Katz has suggested that the general lack of stereospecificity in Lewis acid cocatalyzed metathesis systems is due to a reversible Lewis acid induced cleavage of transient metallacyclobutanes to a 3-metallapropyl cation, which can then undergo C–C bond rotation, ultimately resulting in scrambling of stereochemistry.[16,17] The similarity of Katz's suggestion to our proposal is apparent. The tendency of a given metathesis catalyst system to show high stereospecificity in the presence of Lewis acids may depend on steric and electronic factors that can determine the susceptibility of a transient metallacyclobutane to transmetalation by the Lewis acid cocatalyst.

Acknowledgment. We gratefully acknowledge the support of the National Science Foundation (Grant CHE 8016528), the Department of Energy, and the use of the Southern California Regional NMR Facility (NSF Grant 7916324A1).

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(16) Katz, T. J.; Hersh, W. H. *Tetrahedron Lett.* **1977**, 585.

(17) Not all aluminum alkyl cocatalyzed metathesis systems show such a dependence of stereospecificity on the Lewis acid concentration. For example, the stereochemistry of ring-opening metathesis polymerization of cyclopentene with $MoCl_5/AlEt_3$ is unaffected by raising the $AlEt_3$ concentration: Dall'Asta, G.; Motroni, G. *Angew. Makromol. Chem.* **1971**, *16/17*, 51.

(18) All reactions described herein were followed by NMR spectroscopy with either a Bruker WM–500 (500.13 MHz ^1H, 76.76 MHz ^2H) or a JEOL FX-90Q (89.60 MHz ^1H) spectrometer.

(19) Reaction of *trans*-I-d_1 with 1 equiv of $AlMe_3$ resulted in less than 5% isomerization in 20 min at room temperature. Reaction of *trans*-I-d_1 with $AlCl_3$ resulted in decomposition of the metallacycle, but in the initial stages of reaction, the metallacycle was observed to be isomerized. Reaction of *trans*-I-d_1 with diphenylacetylene resulted in no isomerization of the metallacycle, and *trans*-3,3-dimethyl-1-butene-$_4$-d_1 is observed as the only deuterated olefin. The half-life for thermal isomerization of *trans*-I-d_1 is 2 h at 50 °C: Lee, J. B.; Ott, K. C.; Grubbs, R. H. to be submitted for publication.

Mechanism of the Photochemical Disproportionation Reactions of $(\eta^5\text{-}C_5H_5)_2M_2(CO)_6$ (M = Cr, Mo, W)

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Very little is known about the mechanism of the photochemically induced disproportionation reactions of metal–metal bonded dimers.[1] For this reason we have been investigating the photochemical disproportionation reactions of the $Cp_2M_2(CO)_6$ (M = Cr, Mo, W; Cp = η^5-C_5H_5) complexes, an example of which is shown in eq 1. The photochemical reactions of metal–metal bonded dimers are generally thought to proceed via homolytic cleavage of the metal–metal bond,[2] but the disproportionation reactions might be an exception to this generalization; it has been suggested that these reactions proceed via photoinduced heterolytic cleavage of the metal–metal bond.[1a] We communicate here the results of experiments that strongly suggest that the disproportionation reactions of the $Cp_2M_2(CO)_6$ complexes result from neither homolytic nor heterolytic cleavage of the metal–metal bond but via a third pathway instead.

$$Cp_2Mo_2(CO)_6 \xrightarrow[NEt_3]{h\nu} CpMo(CO)_3^- + CpMo(CO)_2(NEt_3)_2^+ \tag{1}$$

Scheme I

$$Cp_2M_2(CO)_5L \xrightarrow{h\nu} CpM(CO)_3 + CpM(CO)_2L$$
$$CpM(CO)_3 + CpM(CO)_2L \xrightarrow{\text{electron transfer}} CpM(CO)_3^- + CpM(CO)_2L^+$$
$$CpM(CO)_2L^+ + L \rightarrow CpM(CO)_2L_2^+$$

Scheme II

$$Cp_2M_2(CO)_5L \xrightarrow{h\nu} CpM(CO)_3 + CpM(CO)_2L$$
$$CpM(CO)_2L + Cp_2M_2(CO)_5L \rightarrow CpM(CO)_2L^+ + Cp_2M_2(CO)_5L^-$$
$$Cp_2M_2(CO)_5L^- \rightarrow CpM(CO)_2L + CpM(CO)_3^-$$
$$CpM(CO)_2L^+ + L \rightarrow CpM(CO)_2L_2^+$$

Irradiation (λ > 290 nm) of $Cp_2Mo_2(CO)_6$ (1.0×10^{-2} M) in degassed cyclohexane solution containing PPh_3 (5.0×10^{-2} M) proceeds as in eq 2.[3] The substitution product, $Cp_2Mo_2(CO)_5(PPh_3)$, was identified as an intermediate by its infrared absorption bands at 1968, 1900, and 1827 cm^{-1}.[4] The products $CpMo(CO)_2(PPh_3)_2^+$ and $CpMo(CO)_3^-$ were identified by their infrared absorption bands at 1974 and 1895 cm^{-1} and at 1771 cm^{-1}, respectively.[4] Note the small mole ratio of PPh_3 to metal complex (5:1) required to give the disproportionation products. This small ratio shows that the disproportionation is not attributable to a solvent-induced dipolar excited state as originally proposed.[5]

$$Cp_2Mo_2(CO)_6 \xrightarrow[PPh_3]{h\nu} Cp_2Mo_2(CO)_5(PPh_3) \xrightarrow[PPh_3]{h\nu} CpMo(CO)_2(PPh_3)_2^+ + CpMo(CO)_3^- \tag{2}$$

Disproportionation reactions similar to the one in eq 2 occur for the $Cp_2M_2(CO)_6$ (M = Cr, Mo, W) dimers in hexane solution with ligands other than PPh_3. A list of ligands that lead to disproportionation includes NEt_3, CH_3CN, pyridine, aniline, $AsPh_3$, $P(O\text{-}i\text{-}C_3H_7)_3$, and $P(OCH_3)_3$. In each case, irradiation initially produces the monosubstituted dimer, $Cp_2M_2(CO)_5L$ (identified by IR spectroscopy), and then this complex photolyzes to give the ionic products $CpM(CO)_2L_2^+$ and $CpM(CO)_3^-$. In no case were ionic products observed to form without the initial formation of the monosubstituted dimer. In order to check the idea that the monosubstituted dimer is an intermediate in the formation of the ionic products, the complex $Cp_2Mo_2(CO)_5(PPh_3)$ was synthesized[6] and its photochemistry studied. Irradiation (290 nm) of this complex (1.0×10^{-2} M) in hexane solution containing 0.1 M PPh_3 gave $CpMo(CO)_2(PPh_3)_2^+$ and $CpMo(CO)_3^-$. The products were identified by infrared spectroscopy.[4] No infrared bands other than the ones attributable to these products were observed.

The disproportionation reactions show a marked wavelength dependence. Irradiation of $(MeCp)_2Mo_2(CO)_6$[7] in cyclohexane containing excess PPh_3 at 505, 435, 405, and 366 nm[8] does not give the ionic disproportionation products; only the monosubstituted product $(MeCp)_2Mo_2(CO)_5(PPh_3)$ is formed.[9] The quantum yield for substitution of $(MeCp)Mo_2(CO)_6$ by PPh_3 ($[PPh_3] = 0.018$ M, cyclohexane solution) at 405 nm is 0.04 ± 0.01. Disproportionation does not occur until the excitation wavelength is 290 nm. At 290 nm the quantum yield for disproportionation of $(MeCp)_2Mo_2(CO)_5(PPh_3)$ is 0.40 ± 0.04 in

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(1) (a) Allen, D. M.; Cox, A.; Kemp, T. J.; Sultana, Q. *J. Chem. Soc., Dalton Trans.* **1976**, 1189–1193. (b) Hieber, W.; Beck, W.; Zeitler, G. *Angew. Chem.* **1961**, *11*, 364–368.

(2) (a) Wrighton, M. *Chem. Rev.* **1974**, *74*, 401–430. (b) Grinley, D. S.; Wrighton, M. S. *J. Am. Chem. Soc.* **1975**, *97*, 4908–4911. (c) Grinley, D. S.; Bock, C. R.; Wrighton, M. S. *Inorg. Chim. Acta* **1977**, *23*, 85–94. (d) Kidd, C. R.; Brown, T. L. *J. Am. Chem. Soc.* **1978**, *100*, 4095–4103. (e) Hudson, A.; Lappert, M. F.; Nicholson, B. K. *J. Chem. Soc., Dalton Trans.* **1977**, *98*, 551–554. (f) Morse, D. L.; Wrighton, M. S. *J. Am. Chem. Soc.* **1976**, *98*, 3931–3934. (g) Geoffroy, F. L.; Wrighton, M. S. "Organometallic Photochemistry"; Academic Press: New York, 1979.

(3) All irradiations were carried out with a 200-W high-pressure mercury arc. Solutions were degassed with a stream of argon or nitrogen. The 290-nm wavelength band was isolated with a Corion interference filter.

(4) Haines, R. J.; Nyholm, R. S.; Stiddard, M. H. B. *J. Chem. Soc. A* **1968**, 43–46.

(5) The disproportionation reactions were initially observed to occur in neat solvents such as pyridine, Me_2SO, and DMF. It was suggested that the polar solvent molecules induced a dipole in the excited state, $^{\delta-}M\text{–}M^{\delta+}$, which subsequently relaxed to give ionic products.

(6) Barnett, K. W.; Treichel, P. M. *Inorg. Chem.* **1967**, *6*, 294–299.

(7) The methylcyclopentadienyl compounds were used in some of these experiments as they were more soluble in alkane solvents than their cyclopentadienyl counterparts.

(8) These wavelengths were isolated with interference filters from Edmund Scientific Co.

(9) The CO stretching region of the infrared spectrum of $(MeCp)_2Mo_2(CO)_5(PPh_3)$ is identical with that of $Cp_2Mo_2(CO)_5(PPh_3)$.

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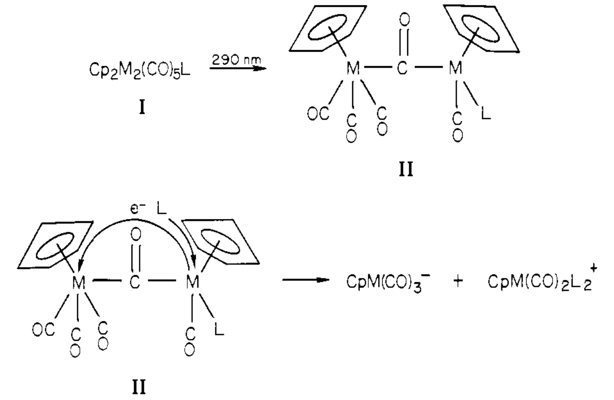
Scheme III



benzene; substitution of $(MeCp)_2Mo_2(CO)_6$ by PPh_3 ($[PPh_3] = 0.018$ M, cyclohexane solution) at 290 nm has a quantum yield of 0.35 ± 0.04. The two lowest energy electronic absorption bands at approximately 500 and 380 nm in the $Cp_2M_2(CO)_5L$ complexes have been assigned to the $d\pi\rightarrow\sigma^*$ and $\sigma\rightarrow\sigma^*$ transitions, respectively.[2g] Because electronic excitation at 505, 435, 405, and 366 nm does not lead to disproportionation, we must conclude that these excited states are inactive toward disproportionation. The dependence of the disproportionation reaction on wavelength is independent of the ligand. Wavelength results similar to those obtained with PPh_3 were also found for the other ligands used in our study.

Homolytic cleavage of the metal–metal bond occurs upon $\sigma\rightarrow\sigma^*$ or $d\pi\rightarrow\sigma^*$ excitation of the $Cp_2M_2(CO)_5L$ complexes.[10] Therefore, the wavelength dependence of the disproportionation reaction has an important mechanistic implication: homolytic cleavage of the metal–metal bond is not sufficient to induce disproportionation. Consequently, the outer-sphere electron-transfer pathway in Scheme I and the radical-chain pathway[11] of Scheme II are not responsible for disproportionation of the $Cp_2M_2(CO)_6$ complexes. In addition, the previously proposed substitution-induced outer-sphere electron-transfer mechanism can also be eliminated from consideration.[12]

The results above suggest that disproportionation results from excitation to an excited state that is higher in energy than the $d\pi\rightarrow\sigma^*$ or $\sigma\rightarrow\sigma^*$ states. A possible pathway is outlined in Scheme III. In this scheme, the effect of 290-nm excitation is to produce intermediate II, a species with no metal–metal bond but a CO bridge. One of the metal atoms in II is coordinatively unsaturated and it undergoes nucleophilic attack by ligand L. This addition of another ligand to the metal puts sufficient electron density[13] on the metal so as to induce an inner-sphere electron transfer. Note that reaction intermediates similar to II have been proposed before in the reactions of binuclear metal carbonyl complexes.[14-16]

The quantum yield data support our suggestion that a coordinatively unsaturated intermediate such as II forms upon 290-nm excitation of the $Cp_2M_2(CO)_5L$ complexes. Note that the quantum yields for substitution of $Cp_2Mo_2(CO)_6$ and disproportionation of $Cp_2Mo_2(CO)_5L$ at 290 nm are identical within experimental error (0.35 ± 0.04 and 0.40 ± 0.04, respectively). This constant value suggests that structurally related intermediates form with constant quantum efficiency when the $Cp_2M_2(CO)_6$ and $Cp_2M_2(CO)_5L$ complexes are irradiated at 290 nm; we suggest that the M–CO–M bridged intermediate is common to both the substitution and disproportionation reactions at 290 nm. When $Cp_2M_2(CO)_6$ is irradiated, attack of L on the intermediate simply leads to substitution. When $Cp_2M_2(CO)_5L$ is irradiated, the bridged intermediate forms with the same quantum efficiency as when $Cp_2M_2(CO)_6$ is irradiated. This time, however, coordination of L (two L's are now coordinated to the same metal) polarizes the M–CO–M unit enough so as to induce electron transfer.[17] Attempts to stabilize II by irradiating $Cp_2M_2(CO)_5L$ in low-temperature glasses are in our laboratory.

Acknowledgment. We thank Professors H. B. Gray, T. L. Brown, and M. S. Wrighton for helpful discussions. S. Brawner McCullen is thanked for sending us a preprint of ref 11. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the Research Corp. for the support of this research.

Registry No. $Cp_2Mo_2(CO)_6$, 12091-64-4; $Cp_2Cr_2(CO)_6$, 12194-12-6; $Cp_2W_2(CO)_6$, 12566-66-4; $Cp_2Mo_2(CO)_5(PPh_3)$, 12119-01-6; $(MeCp)_2Mo_2(CO)_6$, 33056-03-0; PPh_3, 603-35-0; NEt_3, 121-44-8; CH_3CN, 75-05-8; $AsPh_3$, 603-32-7; $P(O\text{-}i\text{-}C_3H_7)_3$, 116-17-6; $P(OCH_3)_3$, 121-45-9; pyridine, 110-86-1; aniline, 62-53-3.

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[10] Our results indicate that homolytic cleavage of the metal–metal bond occurs with low-energy excitation of $Cp_2Mo_2(CO)_5(PPh_3)$. Irradiation (405 nm) of this complex in CCl_4 solution yields $CpMo(CO)_3Cl$ and $CpMo(CO)_2(PPh_3)Cl$. These products were identified by infrared spectroscopy. (See: Burkett, A. R.; Meyer, T. J.; Whitten, D. G. *J. Organomet. Chem.* **1974**, *67*, 67–73.) In addition, irradiation (405 nm) of $Cp_2Mo_2(CO)_5(PPh_3)$ in benzene solution gives $Cp_2Mo_2(CO)_6$. No CO stretching bands attributable to other products were observed in the infrared spectrum. The products of the Cl atom abstraction reaction and the cross-coupling reaction are consistent with initial homolytic cleavage of the metal–metal bond.

[11] McCullen, S. B.; Brown, T. L. *Inorg. Chem.* **1981**, *20*, 3528–3533.

[12] Hepp, A. F.; Wrighton, M. S. *J. Am. Chem. Soc.* **1981**, *103*, 1258–1261.

[13] The electron-donating ability of the entering ligand is the key to whether a particular ligand can induce disproportionation or whether just substitution occurs. This aspect of the mechanism will be discussed in a full paper.

[14] Tyler, D. R.; Schmidt, M. A.; Gray, H. B. *J. Am. Chem. Soc.* **1979**, *101*, 2753–2755.

[15] Stanghellini, P. L.; Rossetti, R.; Mentasti, E.; Pelizzetti, E. *Inorg. Chim. Acta* **1977**, *22*, 19–22.

[16] Fox, A.; Poe, A. *J. Am. Chem. Soc.* **1980**, *102*, 2497–2499.

[17] Although the quantum yield data are consistent with the formation of intermediate II in Scheme III, our results cannot rule out direct heterolysis of the M–M bond at 290 nm. The $\sigma\sigma^*$ singlet excited state of a metal–metal bonded complex is a bound ionic state. Irradiation at 290 nm may excite the molecule to a vibrational energy level of the $\sigma\sigma^*$ singlet state that is above the dissociation limit and ions may result.

Stereoselective Total Synthesis of 1α,25-Dihydroxycholecalciferol

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The isolation and structure determination of the physiologically active vitamin D_3 metabolite 1α,25-dihydroxycholecalciferol (**1**)[1] and its use as a lifesaving drug for osteodystrophy due to renal failure have stimulated significant efforts toward synthesis of this natural product.[2] We report here the first[3] total and chiral synthesis of 1α,25-dihydroxycholecalciferol, which can also be used efficiently in the preparation of other 1α-hydroxy vitamin D metabolites.

Lythgoe and co-workers have shown[4,5] that the lithium phos-

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[3] This synthesis was first presented by us (E.G.B.) at the Gordon Conference on Natural Products, July, 1981.

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