to 10 mL in benzene. A solution for UV−vis irradiation was prepared by diluting 250 μL of the **3a** solution to 5 mL with the **2a** solution. Spectra of this solution (2 mL, 1.6 $\times$ 10^{-4} M **3a** and 8.3 $\times$ 10^{-3} M **2a**) were recorded during 5 min irradiation with the tungsten−halogen lamp (1 min intervals) followed by irradiation with a 300 nm lamp until no significant change was observed (3 min, 30 s intervals). This sequence was repeated twice more for a total of three vis−UV irradiation cycles. Similar experiments were carried out with 1.3 $\times$ 10^{-4} M **3a** in heptane.

3a (No 2a). A stock solution was prepared by diluting **3a** (7 mg, 23 μmol) to 10 mL with benzene. A sample was prepared by diluting 200 μL of the stock solution to 3 mL with benzene (1.5 $\times$ 10^{-4} M). Spectra were recorded after five 1 min intervals of irradiation with the tungsten−halogen lamp and 30 s intervals for subsequent irradiation with a 300 nm lamp.

3b, 2b, and Acetonitrile. A **3b** stock solution was prepared by diluting 7 mg of **3b** (26 μmol) to 10 mL with benzene. A pyridine and acetonitrile stock solution was prepared by diluting 18.5 μL of pyridine (230 μmol) and 12.2 μL of acetonitrile (230 μmol) to 25 mL with benzene. For irradiation, 500 μL of the **3b** stock solution was diluted to 10 mL with the pyridine and acetonitrile stock solution. The pyridine and acetonitrile stock solution was used for background. A 3 mL sample (1.3 $\times$ 10^{-4} M **3b** and 8.7 $\times$ 10^{-3} M pyridine and acetonitrile) was irradiated for 15 min with the tungsten−halogen lamp while spectra were obtained at 60 s intervals and for 2.5 min with a 300 nm lamp while spectra were obtained at 30 s intervals.

IR Analysis of 3a. A solution was prepared by diluting **3a** (6 mg, 19 μmol) to 5 mL with isooctane. The solution was irradiated in a 0.5 mm path length NaCl IR cell with a 300 nm lamp for 30 s, the tungsten−halogen lamp for 3 min, and then the 300 nm lamp for 30 s.

Results

General Observations. Colorless or pale yellow solutions of **1** became red upon UV irradiation if a coordinated or dispersed ligand contained a pyridine group. Visible light bleached these solutions to yellow if dispersed or coordinated ligands had a nitrile or vinyl group (except in the case of **2c**; vide infra). With the change in color, some NMR peaks were found to grow and maintain a constant area ratio while other NMR peaks similarly declined. This assisted in the NMR assignments listed in Tables 1−5, along with the fact that the colors of complexes containing pyridine, nitrile, and vinyl ligands were previously reported.[9,10] NMR

(9) Gross, R.; Kaim, W. *J. Organomet. Chem.* **1987**, *333*, 347−65.
(10) Kelly, J. M.; Long, C. *J. Organomet. Chem.* **1982**, *231*, C9−C11.

Table 1. Proton NMR Data (ppm) for Irradiation of 1 and 2a in Benzene-d_6

	chem shift assignt							
complex	CH_3	CH_2	2,5-Cp′	3,4-Cp′	5-py	4-py	2-py	6-py
1 and **2a**	1.39	2.37	3.82	3.88	6.50	6.87	8.08	8.32
3a[a]	1.25	1.97	3.96	4.14	5.84	6.42	8.22	8.22
4a[a]	1.53	2.25	4.04	4.20	6.64	7.94	*b*	*b*

[a] After UV irradiation. [b] Peak could not be resolved.

Table 2. Proton NMR Data (ppm) for Irradiation of 3b, Acetonitrile, and Pyridine in Benzene-d_6

	chem shift assignt						
complex	CH_3CN	CH_3Cp'	2,5-Cp′	3,4-Cp′	3,5-py	4-py	2,6-py
3b and CH_3CN	0.63	1.22	3.95	4.14	5.95	6.44	8.36
5[a]	0.47	1.58	4.07	4.23	*b*	*b*	*b*

[a] After UV irradiation. [b] Peak could not be resolved.

Table 3. Proton NMR Data (ppm) for Irradiation of 1 and 2c in Cyclohexane-d_{12}

	chem shift assignt				
complex	CH_3	2,5-Cp′	3,4-Cp′	3,5-py	2,6-py
1 and **2c**	1.92	4.41	4.49	7.30	8.68
3c[a]	1.49	4.09	4.18	6.82	8.99
4c[a]	1.81	4.15	4.31	7.07	8.58
3c[b]	1.13	3.86	3.98	5.66	8.10
4c[b]	1.56	4.04	4.24	6.01	8.08

[a] After UV irradiation. [b] In benzene-d_6.[9]

Table 4. Proton NMR Data (ppm) for Irradiation of 1 and 2d in Benzene-d_6

	chem shift assignt							
complex	CH_3	CH_2	2,5-Cp′	3,4-Cp′	5-py	3-py	4-py	6-py
1 and **2d**	1.41	3.09	3.86	3.91	6.51	6.71	6.90	8.25
3d[a]	1.04	4.03	3.77	3.99	5.95	*b*	6.86	8.82
4d[a]	1.63	2.92	4.08	4.27	*b*	6.40	6.86	8.15
1 and **2d**[b]	1.92	3.73	4.41	4.49	7.06	7.39	7.56	8.44
4d[a,c]	1.72	3.88	4.04	4.20	*b*	*b*	*b*	*b*

[a] After UV irradiation. [b] In cyclohexane-d_{12}. [c] Peak could not be resolved.

Table 5. Proton NMR Data (ppm) for Irradiation of 1 and 2f in Benzene-d_6

	chem shift assignt							
complex	CH_3	2,5-Cp′	3,4-Cp′	vinyl	vinyl	vinyl	3,5-py	2,6-py
1 and **2f**	1.39	3.82	3.88	5.03	5.51	6.21	6.72	8.50
3f[a]	1.28	4.00	4.17	4.94	5.33	5.9	6.04	8.31
3f[b]	1.27	4.0	4.2	4.9	5.3	6.0	6.1	8.3
4f[a]	c	3.56	3.56	2.36	2.50	3.3	6.56	*c*
4f[b]	1.37	3.6	3.6	2.25	2.25	3.3	6.0	8.3
1 and **2f**[d]	1.92	4.41	4.49	5.3	5.81	6.57	7.07	8.50
3f[a,d]	1.47	4.01	4.17	*c*	*c*	*c*	6.71	8.71
4f[a,d]	1.88	4.16	4.21	2.79	2.79	3.7	*c*	8.26

[a] After UV irradiation. [b] Reference 10. [c] Peak could not be resolved. [d] In cyclohexane-d_{12}.

peak multiplicities and areas are reported in the Supporting Information. A photochromic response is observed during alternating visible and UV irradiation: visible irradiation of a red solution bleaches it to yellow, and UV irradiation of a yellow solution changes it to red. The NMR, UV−vis, and IR spectral changes that are observed for reactions based on **2a** are indicative of the results observed for the other ligands.

3a/4a. A red solution of **3a** and **2a** in benzene-d_6 changed to yellow upon 8 min irradiation with visible light. During this period, NMR peaks assigned to **3a** decreased while those for **4a** grew (Figure 1), and the area ratio of the methyl peaks at 1.25 (**3a**) versus 1.53 ppm (**4a**) was 0.7. The process was partially reversed upon 10 min UV irradiation, yielding a **3a**:**4a** methyl peak ratio of 2.0. No peaks associated with **1** were observed. Over the course of 10 min UV and 8 min visible irradiation the area ratio of **3a** and **4a** methyl peaks versus the **2a** methylene peak at 2.37 ppm declined from 0.21 to 0.17. Similar results were obtained when **3a** and **4a** where formed in situ during alternating UV and visible irradiation of **1** and **2a** in benzene-d_6.

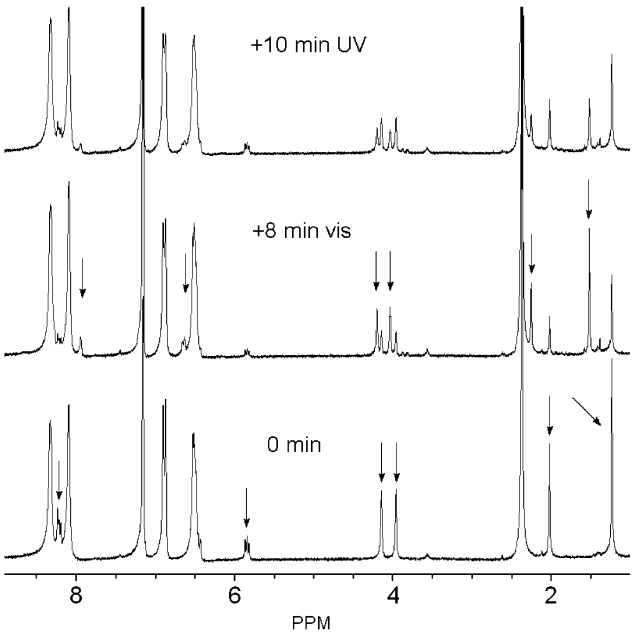


Figure 1. ^{1}H NMR spectral changes upon visible and UV irradiation of **3a** (1.4×10^{-2} M) and **2a** (7.4×10^{-2} M) in benzene-d_6. The 0 min spectrum shows the sample before irradiation. The arrows indicate assignments of **3a** peaks. The remaining peaks are assigned to **2a** or benzene-d_5. The +8 min visible spectrum shows the sample after irradiation for 8 min with visible light, and the arrows indicate new peaks assigned to **4a**. The +10 min UV spectrum shows the sample after a further 10 min irradiation with UV light.

An isosbestic point at 344 nm persists in the UV−vis spectra of a mixture of **3a** and **2a** (Figure 2) in benzene for at least three cycles of alternate UV and visible irradiation.[11] The maximum at 415 nm declined by 50% after 2 min visible irradiation and returned to a steady-state absorbance after 2.5 min UV irradiation. In the absence of free **2a** in benzene, an isosbestic point at 334 nm was maintained during 5 min visible irradiation but was lost immediately during UV irradiation. A different isosbestic point was observed during further visible irradiation but lost again during UV irradiation. For similar experiments with **2a** in heptane, an isosbestic point at 347 nm was observed during 5 min visible irradiation but was also lost immediately upon UV irradiation (data not shown).

Infrared peaks of **3a** in isooctane were observed at 2255 (w), 1932 (s), and 1868 (s) cm^{-1} (Figure 3). Visible

(11) In comparison to the case for irradiation of NMR samples in glass tubes, the concentrations for UV−vis samples are much lower and quartz cuvettes were used. This resulted in much shorter irradiation times.

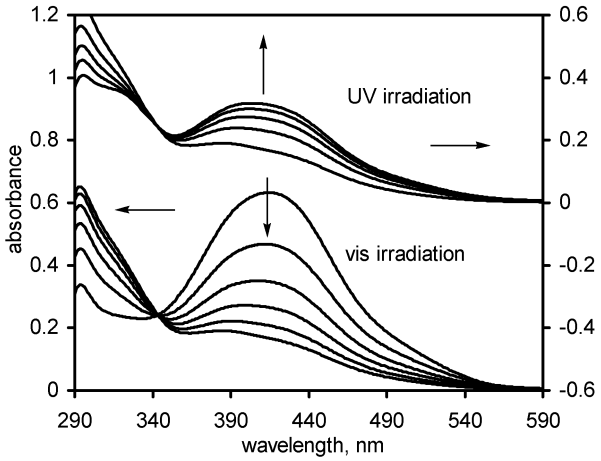


Figure 2. UV−vis spectral changes upon visible and UV irradiation of **3a** (1.6×10^{-4} M) and **2a** (8.3×10^{-3} M) in benzene. The lower spectra were recorded after 0, 1, 2, 3, 4, and 5 min of visible irradiation. The upper spectra were recorded after 5 min of visible irradiation and then 0.5, 1, 1.5, 2.5, and 3 min UV irradiation (spectra at 2.5 and 3 min were identical). Vertical arrows indicate the direction of increasing time, and horizontal arrows indicate the scale for each spectral series.

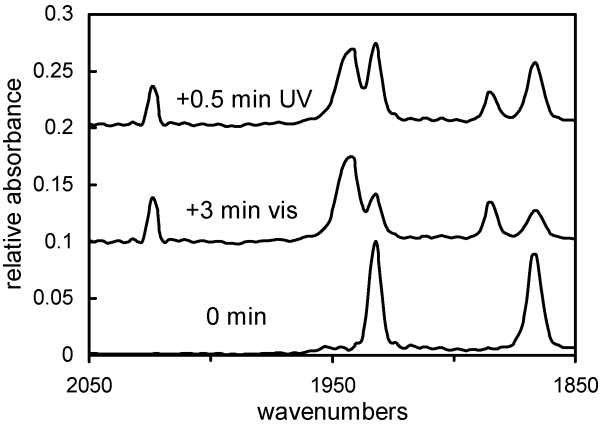


Figure 3. IR spectral changes upon visible and UV irradiation of **3a** (3.8×10^{-3} M) in isooctane. The 0 min spectrum shows the sample before irradiation. The +3 min visible spectrum shows the sample after 3 min of irradiation with visible light. The +0.5 min UV spectrum shows the sample after a further 0.5 min of irradiation with UV light.

irradiation reduced the **3a** peaks as new peaks appeared at 2025 (s), 1943 (s), and 1885 (s) cm^1. UV irradiation partially reversed these spectral changes until a steady-state spectrum was obtained.

3b/5. A red-orange solution of **3b**, **2b**, and acetonitrile in benzene-d_6 noticeably bleached to a pale orange color upon irradiation with visible light. Concurrently, NMR peaks assigned to **3b** decreased while those for **5** ((acetonitrile)dicarbonyl(methylcyclopentadienyl)manganese(I)) grew, yielding an area ratio of 1.3 for the methyl peaks at 1.21 (**3b**) and 1.58 ppm (**5**). Partial reversal of this process occurred with 25 min of UV irradiation; thus, **3b** peaks increased while those for **5** decreased, yielding a methyl peak ratio of 2.8. That ratio returned to 1.3 after 10 min additional visible irradiation. Over the course of the UV and visible photolyses the area ratio of all methyl peaks versus all the 2,6-pyridine hydrogen peaks decreased from 0.38 to 0.21. UV−vis spectra revealed an isosbestic point at 325 nm during a total of 15 min visible and 2.5 min UV irradiation of **3b**, **2b**, and acetonitrile in benzene. A peak at 392 nm decreased to 50% of its original absorbance during the first 14 min of visible irradiation, while the peak returned to a steady-state absorbance after 2 min of UV irradiation.

1/2a, 1/2b/Acetonitrile, and 1/2b/Benzonitrile. NMR spectra were compared for three samples containing **1** and free ligand after 1 min of UV irradiation. The spectra of the first sample containing 0.25 M **2a** had an area ratio of 1.3 for the methyl peaks at 1.25 (**3a**) and 1.53 ppm (**4a**). The spectra for a second sample containing 0.25 M **2b** and 0.25 M acetonitrile had an area ratio of 1.3 for the methyl peaks at 1.22 (**3b**) and 1.58 ppm (**5**). The third sample containing 0.25 M **2b** and 0.25 M benzonitrile had an area ratio of 1.5 for the methyl peaks at 1.22 (**3b**) and 1.62 ppm ((benzonitrile)-dicarbonyl(methylcyclopentadienyl)manganese(I)).

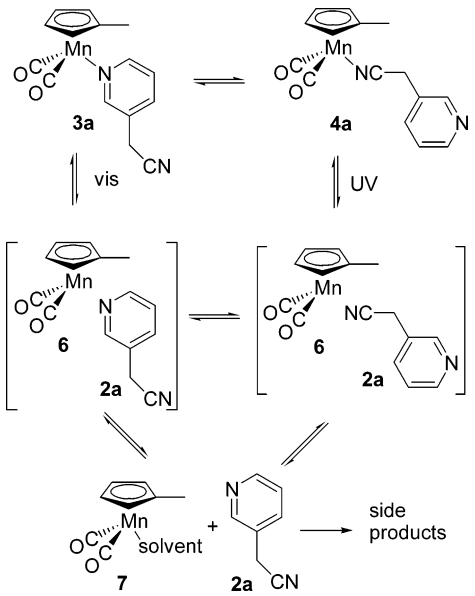
3c/4c. UV irradiation of a colorless solution containing **1** and **2c** turned dark red, and NMR peaks assigned to **3c** and **4c** appeared. The ratio of peak areas assigned to 3,5-pyridine hydrogens at 6.8 (**3c**) and 7.07 (**4c**) ppm was 0.9. After visible irradiation, the sample color became a darker red, but the ratio decreased to 0.11.

3d/4d. UV irradiation of a colorless benzene-d_6 solution of **1** and **2d** led to formation of a red-orange solution and new NMR peaks assigned to **3d** and **4d**. The methyl peaks at 1.04 (**3d**) and 1.63 (**4d**) ppm had a constant area ratio of 0.42 when monitored for up to 60 min of UV irradiation, and the ratio of the methyl peak areas for **3d** and **4d** to that for **1** was 2.2. After 5 min of visible irradiation, the sample color bleached to yellow, and the **3d** to **4d** methyl peak area ratio decreased to 0.29. At the same time the methyl peak area ratio of **3d** and **4d** to **1** was still 2.2 (±10%). Before any irradiation the area ratio of all the methyl peaks to the residual benzene peak was 2.3. After 2.5 irradiation cycles (60 min UV, 5 min vis, 30 min UV, 30 min vis, 100 min UV) the methyl-to-benzene peak area ratio declined to 0.5.

3e/4e. The color of an ethanol-d_6 solution containing **1** and *trans*-**2e** in an NMR tube was cycled 10 times between red and a dark yellow-orange with alternating UV and visible irradiation. During these experiments NMR spectra revealed multiple sets of peaks that increased or decreased which could not be readily identified. After UV irradiation of *trans*-**2e**, new ^1H NMR peaks were observed and assigned to *cis*-**2e** (the coupling constant is 12 Hz for the *cis*-**2e** vinyl peak while it is 16 Hz for the *trans*-**2e** vinyl peak). The area ratio of trans to cis vinyl peaks was 0.4.

3f/4f. UV irradiation for 2 h of a colorless cyclohexane-d_{12} solution of **1** and **2f** led to the formation of a red solution and NMR peaks assigned to **3f** and **4f**. The 2,6-pyridine hydrogens at 8.71 (**3f**) and 8.26 (**4f**) ppm had an area ratio of >10. After 4 h of visible irradiation the sample color bleached to yellow, and the 2,6-arene peak ratio decreased to <0.1. Similar NMR and color changes were observed in benzene-d_6 solutions. During a total irradiation of 20 min for UV and 20 min for visible, the ratio of the total area for the **3f** and **4f** methyl peaks to the solvent peak decreased from 1.4 to 1.1.

Scheme 2



Discussion

The results demonstrate that cyclopentadienylmanganese complexes can be a platform for a bistable photochromic system; a reversible color change was observed during alternate UV and visible irradiation of **1**, **3,** or **4** when ligands had either pyridine and nitrile functional groups or pyridine and vinyl groups (except in the case of **2d**). When effective π-acceptors (nitrile or vinyl groups) were coordinated to the metal fragment, the solutions were yellow (**4**), and when an effective σ-donor (pyridine group) was coordinated, the solutions were red or red-orange (**3**). UV irradiation of a solution containing a π-acceptor, a σ-donor, and **1** produces two complexes: one complex has CO replaced by the π-acceptor and another by the σ-donor. Generally this mixture produces a red solution, indicating significant formation of the σ-donor complex. Because **4** and **5** do not absorb much visible light, irradiation of the mixture with visible light selectively converts the σ-donor complex (**3**) to the π-acceptor complex (**4** or **5**), yielding a yellow solution. On the other hand, UV light is not selective, primarily because all the complexes (**3**−**5**) strongly absorb UV light.

The photochromic response is demonstrated most effectively with **3a** and **4a** (Scheme 2). We propose that a change in the coordination from the pyridine to the nitrile nitrogen of **2a** is responsible for the color change from the red **3a** to the yellow **4a**. This is consistent with the colors we observed for **3b** (red) and **5** (yellow). Pyridine nitrogen coordination for the red **3b** is unambiguous, since **3b** is formed from **1** and pyridine in the absence of nitrile, and the optical properties of **3b** are the same as in a previous report.[12] Similarly, the yellow **5** forms only in the presence of acetonitrile. More generally, previous studies report that (η^5-$C_5H_4CH_3$)-$Mn(CO)_2$ complexes coordinating pyridine functional groups are red, and those coordinating nitrile and olefin groups are yellow.[12−14]

The electronic structures of tricarbonylcyclopentadienylmanganese(I) derivatives have been studied previously, and the addition of a methyl to the cyclopentadienyl ring creates only minor changes to the electronic structures.[12] By analogy to the previous study, the peak at 415 nm may be assigned to a metal-to-pyridine π^* charge transfer for **3a**. For **4a**, where a nitrile is isolobal with carbon monoxide, a peak at 380 nm should correspond to a metal-to-acetonitrile π^* charge transfer. Recent studies suggest that dicarbonylcyclopentadienylmanganese(I) forms nearly degenerate triplet and singlet excited sates, with the triplet reacting with alkanes the slowest at 100 ps.[15] Singlet and triplet states for **3** and **4** should react even faster for a more reactive solvent such as benzene.

The assignments of **3a** and **4a** are also supported by the NMR data. An upfield shift of the methyl peak from 1.39 ppm for **1** to 1.25 ppm for **3a** (Table 1), where CO is substituted by a pyridine nitrogen, is consistent with the 1.22 ppm methyl peak observed for **3b** (Table 2). Likewise, a methyl downfield shift from 1.39 ppm for **1** to 1.53 ppm for **4a** (Table 1), where CO is substituted by a nitrile nitrogen, is consistent with the 1.58 ppm methyl peak observed for **5** (Table 2). The remaining peaks assigned to **3a** or **4a** increase or decrease in constant area ratios with the 1.22 or 1.53 ppm peaks, respectively. The formation of a complex containing two metal fragments bridged by 3-cyanopyridine is inconsistent with the NMR data, where peak areas indicate that the ratio of the methylcyclopentadienyl group to coordinated **2a** is 1:1, not 2:1. Finally, the assignment of **3a** is consistent with the X-ray analysis (Supporting Information) and infrared data (vide infra).

The reversibility of the **3a**−**4a** linkage isomerization is demonstrated by the NMR, UV−vis, and IR results in Figures 1−3. In the presence of free **2a**, an isosbestic point observed during alternating UV and visible irradiation of **3a** indicates that no side products are formed. In the absence of free **2a**, the isosbestic point persists during visible irradiation but not during subsequent UV irradiation. This indicates that, at least during UV irradiation, some other product is formed, which can be inhibited by free **2a**. Because some of the irradiation without free **2a** produces side product and this irradiation otherwise produces linkage isomerization in the presence of free **2a**, we conclude that at least some of the linkage isomerization is bimolecular and occurs by a reaction between an intermediate metal fragment and free **2a**. The side product formation is not simply caused by a process dependent on benzene UV irradiation, since the isosbestic point is also lost in heptane during UV irradiation.

Scheme 2 is a mechanism proposed for **3a** and **4a** photoisomerization. Visible irradiation of **3a** or UV irradiation of **4a** forms what appears to be a common cage intermediate (**6** and **2a**). In each case, the intermediate can recombine to re-form the starting isomer or rearrange in the solvent cage to form the other isomer. On occasion, the ligand escapes, allowing solvent coordination and eventually the formation of some other product. The intermediate from **3a** (UV irradiation) cannot be identical with that from **4a (**visible irradia-

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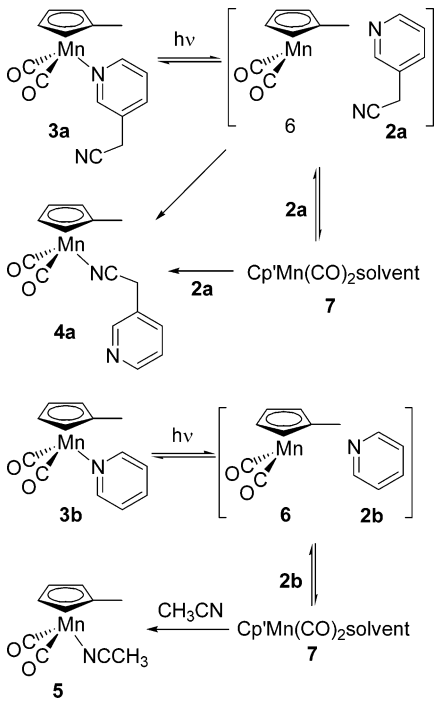
Scheme 3



tion); otherwise, the isosbestic point would be readily lost during visible irradiation as well. There are two likely contributions to the differences in the intermediates. First, immediately upon dissociation of **4a**, the nitrile is near the metal after UV irradiation, while for **3a** the pyridine is near the metal after visible irradiation. A simple rotation moving the nitrile group allows solvent coordination, but virtually the whole ligand must move when the pyridine group is near the metal. Therefore, solvent coordination is more likely after the nitrile dissociation that accompanies UV irradiation. Second, the fragments have greater excess energy after UV irradiation than for visible irradiation; therefore, after UV irradiation there is a greater probability of cage escape leading to subsequent solvent coordination. Thus, solvent coordination and subsequent side product formation are more likely for UV irradiation. Any alternative mechanism that accounts for side product formation must occur via an intermediate that can be captured by free ligand to re-form **3a** or **4a**.[16]

The fact that **3a** converts to **4a** nearly 3 times faster than **3b** to **5** under nearly identical conditions indicates that some of the linkage isomerization is a unimolecular (cage) reaction. Scheme 3 compares the conversions of **3a** and **3b** and reveals two differences. First, the conversion of **3a** to **4a** can occur by a unimolecular (cage) reaction, whereas the conversion of **3b** to **5** cannot. Second, **7**, a common intermediate for both reactions, competes for two functional groups on the same ligand (**2a**) to form **4a** in contrast to two separate ligands (**2b** and acetonitrile) to form **5**. A simple analysis indicates that the conversion of **3a** to **4a** via **7** is not significantly different than the conversion of **3b** to **5**, leading to the conclusion that faster conversion of **3a** to **4a** must be due to the cage reaction (**6** to **4a**). Consider the formation of **7**, the first step for the bimolecular reaction in each case. The yield of **7** is not likely to differ significantly for **3a** and **3b**, since the yield for ligand substitution of $CpMn(CO)_2(RC_5H_5N)$ in a hydrocarbon solvent is nearly independent of the functional groups on the pyridine.[12] Note that the methyl substitution on the Cp ring is unlikely to have an appreciable effect, because the substitution quantum yields for $CpMn(CO)_3$ and **1** in hydrocarbon solvents are the same.[12,17] Our results indicate that the second step, the partitioning of **7** into **3a** and **4a**, is not significantly different than the partitioning of **7** into **3b** and **5**. Specifically, when **7** is generated independently by photolysis of **1** in the presence of **2a**, of **2b** and acetonitrile, or of **2b** and benzonitrile, the ratio of pyridine-nitrogen to nitrile-nitrogen coordination is the same within experimental errors for each case. Hence, the preference for nitrile versus pyridine is not altered when **2a** is replaced by **2b** and free nitrile, and we conclude that the yields for the **3a** to **4a** and **3b** to **5** pathways involving **7** are not significantly different and that the cage linkage isomerization via **6** (Scheme 3) accounts for the faster conversion of **3a** to **4a**.

The isosbestic points also demonstrate that UV or visible irradiation of **3a** or **4a** leads to selective dissociation of the metal−nitrogen bond without significant CO dissociation. While the bond energies for these complexes are not known, the relative bond energies have been reported for other metal carbonyls and show that the metal−CO bond energy is greater than the metal−pyridine and metal−nitrile bond energies.[18] This follows the trend for irradiation of cyclopentadienylmanganese complexes, where the weakest bond breaks.[12]

A ring-slip mechanism might account for the linkage isomerization by providing a vacant site for addition.[19] The addition would have to be bimolecular with free **2b**, since chelation of **2b** is precluded by the geometrical constraint of 1,3-substitution. Presumably ring-slipped **3a** or **4a** will be rapidly solvated as observed with **7**, and subsequent displacement of the solvent by free ligand will be relatively slow.[15,20] It seems likely that photolytic ring slippage does not contribute to the linkage isomerization, since ultrafast studies do not reveal photolytic ring slippage for tricarbonylcyclopentadienylmanganese.[15] Even if ring slippage does occur, it might be reversed before any addition can occur.

Other Nitrile−Pyridine Exchanges. Irradiation of **1** and **2c** resulted in a mixture of two products. In either cyclohexane-d_{12} or benzene-d_6, the peak assigned to the methyl of the pyridine-coordinated **3c** is upfield of the methyl peak assigned to the nitrile-coordinated **4c** (Table 3). This assignment is consistent with those for **3a**, **4a**, **3b**, and **5**. The 3,5-pyridine peak that grows and

(16) There is another distinction between visible and UV irradiation of this system. Visible irradiation can completely convert **3a** to **4a**, since **4a** does not absorb at long wavelengths and cannot be converted to **3a** by visible irradiation. On the other hand, UV irradiation does not completely convert **4a** to **3a**, since the **3a** that is formed also absorbs UV light and converts back to **4a** until a steady-state mixture of **3a** and **4a** is obtained. Therefore, the inner-filter effect of **3a** makes conversion of **4a** to **3a** more inefficient as the steady state is reached. In any event, the loss of isosbestic point is not due to extended UV irradiation, since the isosbestic point is lost when UV irradiation commences.

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declines with the **3c** methyl peak is upfield of the 3,5-pyridine peak that grows and declines with the **4c** methyl peaks for **4c**. Likewise, the 2,6-pyridine peak that grows and declines with the **4c** methyl peak is downfield of that for **3c**. These relative peak positions are also consistent with the assignments for the 5- and 6-pyridine peaks of **3a** and **4a**. Furthermore, these assignments for **3c** and **4c** agree with those reported previously in benzene-d_6.[9] Despite the similarity in the absorption spectra of **3c** and **4c**, visible irradiation of a 50:50 mixture of **3c** and **4c** converts nearly all of **4c** to **3c**. Although pure samples of **3c** and **4c** have not been obtained, this suggests that conversion of **4c** to **3c** is favored by visible irradiation either because **4c** has greater extinction coefficients at long wavelengths or because the quantum yield for linkage isomerization is greater for **4c**.

Two products, **3d** and **4d**, were detected upon UV irradiation of **1** and **2d**. Except for the **3d** methylene peak, the assignments for **3d** and **4d** are consistent with assignments made for the compounds discussed above (Table 4). The large downfield shift of the **3d** methylene peak may be due to methylene occupation of deshielding regions near the Cp′ ring or CO. The NMR results indicate that interconversion of **3d** and **4d** occurs during alternate UV and visible irradiation of a mixture of **1** and **2d**. The decrease in one isomer during the increase of the other cannot be explained simply by the further conversion of **1** into **3d** or **4d** while the other isomer decomposes, since the NMR peak areas indicate that the loss of **1** was not enough to account for the formation of **3d** or **4d**. Thus, **3d** and **4d** are photochromic.

Olefin−Pyridine Exchange. Originally we planned a photochromic ligand exchange of **3e** with pyridine because of the large wavelength shift previously observed for pyridine substitution with (η^6-benzene)-dicarbonyl(η^1-4-(2-phenylethenyl)pyridine)chromium.[5] The exchange was never attempted for two reasons. First, a red solution, not blue, was produced when **1** and **2e** were irradiated; therefore, no significant photochromic response would occur if the product were converted to the red **3b.** Second, and more importantly, a photochromic response was observed with **1** and **2e** without any other dispersed ligand. We propose that a linkage isomerization occurs between the pyridine and vinyl groups, but this system is less than ideal. It is well established that **2e** undergoes cis−trans isomerization while coordinated to other metal fragments, resulting in a mixture of isomers.[21] Furthermore, the free ligand absorbs UV light under the conditions of our experiments, producing the cis isomer before it coordinates to the metal. At least six species involving **2e** may be present to generate a complex NMR spectrum. Finally, the cis−trans isomerization is a sink for excitation energy, which lowers the yield of the photochromic response.

To lend support for the proposed linkage isomerization between the vinyl and pyridinyl groups of **2e**, we investigated the isomerization between **3f** and **4f**. Olefin coordination by $Mn(C_5H_4CH_3)(CO)_2$ has been reported previously, and the products are yellow for simple olefins.[22] **3f** and **4f** have been reported previously; however, a photochromic response has not been reported.[10] The results for irradiation of **1** with **2f** were similar to those for **1** and **2a**, indicating that **3f** and **4f** constitute a photochromic system. A red color correlates with the NMR peaks assigned to the pyridine-coordinated complex, a yellow color correlates with the NMR peaks assigned to the vinyl-coordinated complex, and our NMR assignments agree with those previously reported for **3f** and **4f**. We attribute the photochromic response during irradiation of **1** and **2e** or of **1** and **2f** to the linkage isomerization between pyridine and vinyl coordination.

Conclusions

Ligand substitution of pyridine by vinyl or nitrile groups on $(C_5H_4CH_3)Mn(CO)_2L$ provides a mechanism for a bistable photochromic system. With bifunctional ligands, a linkage isomerization occurs via both unimolecular and bimolecular processes. In the case of **3a** and **4a**, a unimolecular linkage isomerization accounts for a more efficient exchange than is observed for the analogous bimolecular ligand exchange of **3b** and **4b**. To improve the yield and speed of the photochromic response and to eliminate fatigue, we are examining the photochemistry of tethered bifunctional ligands.

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Supporting Information Available: Text giving synthetic procedures, analytical and spectroscopic data for **1**, **2a**−**c**,**f**, **3a**−**d**,**f**, **4b**,**c**,**f**, and *trans*-**2e** and tables giving X-ray crystallographic data for **3a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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