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Preliminary communication

THE ORGANOMETALLIC CHEMISTRY OF PHENALENE

NEUTRAL AND CATIONIC η^2-COMPLEXES OF PHENALENE

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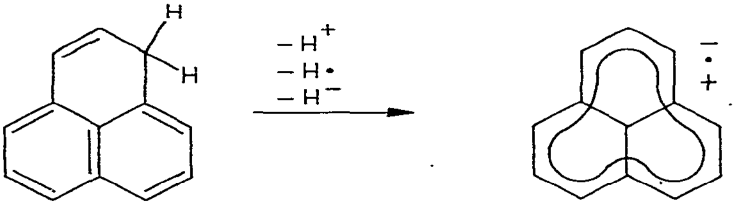
Summary

The first η^2-complexes of phenalene (I) have been prepared and characterized. The most stable of these is (η^2-phenalene)MnCpMe$(CO)_2$ obtained from the photolysis of I and (methylcyclopentadienyl)tricarbonylmanganese(0) in hexane. Two iron complexes were also prepared: (phenalene)tetracarbonyliron(0) and dicarbonyl(η^5-cyclopentadienyl)(η^2-phenalene)iron(II) tetrafluoroborate.

The coordination chemistry of cyclic polyenes has been the focal point of intensive research for nearly three decades. The interest in these ligands is mostly due to their ability to achieve high symmetry and their potential to bond to a large number of metals in a variety of ways. Conspicuously absent from the field of complexed cyclic hydrocarbons is phenalene (I), a unique compound because it can generate an anion, Ia, a radical, Ib, and a cation, Ic, all of which are aromatic, via loss of a proton, hydrogen atom and hydride ion respectively [1]. In spite of this novel property, phenalene has received little attention from organometallic chemists. In fact, other than the report by Maitlis [2] that the ethoxyphenalenium ion forms two isomeric η^3 complexes with platinum, we could find no

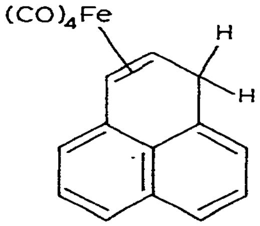


(I) (Ia,Ib,Ic)

other literature on the organometallic chemistry of phenalene or its derivatives*. Although phenalene was first prepared in 1944 [3] (some of its derivatives have been known for a hundred years [4]), it has maintained a low profile in synthetic chemistry because it was difficult to make and is unstable to mild oxidizing agents.

Several years ago we initiated a program to investigate the reactions of I with organometallic reagents. Our need for ready access to this ligand was met when we found that the easily prepared ketone, phenalenone (II) [5] is reduced in high yield to I using diisobutylaluminum hydride or 9-borabicyclononane [6]. In this paper we report the first examples of transition metals complexed to phenalene.

When a pentane solution of I is stirred with an excess of $Fe_2(CO)_9$ under nitrogen for 45 minutes, the unstable complex, η^2-(phenalene)tetracarbonyliron(0) (III) is formed in approximately 11% yield. Filtration to remove $Fe_2(CO)_9$ and evaporation of solvent by bubbling nitrogen through the solution gives yellow crystals containing I and III. Attempts to separate them by column chromatography failed (they have identical R_f's on TLC) as did extensive efforts to purify III by crystallization. High vacuum sublimation at room temperature was tried in an effort to remove I but this resulted in immediate decomposition of III. The complex is stable for several weeks at −78°C but decomposes quickly ($t_{1/2} \approx 1/2$ h) at room temperature, behavior similar to that of η^2-(ethene)tetracarbonyliron(0) [7].



(III)

The structural assignment is based on spectroscopic data obtained on a solution of I and III. The IR spectrum (pentane) shows absorptions at 2072, 2003, 1995 and 1974 cm^{-1}, diagnostic for olefintetracarbonyliron(0) complexes [8]. In the PMR spectrum (toluene-d_8), the coordinated vinyl protons absorb at δ 4.60 (d, J 2.5 Hz) and 3.73 (multiplet overlapped in part by methylene hydrogens in I), 1.80 and 2.03 ppm upfield from the corresponding protons in the uncomplexed phenalene [9]. The magnitude of the upfield shift and the reduction in the coupling constant for the vinyl protons (~1.0 Hz) are similar to those observed for other olefins upon coordination to the $Fe(CO)_4$ group [8,10].

Since a large number of olefins readily form stable cationic complexes with the Fp group (η^5-$C_5H_5Fe(CO)_2$) [11], the coordination of the Fp^+ moiety

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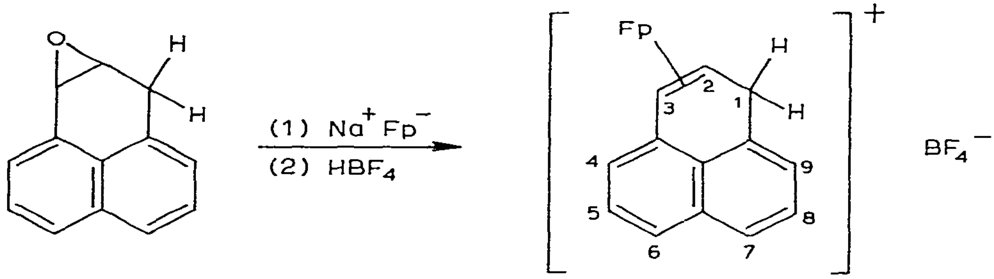
*Recently it was reported that cycloprop[*a*]acenaphthylene rearranges to phenalene in the presence of rhodium dicarbonyl chloride dimer. Deuterium labelling studies strongly suggest the intermediacy of a η^3-phenalenerhodium complex [16].

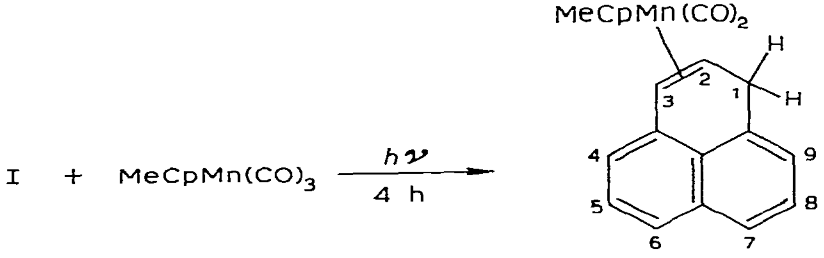
seemed an attractive route to a stable η^2 complex of phenalene. Heating an excess of the olefin with Fp (isobutylene)$^+BF_4^-$ [11], did not give an isolable complex with phenalene. However, an alternate method, utilizing the epoxide of the olefin as an intermediate [12], succeeded.

Phenalene oxide (IV) was prepared by treating I with *m*-chloroperbenzoic acid in $CHCl_3$ at 0°C for three hours*. The crude epoxide (m.p. 72—85°C) was then treated with Na^+Fp^- and HBF_4 [12] to give a 27% yield (based on I) of [dicarbonyl(η^5-cyclopentadienyl)(η^2-phenalene)iron]$^+$[tetrafluoroborate]$^-$ (V). The carbonyl stretching frequencies at 2067 and 2037 (nujol) are in the range for Fp$^+$ (olefin) complexes [13]. The PMR spectrum also is consistent with the proposed structure: (δ in CD_3CN), 7.96—7.30, m, 6H (H^4—H^9); 6.60, d, 1H (H^3); 5.70, m. 1H (H^2); 5.60, s, 5H (η^5-C_5H_5); 4.30, s (H^1). Decomplexation of V with NaI [14] gave phenalene in 52% yield. The complex can be stored indefinitely at −78°C but decomposes at room temperature ($t_{1/2} \approx 2$ h).



(IV) (V)

We were able to obtain a thermally stable complex of phenalene, however, via the photochemical reaction of I with (methylcyclopentadienyl)tricarbonylmanganese(0) (MMT) in hexane.



(VI)

A fifty percent excess of I and MMT dissolved in degassed hexane in a pyrex tube were photolyzed under a sun lamp for 4 h at 20°C. Within one hour yellow crystals of VI precipitated. The crude yield of VI was 13%. Recrystallization from hexane gave 3% of analytically pure VI as yellow crystals, m.p. 92—94°C (dec.). The IR spectrum (hexane) of η^2-(phenalene)dicarbonylcyclopentadienyl-

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*This epoxide is very sensitive to acidic reagents and cannot be dried over $MgSO_4$ like other epoxides [17]. We were able to dry the filtrate, after $NaHSO_3$ and $NaHCO_3$ washings, with $NaSO_4$. IV can be recrystallized from CH_3OH.

manganese(0) (VI) shows characteristic absorptions at 1960 and 1907 cm^{-1} [15] The mass spectrum gives peaks at (m/e): 300 [$(C_{13}H_{10})(CH_3C_5H_4)Mn$]$^+$, 166 [$C_{13}H_{10}$]$^+$, 165 [$C_{13}H_9$]$^+$, 134 [$(CH_3C_5H_4)Mn$]$^+$, 83 [COMn]$^+$, 55 [Mn]$^+$. The PMR spectrum supports the proposed structure for VI: (δ in acetone-d_6); 8.20—6.90, m, 6H (H^4—H^9); 5.30—3.70, m, 1H (H^2), 1H (H^3), 4H (η^5-C_5H_4), 2H (H^1); 1.9, s, 3H. (Found: C, 70.44; H, 4.83. $C_{21}H_{16}MnO_2$ calcd.: C, 70.79; H, 4.78%.)

These observations, coupled with those of Maitlis et al. [2] demonstrate that phenalene is capable of η^2- and η^3-bonding and will form neutral and charged complexes. Work is in progress to expand the coordination chemistry of this interesting ligand and to explore the chemistry of its complexes.

Acknowledgment

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