(hexane/ether = 1/1) gave 222 mg (91% yield) of (*R*)-1-phenylethanol (**2a**) ($[\alpha]^{23}_{D}$ +48.6° (*c* 1.0, dichloromethane)).[16] The regioisomer **3a** was not detected by ^1H NMR analysis of the crude reaction mixture. The enantiomeric purity of **2a** was determined to be 96% by HPLC analysis of 3,5-dinitrophenyl carbamate **4a** (ArNCO/pyridine/toluene) with a chiral stationary phase column (Sumipax OA-4100, hexane/dichloroethane/ethanol = 100/20/1).

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[16] Nagai, U.; Shishido, T.; Chiba, R.; Mitsuhashi, H. *Tetrahedron* **1965**, *21*, 1701.

Photochemical Insertion of Alkynes into $Cp_2Fe_2(CO)_2(\mu\text{-}CO)_2$: A Mechanistic Study by Laser Flash Photolysis

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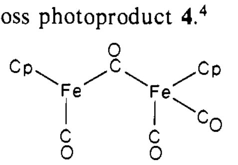
$Cp_2Fe_2(CO)_2(\mu\text{-}CO)_2$ (**1**: Cp = $\eta^5\text{-}C_5H_5$) has a rich and diverse photochemistry, as evidenced by the plethora of synthetic and mechanistic studies of it in the literature.[1] Early photochemical studies of **1** have demonstrated homolysis to the radical $Cp(CO)_2Fe^\bullet$ (**2**).[2] Recent work on metal dimers indicates that a dinuclear species is formed concomitantly. Tyler, Schmidt, and Gray (TSG) first proposed that irradiation of **1** leads to the dinuclear species **3**, which they suggested was the intermediate responsible for phosphine substitution.[3] Research by other individuals has indicated that the substitutionally active species is the CO-loss photoproduct **4**.[4]

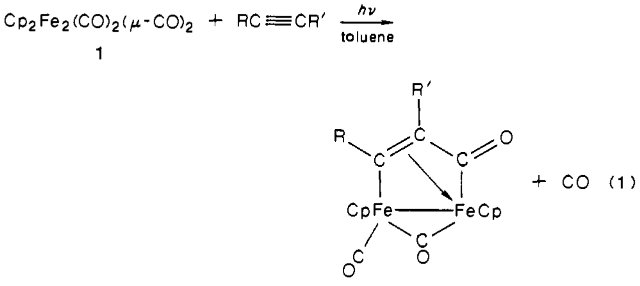


3

$CpFe(\mu\text{-}CO)_3FeCp$

4

Our interest in the photochemistry of **1** stemmed from our theoretical studies on piano-stool dimers.[5] One reaction of particular concern is the photochemical insertion of alkynes into **1** to yield dimetallacyclopentenone **5** (eq 1). On the basis of MO calculations, we proposed a possible "LUMO-controlled" mechanism for this reaction that involved alkyne addition to the TSG transition state **3**, followed by CO loss.[5b] In this contribution, we report initial experimental studies which demonstrate that **4** is the photochemical intermediate responsible for this reaction. We consider this reaction to be a paradigm for photochemical substitution and insertion reactions in such systems.[5b,6]



(1)

5

Laser flash photolysis (LFP)[7] of **1** in toluene shows the formation of an intermediate with a strong absorbance at 515 nm. This absorption is analogous to that observed in previous flash photolytic and matrix isolation studies[4a,8] and is readily assigned to the CO-loss photoproduct $CpFe(\mu\text{-}CO)_3FeCp$ (**4**).

In the absence of alkyne, **4** has a long (ca. 10 ms)[4a] lifetime. However, in the presence of excess phenylacetylene (PHAC), **4** undergoes a very rapid dark reaction (Figure 1). The decay is pseudo-first-order (inset, Figure 1), with a linear dependence of the observed first-order rate constant (k_{obs}) on PHAC concentration. Similar behavior is observed with 1-hexyne and dimethyl acetylenedicarboxylate (DMAD). Measured second-order rate constants and activation parameters for these alkynes are reported in Table I.[9] These rate constants are the same order of magnitude as those reported by Poliakoff et al. for the reaction of **4** with CO ($6 \times 10^4\ M^{-1}\ s^{-1}$) to yield **1**,[11] but they are somewhat smaller than those for the reaction of **4** with CH_3CN, $P(n\text{-}Bu)_3$, and PPh_3.[4c] The activation parameters for the alkyne reactions, obtained from Eyring plots, are very similar to those found for the simple two-electron ligands; in particular, the large negative $\Delta S^\ddagger$ values indicate that the transition state for the reaction of **4** with alkynes has substantial loss in translational and rotational freedom.

The reaction of **4** with L = CO, CH_3CN, and PR_3 is an associative bimolecular process that leads to the substitution photoproducts $Cp_2Fe_2(\mu\text{-}CO)_2(CO)(L)$ (**6**).[4c] By analogy, the kinetic data for the reaction of **4** with alkynes are consistent with the same type of process (Scheme I). The similarities between the reported reaction of **4** with CO, CH_3CN, and PR_3[4c] and those reported here with alkynes suggest the possible formation of an undetected η^2-alkyne substitution product, **7**,[12] a species similar to the unstable ethylene complex $Cp_2Fe_2(\mu\text{-}CO)_2(CO)(\eta^2\text{-}H_2C{=}CH_2)$.[13] That **7** has not been observed suggests that either the presumed unimolecular transformation **7** → **5** is much faster than the bimolecular process **4** → **7**, at least under the conditions of these studies, or that **7** is a poor chromophore for UV-vis detection.

As a complement to the LFP experiments, we have performed competition reactions between pairs of alkynes to compare product

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[1] (a) Geoffroy, G. L.; Wrighton, M. S. *Organometallic Photochemistry*; Academic Press: New York, 1979. (b) Meyer, T. J.; Caspar, J. V. *Chem. Rev.* **1985**, *85*, 187.

[2] (a) Giannotti, C.; Merle, G. *J. Organomet. Chem.* **1976**, *105*, 97. (b) Abrahamson, H. B.; Palazzotto, M. C.; Reichel, C. L.; Wrighton, M. S. *J. Am. Chem. Soc.* **1979**, *101*, 4123.

[3] (a) Tyler, D. R.; Schmidt, M. A.; Gray, H. B. *J. Am. Chem. Soc.* **1979**, *101*, 2753. (b) Tyler, D. R.; Schmidt, M. A.; Gray, H. B. *J. Am. Chem. Soc.* **1983**, *105*, 6018. (c) Poë, A. In *Reactivity of Metal-Metal Bonds*; Chisholm, M. H., Ed.; American Chemical Society: Washington, DC, 1981; ACS Symp. Ser. 155, pp 135-166.

[4] (a) Caspar, J. V.; Meyer, T. J. *J. Am. Chem. Soc.* **1980**, *102*, 7794. (b) Moore, B. D.; Simpson, M. B.; Poliakoff, M.; Turner, J. J. *J. Chem. Soc., Chem. Commun.* **1984**, 972. (c) Dixon, A. J.; Healy, M. A.; Poliakoff, M.; Turner, J. J. *J. Chem. Soc., Chem. Commun.* **1986**, 994. (d) Moore, B. D.; Poliakoff, M.; Turner, J. J. *J. Am. Chem. Soc.* **1986**, *108*, 1819.

[5] (a) Bursten, B. E.; Cayton, R. H. *Organometallics* **1986**, *5*, 1051. (b) Bursten, B. E.; Cayton, R. H. *J. Am. Chem. Soc.* **1986**, *108*, 8241. (c) Bursten, B. E.; Cayton, R. H. *J. Am. Chem. Soc.* **1987**, *109*, 6053. (d) Bursten, B. E.; Cayton, R. H.; Gatter, M. G. *Organometallics* **1988**, *7*, 1342. (e) Bursten, B. E.; Cayton, R. H. *Organometallics* **1988**, *7*, 1349. (f) Bursten, B. E.; Cayton, R. H. *Polyhedron* **1988**, *7*, 943.

[6] (a) Dyke, A. F.; Knox, S. A. R.; Naish, P. J.; Taylor, G. E. *J. Chem. Soc., Chem. Commun.* **1980**, 409. (b) Dyke, A. F.; Knox, S. A. R.; Naish, P. J.; Taylor, G. E. *J. Chem. Soc., Chem. Commun.* **1980**, 803. (c) Dyke, A. F.; Knox, S. A. R.; Naish, P. J.; Taylor, G. E. *J. Chem. Soc., Dalton Trans.* **1982**, 1297. (d) Finnimore, S. R.; Knox, S. A. R.; Taylor, G. E. *J. Chem. Soc., Dalton Trans.* **1982**, 1783. (e) Casey, C. P.; Miles, W. H.; Fagan, P. J.; Haller, K. J. *Organometallics* **1985**, *4*, 559.

[7] Soundararajan, N.; Platz, M. S.; Jackson, J. E.; Doyle, M. P.; Oon, Su-Min; Liu, M. T. H.; Anand, S. M. *J. Am. Chem. Soc.* **1988**, *110*, 7143.

[8] (a) Hooker, R. H.; Mahmoud, K. A.; Rest, A. J. *J. Chem. Soc., Chem. Commun.* **1983**, 1022. (b) Hepp, A. F.; Blaha, J. P.; Lewis, C.; Wrighton, M. S. *Organometallics* **1984**, *3*, 174. (c) Blaha, J. P.; Bursten, B. E.; Dewan, J. C.; Frankel, R. B.; Randolph, C. L.; Wilson, B. A.; Wrighton, M. S. *J. Am. Chem. Soc.* **1985**, *107*, 4561.

[9] Experimental details are presented in the supplementary material.

[10] King, R. B. *Organometallic Syntheses*; Academic Press: New York, 1965; Vol. 1, p 114.

[11] Dixon, A. J.; Healy, M. A.; Hodges, P. M.; Moore, B. D.; Poliakoff, M.; Simpson, M. B.; Turner, J. J.; West, M. A. *J. Chem. Soc., Faraday Trans. 2* **1986**, *82*, 2083.

[12] Preliminary results indicate that **4** undergoes a similar dark reaction with styrene: Bursten, B. E.; McKee, S. D.; Platz, M. S., unpublished results. The reaction of $(C_5Me_4CH_2C_6H_5)Fe(\mu\text{-}CO)_3Fe(C_5Me_4CH_2C_6H_5)$ with ethylene to yield $(C_5Me_4CH_2C_6H_5)_2Fe_2(CO)_3(C_2H_4)$ has also been reported: Randolph, C. L. Ph.D. Thesis, Massachusetts Institute of Technology, 1985.

[13] Gracey, B. P.; Knox, S. A. R.; Macpherson, K. A.; Orpen, A. G.; Stobart, S. R. *J. Chem. Soc., Dalton Trans.* **1985**, 1935.

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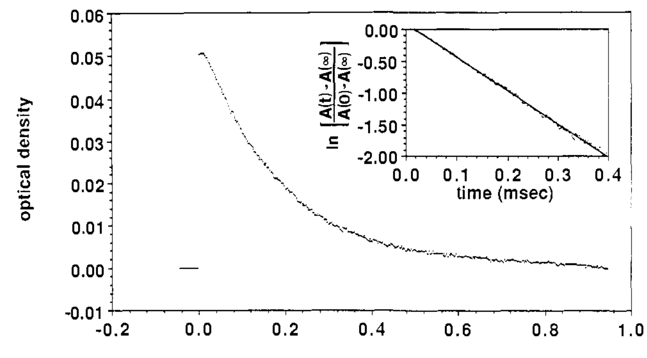


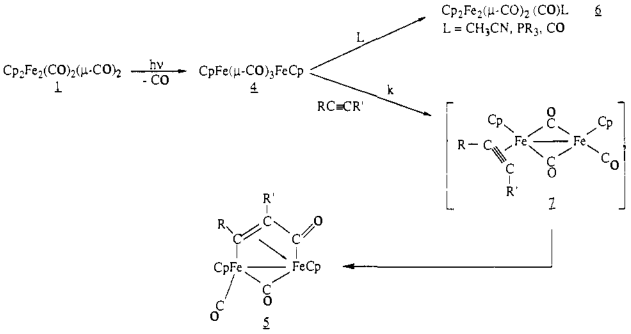
Figure 1. A representative quenching decay between **4** and PHAC (1.785×10^{-1} M) obtained by LFP on a 1.54×10^{-3} M solution of **1** in toluene, monitored at 515 nm. The inset figure shows the pseudo-first-order analysis of the decay curve over more than 1.5 half-lives, with $k_{\text{obs}} = 5711.6\ \text{s}^{-1}$. The time the laser is fired is set to $t = 0$.

Table I. LFP Rate Constants and Activation Parameters for the Photochemical Reaction of **4** with Alkynes[a] and Several Simple Two-Electron Ligands

quencher	k ($M^{-1}\,s^{-1}$)	$\Delta H^{\ddagger}$ (kJ mol^{-1})	$\Delta S^{\ddagger}$ (J mol^{-1} K^{-1})
1-hexyne	$(6.24 \pm 0.59) \times 10^4$	25.9 ± 1.0	-69.4 ± 2.6
PHAC	$(3.63 \pm 0.36) \times 10^4$	28.5 ± 1.1	-61.7 ± 3.3
DMAD	$(3.21 \pm 0.28) \times 10^4$	20.8 ± 1.5	-88.6 ± 4.2
CH_3CN[b,c]	7.6×10^5	24.4	-50.0
P(n-butyl)$_3$[b]	1.25×10^5	28.1	-52.3
$P(C_6H_5)_3$[b]	2.1×10^5	22.3	-64.8

[a] Toluene solution; rate constants reported are at $T = 24 \pm 2$ °C. Activation parameters were obtained from measurements between 0 and 50 °C. [b] Reference 4c. The rate constants and activation parameters are in cyclohexane solution. [c] We have measured a rate constant of $(3.10 \pm 0.29) \times 10^5\ M^{-1}\ s^{-1}$ in toluene.

Scheme I. Proposed Mechanism for the Insertion of Alkynes into **1**



ratios after prolonged irradiation.[9] The photolysis of **1** with an equimolar mixture of 1-hexyne and PHAC yields the corresponding insertion products **5** in the ratio 1-hexyne:PHAC = 1.55 ± 0.15. This is similar to the ratio for the LFP rate constants (1.72 ± 0.14), strong evidence that the observed reaction is under kinetic control. Similar close agreements between the product and kinetic ratios were observed for 1-hexyne/DMAD and PHAC/DMAD competitions. These observations are most consistent with the postulate that the process **4** + alkyne → **5** is irreversible, and that **4** is ultimately responsible for formation of alkyne insertion product **5**. Prolonged irradiation of either the 1-hexyne insertion product with free PHAC or the PHAC insertion product with free 1-hexyne further substantiates this assumption: no crossover of alkynes was observed.

The conclusions of the present studies, i.e. that the alkyne adds to the CO-loss product **4**, run counter to those proposed by us earlier;[5b] our results indicate that **4** (not **3**) is responsible for the alkyne insertion reaction. Experiments are currently in process to better delineate solvent and steric effects and to verify the formation of the proposed η^2-alkyne intermediate **7**.

Acknowledgment. We acknowledge Dr. Karen I. Goldberg for helpful discussions, Dr. James E. Jackson for assistance in obtaining the transient spectrum of **4**, and Mark Glogowski, Kim Lance, and Peter Padolik for assistance with the HPLC apparatus. M.S.P. acknowledges support from the National Science Foundation. B.E.B. is a Camille and Henry Dreyfus Teacher-Scholar (1984–1989).

Registry No. 1, 12154-95-9; **4**, 87985-70-4; PHAC, 536-74-3; DMAD, 762-42-5; CH_3CN, 75-05-8; P(n-Bu)$_3$, 998-40-3; $P(C_6H_5)_3$, 603-35-0; 1-hexyne, 693-02-7.

Supplementary Material Available: Experimental details of the laser flash photolysis and alkyne competition experiments (2 pages). Ordering information is given on any current masthead page.

Detection and Assignments of Diastereotopic Chemical Shifts in Partially Deuteriated Methyl Groups of a Chiral Molecule

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The three protons of a rapidly rotating methyl group in *any* molecule are homotopic[1] from an NMR point of view and thus give rise to a single chemical shift.[2] On the other hand, the two protons in a rapidly rotating CH_2D group in a *chiral* molecule are diastereotopic[1] and are anisochronous, i.e., they have (in principle) different chemical shifts,[3] but an *observable* shift difference in such a system has not been previously reported to our knowledge.

A significant diastereotopic chemical shift difference is most easily induced by having a strong conformational (rotameric) preference for the CH_2D group,[4] together with having very different magnetic environments at the sites occupied by the CH_2D protons. Because lone pairs of electrons on nitrogens that are adjacent to CHD groups in six-membered rings give relatively large isotope effects on conformational equilibria,[5,6] we have investigated the ^{1}H NMR spectrum of a chiral molecule, (RS)-I-d, containing a NCH_2D group. The corresponding undeuteriated compound, (RS)-(±)-1,2-dimethylpiperidine, i.e., (RS)-I, is known to exist at room temperature to the extent of 95% in the diequatorial chair conformation,[7] viz., structure (S)-I-ee for the (S)-(+) enantiomer[8] of I. It is sufficient here to use the racemic

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[1] Mislow, K.; Raban, M. *Top. Stereochem.* **1967**, *1*, 1–38.

[2] It is assumed that the molecule is in an isotropic medium and tumbles rapidly. All symmetry properties in the present paper refer to a time average suitable for proton chemical shifts. Rotation of methyl groups in very sterically hindered molecules can be slow at low temperatures (−150 to −50 °C). Anderson, J. E.; Rawson, D. I. *J. Chem. Soc., Chem. Commun.* **1973**, 830–831. Nakamura, M.; Ōki, M.; Nakanishi, H. *J. Am. Chem. Soc.* **1973**, *95*, 7169–7171. Nakamura, M.; Ōki, M.; Nakanishi, H. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 2415–2419.

[3] Achiral molecules can also have this property provided that there is no plane of symmetry passing through the CH_2D group.

[4] However, a population difference is not required for the observation of a diastereotopic shift difference (Binsch, G.; Franzen, G. R. *J. Am. Chem. Soc.* **1969**, *91*, 3999–4000).

[5] Anet, F. A. L.; Kopelevich, M. *J. Chem. Soc., Chem. Commun.* **1987**, 595–597.

[6] Forsyth, D. A.; Hanley, J. A. *J. Am. Chem. Soc.* **1987**, *109*, 7930–7932. Forsyth, D. A.; Prapansiri, V. *Tetrahedron Lett.* **1988**, *28*, 3551–3554.

[7] From ^{13}C NMR on several C-dimethylated N-methylpiperidines and assuming additivity, Eliel and co-workers deduce a value of 1.9 kcal/mol for the equatorial–axial energy difference of the 2-methyl group in I, the 1-methyl group being almost entirely in the equatorial position (Eliel, E. L.; Kandasamy, D.; Yen, C.; Hargrave, K. D. *J. Am. Chem. Soc.* **1980**, *102*, 3698–3707). They also find that the methyl–methyl interaction energy in the diequatorial form of I is 1.0 kcal/mol. Direct analysis of the ^{13}C NMR spectra of I shows that the diequatorial form is preferred over the 1-equatorial–2-axial form by 1.7 ± 0.1 kcal/mol (Anet, F. A. L.; Dekmezian, A., unpublished work).

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