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## Reactions of pentafluorophenyllithium and cyclopentadienyliron carbonyl cations

The reactions of  $C_5H_5Fe(CO)_3^-BPh_4^-$  and  $C_5H_5Fe(CO)_2^+[(C_6H_5)_3P]^-Cl^-$  with sodium borohydride<sup>1</sup> provide a contrast which illustrates an effect of substitution of triphenylphosphine for carbon monoxide in a metal complex. The former reaction yields  $[C_5H_5Fe(CO)_2]^-$  presumably via the hydride  $C_5H_5Fe(CO)_2H$ , whereas the latter yields a cyclopentadiene derivative,  $C_5H_6Fe(CO)_2^+[(C_6H_5)_3P]^-$ .

We have also observed a contrast in reactions of these two cyclopentadienyliron carbonyl cations with pentafluorophenyllithium. The reaction of this lithium reagent (prepared from butyllithium and bromopentafluorobenzene in diethyl ether<sup>2</sup> at  $-78^\circ$ ) and a slurry of  $C_5H_5Fe(CO)_2^+[(C_6H_5)_3P]^-I^-$  in tetrahydrofuran was run at  $0^\circ$  for 2 h. After removing solvent the residue was chromatographed on an alumina column, with a single yellow band eluting with benzene. This band was collected and evaporated giving a yellow solid. Crystallization from a benzene-octane mixture gave the yellow crystalline cyclopentadiene-iron compound *exo*- $C_6F_5-C_5H_5Fe(CO)_2^+[(C_6H_5)_3P]^-$ , m.p.  $132.5-134.0^\circ$ , in 59.4% yield; this product was characterized by analysis (Calcd. for  $C_{21}H_{20}FeO_2PF_5$ : C, 61.4; H, 3.33; F, 15.7; P, 5.11; Mol. wt., 666. Found: C, 61.6; H, 3.50; F, 15.4; P, 5.00; mol. wt., 610).

The infrared spectrum of this compound in carbon tetrachloride contained bands characteristic of the pentafluorophenyl group and the triphenylphosphine ligand, and contained also two strong carbonyl stretching frequencies at 1960 and 1925  $cm^{-1}$  (compared to 1978 and 1912  $cm^{-1}$  in a Nujol mull spectrum of  $C_5H_6Fe(CO)_2^+[(C_6H_5)_3P]^-$ ). The presence of a single isomer, the *exo*- form, was clear from this spectrum which showed a C-H stretching frequency at 2940  $cm^{-1}$  characteristic of the *endo*- C-H but which lacked an absorption at  $\sim 2750$   $cm^{-1}$  which would be expected\* for an *exo*- C-H. The proton NMR spectrum of this complex contained broad peaks at 2.70 $\tau$  (multiplet), 5.03 $\tau$ , 5.85 $\tau$ , and 7.40 $\tau$  of relative intensities 15:2:1:2. These resonances are assignable to the protons  $C_6H_5$ ,  $H_A$ ,  $H_{endo}$ ,  $H_B$  respectively (Fig. 1).

When a diethyl ether solution of pentafluorophenyllithium was reacted with a slurry of  $C_5H_5Fe(CO)_3^+PF_6^-$  in tetrahydrofuran at  $0^\circ$  for 2 h a reaction was again

\* There appears some doubt in the literature regarding the geometry of substituted cyclopentadiene complexes of metals. The most definitive work is found in a crystal structure determination<sup>1a</sup> of *exo*-1- $C_6H_5C_5H_2CoC_5H_5$ . The infrared band at 2952  $cm^{-1}$  in this compound could logically be assigned to the *endo*-CH-, contrary to the assignment originally made for this compound<sup>2b</sup>, and contrary to most other assignments made in other substituted cyclopentadiene complexes.

observed to occur. The crude product obtained on evaporation of solvent was chromatographed on alumina using benzene as an eluent. Two yellow bands were observed to elute, and the products obtained from each of these bands were crystallized from a benzene-octane mixture. The first product, obtained in 12.7% yield, was identified as the known compound<sup>4</sup>  $C_5H_5Fe(CO)_2C_6F_5$  by analyses and by its infrared spectrum.

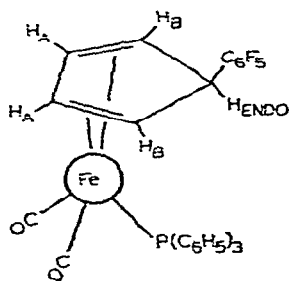


Fig. 1. Endo- $C_6F_5-C_5H_5Fe(CO)_2P(C_6H_5)_3$

The second yellow product, identified as the previously unreported pentafluorobenzoyl derivative  $C_5H_5Fe(CO)_2COC_6F_5$ , m.p. 86–87°, was obtained in 17.6% yield. It was identified by its infrared spectrum and by analyses. (Calcd. for  $C_{14}H_5F_5O_3Fe$ : C, 45.2; H, 1.35; F, 25.5; mol. wt., 372. Found: C, 46.0; H, 1.45; F, 25.4; mol. wt., 374.)

The fact that two products were obtained would suggest that there are two possible routes for this reaction. Pentafluorophenyllithium could displace carbon monoxide as occurred in the reaction of sodium borohydride and this cation, or, alternatively, nucleophilic attack could occur on the carbonyl group to give  $C_5H_5Fe(CO)_2COC_6F_5$ . This latter mode of reaction with cationic carbonyl complexes has been observed in other systems. In the reaction of  $Mn(CO)_5^+[(C_6H_5)_3P]_2^-$  and alkoxide ion<sup>5</sup> the product is found to be  $Mn(CO)_5^+[(C_6H_5)_3P]_2^-COOR$ . Similarly the exchange of oxygen in  $Re(CO)_6^+$  has been suggested to proceed via solvolytic attack on a carbonyl group<sup>6</sup>.

Alternative mechanisms for formation of the two products could involve initial formation of a single product, either  $C_5H_5Fe(CO)_2COC_6F_5$  or  $C_5H_5Fe(CO)_2C_6F_5$ , followed by partial decarbonylation or carbonylation respectively giving the observed mixture of products. We feel the former mechanism can be ruled out since we were able to show that  $C_5H_5Fe(CO)_2COC_6F_5$  does not decarbonylate under conditions of the reaction. The latter possibility (analogous to the formation of  $Mn(CO)_5R$  and  $Mn(CO)_5COR$  from the addition of an alkyl iodide to  $Mn(CO)_5^+$ ) cannot be discounted completely. We do feel that such an explanation is less likely since no fluorocarbon metal carbonyl complexes have yet been carbonylated to the corresponding acyl derivatives<sup>7</sup>, and since in the preparation of  $C_5H_5Fe(CO)_2C_6F_5$  from  $C_5H_5Fe(CO)_2^-$  and hexafluorobenzene<sup>8</sup> no pentafluorobenzoyl species was isolated.

The observed contrast in reactions of  $C_5H_5Fe(CO)_2^+[(C_6H_5)_3P]_2^-$  and  $C_5H_5Fe(CO)_3^+$  with nucleophilic reagents might be due to relative thermodynamic stability of the products. Alternatively the course of the reaction might be determined by mechanistic considerations which could be due either to steric or electronic differences. The steric hindrance presented by the bulky triphenylphosphine ligand to attack at the metal or

at a carbonyl could be the predominate factor here. This seems rather more likely than a postulate of a gross difference in charge distribution in these molecules to explain the position of attack.

*The Department of Chemistry,  
University of Wisconsin, Madison, Wisconsin*

P. M. TREICHEL  
R. L. SHUBKIN

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### Molecular symmetry and crystal structure of dibenzene chromium

There has been considerable discussion concerning the symmetry of the  $\text{Cr}(\text{C}_6\text{H}_6)_2$  molecule in solid dibenzene chromium. A room-temperature X-ray diffraction study by one of the present authors<sup>1,2</sup> indicated a distortion from  $D_{6h}$  molecular symmetry; in the ligand rings carbon-carbon bonds of  $1.436 \pm 0.012$  Å were found to alternate with bonds of  $1.366 \pm 0.012$  Å. Another determination of the crystal structure of dibenzene chromium at room temperature was undertaken by Cotton *et al.*<sup>3</sup> In this investigation no significant deviation from  $D_{6h}$  symmetry was observed; the length of both independent sets of carbon-carbon bonds was given as  $1.387 \pm 0.017$  Å. Cotton's experimental data were also refined and analyzed by Ibers<sup>4</sup>, who found these data to provide no evidence for significant deviations from  $D_{6h}$  symmetry of the dibenzene chromium molecule.

A critical comparison and analysis of Cotton's<sup>3</sup> and Jellinek's<sup>2</sup> data and results was undertaken by Wheatley<sup>5</sup>. His independent refinement of the structure, based on Jellinek's experimental data, confirmed the apparent distortion of the benzene ligands and led to essentially the same interatomic distances and standard deviations as those published previously<sup>2</sup>. Wheatley's results confirmed our view<sup>2</sup> that more and better experimental data were needed to solve the problem. We had, therefore, started a study of the crystal structure of dibenzene chromium at low temperatures, in order to suppress thermal motion which puts a serious limitation on the accuracies with which the atomic positions can be determined at room temperature.

It has been suggested<sup>2</sup> that the discrepancy between Cotton's<sup>3</sup> and Jellinek's<sup>2</sup> experimental data might be caused by orientational disorder in the crystals studied by Cotton *et al.* Since mesitylene is frequently used as a catalyst in the synthesis of