Journal of Organometallic Chemistry, 228 (1982) 273—279
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

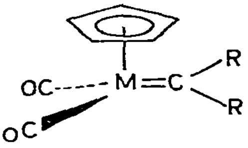
ROTATION BARRIERS AROUND THE CARBENE—METAL BOND OF TRANSITION METAL COMPLEXES OF CYCLOHEPTATRIENYLIDENES

FRANK J. MANGANIELLO, MARC D. RADCLIFFE and W.M. JONES
Department of Chemistry, University of Florida, Gainesville, Florida 32611 (U.S.A.)
(Received September 21st, 1981)

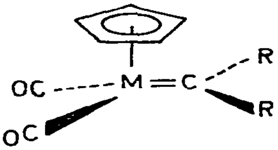
Summary

Rotation around the carbon—metal bond of a cycloheptatriene and three cycloheptatrienylidene complexes of iron have been examined using temperature-dependent NMR studies. Neither η^1-cycloheptatrienylidene-η^5-cyclopentadienyldicarbonyliron hexafluorophosphate (**3**) nor 1,2-benzo-5-(η^5-cyclopentadienylcarbonyltri-n-butylphosphineiron)cycloheptatriene (**10**) showed any temperature dependence to —105°C. From this it is concluded that the former probably prefers the electronically less favored (but sterically preferred) conformation **3b** while the rotation barrier for the latter is too small to be observed in this temperature range. Both η^1-cycloheptatrienylidene-η^5-cyclopentadienylcarbonyltri-n-butylphosphineiron hexafluorophosphate (**11**) and η^1-4,5-benzocycloheptatrienylidene-η^5-cyclopentadienylcarbonyltri-n-butylphosphineiron hexafluorophosphate (**12**) showed rotation barriers that could be measured in the temperature range employed (RT to —105°C). The barrier in the benzannelated complex **12** is greater than in **11**. This is consistent with Hoffmann's [2] prediction that an electronic component should contribute to conformational preferences and rotational barriers in carbene complexes of unsymmetrically substituted transition metals.

Conformational preferences and rotation barriers around carbene—metal bonds of transition metal complexes are currently areas of both theoretical [1—4] and experimental interest [5—10]. From both single crystal X-ray analysis [10] and low-temperature NMR studies [7], carbene-metal complexes of type 1 apparently prefer a conformation in which the plane described by the metal, the carbene carbon and the groups bonded to it describe the mirror plane of the molecule (conformation 1a). Preference for this conformation, which is probably the sterically less favorable (e.g. sterically congested complex 2 does not prefer this conformation [8]) has been rationalized by Hoffmann and his coworkers [2] as resulting from more favorable back-bonding from the appropriately oriented *d*-hybrid (a'') into the vacant orbital of the carbene in 1a than

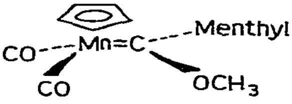


(1a)

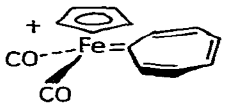


(1b)

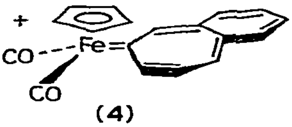
from the lower energy 1*a*′ orbital in conformation **1b**. Consistent with this electronic explanation is our finding that, in the crystal, both **3** and **4** prefer conformations corresponding to **1b** [9]. In these examples, back-bonding should be reduced due to the aromaticity of the tropylium ions.



(2)

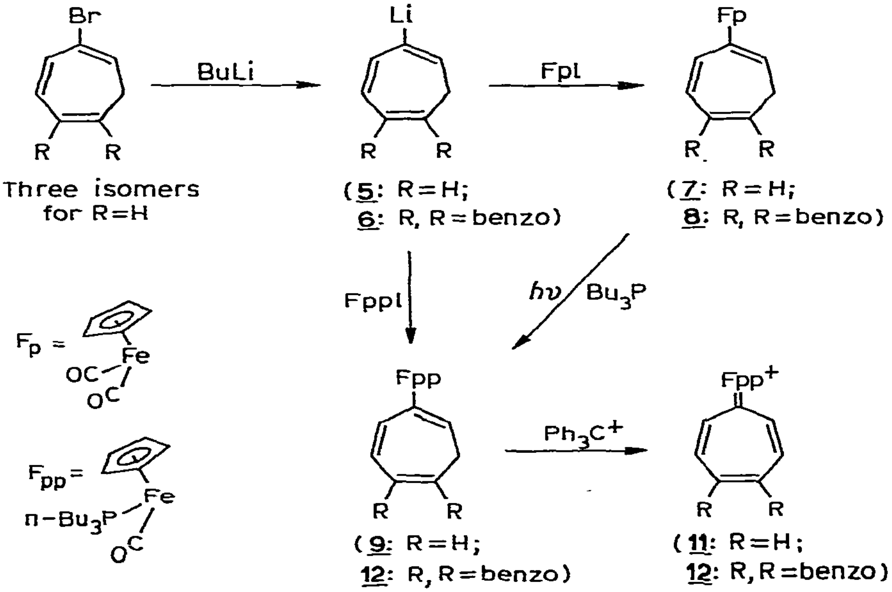


(3)



(4)

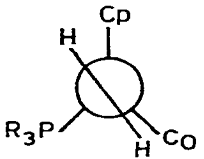
At this time we report the synthesis of two iron complexes of cycloheptatrienylidene (**11** and **12**) that are sufficiently devoid of symmetry to permit an examination of rotation barriers about their carbon—metal bonds using variable temperature NMR. These two compounds are of particular interest because while steric hindrance to rotation should be essentially the same, electronic demands for back bonding from the metal should be greater for **12** than for **11**. The two complexes (**11** and **12**) were synthesized as summarized in Scheme 1.



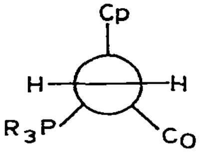
SCHEME 1.

Intermediates **5**, **6**, **7** and **8** were prepared as previously reported [9,11]. Substitution of one carbonyl with tri-n-butylphosphine was satisfactorily accomplished by either photolysis of **7** or **8** in the presence of tri-n-butylphosphine (room temp., THF) or reaction of lithium reagents **5** or **6** with FppI [12] (THF, 1 h, −78°C, 49 h, room temp.). Hydride abstraction with triphenylcarbenium hexafluorophosphate was conducted as previously reported [9,11] for **7** and **8**. Complex **11** is a purple solid which slowly decomposes in solution but appears to be stable indefinitely in the crystalline form. Hydride abstraction from **10** gave **12** as a blue-purple solid that is much less stable than **11**. It rapidly decomposes when it is either exposed to air or permitted to warm to room temperature.

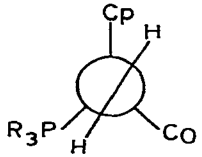
The barriers to rotation in **11** and **12** were measured by variable temperature ^{1}H NMR. The proton NMR of **11** at room temperature revealed a doublet (9.60 ppm) attributable to the pair of protons adjacent to the carbon—iron bond. Although these protons are in different environments regardless of conformation [13] they are equivalent due to rapid rotation. Upon cooling, this doublet broadened to sharpen eventually to an apparent broad triplet (actually an overlapping doublet of doublets broadened by solvent viscosity). By irradiating the protons of C(3) and C(6) and using the standard coalescence equation given in eq. 1 [14], a value for $\Delta G^{\neq}$ was determined



(11a, 12a)



(11b, 12b)



(11c, 12c)

$$\Delta G^{\neq} = RT_c[(22.96) + \ln(T_c/\Delta\nu)] \tag{1}$$

to be 9.6 ± 0.2 kcal/mol [15]. Coalescence occurred at −84°C. At −105°C the spectrum showed two broad singlets separated by 13 ± 2 Hz [17]. Application of the same procedure to **12** gave a value for $\Delta G^{\neq}$ of 10.4 ± 0.2 kcal/mol with coalescence occurring at −68°C and singlets separated by 15 ± 2 Hz from −85 to −104°C.

The barriers to rotation in **11** and **12** are interesting in their own right. However, the significant question is: are they different? Based only on absolute magnitudes, conclusions would be dangerous indeed because the size of the energy difference is not statistically certain. However, the fact that the separations of the singlets at low temperature are nearly identical while the coalescence temperatures are without question significantly different convinces us that the barrier to rotation in **12** is greater than **11**, although the magnitude of the difference is not known.

The origin of the difference in rotational barriers is a point of interest. From the calculations of Hoffmann et al. [2,3], in unsymmetrical carbene complexes **11** and **12**, conformations **11a** and **12a** should be favored [13] over **11b**, **11c**, **12b** and **12c** as a result of more favorable back-bonding in the former. This, in turn, leads to the prediction that the barriers to rotation should have an electronic as well as the obvious steric component. Our result supports this prediction since benzannelation of cycloheptatrienylidene should lead to an increase in back-bonding from the metal while leaving the steric effect unchanged. It must be emphasized, though, that this is not to say that the electronic component is the dominant force in these rotational barriers. In fact, in complexes such as **11** and **12** it has been found [18] that back-bonding is rather weak. It is therefore likely that the principal restriction to rotation is steric in origin with a minor electronic component superimposed.

The temperature-dependent NMR spectrum of **3** was also examined. In this case no kinetically induced broadening was observed as the temperature was lowered to −105°C. Absence of an observable rotation barrier in this case was expected since an X-ray study [9] showed **3** to prefer the conformation depicted (note the equivalence of the *ortho*-hydrogens) in the crystal and there is no reason to assume a different preference in solution.

Finally, the temperature-dependent NMR spectrum of **10** was examined. In this case the CH_2 hydrogens were irradiated to give the adjacent vinyl hydrogen as a singlet. As the temperature was lowered no kinetically induced broadening was observed to −105°C. This suggests a substantially lower rotation barrier than was observed for the corresponding carbene complex **12**. Although it isn't possible to assess how much of the difference is due to different carbon—metal bond lengths, it clearly is in the direction expected if back-bonding contributes to the barrier in **12**.

Experimental section

General procedure

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 NMR 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. Benzene was refluxed over CaH_2 and distilled. Methylene chloride was dried over P_4O_{10} and distilled under nitrogen, passed through basic alumina (Brockman Activity I) and then degassed by bubbling N_2 through the solvent.

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. η^5-Cyclopentadienyliron dicarbonyl iodide was obtained from Alfa Products and used without further purification.

η^5-Cyclopentadienyliron carbonyl tri-n-butylphosphine iodide

To a solution of cyclopentadienyliron dicarbonyl iodide (10.0 g; 0.033 mol) in 200 ml of benzene was added tri-n-butylphosphine (6.7 g). This mixture was refluxed for 20 hours at which time the solvent was removed under reduced pressure, followed by recrystallization (petroleum ether, 60°—90°C), to yield 14.0 g (89%) of a brown solid: m.p. 75—76°C, ^1H NMR ($CDCl_3$): δ 0.70—2.20 (m, n-butyl group, 27 H), 4.50 ppm (d, $J(HP) = 1.10$ Hz, Cp, 5 H); IR (KBr): 2975, 2240, 2050, 1900, 1460, 1405, 1375, 1340, 1300, 1205, 1090, 1050, 1000, 960, 880, 840 cm^{-1}.

Tropone

Tropone was prepared according to the method of Radlich [20] with the single variation that the reaction mixture was stirred with a mechanical stirrer in a Morton flask (37%).

Preparation of a mixture of 1-, 2-, and 3-bromocycloheptatrienes

These were synthesized and purified according to published procedures from the reduction of bromotropylium bromide [21,22].

Preparation of a mixture of 1-, 2-, and 3-lithiocycloheptatrienes (5)

To a cold (—78°C) mixture of 1-, 2-, and 3-bromocycloheptatrienes (3.21 g; 18.8 mmol) in 30 ml of THF was added 15 ml of n-butyllithium (24.0 mmol; 1.6 molar solution in hexane) dropwise (~15 min). The resulting solution was stirred for 30 minutes at —78°C and used immediately.

Preparation of a mixture of 1-,2-, and 3-(η^5-cyclopentadienyliron carbonyl tri-n-butylphosphine)cycloheptatrienes (9)

Method A: Cyclopentadienyliron carbonyl tri-n-butylphosphine iodide (9.20 g; 19.5 mmol) in 20 ml of THF was added to a solution of 1-, 2-, and 3-lithiocycloheptatrienes dropwise (~15 min) at —78°C. The reaction was stirred for 12 hours at —78°C after which it was allowed to stir for 1 hour at room temperature. The solution was then poured into a 250 ml round bottom flask containing 45 g of alumina followed by removal of the solvent in vacuo. The coated alumina was then placed on a column (12 inch X 1 inch) of alumina and eluted with pentane. A reddish orange band was collected. Removal of the solvent, in vacuo, gave 2.0 g (24%) of a reddish orange, air-sensitive oil: ^{1}H ($CDCl_3$): δ 0.50—2.80 (m, methylene and n-butyl groups, 29 H), 4.20, 4.28 and 4.40 (s, s, s, Cp, 5H), 4.60—4.80 ppm (m, olefin, 5 H); IR (neat): 2960, 1910, 1470, 1380, 1095, 1015, 910, 730 cm^{-1}; Mass spec.: *m/e* 442.20370 (calcd. M^+, 442.20879), 414.21098 (calcd. $M^+ - CO$, 414.21388).

Method B: η^5-Cyclopentadienyliron dicarbonyl iodide (0.38 g; 0.01 moles) in 60 ml of THF was added by syringe (~15 min) to a cold (—78°C) mixture of 1-, 2-, and 3-lithiocycloheptatrienes (1.80 g; 0.01 mol) in 30 ml of THF. After addition, the mixture was stirred for 1 hour at —78°C followed by 1 hour at room temperature. To this mixture was added by syringe 4 ml of tri-n-butylphosphine. Irradiation for 3 hours using a 450 watt Hg lamp followed by purification as above gave 0.89 g (20%) of the sigma complexes.

η^1-Cycloheptatrienylidene-η^5-cyclopentadienylcarbonyltri-n-butylphosphineiron hexafluorophosphate (11)

To a solution of 1-, 2-, and 3-(cyclopentadienyliron carbonyl tri-n-butylphosphine)cycloheptatrienes (2.0 g; 4.6 mmol) in 25 ml of methylene chloride was added triphenylcarbenium hexafluorophosphate (2.5 g; 6.4 mmol) in 30 ml of methylene chloride dropwise (~20 min) at —78°C. The reaction mixture was allowed to stir at —78°C for 1 hour followed by 1 hour at room temperature at which time 45 ml of solvent was removed in vacuo. To this was added 90 ml of diethyl ether by syringe to precipitate the complex. The solid was collected on a glass frit and was washed with several portions of diethyl ether to give 0.902 g

(54%) of a purple solid. Recrystallization from CH_2Cl_2 and diethyl ether gave purple plates: ^1H NMR (acetone-d_6): δ 0.70—2.00 (m, n-butyl groups, 27 H), 5.10 (d, J(HP) = 1.1 Hz, Cp, 5 H), 7.0—8.0 (m, olefinic, 4 H), 9.6 ppm (d, olefinic, 2 H); IR (neat): 2995, 1920, 1450, 1090, 840 cm^{-1}. ^{13}C NMR (ppm from Me_4Si, acetone-d_6, 25.0 MHz, RT broadband ^1H decoupled): 278.8 (d, $J(^{13}C—^{31}p)$ = 22.5 Hz, C(1), 217.5 (d, $J(^{13}C—^{31}p)$ = 27.5 Hz, CO), 167.0 (C(2)), 143.0 (C(3)), 128.9 (C(4)) and 86.7 (Cp).

Anal. Found: C, 48.95; H, 6.25. Calcd. for $C_{25}H_{38}F_6FeOP_2$: C, 51.21; H, 6.53%.

Benzotropone

This material was synthesized and purified according to published procedures [23].

1,2-Benzo-5-bromocycloheptatriene

This was prepared according to the method of Fohlisch et al. by the reduction of the dibromide salt [24].

Preparation of 1,2-benzo-5(η^5-cyclopentadienyl ironcarbonyl tri-n-butylphosphine)cycloheptatriene (10)

Method A. To a cold (—78°C) solution of 1,2-benzo-5-bromocycloheptatriene (0.7 g; 3.2 mmol) in 20 ml of THF was added dropwise over ca. 20 min 2.3 ml of n-butyllithium (1.6 molar in hexane). The cold (—78°C) solution was stirred for 30 minutes at which time cyclopentadienyliron carbonyl tri-n-butylphosphine in 55 ml of THF was added by syringe (~10 min). This mixture was then stirred for 1 hour at —78°C and 49 hours at room temperature. The solution was then poured into a 500 ml round bottomed flask with 40 g of alumina followed by the removal of the solvent in vacuo. The product coated on the alumina was purified by column chromatography (7 in × 1 in) with pentane as the eluent. A yellow band was collected and removal of the solvent gave 0.401 g (27%) of a yellow-orange, air-sensitive oil: ^1H NMR ($CDCl_3$): δ 0.50—1.50 (m, n-butyl groups, 27 H), 2.80 (br. d, methylene, J = 6.4 Hz, J(HP) = 1.8 Hz, 2 H), 4.25 (s, Cp, 5 H), 5.40 (d of t, olefinic, J = 6.4 Hz, J(HP) = 2.8 Hz, 1 H), 6.2—6.7 (AB system, olefinic, J = 10.9 Hz, 2 H), 6.70—7.10 (m, aromatic, 4 H); IR (neat): 2950, 2300, 1925, 1460, 1380, 1050, 910, 785, 730 cm^{-1}; mass spec. m/e 464.22953 (calcd. M^+ — CO, 464.22953).

Method B. To a cold (—78°C) solution of 1,2-benzo-5-lithiocycloheptatriene (1.5 g; 6.8 mmol) in 30 ml of THF was added a mixture of cyclopentadienyliron dicarbonyl iodide (1.5 g; 8.2 mmol) in 20 ml of THF dropwise (~15 min). This was stirred for 16 hours at —78°C and 1 hour at room temperature at which time 6 ml of tri-n-butylphosphine was added by syringe. The resulting solution was irradiated for 5 hours (450 watt Hg lamp). Purification as above gave 0.50 g (15%) of the sigma complex.

η^1-4,5-Benzocycloheptatrienylidene-η^5-cyclopentadienylcarbonyltri-n-butylphosphineiron hexafluorophosphate (12)

To a solution of 1,2-benzo-5-(cyclopentadienyliron carbonyl tri-n-butylphosphine)cycloheptatriene (0.50 g; 1.1 mmol) in 15 ml of methylene chloride at

—78° C was added dropwise by syringe a solution of triphenylcarbenium hexafluorophosphate (0.4981 g; 1.28 mmol) in 20 ml of methylene chloride. The reaction mixture was stirred for 20 hours at —78° C and then allowed to warm to room temperature (~20 min) at which time ~30 ml of the methylene chloride was removed in vacuo. To the residue was added 80 ml of cold (0° C) ethyl ether by syringe after which the solution was cooled to 0° C. The mixture was filtered to yield 0.25 g (45%) of a blue-purple solid that is sensitive to air and thermally decomposes at room temperature: ^{1}H NMR (acetone-d_6): δ 0.70—2.00 (m, n-butyl group, 27 H), 5.3 (s, Cp, 5 H), 7.30 (d, olefinic, 2 H), 7.70—8.00 (AA'BB' system, aromatic, 4 H), 9.10 (d, olefinic, 2 H); IR (neat): 3060, 2995(sh), 1980, 1720, 1520, 1560, 1240, 1080, 990, 830 cm^{-1}; ^{13}C NMR (ppm from Me$_4$Si, acetone-d_6 (—10° C) broadband ^{1}H decoupled): 157.6 (C(2)), 139.4 (C(3)), 135.5 (C(4)), 133.6 (C(5)), 129.3 (C(6)), and 89.5 (Cp); instability of this complex precluded detection of the weak CO and C(1) resonances.

Acknowledgement

Financial support of this research by the National Science Foundation is gratefully acknowledged.

References

1 D. Spangler, J.J. Wendlolski, M. Dupuis, M.M.L. Chen and H.F. Schaefer, III J. Amer. Chem. Soc., 103 (1981) 3985.
2 B.E.R. Schilling, R. Hoffmann and D.L. Lichtenberger, J. Amer. Chem. Soc., 101 (1979) 585.
3 B.E.R. Schilling, R. Hoffmann and J.W. Falla, J. Amer. Chem. Soc., 101 (1979) 592.
4 J.W. Lauher and R.J. Hoffmann, J. Amer. Chem. Soc., 98 (1976) 1729.
5 M. Brookhart and J.R. Tucker, J. Amer. Chem. Soc., 103 (1981) (1979).
6 W.A. Kiel, G.Y. Lin and J.A. Gladysz, J. Amer. Chem. Soc., 102 (1980) 3299.
7 M. Brookhart, J.R. Tucker, T.C. Flood and J. Jensen, J. Amer. Chem. Soc., 102 (1980) 1203.
8 S. Fontana, U. Schubert and E.O. Fischer, J. Organometal. Chem., 146 (1978) 39.
9 P.W. Riley, R.E. Davis, N.T. Allison and W.M. Jones, J. Amer. Chem. Soc., 102 (1980) 2458.
10 A.D. Redhouse, J. Organometal. Chem., 99 (1975) C29; E. Hadicke and E. Hoppe, Acta Crystallog., B 27 (1972) 1960.
11 Cf. N.T. Allison, Y. Kawada and W.M. Jones, J. Amer. Chem. Soc., 100 (1978) 5224.
12 R.J. Haines, A.L. DuPreez and I.L. Marais, J. Organometal. Chem., 28 (1971) 405.
13 The carbene is calculated [3] to be titled as shown in 11a and 12a when one carbonyl is substituted by phosphine.
14 Line shape simulation programs were not used because they were not readily available and it was felt that enthalpy and entropy information obtained in this way was not likely to be accurate due to the limited temperature range over which kinetically dependent line shapes could be observed.
15 Analysis of the fast exchange line shape behavior produced an approximate value (possibly affected by the decoupling irradiation [16]) of 9.7 kcal/mol for the activation barrier.
16 L.M. Jackman and F.A. Cotton, Dynamic Nuclear Magnetic Resonance Spectroscopy, Academic Press, New York, 1975, p. 64.
17 Low-temperature induced line broadening introduced some uncertainty into this number. However, varying it from the extremes of 11 to 15 Hz (13 to 17 Hz for 12) did not cause the calculated $\Delta G^{\neq}$'s to overlap.
18 P.E. Riley, R.E. Davis, T. Allison and W.M. Jones, J. Amer. Chem. Soc., 102 (1980) 2458.
19 A referee has pointed out that a lack of broadening in 10 could also be due to a large difference in populations of the possible conformers. Although the steric requirements of the two *ortho*-positions in 10 are similar, they are not identical, making this a viable alternative.
20 P. Radlich, J. Org. Chem., 29 (1961) 960.
21 B. Fohlisch, P. Burgle and D. Krackenberger, Chem. Ber., 101 (1968) 2727.
22 B. Fohlisch and E. Haug, Chem. Ber., 104 (1971) 2324.
23 L.A. Paquette and G.D. Ewing, J. Org. Chem., 40 (1975) 2965.
24 B. Fohlisch, C. Fisher, E. Widman and E. Wolf, Tetrahedron, 34 (1978) 533.