Journal of Organometallic Chemistry, 235 (1982) 327—334
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

SYNTHESIS OF CYCLOPROPYL-IRON σ COMPLEXES BY DECARBONYLATION OF ACYL COMPLEXES

FRANK J. MANGANIELLO, LARRY W. CHRISTENSEN and W.M. JONES

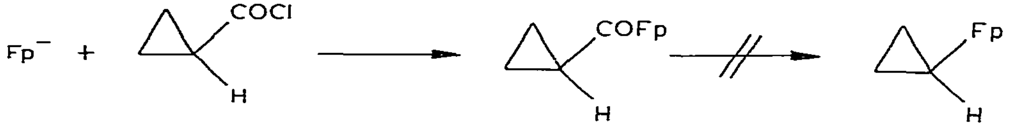
Department of Chemistry, University of Florida, Gainesville, FL 32611 (U.S.A.)

(Received February 16th, 1982; in revised form April 1st, 1982)

Summary

Contrary to earlier reports [1,2] cyclopropyliron σ complexes can be conveniently prepared in fair to excellent yields by photodecarbonylation of the corresponding acyl complexes.

Some years ago Bruce, Iqbal and Stone [1] reported that although the parent cyclopropanoyl complex of dicarbonyl-η^5-cyclopentadienyl iron (2) is readily made form the corresponding acyl chloride, all attempts to effect its decarbonylation to the corresponding σ complex failed. These attempts included thermolysis, photolysis and reaction with $(Ph_3P)_3RhCl$. Failure of the latter reagent to cause decarbonylation was later confirmed by Iqbal [2].



Fp = $CpFe(CO)_2$

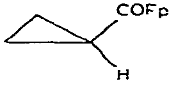
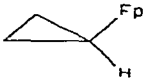
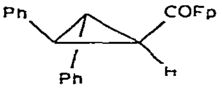
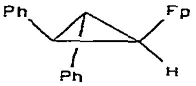
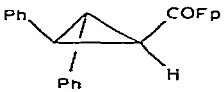
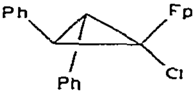
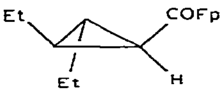
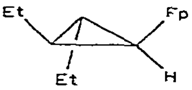
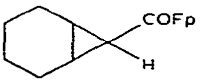
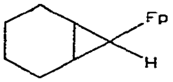
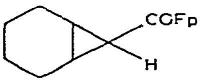
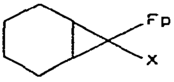
(2)

(1)

We recently had a need to synthesize some substituted dicarbonyl-η^5-cyclopentadienyliron cyclopropane using as our starting material the corresponding cyclopropane carboxylic acids. In view of the results of Stone et al., we expected formation of the acyl complexes to be straight-forward but were pessimistic that we could achieve our final goal by decarbonylation. Nonetheless, in view of anticipated synthetic difficulties using alternate routes [3], we elected to attempt this method in hopes that the substituents on the cyclopropane rings might cause the acyl complexes to show behavior different from that reported for the parent. To our pleasant surprise all new acyl complexes that we succeeded in preparing (4, 7 and 9) underwent smooth photoinduced decarbonylation in acetone-d_6 to give fair to excellent yield (52—97%) of the desired σ com-

TABLE 1

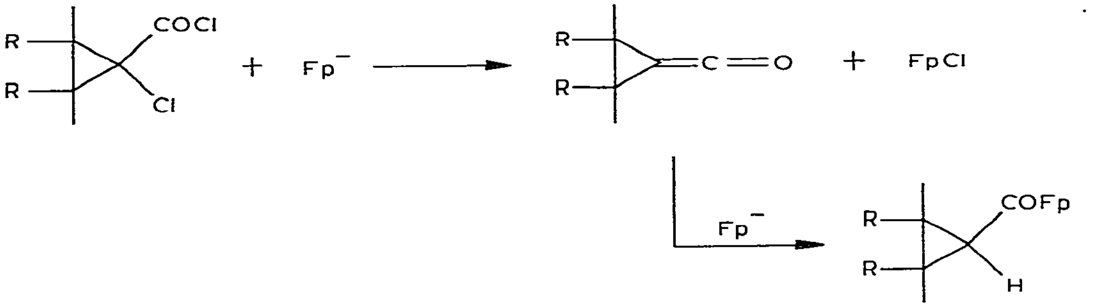
PRODUCTS FROM REACTION OF Fp^- WITH ACYL HALIDES AND YIELDS FROM PHOTOLYSIS OF ACYL COMPLEXES

Product of Fp^- + corresponding acyl halide	Yield (%)	Desired σ complex	Photolysis solvent	Yield of σ complex (%)
 (2)	20^{a}	 (1)	acetone-d_6 benzene-d_6 petroleum ether	75 52 16
 (4)	77	 (3)	acetone-d_6 benzene-d_6 petroleum ether	97 64 51
 (4)	15	 (5)		
 (7)	63	 (6)	acetone-d_6	75
 (9)	18	 (8)	acetone-d_6	52
 (9)	17 (X = Cl) 3 (X = Br)	 X = Cl, Br (10)		

plexes (see Table 1). As a result of these encouraging results we also examined the parent and, again, obtained a good yield (75%) of the σ complex. Since our photolyses were conducted in acetone-d_6 while those of Stone et al. were carried out in petroleum ether, we suspected that our success was probably due to the change in solvents. We therefore repeated our experiments on two of the complexes (2 and 4) in petroleum ether. Indeed, yield were significantly lower and in the case of the parent the yield was low enough (16%) that the σ complex might well have been overlooked. In the two cases studied, benzene-d_6 as the solvent was found to give yields intermediate between acetone-d_6 and petroleum ether.

In addition to **3**, **6** and **8**, we also had a need for the halogen substituted σ complexes **5** and **10** (X = Cl or Br). Unfortunately, despite many variations in conditions all attempts to prepare the necessary acyl complexes failed; the only characterizable materials formed were the corresponding reduced cyclopropanoyl complexes **4** and **9**.

The surprising reduction in our attempts to prepare the α-haloacyl complexes finds apparent precedent in the very recently reported Fp^- reduction of 1,1-dichlorocyclopropanes to 1-chlorocyclopropanes [5a]. However, this may be only apparent since the α-haloacyl chlorides could undergo reduction by a rather attractive ketene mechanism that is not available to Marten's compounds [5b]. Such an elimination could also explain Rosenblum's failure to obtain



characterizable products form reaction of Fp^- with chloroacetyl chloride [6].

Experimental

All operations were carried out in a nitrogen atmosphere. Proton magnetic resonance spectra were obtained with a Jeol FX-100 or a Jeol PMX-60 spectrometer and referenced to tetramethylsilane. The Jeol FX-100 spectrometer was also employed for recording of ^{13}C spectra. Infrared spectra were recorded on a Perkin—Elmer 137 spectrophotometer. Elemental analyses were performed by Atlantic Microlab; Atlanta, Georgia. All solvents were reagent grade. Tetrahydrofuran (THF) was dried over $CaH_2/LiAlH_4$ and distilled over sodium potassium alloy just before using.

The alumina used for column chromatography was Fisher certified neutral alumina, Brockman Activity I, to which 3% water was added. This was stored under nitrogen for no less than one day.

Photolysis was done with a 450 watt Hg Hanovia Lamp in a pyrex well.

Preparation of acyl halides

All acyl halides were prepared in the same way. The procedure is exemplified by the following preparation of 7-chlorobicyclo[4.1.0]heptyl-7-carboxylic acid chloride.

To a solution of 7-chlorobicyclo[4.1.0]heptyl-7-carboxylic acid [7] (6.0 g; 0.03 mol) in benzene (10 ml) was added oxalyl chloride (7.0 g; 0.05 mol) dropwise with stirring. The reaction mixture was then stirred for 2 h at room temperature at which time 2 drops of *N,N*-dimethylformamide were added. The mixture was then refluxed for 1.5 h followed by the removal of the solvent (in vacuo) which left a dark oil. The oil was purified by vacuum distillation (~0.1 Torr, 80—88°C) to give a clear liquid (~2.0 g; 28%); ^{1}H NMR ($CDCl_3$) δ 2.5—1.7 (m); IR (neat) 1780 cm^{-1} (CO).

7-Bromobicyclo[4.1.0]heptyl-7-carboxylic acid chloride, prepared from the known acid [8] is an orange oil isolated in 87% yield. *trans*-2,3-Diphenylcyclopropane carboxylic acid chloride [9] is a cream colored solid, m.p. 185—187°C (86%). *trans*-2,3-Diethylcyclopropanecarboxylic acid chloride, prepared from the known acid [10] is a clear, nearly colorless oil (75%).

Preparation of dicarbonyl-η^5-cyclopentadienyl(cyclopropylcarbonyl)iron (2)

A solution of cyclopropanecarboxylic acid chloride [11] (2.00 g; 0.02 mol) in 5 ml dry THF was added dropwise to a stirring suspension of 3.00 g (0.01 mol) of potassium η^5-cyclopentadienyldicarbonylferrate in 30 ml THF at 0°C. The resulting mixture was then stirred for 1.5 h at 0°C followed by 45 min at room temperature. The reaction mixture was then transferred to a 100 ml round bottom flask containing 20 g alumina followed by the removal of the solvent in vacuo. The reaction products coated on the alumina were chromatographed on an alumina column (1 inch × 6 inch) eluting with a mixture of hexane/dichloromethane (50/50).

The first band (red) was bis[(dicarbonylcyclopentadienyl)iron]. This was followed immediately by an orange band. Removal of the solvent (in vacuo) gave 0.682 g (20%) of an orange-brown air sensitive liquid.

^{1}H NMR ($CDCl_3$) δ 5.0 (s, Cp, 5 H); 2.75 (m, CH, 1 H), 0.70 (m, CH_2, 4 H); IR (neat) 3220, 3020, 2020, 1965, 1785, 1640, 1440, 1420, 1330, 1190, 1030, 940, 825, 680, 660, 620, 570 cm^{-1}; decoupled ^{13}C NMR ($CDCl_3$) 255.7 ppm (acyl-CO), 214.0 (Fe—CO), 85.9 (Cp), 39.2 (C(1)), 10.5 (C(2)—C(3)); MS *m/e* 218.0010 (calcd. M^+ — CO, 218.0030); Anal. Found: C, 53.62; H, 4.19. $C_{11}H_{10}FeO_3$ calcd: C, 53.70; H, 4.09%.

Preparation of dicarbonyl-η^5-cyclopentadienyl(bicyclo[4.1.0]hepta-7-ylcarbonyl)iron (9)

To a cold (—78°C) stirring suspension of potassium η^5-cyclopentadienyldicarbonylferrate (2.578 g; 0.012 mol) in 30 ml of THF was added dropwise a solution of bicyclo[4.1.0]heptyl-7-carboxylic acid chloride [12] (1.900 g; 0.012 mol) in 20 ml of THF. This solution was stirred for 2 h at —78°C followed by 5 h at room temperature. The mixture was then transferred to a 100 ml round bottom flask containing 25 g alumina followed by the removal of the solvent in vacuo. The reaction products coated on the alumina were chromatographed on an alumina column (1 inch × 6 inch) eluting with a mixture of hexane/dichloromethane (80/20).

A red band was first collected which was bis[(dicarbonylcyclopentadienyl)-iron]. This was followed immediately by a yellow band. Removal of the solvent (in vacuo) gave 0.650 g (18%) of a brown air sensitive solid.

^{1}H NMR ($CDCl_3$) δ 4.88 (s, Cp, 5 H), 2.42 (m, H(7), 1 H), 1.70 (m, 6 H), 1.25 (m, 4 H); IR (in $CDCl_3$) 2940, 2865, 2015, 1970, 1630, 1450, 1395, 1285, 1270, 1205, 1090, 1005, 905, 870, 730, 650, 570 cm^{-1}; decoupled ^{13}C NMR ($CDCl_3$) 253.0 ppm (acyl-CO), 215.0 (Fe—CO), 85.9 (Cp), 54.3 (C(7)), 24.7 (C(1) + C(6)), 22.2 and 20.8 (C(2)—C(5)); MS *m/e* 272.0495 (calcd.

M^+ — CO, 272.0499); m.p. 56—57°C (sealed in a vacuum cap. tube); Anal. Found: C, 59.79; H, 5.42. $C_{15}H_{16}FeO_3$ calcd.: C, 60.03; H, 5.37%.

Reaction of potassium η^5-cyclopentadienyldicarbonylferrate with 7-chlorobicyclo[4.1.0]heptyl-7-carboxylic acid chloride

To a cold (0°C) stirred suspension of potassium η^5-cyclopentadienyldicarbonylferrate (2.00 g; 9.6 mmol) in 80 ml of THF was added dropwise a solution of 7-chlorobicyclo[4.1.0]heptyl-7-carboxylic acid chloride (3.50 g; 16.2 mmol) in 30 ml of THF. This mixture was allowed to stir 30 min at 0°C followed by 3 h at room temperature. Work-up as above gave bis[(dicarbonylcyclopentadienyl)iron] and 0.498 g (17%) of dicarbonyl-η^5-cyclopentadienyl-(bicyclo[4.1.0]hepta-7-ylcarbonyl)iron (**9**).

Reaction of potassium η^5-cyclopentadienyldicarbonylferrate with 7-bromobicyclo[4.1.0]heptyl-7-carboxylic acid chloride

To a suspension of potassium η^5-cyclopentadienyldicarbonylferrate (2.00 g; 0.010 mol) in 60 ml of THF at 0°C was added dropwise a solution of 7-bromobicyclo[4.1.0]heptyl-7-carboxylic acid chloride (2.40 g; 0.008 mol) in 15 ml of THF. This was then allowed to stir 2 h at 0°C followed by 1 h at room temperature. Work-up as above gave bis[(dicarbonylcyclopentadienyl)iron] and 100 mg (3%) of dicarbonyl-η^5-cyclopentadienyl(bicyclo[4.1.0]hepta-7-ylcarbonyl)iron (**9**).

Preparation of dicarbonyl-η^5-cyclopentadienyl(trans-2,3-diethylcyclopropylcarbonyl)iron (7).

To a suspension (at 0° C) of potassium η^5-cyclopentadienyldicarbonylferrate (2.012 g; 9.35 mmol) in 20 ml of THF was added over ca. 10 min a solution of *trans*-2,3-diethylcyclopropanecarboxylic acid chloride (1.012 g; 6.23 mmol) in 10 ml of THF. This mixture was stirred for 2.5 h at 0°C followed by 45 min at room temperature. The usual workup using an alumina column (1 inch × 6 inch) and eluting with hexane/methylene chloride (75/25) gave a yellowish-orange band. Removal of the solvent gave 1.20 g (63%) of an orange-brown air sensitive oil.

^{1}H NMR ($CDCl_3$) δ 4.80 (s, Cp, 5H), 2.50 (m, C(1), 1H), 1.20 (m, 12 H); IR (neat) 2970, 2940, 2880, 2005, 1965, 1640, 1470, 1430, 1420, 1380, 1320, 1240, 1205, 1140, 1070, 1020, 985, 950, 830, 735, 620, 660, 580 cm^{-1}; decoupled ^{13}C NMR (acetone-d_6) 253.0 ppm (acyl-CO), 214.4 (Fe—CO), 214.1 (Fe—CO), 86.0 (Cp), 53.7 (C(1)), 35.8 (CH_3), 31.8 (CH_3), 26.5 (CH_2), 28.1 (CH_2), 14.1, 13.1 (C(2)—C(3)); MS *m/e* 274.0643, (calcd. M^+ — CO 274.0656); Anal. Found: C, 59.73; H, 6.05. $C_{15}H_{18}FeO_3$ calcd.: C, 59.63; H, 6.01%.

Preparation of dicarbonyl-η^5-cyclopentadienyl(trans-2,3-diphenylcyclopropylcarbonyl)iron (4)

To a suspension of potassium η^5-cyclopentadienyldicarbonylferrate (2.10 g; 9.80 mmol) in 35 ml of THF at 0°C was added a mixture of *trans*-2,3-diphenylcyclopropanecarboxylic acid chloride (1.56 g, 6.00 mmol) in 20 ml of THF dropwise (~20 min). This was allowed to stir 2.5 h at 0°C followed by 45 min at room temperature. Usual work-up gave 1.832 g (77%) of an orange-brown air sensitive oil.

^1H NMR (acetone-d_6) δ 7.25 (s, aromatic, 10 H), 4.85 (s, Cp, 5 H), 3.50 (m, 2 H), 3.12 (m, 1 H); IR (acetone-d_6) 3110, 3090, 3060, 3040, 2255, 2010, 1955, 1705, 1635, 1500, 1450, 1420, 1310, 1250, 1155, 1080, 1020, 950, 910, 830, 790, 750, 735, 695, 580, 515 cm^{-1}; decoupled ^{13}C NMR (acetone-d_6) 249.8 ppm (acyl-CO), 213.9 (Fe—CO), 213.8 (Fe—CO), 140.0, 135.6, 128.4, 129.1, 126.1, 125,8 (aromatic C's), 85.9 (Cp), 58.3 (C(1)), 36.1 and 29.7 (C(2)—C(3)); MS *m/e* 314.0756 (calcd. $M^+ - 3CO$) 314.0758); Anal. Found: C, 69.17; H, 4.64. $C_{23}H_{18}FeO_3$ calcd.: C, 69,37; H 4.56%.

Reaction of potassium η⁵-cyclopentadienyldicarbonylferrate with trans-2,3-diphenyl-1-chlorocyclopropanecarboxylic acid chloride

To a mixture of potassium η^5-cyclopentadienyldicarbonylferrate (0.50 g; 2.3 mmol) at 0°C in 50 ml of THF was added a mixture of *trans*-2,3-diphenyl-1-chlorocyclopropanecarboxylic acid chloride (0.50 g; 1.7 mmol) dropwise (~30 min). This mixture was allowed to stir 2.5 h at 0°C followed by 45 min at room temperature. The usual work-up gave 0.104 g (15%) of dicarbonyl-η^5-cyclopentadienyl(*trans*-2,3-diphenylcyclopropylcarbonyl)iron (4).

Preparation of η⁵-cyclopentadienyl(bicyclo[4.1.0]hepta-7-yldicarbonyl)iron (8) [6]

Dicarbonyl-η^5-cyclopentadienyl(bicyclo[4.1.0]hepta-7-ylcarbonyl)iron (0.256 g; 0.86 mmol) was dissolved in acetone-d_6. This mixture was then filtered into an NMR tube and photolyzed at 0°C for 3 h (under a N_2 atmosphere). The reaction mixture was then added to a 50 ml round bottom with 2 g of alumina followed by removal of the solvent in vacuo. The reaction products coated on the alumina were chromatographed on an alumina column (0.5 inch × 3 inch) eluting with hexane. Only one yellow band was collected which gave 0.122 g (52%) of an orange brown liquid (not air sensitive) after the removal of the solvent.

^1H NMR ($CDCl_3$) δ 4.70 (s, Cp, 5 H), 1.7 (m), 1.2 (m), and 0.56 m; IR (neat) 2930, 2860, 2360, 2005, 1950, 1190, 1050, 900, 720 cm^{-1}; decoupled ^{13}C NMR (acetone-d_6) 205.8 ppm (Fe—CO), 86.3 (Cp), 26.2, 22.1, 21.4 (C(1)—C(6)) and 4.6 (C(7)); MS *m/e* 272.0499, (calcd. M^+, 272.0495); Anal. Found: C, 61.57; H, 5.97. $C_{14}H_{16}FeO_2$ calcd.: C, 61.79, H, 5.93%.

Preparation of dicarbonyl-η⁵-cyclopentadienyl(cyclopropyl)iron (1) [6]

Dicarbonyl-η^5-cyclopentadienyl(cyclopropylcarbonyl)iron (0.206 g; 0.84 mmol) was dissolved in acetone-d_6. This mixture was filtered into a NMR tube and photolyzed for 1 h and 10 min at 10°C. Work-up as above gave 0.135 g (75%) of an orange-brown solid.

^1H NMR (acetone-d_6) δ 4.90 (s, Cp, 5H), 0.58 (m, 3H), −0.05 (m, 2 H), (these values correspond with the values reported by Rosenblum [6]; IR (neat) 3128, 3060, 2990, 2010, 1950, 1450, 1435, 1422, 1365, 1210, 1110, 1075, 1045, 1015, 1000, 925, 830, 635, 595, 585, 520, 465 cm^{-1}; decoupled ^{13}C NMR (acetone-d_6) 218.1 ppm (Fe—CO), 86.9 (Cp), 8.6 (CH_2), −9.8 (CH); Anal. Found: C, 55.21 H, 4.68. $C_{10}H_{10}FeO_2$ calcd.: C, 55.09; H, 4.62%.

Using benzene-d_6 photolysis (2 h) of 0.1127 g of acyl complex gave 0.0518 g (52%) of isolated σ complex.

Using petroleum ether (38—56° C) photolysis (1 h and 45 min) of 0.1996 g of the acyl complex gave 0.0265 g (16%) of isolated σ complex.

Preparation of dicarbonyl-η^5-cyclopentadienyl(trans-2,3-diethylcyclopropyl)-iron (6)

Dicarbonyl-η^5-cyclopentadienyl(*trans*-2,3-diethylcyclopropylcarbonyl)iron (0.5012 g; 1.65 mmol) was dissolved in acetone-d_6. The resulting mixture was then filtered into an NMR tube and photolyzed for 2 h at 0°C. The usual work-up gave 0.3428 g (75%) of a brownish oil.

^{1}H NMR δ 4.85 (s, Cp, 5 H), 1.10 (m, 12 H), 0.2 (m, 1 H); IR (neat), 2960, 2940, 2880, 2860, 2000, 1950, 1455, 1375, 1300, 1250, 1200, 1170, 1020, 1000, 840, 825, 775, 635, 590, 560 cm^{-1}; decoupled ^{13}C NMR (acetone-d_6) 218.5 ppm (Fe—CO), 218.2 (Fe—CO), 86.4 (Cp), 30.3, 30.1 (CH_2), 27.4 (CH_3), 15.1, 14.1 (C(2) + C(3)), 7.5 (C(1)); MS *m/e* 274.0657, calcd. M^+, 274.0656). Anal. Found:, C, 61.49; H, 6.71. $C_{14}H_{18}FeO_2$ calcd.: C, 61.34; H, 6.62%.

Preparation of dicarbonyl-η^5-cyclopentadienyl(trans-2,3-diphenylcyclopropyl)-iron (5)

Dicarbonyl-η^5-cyclopentadienyl(*trans*-2,3-diphenylcyclopropylcarbonyl)iron (0.50 g; 1.26 mmol) was dissolved in acetone-d_6. This mixture was then filtered into an NMR tube which was photolyzed for 2 h at 0°C. Work-up as usual gave 0.452 g (97%) of an air stable orange solid.

^{1}H NMR ($CDCl_3$) δ 7.12 (m, aromatic, 10 H), 4.4 (s, Cp, 5 H), 2.45 (cyclopropyl H *trans* to Fp, d of d, $^3J_{cis\,H's}$ 5.2 Hz; $^3J_{trans\,H's}$ 2.3 Hz), 2.1 (cyclopropyl H *cis* to Fp, d of d), 1.5 (cyclopropyl H α to Fp, d of d); IR ($CDCl_3$) 3100, 3070, 3040, 3000, 2970, 2260, 2010, 1950, 1580, 1495, 1435, 1420, 1360, 1270, 1075, 1020, 1000, 910, 885, 830, 755, 730, 700, 635, 590, 570 and 530 cm^{-1}; decoupled ^{13}C NMR (acetone-d_6) 216.4 ppm (Fe—CO), 215.7 (Fe—CO), 145.8, 143.6, 129.2, 128.1, 127.7, 125.8, 125.2, 124.9 (aromatic C's), 85.1 (Cp), 34.9, 31.2 (C(2)—C(3)), 15.8 (C(1)); MS *m/e* 314.0739 (calcd. M^+, 314.0729); Anal. Found: C, 71.14; H, 4.94. $C_{22}H_{18}FeO_2$ calcd.: C, 71.34; H, 4.90%.

Using benzene-d_6 photolysis (2.5 h) of 0.306 g of the acyl complex gave 0.148 g (64%) of the alkyl complex.

Using petroleum ether (38—56°C) as solvent, photolysis (2.5 h) on 0.046 g of the acyl complex gave 0.022 g (51%) of the alkyl complex.

Acknowledgment

Financial support of this research by the National Science Foundation is gratefully acknowledged. The authors are also indebted to Mr. Marc D. Radcliffe for assistance in obtaining some of the NMR data.

References

1 F.G.A. Stone, M. Bruce and M. Iqbal, J. Organometal. Chem., 161 (1969) 20.
2 M. Iqbal, Pakistan J. Scientific Research, 81, (1973) 25.
3 Rosenblum [4] synthesized both 1 and 8 by allowing FpNa to react with the appropriate cyclopropyl

bromide and, in one case, from reaction of FpBr with cyclopropyllithium. To use either of these methods and still meet our limitation of beginning with the carboxylic acid would be formidable.

4 A. Cutler, R. Fish, W. Giering and M. Rosenblum, J. Am. Chem. Soc., 4354 (1972) 94.

5 (a) D. Marten, E. Dehmlow, D. Hanlon, M. Bilayet and D. van der Helm, J. Am. Chem. Soc., 4940 (1981) 103; (b) A referee has suggested that this reduction might also occur by a radical mechanism with FpH (as an impurity in the Fp^-) as the hydrogen source. We have no evidence to either support or refute this suggestion.

6 A. Cutler, S. Raghu and M. Rosenblum, J. Organometal. Chem., 381 (1974) 77.

7 G. Kobrich and W. Goyert, Tetrahedron, 4327 (1968) 24.

8 D. Seyferth, R. Lambert and M. Massol, J. Organometal. Chem., 255 (1975) 88.

9 I.A. D'yakanov, M.I. Komendantov, Fu Gui-siya and G.L. Korichev, J. Gen. Chem. USSR, 917 (1962) 32.

10 J. Walbrick, J. Willison Jr. and W.M. Jones, J. Am. Chem. Soc., 2895 (1968) 90; E. York, W. Dittmar, J. Stevenson and R. Bergman, J. Am. Chem. Soc., 5680 (1973) 95.

11 Obtained from Aldrich Chemical Company and used without further purification.

12 Hodgkins and Flores, J. Org. Chem., 3356 (1963) 28.