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Some aspects of the chemistry of binuclear bridging iron complexes

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addition was complete, the flask was slowly warmed to room temperature and allowed to stand until the bromine color was gone (12 days). The solvent was removed by rotary evaporation and the residue heated at 60 °C and 0.01 torr to yield crude product which was recrystallized from methylene chloride: light yellow crystals (2.3 g., 95%): mp 166–168 °C; ^1H NMR ($(CD_3)_2CO$) δ 1.50 (s, 6, $^2J(^{119}Sn–C–H)$ = 92.0 Hz, SnMe), 1.54 (s, 6, $^2J(^{119}Sn–C–H)$ = 92.0 Hz, Sn–Me); IR (KBr, cm^{-1}. ν_{SO} 950.0.

Anal. Calcd for $C_7H_{16}Br_4OSSn_2$: C, 11.92; H, 2.28; mol wt, 705. Found: C, 12.10; H, 2.32; mol wt, 858 (osmometric in toluene at 40 °C).[21]

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Registry No. 1, 85293-94-3; 2, 85293-95-4; 3, 85293-96-5; 4, 85293-97-6; 5, 85293-98-7; 6, 85293-99-8; 7, 85294-00-4; 8, 85294-01-5; 9, 85294-02-6; 10, 85294-03-7; 11, 85294-04-8; 12, 85294-05-9; 13, 16812-43-4; 14, 83135-43-7; trimethylstannane, 1631-73-8; propargyl acetate, 627-09-8; 3,3-bis(trimethylstannyl)propyl tosylate, 85294-06-0; chlorodimethylstannane, 16561-41-4.

Some Aspects of the Chemistry of Binuclear Bridging Iron Complexes[1a]

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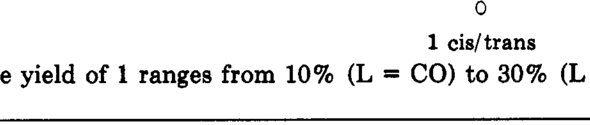
The formation of hydrocarbons from binuclear iron complexes $Cp(CO)Fe(\mu-CH_2)Fe(CO)Cp$, $Cp(CO)_2Fe(CH_2)_nFe(CO)_2Cp$ (n = 3, 4), and $Cp(CO)_2Fe(C{=}O)(CH_2)_n(C{=}O)Fe(CO)_2Cp$ (n = 2–4) (Cp = $\eta^5-C_5H_5$) under photolytic and thermolytic conditions was investigated. The studies indicate that bimetallacyclic species $Cp(CO)Fe(\mu-CO)(CH_2)_nFe(CO)Cp$ (n = 3, 4) might be involved in the reaction sequence which leads to the formation of cyclopropane (n = 3) and olefins (n = 2, 3, 4).

Introduction

To a large extent, the importance of organometallic chemistry is based upon the unique chemical properties of alkyl, alkylidene, or alkylidyne groups when attached to a transition metal, and this area continues to receive much attention.[3] An extension of this field that has been less well developed is where two transition-metal centers are involved. Several interesting aspects appear to exist in this class of compounds, particularly the interactions between the metal centers and the effects of this interaction on the chemical properties of the attached hydrocarbon moieties. Other aspects include the possible relationship of this system to the alkyl groups bonded to metal surfaces which make up most heterogeneous systems.[4] We now wish to report some results from these laboratories pertaining to this class of compounds.[5]

Results and Discussion

Recently, we[6] and others[7] have described the synthesis of the novel organometallic compound $Cp(CO)Fe(\mu-CO)(\mu-CH_2)Fe(CO)Cp$ (1, Cp = $\eta^5-C_5H_5$) in which a CH_2 group bridges two iron atoms linked by a single bond. We have found that 1 can also be prepared by the reaction of $CpFe(CO)(L)CH_2Cl$ (L = CO, PPh_3) and $CpFe(CO)_2K$ in tetrahydrofuran (THF) (eq 1). Depending on ligand L, the yield of 1 ranges from 10% (L = CO) to 30% (L = PPh_3). Other products identified in this reaction (L = CO) are methane (2%), ethylene (7%), $CpFe(CO)_2CH_3$ (15%), and $[CpFe(CO)_2]_2$ (65%). As noted by other workers,[7b] separation of 1 from $[CpFe(CO)_2]_2$ was difficult but was accomplished by treating the crude product mixture with excess 1,2-bis(diphenylphosphino)ethane (diphos) prior to separation. This procedure selectively converted $[CpFe(CO)_2]_2$ into its diphos derivative while leaving 1 intact. Complex 1 and the diphos derivative of $[CpFe(CO)_2]_2$ can be easily separated by chromatography.



(1)

1 cis/trans

One mechanism which could explain most of the side products in the synthesis of 1 involves an electron transfer from the $CpFe(CO)_2^-$ to the (chloromethyl)iron complex, followed by loss of chloride ion from the radical anion, to give rise to $CpFe(CO)_2CH_2\cdot$(2) and $CpFe(CO)_2\cdot$(3). Recombination of 3 would yield the observed $[CpFe(CO)_2]_2$. There are at least three different modes of reaction for species 2. It can abstract a hydrogen from solvent to form $CpFe(CO)_2CH_3$ or react with radical 3 to give the bridging methylene complex 1. A third pathway is to couple with

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[1] (a) Taken in part from the Ph.D. dissertation of S. C. Kao, The University of Texas at Austin, 1981. (b) NATO Postdoctoral Fellow, 1981–1982.

[2] Deceased December 10, 1981.

[3] (a) Schrock, R. R.; Parshall, G. W. *Chem. Rev.* 1976, *76*, 243. (b) Davidson, P. J.; Lappert, M. F.; Pearce, R. *Chem. Rev.* 1976, *76*, 219. (c) Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 4th ed.; Wiley: New York, 1980; p 1119.

[4] Brady, R. C.; Pettit, R. *J. Am. Chem. Soc.* 1980, *102*, 6191; 1981, *103*, 1287.

[5] Analogous results of a portion of this work have been reported recently: Cooke, M.; Forrow, N. J.; Knox, S. A. R. *J. Organomet. Chem.* 1981, *222*, C21.

[6] Kao, S. C.; Lu, P. P. Y.; Pettit, R. *Organometallics* 1982, *1*, 911.

[7] (a) Jorswagen, R.; Alt, R.; Speth, D.; Ziegler, M. L. *Angew. Chem., Int. Ed. Engl.* 1981, *20*, 1049. (b) Casey, C. P.; Fagan, P. J.; Miles, W. H. *J. Am. Chem. Soc.* 1982, *104*, 1134.

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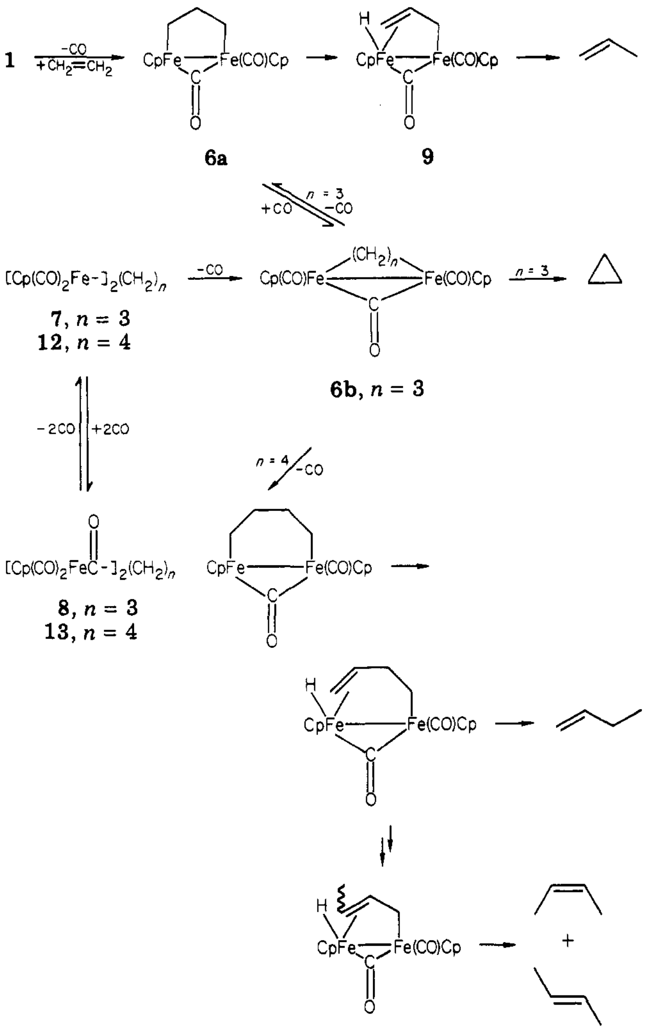
Scheme I



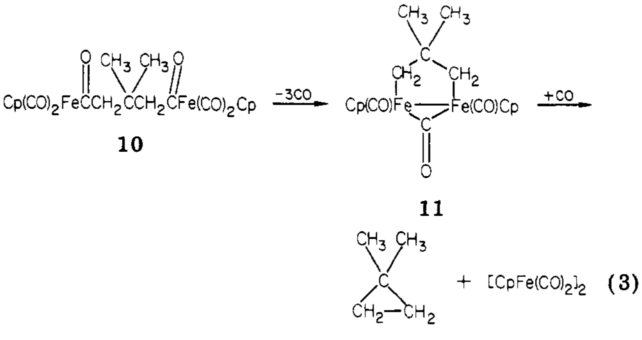
another molecule of **2** to afford an intermediate bridging ethylene complex $Cp(CO)_2FeCH_2CH_2Fe(CO)_2Cp$ (**4**), which upon spontaneous decomposition, could be the source of the observed ethylene. Such behavior is not unusual for bimetallic complexes containing a σ-bonded ethylene moiety; Beck and Olgemoller[8] have shown that the analogous complexes MCH_2CH_2M' (M, M' = Mo, W, Re) upon heating result in the formation of ethylene and corresponding organometallic products. In support of this, we have found that the photolysis of the corresponding diacyl complex $Cp(CO)_2Fe(C{=}O)\,CH_2CH_2(C{=}O)Fe(CO)_2Cp$ (**5**) results in the production of ethylene (70%) and $[CpFe(CO)_2]_2$. The reaction is believed to proceed via a double decarbonylation of diacyl **5** to give **4**, which, under the reaction conditions, decomposes to give the observed products (eq 2).[9]

$$\underset{\mathbf{5}}{Cp(CO)_2FeC({=}O)CH_2CH_2C({=}O)Fe(CO)_2Cp} \xrightarrow{-2CO} \underset{\mathbf{4}}{Cp(CO)_2FeCH_2CH_2Fe(CO)_2Cp}CH_2{=}CH_2 + [CpFe(CO)_2]_2 \quad (2)$$

Reaction of **1** with ethylene (350 psi, 150 °C) gave a small amount of propylene (5%), which may involve a reaction sequence similar to that proposed for reaction of $Fe_2(CO)_8CH_2$ and ethylene.[10] A plausible mechanism for this reaction involves the insertion of an ethylene molecule into one Fe–CH_2 bond of **1** to generate a bimetallacyclopentane **6a** (Scheme I). Although neither **6a** nor **6b** was detected in this reaction, the recent isolation of a bicobaltacyclopentane complex by Bergman and Theopold[11] lends support to the possible intermediacy of such complexes.

In principle, **6b** can be prepared alternatively from the bridging trimethylene complex **7** if a CO ligand is removed selectively and a metal–metal bond is formed. Complex **7** was found to be stable in both refluxing THF and in the presence of trimethylamine oxide, an effective reagent for removing CO ligands.[12] Under photolytic conditions (THF, 45 °C), it did decompose, but the products recovered from the reaction were propylene (72%), cyclopropane (2.5%), and $[CpFe(CO)_2]_2$ (70%), but no **6b** was detected. At higher temperatures (120 °C, THF), in a sealed system, **7** decomposed to give propylene (4%), cyclopropane (80%), and $[CpFe(CO)_2]_2$ (70%); again, no **6b** was observed. When carbon monoxide (575 psi) was included in the reaction, the yields of both C_3 hydrocarbons and $[CpFe(CO)_2]_2$ markedly decreased and the double CO insertion product **8** was isolated. Upon photolysis, **8** was found to produce propylene, cyclopropane, and $[CpFe(CO)_2]_2$; presumably under these conditions **7** was regenerated to yield the observed products. Formation of propylene and cyclopropane from **7** can be explained by the involvement of bimetallacyclopentanes **6** (Scheme I, $n = 3$).

The bimetallacyclopentane **6b** generated from **7** can undergo either reductive elimination to give cyclopropane or dissociation of another CO ligand to yield **6a**, which would give **9** upon β-hydride abstraction. Reductive elimination from **9** would then produce propylene. Consistent with this scheme, we have found that 1,1-dimethylcyclopropane (70%) and $[CpFe(CO)_2]_2$ were the major products formed from the photolysis of diacyl complex **10**. In this transformation, the in situ generated bimetallacyclopentane **11**, bearing no β-hydrogens, cannot rearrange to a species analogous to **9**, but reductively eliminates 1,1-dimethylcyclopropane (eq 3).



In order to determine the extent of the possible interactions between two metal centers which are bridged by carbon–carbon bonds, the related chemistry of compound **12** (Scheme I), where the two iron atoms are separated by four methylene units, was studied. This species was thermally stable, and only trace amounts of decomposition were detected even at 120 °C in THF. Decomposition of

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[8] Beck, W.; Olgemoller, B. *J. Organomet. Chem.* **1977**, *127*, C45.

[9] King and Braitsch observed the formation of ethylene in the reaction of $CpFe(CO)_2Na$ with 1,2-dihaloethanes, which might also be interpreted to involve **4**, although alternate pathways are conceivable. King, R. B.; Braitsch, D. M. *J. Organomet. Chem.* **1973**, *54*, 9.

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12 under photolytic conditions proceeded at a lower rate than did **7** and produced 1-butene (40%), *cis*-2-butene (1.5%), *trans*-2-butene (10%), butane (5%), and $[CpFe(CO)_2]_2$. Under carbon monoxide pressure (575 psi, 120 °C), **12** gave rise to the double CO insertion product **13** (70%). Photolysis of **13** regenerated **12** plus C_4 hydrocarbons and $[CpFe(CO)_2]_2$. A reaction scheme analogous to the one proposed for **7** might provide an interpretation for the formation of the various C_4 hydrocarbons (Scheme I, $n = 4$).

In summary, our work here indicates that the binuclear bridging methylene complexes can serve as sources of hydrocarbons. The studies also indicate that bimetallacyclic intermediates might be involved in the reaction sequences which lead to product formation.

Experimental Section

General Procedure. Melting points were obtained on a Fisher-Johns Melting Point apparatus and were uncorrected. Infrared spectra were recorded on a Perkin-elmer Model 257 or 298 grating infrared spectrophotometer. Nuclear magnetic resonance spectra were recorded on a Perkin-elmer R-12 (60 MHz) or a Varian EM-390 (90 HMz) spectrophotometer. Microanalyses were performed by Galbraith Laboratories, Knoxville, TN. Pressure reactions were run in a 58-mL stainless-steel autoclave. Photolysis reactions were carried out quartz tubes using a Rayonet-RS-Photochemical Reactor with 3000-A or 3500-A lamps. Standard Schlenk techniques for handling air-sensitive compounds as described by Brown[13] and Schriver[14] were routinely followed. Reactions were run under argon, unless otherwise specified. $C_5H_5Fe(CO)_2CH_2Cl$,[15] $C_5H_5Fe(CO)(PPh_3)CH_2Cl$,[16] $C_5H_5Fe(CO)_2K$,[17] $[C_5H_5(CO)_2Fe(CH_2)_nFe(CO)_2C_5H_5]$ (n = 3, 4),[18] and 3,3-dimethylglutaryl chloride[19] were prepared according to literature procedures.

Gas chromatographic analyses were performed on Hewlett-Packard Model 5830A or Varian Aerograph series 1200 gas chromatographs, equipped with flame ionization detectors. Columns used in hydrocarbon studies were (1) 5 ft × 0.125 in. Porapak Q on 80/100 Chromosorb W and (2) 7 ft × 0.125 in. 0.18% picric acid on Carbopak C. Peak areas from the GC studies were digitally integrated by using one of the following systems: (a) Hewlett-Packard 18850A GC terminal, (b) Spectra-Physics Autolab Minigrator, or (c) Spectra-Physics Autolab System IV. All gaseous products were identified by GC through coinjection with authentic samples on the two columns mentioned. Unless otherwise noted, reaction products were quantified by means of an external standard of known concentration of the compound being analyzed, dissolved in the solvent used for the reaction.

Preparation of $[C_5H_5(CO)Fe(\mu\text{-}CO)(\mu\text{-}CH_2)Fe(CO)C_5H_5]$ (1) To a solution of $C_5H_5Fe(CO)_2K$ (1.070 g, 4.95 mmol) in THF (30 mL) was added $C_5H_5Fe(CO)_2(CH_2Cl)$ (1.120 g, 4.95 mmol) in THF (15 mL). The reaction mixture was stirred at 5 °C for 1 h before warming up to room temperature. The gas phase over the reaction mixture was checked by VPC, and methane (2%) and ethylene (7%) were found. The solvent was removed, and the residue was taken up in benzene and refluxed with excess 1,2-bis(diphenylphosphino)ethane (diphos). After cooling, CH_3I was added to remove the excess diphos. The solution was filtered, concentrated, and chromatographed on alumina. Three components were identified: (1) $C_5H_5Fe(CO)_2CH_3$ (0.142 g, 15%, eluted with hexane), (2) **1** (0.160 g, 10%, eluted with 20% CH_2Cl_2/hexane), and (3) $(C_5H_5)_2Fe_2(CO)_2(diphos)$[20] (2.237 g, 65%, eluted with CH_2Cl_2). Compound **1**, isolated as a cis/trans mixture, displayed the same spectroscopic data as that prepared by alternative routes.[6]

A similar procedure was followed on the reaction of $C_5H_5Fe(CO)(PPh_3)(CH_2Cl)$ with $C_5H_5Fe(CO)_2K$. The yields of the various products were $C_5H_5Fe(CO)_2CH_3$ (10%), **1** (30%), and $(C_5H_5)_2Fe_2(CO)_2(diphos)$ (50%).

Preparation of $[C_5H_5(CO)_2Fe(C{=}O)CH_2CH_2(C{=}O)Fe(CO)_2C_5H_5]$ (5). To a solution of $C_5H_5Fe(CO)_2K$ (3.000 g, 13.88 mmol) in THF (60 mL) was added succinyl chloride (1.000 g, 6.45 mmol) in THF (10 mL). The reaction mixture was stirred at room temperature for 2 h and a brown residue was obtained after the solvent was removed; the residue was extracted with dichloromethane and chromatographed on alumina. Two components were isolated from the column: (1) $[C_5H_5Fe(CO)_2]_2$ (1.858 g, 75%, eluted with benzene) and (2) **5** (0.460 g, 15%, eluted with 50% ether/benzene). Recrystallization of **5** from diethyl ether–hexane gave air-stable yellow crystals: mp 167–169 °C dec; IR (THF) 2015 (vs), 1950 (vs), 1650 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.95 (s, 4 H), 4.90 (s, 10 H). Anal. Calcd for $C_{18}H_{14}Fe_2O_6$: C, 49.36; H, 3.22; Fe, 25.50. Found: C, 49.39; H, 3.36; Fe, 25.22.

Photolysis of $[C_5H_5(CO)_2Fe(C{=}O)(CH_2)_2(C{=}O)Fe(CO)_2C_5H_5]$ (5). A solution of **5** (0.025 g, 0.06 mmol) in THF (5 mL) was subjected to photolysis for 2 h at 45 °C. VPC analysis of the gas phase over the resulting dark red solution revealed the presence of ethylene (70%). The major component in the liquid phase was $[C_5H_5Fe(CO)_2]_2$ as indicated by the infrared spectrum of the solution.

Reaction of $[C_5H_5(CO)Fe(\mu\text{-}CO)(\mu\text{-}CH_2)Fe(CO)C_5H_5]$ (1) with C_2H_4. Complex **1** (0.050 g, 0.15 mmol) in THF (15 mL) was charged with C_2H_4 (350 psi) and heated at 160 °C for 3 h. Methane (20%) and propylene (5%) were obtained, along with cyclopentadiene as analyzed by gas chromatography. Infrared analysis of the liquid phase indicated the presence of $[C_5H_5Fe(CO)_2]_2$ (40%).

Photolysis of $[C_5H_5(CO)_2Fe(CH_2)_3Fe(CO)_2C_5H_5]$ (7). A solution of **7** (0.300 g, 0.75 mmol) in THF (15 mL) was subjected to photolysis for 3 h at 45 °C. VPC analysis of the gas phase over the resulting dark red solution revealed the presence of propylene (72%) and cyclopropane (2.5%). The major component in the liquid phase was $[C_5H_5Fe(CO)_2]_2$ (ca. 70%).

Thermolysis of $[C_5H_5(CO)_2Fe(CH_2)_3Fe(CO)_2C_5H_5]$ (7). A solution of **7** (0.200 g, 0.50 mmol) in THF (15 mL) was placed in an autoclave and heated at 120 °C for 3 h. The gas phase over the final product mixture was analyzed by VPC, and propylene (3.9%) and cyclopropane (81%) were found. In the liquid phase the major component was $[C_5H_5Fe(CO)_2]_2$ (70%).

Thermolysis of $[C_5H_5(CO)_2Fe(CH_2)_3Fe(CO)_2C_5H_5]$ (7) under CO. A solution of **7** (0.500 g, 1.26 mmol) in THF (15 mL) was charged with CO (575 psi) and heated at 120 °C for 5 h. VPC analysis of the gas phase over the product mixture revealed the presence of cyclopropane (20%) and propylene (2.5%). The liquid phase was concentrated and chromatographed on alumina. Three compounds were isolated from the column: (1) **7** (0.095 g, 20%, eluted with 50% hexane/benzene), (2) $[C_5H_5Fe(CO)_2]_2$ (0.150 g, 30% eluted with benzene), and (3) $[C_5H_5(CO)_2Fe(C{=}O)(CH_2)_3(C{=}O)Fe(CO)_2C_5H_5]$ (**8**)[21] (0.254 g, 40%, eluted with 50% diethyl ether–benzene).

Photolysis of $[C_5H_5(CO)_2Fe(C{=}O)(CH_2)_3(C{=}O)Fe(CO)_2C_5H_5]$ (8). A solution of **8** (0.040 g, 0.09 mmol) in THF (5 mL) was photolyzed for 3 h at 45 °C. VPC analysis revealed the presence of propylene (50%) and cyclopropane (1.8%). The IR spectrum of the liquid phase indicated the presence of $[C_5H_5Fe(CO)_2]_2$ which amounted to a 60% yield after isolation by column chromatography as described above.

Preparation of $[C_5H_5(CO)_2Fe(C{=}O)\{CH_2C(CH_3)_2CH_2\}(C{=}O)Fe(CO)_2C_5H_5]$ (10). To a solution of $C_5H_5Fe(CO)_2K$ (3.025 g, 14.00 mmol) in THF (60 mL) was added 3,3-dimethylglutaryl chloride (1.200 g, 7.00 mmol) in THF (15 mL). The reaction mixture was stirred at room temperature for 2 h and a yellow-brown residue was obtained after the solvent was removed: the

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[20] Haines, R. J.; DuPreez, J. L. *J. Organometal. Chem.* **1970**, *21*, 181.

[21] Compounds **8** and **13** have been previously prepared by the reaction of the corresponding diacid chlorides and $CpFe(CO)_2Na$. Our data on these two compounds are consistent with those reported: King, R. B. *J. Am. Chem. Soc.* **1963**, *85*, 1918.

residue was extracted with dichloromethane and chromatographed on alumina. Two components were isolated from the column: (1) $[C_5H_5Fe(CO)_2]_2$ (1.734 g, 80%, eluted with benzene) and (2) **10** (0.504 g, 15%, eluted with 50% diethyl ether–benzene). Recrystallization of **10** from CH_2Cl_2–hexane gave air-stable yellow crystals: mp 122–123 °C; IR (THF) 2015 (vs), 1950 (vs), 1640 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.88 (s, 6 H), 3.15 (s, 4 H), 4.80 (s, 10 H). Anal. Calcd for $C_{21}H_{20}Fe_2O_6$: C, 52.50; H, 4.16; Fe, 23.28. Found: C, 52.17; H, 4.35; Fe, 22.86.

Photolysis of $[C_5H_5(CO)_2Fe(C{=}O)\{CH_2C(CH_3)_2CH_2\}(C{=}O)Fe(CO)_2C_5H_5]$ (10). A solution of **10** (0.200 g, 0.41 mmol) in THF (15 mL) was photolyzed for 3 h at 45 °C. VPC analysis revealed the presence of 1,1-dimethylcyclopropane (70%) and isobutylene (6%). The infrared analysis of the solution revealed $[C_5H_5Fe(CO)_2]_2$ (65%) as well as **10** (10%) as the products.

Photolysis of $[C_5H_5(CO)_2Fe(CH_2)_4Fe(CO)_2C_5H_5]$ (12). A solution of **12** (0.300 g, 0.73 mmol) in THF (30 mL) was subjected to photolysis for 3 h at 45 °C. VPC analysis revealed the presence of 1-butene (40%), *cis*-2-butene (1.5%), and *trans*-2-butene (10%). The infrared of the solution was checked, and the major products were found to be $[C_5H_5Fe(CO)_2]_2$ (60%) and **12** (30%).

Thermolysis of $[C_5H_5(CO)_2Fe(CH_2)_4Fe(CO)_2C_5H_5]$ (12). A solution of **12** (0.200 g, 0.48 mmol) in THF (15 mL) was placed in an autoclave and heated at 120 °C for 3 h. The gas phase over the final product mixture was analyzed by VPC, and only a trace amount of 1-butene was found. The infrared of the solution indicated that almost all the starting material was intact.

Thermolysis of $[C_5H_5(CO)_2Fe(CH_2)_4Fe(CO)_2C_5H_5]$ (12) under CO. A solution of **12** (0.500 g, 1.22 mmol) in THF (15 mL) was charged with CO (450 psi) and heated at 120 °C for 5 h. VPC analysis of the gas phase over the product mixture found only trace amounts of C_4 hydrocarbon. The liquid phase concentrated to give a dark yellow solid. This dark yellow solid was recrystallized from THF–hexane to give yellow crystals of **13** (70%).[21]

Photolysis of $[C_5H_5(CO)_2Fe(C{=}O)(CH_2)_4(C{=}O)Fe(CO)_2C_5H_5]$ (13). A solution of **13** (0.500 g, 1.07 mmol) in THF (30 mL) was subjected to photolysis at 45 °C for 2 h. VPC analysis of the gas phase over the resulting solution revealed the presence of 1-butene (25%), *cis*-2-butene (1.2%), and *trans*-2-butene (6%). The liquid phase was concentrated and chromatographed on alumina. Three components were isolated from the column: (1) $[C_5H_5(CO)_2Fe(CH_2)_4Fe(CO)_2C_5H_5]$ (0.176 g, 40%, eluted with 50% hexane–benzene), (2) $[C_5H_5Fe(CO)_2]_2$ (0.150 g, 40%, eluted with benzene), and **13** (0.085 g, 17%, eluted with 50% diethyl ether–benzene).

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Registry No. *cis*-**1**, 79839-80-8; *trans*-**1**, 79896-43-8; **5**, 85293-84-1; **7**, 12117-43-0; **8**, 85293-85-2; **10**, 85293-86-3; **12**, 36655-41-1; **13**, 36655-42-2; $C_5H_5Fe(CO)_2K$, 60039-75-0; $C_5H_5Fe(CO)_2(CH_2Cl)$, 12107-38-9; Fe, 7439-89-6; succinyl chloride, 543-20-4; 3,3-dimethylglutaryl, 53120-75-5.

Formation of a Chelating σ-Allyl by the Intramolecular Activation of a Cyclopropylphosphine. Synthesis and Crystal Structure of $[PdCl(P(t\text{-}Bu)_2CH{=}C(CH_3)CH_2)]_2$

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The cyclopropyl-containing phosphine di-*tert*-butyl(cyclopropylmethyl)phosphine, $P(t\text{-}Bu_2CH_2CHCH_2CH_2$, reacts with $PdCl_2$ to afford *trans*-$PdCl_2(P(t\text{-}Bu)_2CH_2CHCH_2CH_2)_2$. When this complex is refluxed in $MeOCH_2CH_2OH$ or glacial acetic acid, a cyclometalated dimer, $[PdCl(P(t\text{-}Bu)_2CH{=}C(CH_3)CH_2)]_2$, is formed, as deduced from spectroscopic and X-ray analysis. This complex crystallizes in the monoclinic space group $C_{2h}{}^5$—$P2_1/n$ ($a = 7.957$ (4) Å, $b = 15.780$ (2) Å, $c = 12.169$ (1) Å, and $\beta = 99.11$ (2)°) with two molecules per unit cell (imposed crystallographic symmetry, $\bar{1}$). The final agreement indices for 2493 reflections having $F_o{}^2 > 3\sigma(F_o{}^2)$ are $R(F) = 0.031$ and $R_w(F) = 0.041$ (136 variables). The five-atom chelate ring Pd—P—C=C—C is planar to within 0.011 (4) Å with a bond length pattern of Pd—P = 2.218 (1) Å, P—C = 1.781 (4) Å, C=C = 1.328 (5) Å, C—C = 1.493 (5) Å, and C—Pd = 2.016 (3) Å. The Pd–Cl distance trans to the P atom is 2.416 (1) Å and that trans to the C atom is 2.457 (1) Å. In the formation of the complex the chelating σ-allyl group probably results from C–C bond activation of the cyclopropyl group.

Introduction

A variety of strained ring molecules have been shown to undergo rearrangements in the presence of transition-metal complexes. The metal-assisted conversion of cyclopropanes to olefins (eq 1)[1] and the metal-assisted isomerizations of olefins (eq 2)[2] have received much at-

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[1] Bishop, K. C., III *Chem. Rev.* **1976**, *76*, 461–486.