

Conclusions

At a 1:1 ratio of $\text{Co}_2(\text{CO})_8$ to PR_3 , product selectivity in the hydroformylation reaction reveals a strong dependence on the cone angle of PR_3 and the CO pressure. Increased formate selectivity is explained by a stabilization of carboalkoxycobalt intermediates by organophosphines of small cone angles and a destabilization by organophosphines having large cone angles. No 1,2-diol products are observed.

Experimental Section

All operations were conducted under purified argon or nitrogen, using standard inert-atmosphere techniques. The cobalt octacarbonyl (Strem Chemical) was either sublimed or recrystallized from hexane prior to use. The 1-hexene (Aldrich, Gold Label) was checked for peroxides and purified, if needed, by extraction with aqueous ferrous sulfate. The 1-hexene and toluene were flushed with argon and stored over 4A molecular sieves. The trialkylphosphine cocatalysts were purchased from Strem Chemical and checked by ^{31}P NMR prior to use. The hydrogen (UHP) and carbon monoxide (UHP) were obtained from Matheson and used as received.

Infrared spectra were determined on a Beckman IR4240 spectrometer. NMR spectra were recorded on a JEOL FX90-Q spectrometer equipped with a broad-band, tunable probe. Phosphorus-31 chemical shifts were referenced to external 85% H_3PO_4 .

1-Hexene Hydroformylation. In a typical reaction, a mixture of 4.0 g of 1-hexene, 1.0 g of decane (internal standard), 0.08 g of $\text{Co}_2(\text{CO})_8$, 1 or 2 equiv of PR_3 , and 20 mL of toluene was loaded into a glass reactor vessel in an inert atmosphere drybox. The vessel was placed into a 300 cm^3 stirring reactor (Autoclave Engineers), and the system was purged with argon. The reactor was pressurized to 1600 psig of syn-gas and heated to 195–200 °C in about 20 min. At that temperature, the reactor pressure was ~2000 psig. Reaction times were 4 h. The reactor was then cooled to room temperature and depressurized to give a red solution which was analyzed.

(28) (a) Allman, T.; Goel, R. G. *Can. J. Chem.* **1982**, *60*, 716. (b) Henderson, W. A.; Streuli, C. A. *J. Am. Chem. Soc.* **1960**, *82*, 5791.
(29) Tollman, C. A. *Chem. Rev.* **1977**, *77*, 3.

Product Analysis. The hydroformylation products were determined by GLC analysis that were performed on a Hewlett-Packard 5730A gas chromatograph using a 30-m SE30 capillary column. These products were characterized by GC/MS (Hewlett-Packard 5985) and ^{13}C NMR/JEOL (FX90-Q) comparison with authentic samples obtained from Aldrich. The heptyl formate was prepared by esterification of heptanol with formic acid. Yields were determined vs. an internal standard with experimentally determined response factors.

Preparation of $[\text{Co}(\text{CO})_3(\text{PR}_3)_2]^+[\text{Co}(\text{CO})_4]^-$. These compounds were prepared as described in the literature.²³ For example, a toluene solution containing 0.50 g of $\text{Co}_2(\text{CO})_8$ was treated with 0.82 g of $\text{P}(\text{C}_6\text{H}_{11})_3$ and stirred for 1 h. Filtering the mixture gave 0.90 g of yellow $[\text{Co}(\text{CO})_3\text{P}(\text{C}_6\text{H}_{11})_3]_2^+[\text{Co}(\text{CO})_4]^-$ (70% yield).

Preparation of $[\text{Co}(\text{CO})_3\text{PR}_3]_2$. These products were prepared as described in the literature.²³ For example, a toluene solution of 0.50 g of $\text{Co}_2(\text{CO})_8$ and 0.82 g of $\text{P}(\text{C}_6\text{H}_{11})_3$ was heated to reflux under nitrogen for 2 h. The toluene was concentrated in vacuo, and 1.1 g of red $[\text{Co}(\text{CO})_3\text{P}(\text{C}_6\text{H}_{11})_3]_2$ was isolated by filtration (90% yield).

Preparation of $\text{Co}_2(\text{CO})_7\text{PR}_3$. For example, a mixture of 0.10 g of $[\text{Co}(\text{CO})_3\text{P}(\text{C}_6\text{H}_{11})_3]_2$ and 0.6 g of $\text{Co}_2(\text{CO})_8$ in 10 mL of toluene was heated to 60 °C for 4 h under CO. A red solution was isolated, and IR analysis confirmed the presence of $\text{Co}_2(\text{CO})_7\text{P}(\text{C}_6\text{H}_{11})_3$.²¹

Characterization of $\text{HCo}(\text{CO})_3\text{PR}_3$. A mixture of 0.20 g of $\text{Co}_2(\text{CO})_8$ and 0.32 g of $\text{P}(\text{C}_6\text{H}_{11})_3$ in 20 mL of toluene was heated in the stirring autoclave at 200 °C for 0.5 h under 2000 psig syn-gas. The reactor was cooled to 0 °C via an ice bath, and the contents were isolated. The toluene was removed in vacuo at -78 °C to remove the dimer and salt products. The solution was then analyzed by ^1H and ^{31}P NMR spectroscopy at -50 °C.

Registry No. 1-Hexene, 592-41-6; heptyl formate, 112-23-2; PPh_3 , 603-35-0; $\text{P}(\text{4-ClC}_6\text{H}_4)_3$, 1159-54-2; $\text{P}(\text{4-MeOC}_6\text{H}_4)_3$, 855-38-9; PPh_2Et , 607-01-2; PPhEt_2 , 1605-53-4; $\text{P}(\textit{n}\text{-C}_4\text{H}_9)_3$, 998-40-3; PMe_3 , 594-09-2; PEt_3 , 554-70-1; PCy_3 , 2622-14-2; $\text{P}(\textit{t}\text{-C}_4\text{H}_9)_3$, 13716-12-6; $\text{P}(\textit{o}\text{-CH}_3\text{C}_6\text{H}_4)_3$, 6163-58-2; $\text{Co}_2(\text{CO})_8$, 10210-68-1; $\text{Co}_2(\text{CO})_7\text{PPh}_3$, 15906-55-5; $[\text{Co}(\text{CO})_3\text{PPh}_3]_2$, 10170-27-1; $\text{HCo}(\text{CO})_3\text{PPh}_3$, 19537-79-2; $\text{Co}_2(\text{CO})_7\text{PCy}_3$, 18947-76-7; $[\text{Co}(\text{CO})_3\text{PCy}_3]_2$, 32875-65-3; $[\text{Co}(\text{CO})_3(\text{PCy}_3)_2]^+[\text{Co}(\text{CO})_4]^-$, 22900-17-0; $\text{HCo}(\text{CO})_3\text{PCy}_3$, 87615-25-6; $\text{Co}_2(\text{CO})_7\text{PEt}_3$, 16456-69-2; $[\text{Co}(\text{CO})_3\text{PEt}_3]_2$, 16456-70-5; $[\text{Co}(\text{CO})_3(\text{PEt}_3)_2]^+[\text{Co}(\text{CO})_4]^-$, 54438-20-9; $\text{HCo}(\text{CO})_3\text{PEt}_3$, 87615-26-7; $[\text{Co}(\text{CO})_3(\text{PPh}_3)_2]^+[\text{Co}(\text{CO})_4]^-$, 55397-73-4.

Communications

Photochemistry of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_4$ and Related Complexes in Rigid Matrices at Low Temperature: Loss of Carbon Monoxide from the Trans Isomer to Yield Triply CO-Bridged Species

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Summary: Near-UV irradiation of $(\eta^5\text{-C}_5\text{R}_5)_2\text{Fe}_2(\text{CO})_4$ (R = H, Me, Bz) in an organic matrix at 77 K yields formation of $(\eta^5\text{-C}_5\text{R}_5)_2\text{Fe}_2(\text{CO})_3$ having a symmetrical triply CO-bridged structure. Interestingly, only the trans isomer of the starting species undergoes efficient photoreaction.

Metal complexes having a two-electron metal-metal

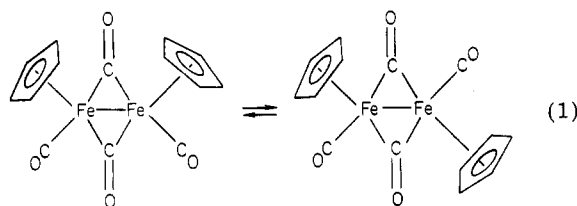
bond are known to be generally reactive upon photoexcitation to give metal-centered radicals.¹ Recently, results in this laboratory have shown that photoexcitation of $\text{Mn}_2(\text{CO})_{10}$ in rigid matrices at low temperature yields only net loss of CO, not $\text{Mn}(\text{CO})_5$ radicals found to dominate the photoproducts in fluid solution at 298 K.² Presumably, the cage effect associated with the rigid matrix contributes to the dramatic change in the net photoreaction. Thus, even though extrusion of a small two-electron donor ligand has a low quantum efficiency, it is possible to bring about clean formation of coordinatively unsaturated dinuclear molecules.

We now report that *trans*- $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_4$ and related complexes lose CO upon photoexcitation in rigid media at low temperature to yield triply CO-bridged

(1) Geoffroy, G. L.; Wrighton, M. S. "Organometallic Photochemistry"; Academic Press: New York, 1979.

(2) Hepp, A. F.; Wrighton, M. S. *J. Am. Chem. Soc.* **1983**, *105*, 5934.

complexes.³ The $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_4$ exists in two limiting geometrical structures that interconvert in fluid solution at 298 K (eq 1).⁴ Alkane solvents give a mixture of the



isomers that is about 1:1, while more polar media give a cis-rich distribution. In rigid media at low temperature the cis and trans isomers do not thermally interconvert.

The photochemistry of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_4$ in fluid solution has been investigated, and net bond homolysis occurs upon irradiation in the presence of CCl_4 to yield $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Cl}$.⁵ When alkane solutions of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Mo}_2(\text{CO})_6$ and $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_4$ are irradiated, $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Mo}(\text{CO})_3(\eta^5\text{-C}_5\text{H}_5)$ is formed.⁶ However, irradiation of the $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_4$ in tetrahydrofuran solution containing $\text{P}(\text{O}-i\text{-Pr})_3$ at 196 K is reported to yield an IR-detectable species formulated as a CO-bridged Fe_2 species without a metal-metal bond.⁷ The species generated at 196 K was proposed to be the reactive intermediate in light-induced substitution of CO by P-donor ligands. Our new results show that dissociative loss of CO upon photoexcitation is an important process under some conditions, as deduced from earlier⁸ flash photolysis experiments in fluid solution.

We have investigated three complexes in our study: $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_4$, I, $(\eta^5\text{-C}_5\text{H}_4\text{Bz})_2\text{Fe}_2(\text{CO})_4$ (Bz = CH_2Ph), II, and $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Fe}_2(\text{CO})_4$, III.⁹ IR band positions in the CO stretching region and their relative intensities are given in Table I. On the basis of IR data, the relative importance of the cis and trans isomers is quite different among the three complexes. The noteworthy difference is that I and II both have a significant fraction of the cis isomer present at 298 K in alkane media,⁴ whereas III is apparently exclusively trans in the same media based on the fact that the IR spectra show only two bands.¹⁰ Moreover, III remains exclusively trans in the more polar 2-methyltetrahydrofuran (2-MeTHF), while I and II become cis-rich in 2-MeTHF. The barrier to interconversion of the cis and trans isomers of I is of the order of 40

Table I. Spectral Features for Dinuclear Fe Species

compound	medium (T, K) ^a	IR, cm^{-1} (ϵ or rel abs)	UV-vis, nm (ϵ or rel OD) ^e
$(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_4$ ^b	MCH (298)	2006 (3000), 1962 (6400), 1794 (6200)	520 (770), 407 (2070), 348 (8320)
	90% MCH/10% 3-MP (77)	1992 (0.7), 1957 (1.0), 1772 (1.0)	
	2-MeTHF (298)	1994 (0.8), 1953 (0.4), 1784 (1.0)	505 (620), 398 (1930), 343 (8350)
	2-MeTHF (77)	1980 (1.0), 1937 (0.2), 1770 (1.0)	
$(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_3$ ^c	90% MCH/10% 3-MP (77)	1811	~885 (0.2), 505 (1.0), 385 (..)
	MCH (298)	1933 (12 700), 1765 (7380)	533 (1520), 420 (2980), 362 (10 100)
	MCH (77)	1926 (1.0), 1754 (0.7)	522 (0.2), 390 (0.5), 355 (1.0)
	2-MeTHF (298)	1925 (3570), 1757 (2400)	532 (1520), 420 (3030), 362 (9900)
$(\eta^5\text{-C}_5\text{Me}_5)_2\text{Fe}_2(\text{CO})_4$ ^d	2-MeTHF (77)	1921 (1.0), 1745 (0.8)	520 (0.2), 390 (0.5), 355 (1.0)
	MCH (77)	1785	880 (0.2), 512 (1.0), 390 (..)
	2-MeTHF (77)	1766	880 (0.2), 512 (1.0), 390 (..)
	2-MeTHF (77)	1999 (0.6), 1955 (1.0), 1781 (0.8)	510 (0.2), 400 (0.5), 350 (1.0)
$(\eta^5\text{-C}_5\text{H}_4\text{Bz})_2\text{Fe}_2(\text{CO})_4$ ^b	67% MCH/33% 3-MP (298)	1989 (0.7), 1945 (0.8), 1764 (1.0)	490 (0.4), 353 (1.0)
	2-MeTHF (298)	1989 (1.0), 1948 (0.6), 1775 (1.0)	520 (0.1), 400 (0.4), 345 (1.0)
$(\eta^5\text{-C}_5\text{H}_4\text{Bz})_2\text{Fe}_2(\text{CO})_3$ ^c	2-MeTHF (77)	1976 (1.0), 1934 (0.1), 1765 (0.6)	500 (0.1), 390 (0.4), 342 (1.0)
	67% MCH/33% 3-MP (77)	1797	910 (0.2), 510 (1.0)

^a MCH = methylcyclohexane; 3-MP = 3-methylpentane; 2-MeTHF = 2-methyltetrahydrofuran. ^b Mixture of cis and trans isomers in alkane media and mainly cis in 2-MeTHF. ^c Generated photochemically by near-UV irradiation of tetracarbonyl precursor at 77 K. ^d Only trans in all media. ^e OD = optical density.

(3) Hooker, R. H.; Rest, A. J. *J. Chem. Soc., Chem. Commun.*, 1983, 1022. We thank Dr. Rest for communicating these results prior to publication showing the formation of a CO loss product from photolysis of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_4$ in a polyvinyl chloride matrix at 12–77 K. They too find a triply CO-bridged photoproduct.

(4) (a) Manning, A. R. *J. Chem. Soc. A* 1968, 1319. (b) Bryan, R. F.; Greene, P. T.; Lewlands, M. J.; Field, D. S. *Ibid.* 1970, 3068. (c) Bullitt, J. G.; Cotton, F. A.; Marks, T. J. *Inorg. Chem.* 1972, 11, 671; *J. Am. Chem. Soc.* 1970, 92, 2155.

(5) (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, 423.

(6) Abrahamson, H. B.; Wrighton, M. S. *Inorg. Chem.* 1978, 17, 1003; *J. Am. Chem. Soc.* 1977, 99, 5510.

(7) Tyler, D. R.; Schmidt, M. A.; Gray, H. B. *J. Am. Chem. Soc.* 1979, 101, 2753; 1983, 105, 6018.

(8) Caspar, J. V.; Meyer, T. J. *J. Am. Chem. Soc.* 1980, 102, 7794.

(9) (a) Complex II was synthesized by using a modification of the procedure reported by: Hallam, B. F.; Pauson, P. L. *J. Am. Chem. Soc.* 1956, 3030, where $\text{C}_5\text{H}_5\text{Bz}$ was refluxed with $\text{Fe}_2(\text{CO})_9$ in *n*-decane. (b) The known complex III (King, R. B.; Bisnette, M. B. *J. Organomet. Chem.* 1967, 8, 287) was synthesized by refluxing $\text{C}_5\text{Me}_5\text{H}$ with $\text{Fe}_2(\text{CO})_9$ in *n*-decane as for related complexes: King, R. B.; Iqbal, M. Z.; King, A. D., Jr., *J. Organomet. Chem.* 1979, 171, 53.

(10) The trans structure was previously assigned to III.^{9b} A crystal structure has been done showing that the structure is trans in the crystalline state: Teller, R. G.; Williams, J. M. *Inorg. Chem.* 1980, 19, 2773.

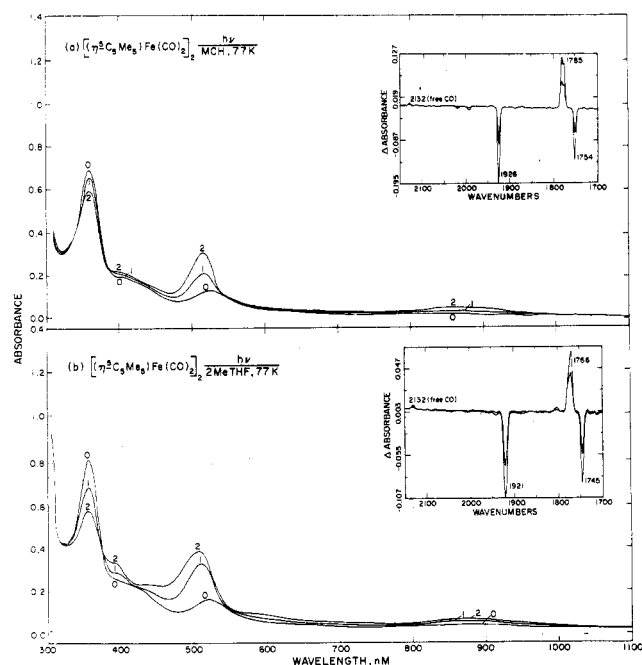


Figure 1. UV-vis-near-IR and IR (inset) spectral changes accompanying near-UV irradiation of $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Fe}_2(\text{CO})_4$ in methylcyclohexane (top) and 2-methyltetrahydrofuran (bottom) at 77 K.

kJ/mol^4 . Thus, interconversion at 77 K has a negligible rate and matrices containing the two isomers can be regarded as thermally inert with respect to such interconversion. IR data for the three complexes at 77 K are included in Table I showing that I and II exist as a mixture of cis and trans isomers in alkane media and mainly as the cis isomer in 2-MeTHF. At 77 K III is exclusively trans.

Figure 1 shows the IR and UV-vis-near-IR spectral changes accompanying near-UV irradiation of III in alkane or 2-MeTHF at 77 K.¹¹ The IR reveals the generation of CO (2132 cm^{-1})¹² in the matrix, and an analysis of the absorbance for the free CO compared to the fraction of the starting material consumed shows that one CO molecule is liberated for each molecule of III consumed.¹³ The CO stretching region shows an absorption at 1785 cm^{-1} , in the bridging CO region, attributable to the metal-containing photoproduct $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Fe}_2(\text{CO})_3$. Essentially the same results are obtained in both alkane and 2-MeTHF matrices. The UV-vis-near-IR spectral changes show the growth of significant vis and near-IR absorption (Table I). The doubly NO-bridged $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{NO})_2$ complex also shows a low intensity near-IR absorption.¹⁴ The single CO band in the bridging CO region, the lack of a significant difference in alkane and 2-MeTHF, and the near-IR absorption lead to the conclusion that the metal-containing product is a triply CO-bridged species that is isoelectronic

(11) Complexes were dissolved at 298 K to $\sim 1\text{ mM}$ to ensure site-site isolation upon cooling to 77 K. Cooling to 77 K often caused precipitation of complexes I and II in alkane media. Samples were run at several concentrations to ensure that results are not a consequence of aggregation. IR spectra were recorded at 77 K by using a Nicolet 7199 FTIR, and UV-vis-near-IR spectrum were recorded by using a Cary 17. The Dewar and irradiation procedures have been described previously: Kazlauskas, R. J.; Wrighton, M. S. *J. Am. Chem. Soc.* **1982**, *104*, 6005.

(12) Leroi, G. E.; Ewing, G. E.; Pimental, G. C. *J. Chem. Phys.* **1964**, *40*, 2298.

(13) The absorptivity of CO in the matrices used is $\sim 300\text{ M}^{-1}\text{ cm}^{-1}$. This allows quantitative determination of the number of CO's lost per molecule. The details of the determination of CO absorptivity will be published elsewhere.

(14) (a) Brunner, H. *J. Organomet. Chem.* **1968**, *14*, 173. (b) Calderon, J. L.; Fontana, S.; Frauendorfer, E.; Day, V. W.; Iske, S. D. *A. Ibid.* **1974**, *64*, C16.

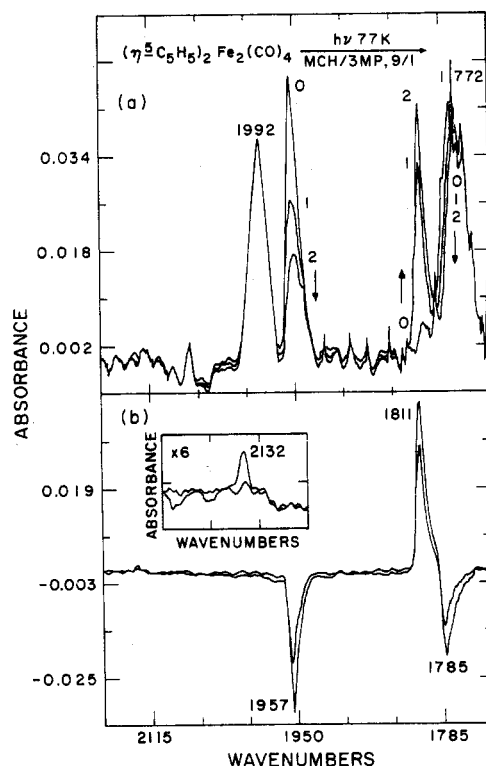


Figure 2. IR spectral changes accompanying irradiation of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_4$ in 90% methylcyclohexane/10% 3-methylpentane at 77 K. The top shows the actual spectral changes, and the bottom shows the difference spectra. Note the feature at 1992 cm^{-1} due to the cis isomer does not change while the 1957 cm^{-1} feature mainly due to the trans isomer does decline.

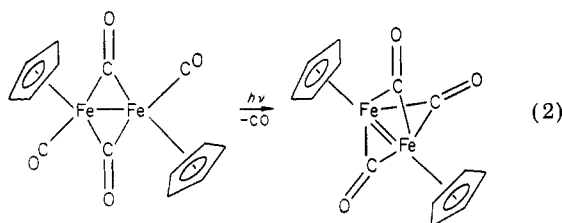
with the doubly NO-bridged species formulated as having an Fe-Fe double bond. The structurally characterized $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Re}_2(\mu\text{-CO})_3$ has a single CO absorption in the bridging CO region at 1748 cm^{-1} ,¹⁵ as we find for the tricarbonyl complexes here.

Note that the irradiation of III in either the alkane or 2-MeTHF matrices results in essentially complete consumption to cleanly yield the CO loss product. The photochemistry of I and II differs considerably. Figure 2 shows the IR spectral changes accompanying irradiation of I in an alkane medium at 77 K. Like III, irradiation of I yields CO (2132 cm^{-1}) in the matrix and a single CO band in the bridging region appears. However, there is essentially no change in the highest energy CO absorption of I, while the two low-energy bands decline. The highest energy band in I is assigned to the cis isomer.⁴ Thus, the trans isomer undergoes loss of CO, but the cis isomer is photoinert on the same time scale. Likewise, irradiation of II in an alkane medium yields free CO and a triply CO-bridged Fe_2 species, but only the trans isomer is photosensitive under the conditions employed. In a 2-MeTHF matrix at 77 K I and II yield only small amounts of product. This is consistent with the fact that the cis isomer appears to be photoinert, since the low-temperature 2-MeTHF medium gives a cis-rich distribution of the two isomers of I and II.

While it is experimentally evident that the cis and trans isomers differ dramatically in photosensitivity under the conditions used, it is not clear why there is such a difference. It is possible that cis undergoes CO loss but the reaction is rapidly reversed. This seems implausible, since 2-MeTHF should effectively trap the resulting metal tricarbonyl. It is possibly significant that the trans isomer

(15) Hoyano, J. K.; Graham, W. A. G. *J. Chem. Soc., Chem. Commun.* **1982**, 27.

can form a symmetrical $(\mu\text{-CO})_3$ complex without gross movement of the C_5 rings (eq 2), whereas reaction of the



cis isomer would require large movement of the C_5 rings. The inability to capture the tricarbonyl from photolysis of III with 2-MeTHF suggests that the loss of CO and rearrangement to form the $(\mu\text{-CO})_3$ structure is concerted. The difference in photosensitivity of the cis and trans species and the role of the tricarbonyl photoproduct in solution photochemistry are presently under study in this laboratory.

Acknowledgment. We thank the National Science Foundation for support of this research.

Registry No. *cis*-I, 33221-55-5; *trans*-I, 32757-46-3; *cis*-II, 88080-00-6; *trans*-II, 87985-72-6; III, 12132-03-5; $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_3$, 87985-70-4; $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Fe}_2(\text{CO})_3$, 87985-71-5; $(\eta^5\text{-C}_5\text{H}_4\text{Bz})_2\text{Fe}_2(\text{CO})_3$, 87985-73-7; Fe, 7439-89-6.

Carbon Chain Growth via Methylene (CH_2) Additions to Cluster-Bound Unsaturates: Conversion of $\mu_3\text{-}\eta^2$ -Acetylides to $\mu_3\text{-}\eta^3$ -Allenyl and $\mu_3\text{-}\eta^4$ -2,3-Butadienyldene Complexes with Diazomethane

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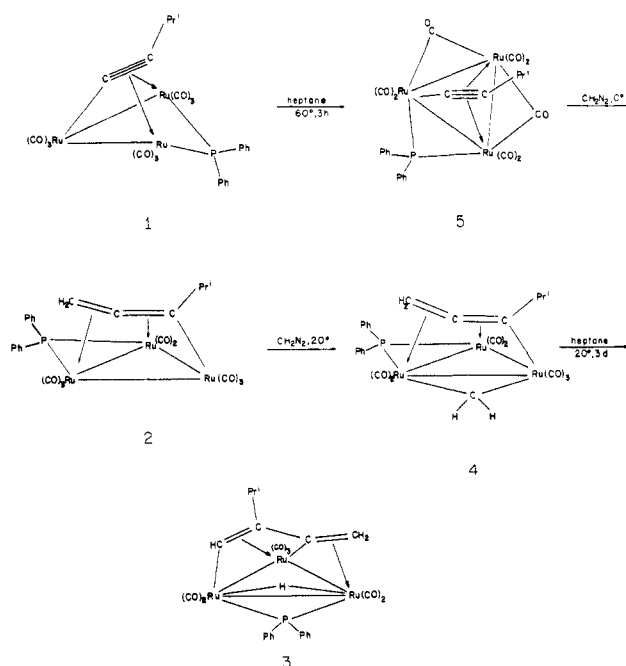
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Summary: The synthesis of a cluster-bound $\mu_3\text{-}\eta^3$ -allenyl ligand in $\text{Ru}_3(\text{CO})_8(\mu_3\text{-}\eta^2\text{-CH}_2\text{=C=C-}i\text{-Pr})(\mu\text{-PPh}_2)$ (**2**) from a $\mu_3\text{-}\eta^2$ -acetylide, $\text{Ru}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{-C}\equiv\text{C-}i\text{-Pr})(\mu\text{-PPh}_2)$ (**1**), via methylene (CH_2) addition and the subsequent conversion of **2** to the 2,3-butadienyldene²¹ cluster $(\mu\text{-H})\text{-Ru}_3(\text{CO})_7(\mu_3\text{-}\eta^4\text{-CH}_2\text{=CC}(i\text{-Pr})\text{=CH})(\mu\text{-PPh}_2)$ (**3**) by methylidyne (CH) transfer from the μ -methylene intermediate $\text{Ru}_3(\text{CO})_7(\mu_3\text{-}\eta^3\text{-CH}_2\text{=C=C-}i\text{-Pr})(\mu\text{-CH}_2)(\mu\text{-PPh}_2)$ (**4**) are described. The structures of the new clusters **2**, **3**, and **4** have been determined by X-ray diffraction. Facile carbon-carbon bond formation between multisite-bound unsaturated ligands and diazomethane-derived methylene or methylidyne fragments may offer new opportunities for cluster-mediated ligand synthesis.

Currently favored mechanisms for carbon-carbon chain growth in Fischer-Tropsch synthesis¹ and C-C bond cleavage in hydrocarbon hydrogenolysis² involve the intermediacy of surface-bound μ -methylenes. In the case of hydrocarbon synthesis, C-C bond formation may occur via

Scheme I



CH_2 insertion into a metal-alkyl bond,¹ coupling with a surface olefin,³ or migrations to other surface ligands including carbides or carbynes. Molecular models for some of these processes have recently been discovered in the chemistry of binuclear μ -methylene complexes^{4,5} and in the reactions of transition-metal compounds with methylene precursors.^{5,6}

Somewhat surprisingly, in view of the metal cluster-metal surface analogy, few reports of C-C bond formation involving methylene groups and unsaturated fragments in polynuclear clusters have appeared⁸ despite the obvious relevance of such reactions to cluster-mediated synthesis, ligand elaboration, and catalysis. As a continuation of our studies on reactivity patterns for multisite-bound unsaturates,⁷ we have examined the behavior of the cluster acetylide $\text{Ru}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{-C}\equiv\text{C-}i\text{-Pr})(\mu\text{-PPh}_2)$, **1**, toward diazomethane. In this communication we report the facile transformation of **1** to the allenyl complex $\text{Ru}_3(\text{CO})_8(\mu_3\text{-}\eta^3\text{-CH}_2\text{=C=C-}i\text{-Pr})(\mu\text{-PPh}_2)$, **2**, and subsequently to the hydrido 2,3-butadienyldene cluster $(\mu\text{-H})\text{Ru}_3(\text{CO})_7(\mu_3\text{-}\eta^4\text{-CH}_2\text{=CC}(i\text{-Pr})\text{=CH})(\mu\text{-PPh}_2)$, **3**, via the intermediacy of a μ -methylene compound, $\text{Ru}_3(\text{CO})_7(\mu_3\text{-}\eta^3\text{-CH}_2\text{=C=C-}i\text{-Pr})(\mu\text{-CH}_2)(\mu\text{-PPh}_2)$, **4**. These reactions support the

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