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Communications

Photochemical Rearrangement of a Rhenium Dimetallacyclobutene Studied by Time-Resolved Infrared Spectroscopy

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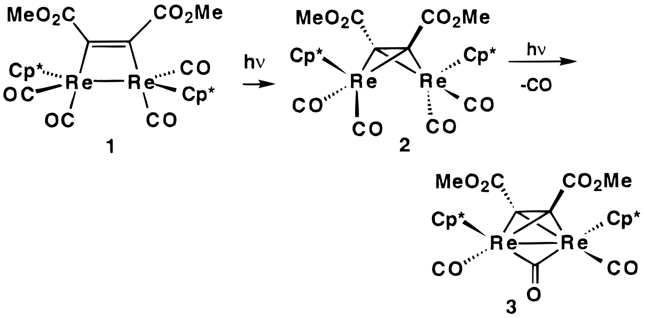
Summary: Time-resolved infrared spectral studies of the photochemical transformation (quantum yield 0.41 for 366 nm photolysis in cyclohexane) of the 3,4-dirhenacyclobutene complex **1** *to the 2,4-dirhena[1.1.0]bicyclobutane complex* **2** *demonstrate the prompt formation of the short-lived intermediate* ***I*** *proposed to be a bis(metallacarbene).*

Time-resolved infrared (TRIR) spectroscopy has proven to be a valuable tool in probing the structures and reactivities of short-lived intermediates generated by the flash photolysis of organometallic complexes.[1] Recently, the preparation of the dirhenacyclobutene $Cp^*(CO)_2Re(\mu\text{-}\eta^1{:}\eta^1\text{-}CH_3O_2CC{=}CCO_2CH_3)Re(CO)_2Cp^*$ (**1**; $Cp^* = \eta^5\text{-}Me_5C_5$) was described.[2] This complex undergoes both thermally induced and photoinduced isomerization to the 2,4-dirhenabicyclo[1.1.0]butane complex $Cp^*(CO)_2Re\text{-}(\mu\text{-}\eta^2{:}\eta^2\text{-}CH_3O_2CC{\equiv}CCO_2CH_3)Re(CO)_2\text{-}Cp^*$ (**2**) and subsequent photochemical decarbonylation to the carbonyl-bridged analog $Cp^*(CO)Re(\mu\text{-}\eta^2{:}\eta^2\text{-}CH_3O_2CC{\equiv}CCO_2CH_3)(\mu\text{-}CO)Re(CO)Cp^*$ (**3**).[2]



Described here are TRIR studies of the **1** → **2** photoisomerization which demonstrate the efficient formation of a short-lived intermediate proposed to be a bis(metallocarbene) species formed by "homolytic" cleavage of the Re−Re bond.

Continuous-wave photolysis[3] (λ_{irr} 366 nm) of room-temperature cyclohexane solutions of **1** (2×10^{-4} M) under argon resulted in clean conversion to **2**, as determined by FTIR (N_{CO}(c-C_6H_{12}): **1**, 1975, 1948, 1902, 1882 cm^{-1}; **2**, 2000, 1973, 1920, 1895 cm^{-1}) and UV/visible spectroscopy (λ_{max} (ϵ): **1**, 326 nm (5.5×10^3 M^{-1} cm^{-1}); **2**, 326 nm (7.0×10^3)). The quantum yield for formation of **2** was 0.41 ± 0.03 under these conditions.[3] An analogous experiment carried out under 1 atm of CO gave experimentally indistiguishable spectroscopic changes and quantum yield (0.40 ± 0.04). When the reaction was monitored by infrared spectroscopy, **2** was the only product observed to ~90% consumption of **1**. When the reaction was monitored by electronic spec-

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[1] (a) Poliakoff, M.; Weitz, E. *Adv. Organomet. Chem.* **1986**, *25*, 277−316. (b) DiBenedetto, J. A.; Ryba, D. W.; Ford, P. C. *Inorg. Chem.* **1989**, *28*, 3503. (c) Weiller, B. H.; Wasserman, E. P.; Bergman, R. G.; Moore, C. B.; Pimentel, G. C. *J. Am. Chem. Soc.* **1989,** *111*, 8288−8289. (d) Belt, S. T.; Ryba, D. W.; Ford, P. C. *J. Am. Chem. Soc.* **1991**, *113*, 9524−9528. (e) Boese, W. T.; Lee, B. L.; Ryba, D. W.; Belt, S. T.; Ford, P. C. *Organometallics* **1993**, *12*, 4739−4741.

[2] Casey, C. P.; Cariño, R. S.; Hayashi, R. K.; Schladetzky, K. D. *J. Am. Chem. Soc.* **1996**, *118*, 1617−1623.

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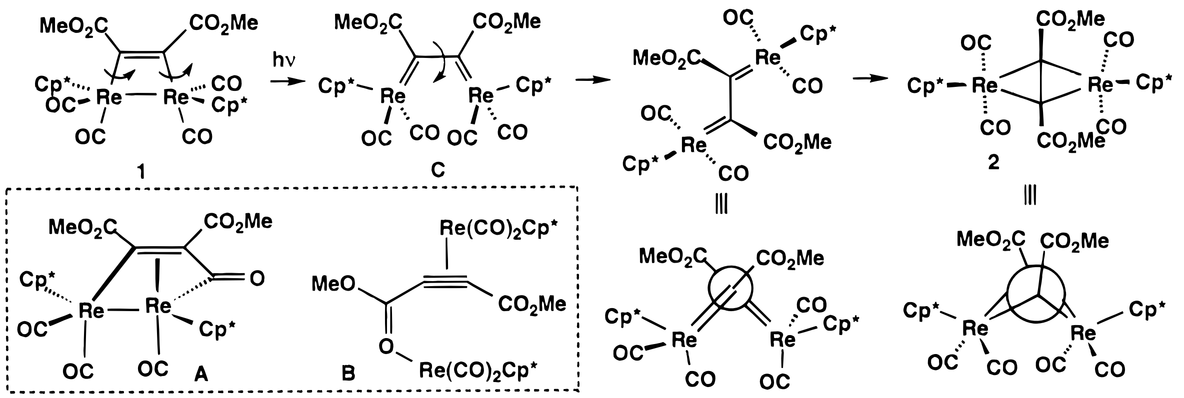
Scheme 1



troscopy, clean isosbestic points were observed at 261 and 313 nm until most of **1** was consumed. Prolonged 366 nm photolysis resulted in eventual conversion of **2** to **3** as determined from spectral changes, but with much lower efficiency ($\Phi = \sim 0.005$). The quantum yield for the second process was also little affected by added CO, although the uncertainty in this value is higher due to the increased absorbance at 366 nm of **3** relative to **2**.[4]

Laser flash photolysis of **1** in cyclohexane solution under argon was carried out using 355 nm excitation (third harmonic of a Nd/YAG laser, 10 ns pulse width) and TRIR detection.[5] The resulting transient IR spectral changes are indicated in Figure 1. The ν_{CO} bands corresponding to **1** were bleached at the earliest observation time (<150 ns), and new bands corresponding to the transient species **I** were observed at ν_{CO} 1992, 1970, and 1895 (broad) cm^{-1} (Figure 1). The latter bands underwent exponential decay over a few picoseconds with the comcomitant appearance of ν_{CO} bands with frequencies and relative intensities corresponding to formation of **2** (eq 1). Prompt formation of **2** was not seen; furthermore, there was little recovery of the ν_{CO} absorbances corresponding to **1**.

$$\mathbf{1} \xrightarrow{h\nu} \mathbf{I} \xrightarrow{k_{obs}} \mathbf{2} \qquad (1)$$

The first-order rate constants k_{obs} for the exponential disappearance of **I** were identical with those determined by following the appearance of **2**. At 296 K, rate constants in cyclohexane ($k_{obs} = (4.4 \pm 0.4) \times 10^4$ s^{-1}) and in *n*-hexane were essentially identical ($k_{obs} = (4.3 \pm 0.4) \times 10^4$ s^{-1}). Rate constants were somewhat higher in the more polar solvents dichloromethane ($k_{obs} = (6.0 \pm 0.6) \times 10^4$ s^{-1}) and tetrahydrofuran ($k_{obs} = (8.1 \pm 0.8) \times 10^4$ s^{-1}).

According to earlier studies of polynuclear metal carbonyls,[6] the most likely primary reactions resulting from photolysis of **1** are CO dissociation or fragmentation of a metal–metal bond. The former would not seem to be the likely predecessor of the **1** → **2** isomerization, and this supposition gains some credibility from the failure of CO to affect the quantum yield for photoisomerization. Furthermore, the relative insensitivity of the lifetime of **I** to solvent nature points to a pathway where the **I** → **2** transformation does not involve a major change in bonding of a solvent molecule to one or both of the metal centers. Notably, k_{obs} for the relatively good donor THF is somewhat larger than that determined in alkane. Thus, the most probable explanation would be that the primary photochemical process leading to the formation of the intermediate **I** does not create unsaturated metal centers.

There are three plausible structures for the observed intermediate **I** that do not involve CO loss (see Scheme 1): the dimetallacyclopentenone $Cp^*(CO)_2Re[\mu\text{-}\eta^1\text{:}\eta^3\text{-}(CH_3O_2C)C{=}C(CO_2CH_3)CO]Re(CO)Cp^*$ (**A**), an alkyne complex in which one Re binds to the C≡C bond of DMAD and the other Re binds to an ester carbonyl (**B**), and the bis(metallacarbene) complex $Cp^*(CO)_2Re{=}C(CO_2CH_3)(CO_2CH_3)C{=}Re(CO)_2Cp^*$ (**C**). The reaction of $Cp^*(CO)_2Re{=}Re(CO)_2Cp^*$ with some alkynes, including $HC{\equiv}CC(CH_3){=}CH_2$[7] and $CH_3C{\equiv}CCO_2CH_3$,[8] produces dimetallacyclopentenones such as $Cp^*(CO)_2Re[\mu\text{-}\eta^1\text{:}\eta^3\text{-}(CH_3O_2C)C{=}C(CH_3)CO]Re(CO)Cp^*$ (**4**). Since the infrared spectrum of **4** with bands at 1944 (s), 1909 (vs), 1867 (m), and 1701 (m) cm^{-1} is qualitatively different from that seen for intermediate **I**, dimetallacyclopentenone **A** can be excluded as the reactive intermediate. The infrared spectrum of **B** would be expected to be similar to the sum of the spectra for $Cp^*Re(CO)_2(MeO_2CC{\equiv}CCO_2Me)$[9] (1989 (s) and 1901 (s) cm^{-1}) and for

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[3] Continuous photolysis studies were carried out on an optical train with a high-pressure short-arc mercury lamp with a 366 nm Hg line interference filter for wavelength selection. Actinometry was carried out using Aberchrome 540. (Heller, H. G.; Langan, J. R. *J. Chem. Soc., Perkin Trans. 2* **1981**, 341–343). All solvents were dried and distilled prior to use using standard techniques. Solutions for photolysis were prepared in subdued light, degassed rigorously in a quartz cuvette, and stirred constantly during irradiation. Quantum yields were determined from photolysis-induced concentration changes calculated from quantitative differences in the absorption spectra in a manner similar to that described previously.[1d]

[4] Qualitative studies using a Rayonette photoreactor with maximum emission ~300 nm indicated that the relative efficiency of the **2** → **3** conversion in benzene is higher than indicated in the present case. This would be expected given the common feature observed in metal carbonyl cluster chemistry that shorter wavelength irradiation leads to higher quantum yields of CO labilization.

[5] (a) Boese, W. T.; Ford, P. C. *Organometallics* **1994**, *13*, 3525–3531. (b) Boese, W. T.; Ford, P. C. *J. Am. Chem. Soc.* **1995**, *117*, 8381–8391.

[6] (a) Ford, P. C.; Boese, W.; Lee, B.; McFarlane, K. In *Photosensitization and Photocatalysis Using Inorganic and Organometallic Compounds* Kalyanasundaram, K., Graetzel, M., Eds.; Kluwer Academic: Dordrecht, The Netherlands, 1993; Chapter 12, pp 359–390. (b) Kobayashi, T.; Yasufuku, K.; Iwa, J. Yesaka, H.; Noda, H.; Ohtani, H. *Coord. Chem. Rev.* **1985**, *64*, 1–19. (c) Geoffroy, G. L.; Wrighton, M. S. *Organometallic Photochemistry*; Academic Press: New York, 1979.

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[8] Casey, C. P.; Cariño, R. S.; Sakaba, H. Manuscript in preparation.

[9] Casey, C. P.; Cariño, R. S. Unpublished results.

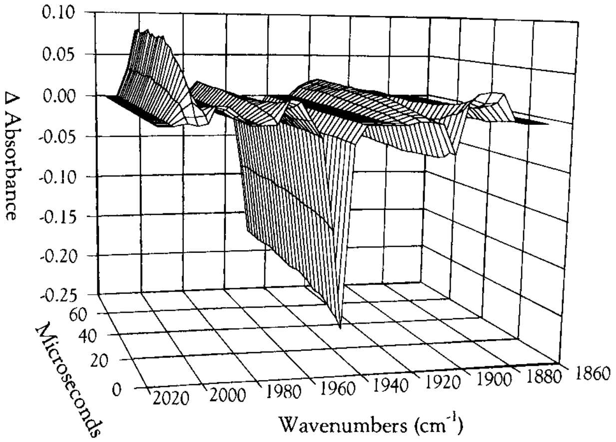

Figure 1. Transient IR spectral changes following 355 nm laser flash photolysis of **1** in *n*-hexane from a composite of the temporal IR absorbance changes in the region beween 1860 and 2020 cm^{-1} with a resolution of ~4 cm^{-1}. The negative bands (1948 (vs), 1900 (m), and ~1880 (w) cm^{-1}), appearing subsequent to the flash, correspond to the irreversible depletion of **1**. Immediately after the flash (~150 ns) positive bands (1992 (m), 1970 (m), and ~1895 (vb, m) cm^{-1}) corresponding to intermediate **I** are seen. These decay exponentially to the base line, while new bands (2000 (s), 1970 (m), and 1920 (m) cm^{-1}) corresponding to **2** appear at the same rate.

$Cp^*Re(CO)_2(THF)$[10,11] (1893 (s), 1823 (s) cm^{-1}) and is also qualitatively different from that observed for intermediate **I**. The infrared spectrum of bis(metallacarbene) complex **C** would be expected to have carbonyl bands similar to those seen for $Cp^*(CO)_2Re{=}CHCH_2CH_2CMe_3$ at 1960 (s) and 1880 (s) cm^{-1}.[12] The infrared bands seen for **I** at 1992 (m), 1970 (m), and 1895 (m) cm^{-1} are in a range consistent with **C**.

The formation of **C** in the photolysis of **1** is very plausible. Homolytic photofragmentation of the Re-Re bond of dimers such as $Re_2(CO)_{10}$ leads to formation of metal-centered radicals.[6b] In the case of **1**, the two metal-centered "radicals" generated by cleavage of the metal−metal bond of **1** would be coupled through the carbon−carbon double bond to give the bis(metallacarbene) **C**. (A true biradical might be expected to undergo rapid ring closure.) Conrotatory ring opening of **1** would generate the *s-cis* rotamer of **C**, in direct analogy with the ring opening of organic cyclobutenes. Rotation about the Re−Re bond to widen the Re−C−C−Re dihedral angle and interaction of each Re with a second carbon center would then lead to the the dimetallabicyclobutane **2**.

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(10) Casey, C. P.; Sakaba, H.; Hazin, P. N.; Powell, D. R. *J. Am. Chem. Soc.* **1991**, *113*, 8165.

(11) THF and esters have comparable donor-acceptor properties in metal carbonyl complexes. For example, $Cp(Ph_3P)(CO)Ru(THF)^+BF_4^-$ (1979 cm^{-1}) and $Cp(Ph_3P)(CO)Ru(ethyl\ acetate)^+BF_4^-$ (1981 cm^{-1}) have similar CO stretching frequencies: Milke, J.; Missling, C.; Sunkel, K.; Beck, W. *J. Organomet. Chem.* **1993**, *445*, 219.

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