Organotransition-Metal Complexes of Very Basic Ketones. The Synthesis of Dicarbonylcyclopentadienyliron Complexes of Diphenylcyclopropenone, Tropone, and Phenalenone. The Crystal and Molecular Structure of Dicarbonylcyclopentadienyliron Tropone Tetrafluoroborate

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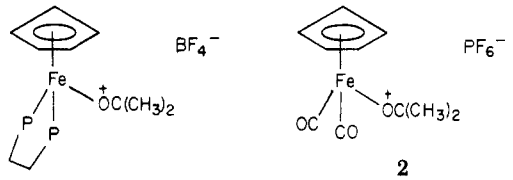
The synthesis and properties of three new ketone complexes of dicarbonylcyclopentadienyliron tetrafluoroborate are described. Diphenylcyclopropenone, tropone, and phenalenone were studied because of their high basicity and potential for extensive delocalization of charge. The structure of the tropone complex ($FeC_{14}H_{11}BF_4$) was determined confirming oxygen to iron σ bonding and that there is no signficant reduction in C–C bond alternation in the tropone ring upon coordination. The complex crystallizes in space group $P2_1/c$ with $Z = 4$ and lattice constants of $a = 7.408$ (4), $b = 16.69$ (1), $c = 12.466$ (9) Å, and $\beta = 92.86$ (4)°.

Introduction

Metal complexes of ketones in the form of simple adducts such as $MgBr_2 \cdot 3(CH_3)_2CO$ and $FeCl_3 \cdot (C_6H_5)_2CO$ have been known for over 70 years, and this class of compounds is highly populated.[1] In all of these cases, the oxygen is presumed to be σ bound to the metal ion.

In the last decade an interest in complexes of the carbonyl function with organotransition-metal groups has developed. In 1971 Silverthorn reported the iron complex **1**, a novel species so labile that the acetone ligand was



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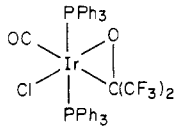
displaced by N_2.[2] Later, Williams and Lalor isolated the more stable $Fp(acetone)^+PF_6^-$ salt (**2**) ($Fp = CpFe(CO)_2$).[3] Recently, Rosenblum and co-workers prepared a variety of $Fp(carbonyl)^+$ complexes that included simple and conjugated ketones, aldehydes, esters, and amides, as part of an effort to enhance the reactivity of the carbonyl group.[4] Shortly after this paper was published, Schmidt and Thiel described the synthesis of similar complexes[5] and we reported the isolation of a Fp^+ complex of diphenylcyclopropenone.[6]

Spectral data indicate that oxygen is σ bound to the iron in these complexes and the crystal structure of one of them, $Fp(3\text{-methylcyclohexenone})^+PF_6^-$ supports that assignment.[4] However, while σ bonding is the dominant type of interaction in all metal carbonyl complexes, side or π bonding has been observed occasionally in complexes such as **3**[7] and **4**[8] in which the ketones are electron deficient.



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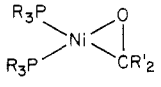
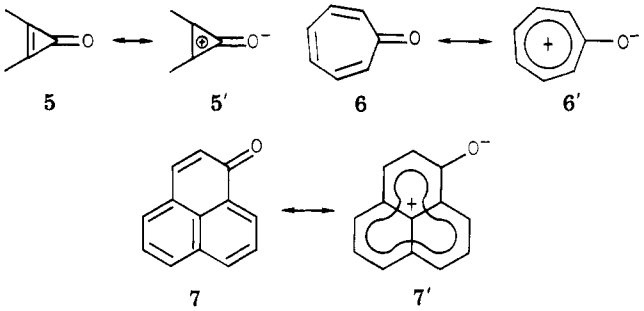


4a, R = C_6H_5, R′ = CF_3
b, R = C_2H_5, R′ = C_6H_5

Apparently the role of the metal is significant, because, in contrast to the side attachment of nickel in **4b**, when the Fp^+ group is used to complex benzophenone the iron is coordinated through the oxygen only.[5]

Before publication of the more recent papers on $Fp(carbonyl)^+$ complexes,[4,5] we had investigated the reactions of diphenylcyclopropenone (DPCPO), **5**, tropone (TROPO), **6**, and phenalenone (PNLNO), **7**, with Fp^+ reagents.



5 5′ 6 6′

7 7′

We envisioned that the highly polar nature of the carbon–oxygen bonds and the resulting increased donor capabilities of the oxygen atoms, due to a significant degree to the contributions of resonance forms **5′**, **6′**, and **7′**, would favor rapid formation of very stable oxygen–iron bonds. Moreover, we wished to examine the effect of coordination of oxygen to iron on the C–C bond lengths in the ketone to see if bond alternation were significantly reduced as a result of charge delocalization in the ring.

Prior to this work no organotransition-metal complexes of **5** and **7** were well characterized although Lewis acid

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Table I. Bond Distances (Å)

Fe-O_1	1.983 (5)	C_4-C_5	1.311 (13)
Fe-C_{13}	1.796 (7)	C_6-O_1	1.238 (8)
Fe-C_{14}	1.796 (7)	C_6-C_7	1.431 (10)
Fe-C_1	2.089 (8)	C_6-C_{12}	1.441 (9)
Fe-C_2	2.096 (8)	C_7-C_8	1.359 (10)
Fe-C_3	2.065 (7)	C_8-C_9	1.400 (13)
Fe-C_4	2.048 (8)	C_9-C_{10}	1.351 (14)
Fe-C_5	2.068 (8)	C_{10}-C_{11}	1.380 (14)
C_1-C_2	1.434 (16)	C_{11}-C_{12}	1.340 (11)
C_1-C_5	1.375 (16)	C_{13}-O_2	1.117 (8)
C_2-C_3	1.412 (15)	C_{14}-O_3	1.135 (9)
C_3-C_4	1.330 (13)		

Table II. Selected Bond Angles (Deg)

O_1FeC_{13}	97.9 (2)	$C_7C_6C_{12}$	122.8 (6)
O_1FeC_{14}	97.3 (3)	$C_6C_7C_8$	129.2 (7)
$C_{13}FeC_{14}$	95.9 (3)	$C_7C_8C_9$	131.4 (8)
FeO_1C_6	136.9 (4)	$C_8C_9C_{10}$	126.7 (8)
$FeC_{13}O_2$	175.8 (7)	$C_9C_{10}C_{11}$	128.7 (7)
$FeC_{14}O_3$	173.8 (7)	$C_{10}C_{11}C_{12}$	130.4 (8)
		$C_{11}C_{12}C_6$	130.7 (8)

adducts of these ketones employing simple metal halides σ bound to the oxygen have been reported.[9,10] Similar adducts of tropone (6) have also been prepared[11] as well as some organotransition complexes in which the metal is π complexed to the ring system as in tropone tricarbonylchromium.[12] Attempts to synthesize organotransition-metal complexes of diphenylcyclopropenone (5), first prompted by suggestions that they may be involved in carbonylation reactions of acetylenes,[13] met with limited success because the reagents either opened the ring or formed species too unstable to permit characterization.[14-17] In this paper we report the synthesis and characterization of organoiron complexes of 5, 6, and 7 including the crystal and molecular structure of one of them, dicarbonylcyclopentadienyliron tropone tetrafluoroborate.

Results and Discussion

Molecular Structure of Fp(TROPO)BF_4. An ORTEP[18] diagram of the Fp(TROPO) cation as it exists in crystals of its BF_4^- salt is given in Figure 1. The structural features most relevant to this study are that the iron atom is σ bound to the tropone oxygen and that the tropone ring shows no significant reduction in bond alternation from that observed in free tropone at −60 °C.[19] Pertinent bond distances and angles are given in Tables I and II.[20]

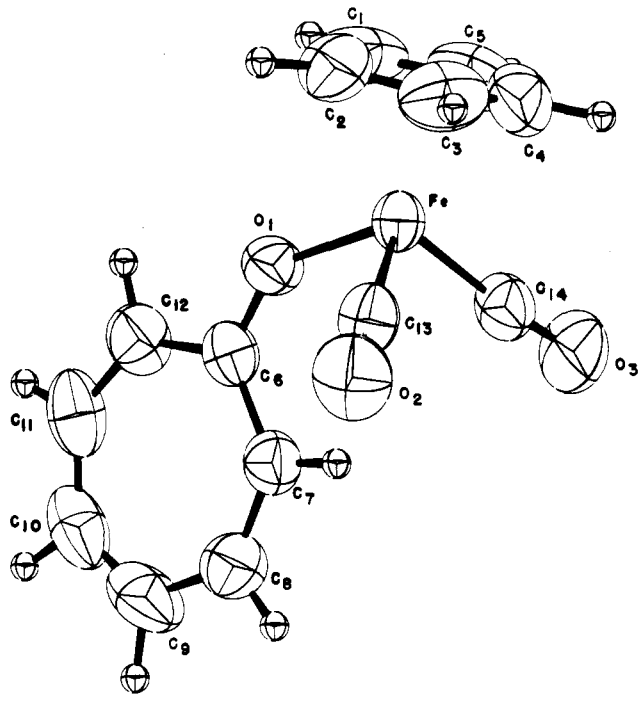

Figure 1. An ORTEP drawing of the $[CpFe(CO)_2C_7H_6O]^+$ cation as it exists in crystals of its BF_4^- salt. Anisotropic ellipsoids are drawn at 50% probability, and the hydrogen atoms have been deliberately reduced in size for clarity.

Bond parameters in the tropone ring display the same trend as that observed in the free tropone at −60 °C.[19] Relatively short C–C distances occur at C_7–C_8, C_9–C_{10}, and C_{11}–C_{12}. Carbon atoms of the tropone ring are planar, with the maximum deviation being 0.014 (10) Å and the average deviation being 0.008 (9) Å. The oxygen atom (O_1), however, is displaced 0.05 Å out of this plane toward the iron atom. The observed ketonic C–O bond length of 1.238 (8) Å is the same as that observed for the π-complexed tropone in tricarbonyl(tropone)chromium of 1.23 Å.[12] The plane of the tropone ligand is rotated slightly, by 1.9°, from the plane defined by Fe, O_1, and C_6. The cyclopentadienyl ligand is approximately perpendicular to this plane, the angle being 89.5°.

The Fe–O_1 distance of 1.983 (5) Å is the same as the corresponding distance in the (3-methylcyclohexenone)Fp cation of 1.980 (6) Å, which is considered a single bond.[4] However, the Fe–O_1–C_6 angle of 136.9 (4) is ~3° larger than in the cyclohexenone complex.[4] The cyclopentadienyl ring is planar, and the average C–C distance is 1.373 (16) Å while the average internal ring angle is 108.0 (9)°. The iron atom is 1.71 Å from the cyclopentadienyl plane, and the average Fe-C_{cp} distance of 2.073 (8) Å is the same as that reported for tricarbonylcyclopentadienyliron hexafluorophosphate.[21]

The shortest nonbonded contacts occur between fluorines and hydrogens. The shortest of these is the $F_1 \cdots H_4^I$ distance of 2.3 Å, where I = 1 − x, 1 − y, and 1 − z. This contact would be 0.10 Å shorter if H_4 were placed at its true internuclear distance from C_4. Unfortunately, the excessive values for the thermal parameters of the fluorines

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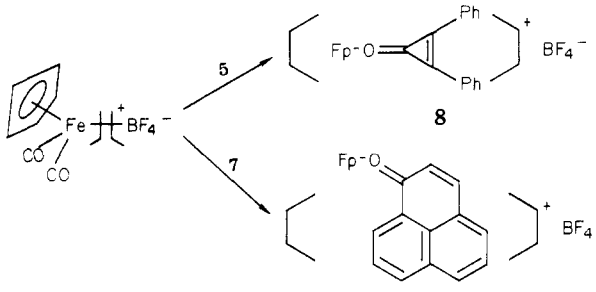
Table III. Comparison of Solvolytic Stabilities of Fp(ketone)$^+$ Complexes with pK_a's of Protonated Ketones

complex	$t_{1/2}$,[a] min	pK_a
Fp(TROPO)$^+$ (**10**)	120	−0.60[23]
Fp(DPCPO)$^+$ (**8**)	45	−3.20[23]
Fp(PNLNO)$^+$ (**9**)	30	−1.40[24]

[a] Rate of displacement measured by NMR at 20 °C in CD_3CN.

precludes any detailed analysis and the calculated contacts are not necessarily a reliable estimate of the average internuclear separations.

Synthesis and Properties. The Fp$^+$ complexes of ketones **5** and **7** were prepared in good yields by treating an excess of the free ketone with Fp(isobutylene)$^+$BF$_4^-$ for 10 min at 65–70 °C in dichloroethane.



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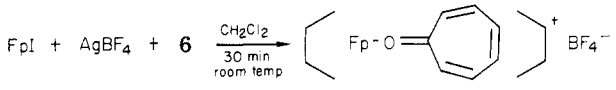
Our attempts to prepare the tropone complex **10** by the



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same reaction failed. However, using the method recently developed by Reger,[22] in which the Fp$^+$ intermediate is generated from FpI and AgBF$_4$ in CH_2Cl_2, we were able to prepare Fp(TROPO)$^+$BF$_4^-$ (**10**) in modest yield (18%).

Complexes **9** and **10** are bright red solids and **8** is orange-red. All are air stable. Fp(DPCPO)BF$_4$ (**8**) and Fp(PNLNO)BF$_4$ (**9**) are microcrystalline materials whereas Fp(TROPO)BF$_4$ (**10**) can be isolated as long needles. Only **10** produced crystals suitable for analysis by X-ray diffraction. Complexes **8**, **9**, and **10** are the most soluble adducts of these ketones. While numerous simple metal halide adducts of **5**,[9] **6**,[11] and **7**,[10] all presumably σ bound to oxygen have been prepared they are characterized by very low solubility. In contrast, **8**, **9**, and **10** dissolve readily in acetonitrile and nitromethane. Dichloromethane will solubilize **8** and **10** but not **9**. None of the three dissolve in solvents such as ether, benzene, or hexane.

Decomplexation of ketone by solvent occurs in each case but the relative stabilities do not parallel the basicities of the free ketones as expected (Table III). Steric factors appear to dominate since the largest ligand, PNLNO, is most readily displaced, and the smallest, TROPO, is most tightly bound. TROPO is also the strongest base but the relative importance of nonbonded interactions was clearly indicated when we tried unsuccessfully to prepare the Fp$^+$ complex of 2-methyltropone. These observations parallel those made on Fp(olefin)$^+$ complexes which exhibit destabilization of the metal–olefin bond with increasing alkyl substitution.[25]

Table IV. Comparison of Carbonyl Stretching Frequencies

ketone, νCO (cm^{-1})	$\Delta\nu$ R$_2$CO-Fp	$\Delta\nu$ R$_2$CO-MX$_n$
tropone, 1583	75[a]	~55[b,11]
diphenylcyclopropenone, 1640	85[a]	~60[c,9]
phenalenone, 1641	151[a]	120-160[b,10]

[a] Spectra obtained in perfluorokerosene mulls. [b] KBr pellets. [c] Nujol mulls. M = Li, Ca, B, Ga, Sn, Ti, Zn, Cd, Cu, Co, Mn, Ni; X = Cl, Br, F.

Table V. Comparison of Ultraviolet Spectra

	λ_{max}, nm (log ϵ), in CH_3CN
DPCPO	227 (4.32), 285 (4.41), 297 (4.46), 310 (sh)
Fp(DPCPO)BF$_4$	226 (4.77), 286 (4.72), 296 (4.73), 312 (sh)
TROPO	224 (4.26), 228 (4.24), 231 (4.21), 303 (3.78), 314 (sh)
Fp(TROPO)BF$_4$	224 (4.53), 228 (4.52), 231 (4.51), 331 (4.03)
PNLNO	313 (3.54), 356 (4.01), 377 (3.94)
Fp(PNLNO)BF$_4$	337 (3.64), 376 (3.73), 445 (3.80)
F$_3$B(PNLNO)[a]	347, 3.93 (4.20), 4.42 (4.04)

[a] Spectrum recorded on ether solution of adduct.[10]

Spectral Properties. Comparison of the infrared spectra of the complexed and free ketones showed the reduction in the carbonyl stretching frequency expected for attachment of the metal to the oxygen. The magnitudes of the $\Delta\nu$(CO)'s parallel closely those observed for simple metal halide adducts of these ketones (Table IV).

The ultraviolet spectra of Fp(TROPO)BF$_4$ and Fp(DPCPO)BF$_4$ resemble those of the free ketones with one exception: the long wavelength absorption at 303 nm in the free tropone is shifted to lower energy ($\Delta\nu$ = 28 nm) upon complexation (Table V). The Fp(PNLNO)BF$_4$ complex shows significant differences in the UV spectrum in that all three absorptions above 300 nm in the free ketone experience a bathochromic shift. These shifts are similar to those reported for gallium trichloride and boron trifluoride adducts of PNLNO.[10] While absorption data above 500 nm were recorded for similar Lewis acid adducts of TROPO[11] and DPCPO,[9] no absorptions in the 300–500-nm region were reported to permit a comparison with our Fp$^+$ complexes.

Experimental Section

X-ray Structure. Red needle shaped crystals of **10** were cut under a microscope and wedged inside 0.30-mm glass capillaries. The crystal used for data collection was a parallellpiped with dimensions of 0.87 × 0.33 × 0.33 mm. A photographic examination followed by an examination of the reciprocal lattice net with the diffractometer indicated the space group was $P2_1/c$ (No. 14).[26] The corresponding lattice constants obtained from the centering of 12 reflections (λ = 0.709 26 Å) were a = 7.408 (4) Å, b = 16.69 (1) Å, c = 12.466 (9) Å, and β = 92.86 (4)°. This unit cell containing four molecules of [(C$_5$H$_5$)(C$_7$H$_6$O)(CO)$_2$Fe]BF$_4$ yields as

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Table VI. Atomic Coordinates[a]

atom	10^4x	10^4y	10^4z
Fe	3517.4 (10)	3826.8 (5)	3274.8 (6)
C_1	3837 (23)	2603 (5)	2986 (7)
C_2	5496 (13)	2932 (6)	3435 (10)
C_3	5041 (12)	3224 (5)	4449 (7)
C_4	3296 (12)	3084 (6)	4569 (7)
C_5	2549 (13)	2721 (6)	3727 (9)
C_6	2895 (8)	4478 (4)	1036 (5)
C_7	2551 (9)	5282 (4)	1365 (5)
C_8	2217 (11)	5944 (5)	751 (7)
C_9	2094 (13)	6048 (6)	-364 (9)
C_{10}	2244 (11)	5474 (7)	-1118 (7)
C_{11}	2588 (11)	4667 (6)	-977 (6)
C_{12}	2871 (12)	4238 (5)	-75 (6)
C_{13}	4901 (8)	4695 (4)	3538 (5)
C_{14}	1420 (9)	4294 (5)	3581 (6)
O_1	3245 (7)	3934 (3)	1691 (3)
O_2	5808 (8)	5211 (4)	3754 (5)
O_3	38 (8)	4521 (5)	3792 (6)
B	863 (11)	6783 (6)	3558 (7)
F_1	2329 (9)	6287 (5)	3527 (6)
F_2	-673 (9)	6385 (4)	3184 (6)
F_3	713 (7)	7035 (4)	4577 (4)
F_4	1098 (9)	7424 (4)	2893 (5)
H_1	1314	2566	3642
H_2	3659	2351	2304
H_3	6638	2947	3121
H_4	5844	3478	4960
H_5	2669	3229	5187
H_7	2558	5366	2119
H_8	2033	6419	1150
H_9	1881	6579	-619
H_{10}	2095	5648	-1842
H_{11}	2630	4367	-1623
H_{12}	3093	3684	-187

[a] Estimated standard deviations are given in parentheses for the least significant digit.

a calculated density of 1.595 g/mL. The experimental density, by flotation, was 1.60 (2) g/mL.

Intensity data were collected as described previously[27] at ambient room temperature (22 ± 2 °C). Background counts were of 10-s duration and the standard reflections remained statistically constant during the collection of $h,k,\pm l$ data to a limiting 2θ of 52.87°. From the entire data set, two reflections (the 104 and 106) appeared as double peaks which were not the result of overlap with a β peak from higher angle data and thus remain unexplained. Both were included in the processed data; however, the 106 had $I < 3\sigma(I)$ and was therefore judged unobserved. Standard deviations were calculated according to

$$\sigma(F) = [C + k^2B + (0.01I)^2/4|F_o|^2Lp^2]^{1/2}$$

where C and B are the counts of the scan and sum of the background, respectively, k is the ratio of scan time to background counting time, and I is the net intensity of the peak. Of the 3183 unique data measured, a total of 2188 with $I < 3\sigma(I)$ were taken as observed. The solution and refinement of the structure were also done as described previously.[27] However, final cycles utilized full matrix[28] refinement and were done as a two-step process, varying all nonhydrogen parameters except for the four fluorines in the first step followed by a cycle varying all nonhydrogen parameters except the oxygens and two carbonyl carbons. Theoretical coordinates for all hydrogen atoms were derived at a distance of 0.95 Å from the respective carbon atoms and thermal parameters were taken as 7 Å^2. All hydrogen parameters were fixed in further refinement which converted with R = 8.2% and R_w = 11.1%. The error of fit was 1.31 and residual electron density from a final difference synthesis ranged from 0.99 e/Å^{-3} in the region of the metal to -0.76 e/Å^3. The resulting atomic coordinates are listed in Table VI.

Syntheses. Fp(isobutylene)$^+BF_4^-$ was prepared by treating Fp(isobutylene) with HBF_4.[29] We found that it was essential to remove excess HBF_4 for successful isolation of the intermediate. FpI[30] was purified according to Reger's procedure.[22] $AgBF_4$ was obtained from Ozark-Mahoning and used only in a dry glovebag filled with nitrogen. Methylene chloride and 1,2-dichloroethane were refluxed over P_2O_5 and distilled immediately before use. PMR spectra were recorded on a Varian EM 390 spectrometer using Me_4Si as an internal standard. IR spectra were recorded on a Perkin-Elmer 137 spectrophotometer, and UV data were obtained from a Beckman DK-2A spectrophotometer.

Dicarbonylcyclopentadienyliron Tropone Tetrafluoroborate (10). A 100-mL Schlenk flask that had been oven dried and purged with nitrogen was charged with FpI (0.82 g, 2.69 mmol), $AgBF_4$ (0.57 g, 2.92 mmol), and CH_2Cl_2 (50 mL) and stirred for 30 min at room temperature. The reaction mixture was then filtered under nitrogen using a Schlenck filter funnel and filter aid (Celite) into a three-neck 100-mL round-bottomed flask. To this solution was added tropone[31] (0.85 g, 8.02 mmol), and the resulting solution was stirred for 15 min. Filtration, followed by the addition of 400 mL of dry ether to the filtrate, gave a turbid mixture. Storage at 5 °C for 3 days produced 0.17 g of bright red crystals which were isolated by filtration. The filtrate contained a brown oily layer that also gave red crystals when mixed with CH_2Cl_2 and ether and chilled to 5 °C. The following procedure, repeated twice, gave analytically pure **10**. The red crystals were dissolved in a minimum of CH_2Cl_2 and filtered in a pipette containing a small piece of microwipe. Enough ether was added to the filtrate to make it turbid. Cooling to 5 °C overnight gave crystalline product. Application of this procedure to the brown oil also gave analytically pure **10**. From these steps 0.18 g (0.49 mmol, 18% yield) was obtained: ^{1}H NMR (CD_3CN, 0 °C) δ 7.95–6.70 (m, 6 H), 5.40 (s, 5 H); IR ν(C≡O) (CH_3CN solution) 2061, 2016 cm^{-1}, (C=O) (perfluorokerosene mull) 1508 cm^{-1}. Anal. Calcd for $FeC_{14}H_{11}BF_4$: Fe, 15.14; C, 45.41; H, 2.97. Found: Fe, 14.97; C, 45.38; H, 3.08.

Dicarbonylcyclopentadienyliron Phenalenone Tetrafluoroborate (9). Fp(isobutylene)BF_4 (1.00 g, 3.13 mmol) and phenalenone[32] (1.00 g, 5.55 mmol) in 40 mL of 1,2-dichloroethane were stirred at ~65 °C for 10 min. After being cooled to room temperature, the reaction mixture was filtered and ether was added to the filtrate which precipitated a red solid. The solid was collected and washed with benzene until the washings were colorless, leaving 0.9 g (65% yield) of crude product. The following procedure was repeated three times to obtain analytically pure **9**. The red solid (0.2 g) was dissolved in 5 mL of CH_3CN at 0 °C under nitrogen and filtered through a pipette containing a small piece of microwipe. Ether was then added to precipitate the product: ^{1}H NMR (CD_3CN, 0 °C) δ 8.68–7.88 (m, 7 H), 7.00 (d, 1 H), 5.51 (s, 5 H); IR ν(C≡O) (CH_3CN solution) 2061, 2016 cm^{-1}, ν(C=O) (perfluorokerosene mull) 1490 cm^{-1}. Anal. Calcd for $FeC_{20}H_{13}O_3BF_4$: Fe, 12.42; C, 54.05; H, 2.93. Found: Fe, 12.42; C, 54.06; H, 3.00.

Dicarbonylcyclopentadienyliron Diphenylcyclopropenone Tetrafluoroborate (8). The procedure described above was followed by using 0.5 g (1.56 mmol) of Fp(isobutylene)BF_4 and 0.96 g (4.68 mmol) of diphenylcyclopropenone[33] and 20 mL of dichloroethane producing 0.39 g (0.83 mmol, 53% yield) of crude **10**. Analytically pure sample was obtained by recrystallizing 3 times from CH_2Cl_2–ether at room temperature: ^{1}H NMR (CD_3CN, 0 °C) δ 8.37–8.03 (m, 4 H), 8.03–7.63 (m, 6 H); 5.50 (s, 5 H); IR (perfluorokerosene mull) ν(C≡O) 2053, 2004, ν(C=O) 1555 cm^{-1}. Anal. Calcd for $FeC_{22}H_{15}O_3BF_4$: Fe, 11.91; C, 56.17; H, 3.19. Found: Fe, 12.02; C, 55.96; H, 3.32.

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Supplementary Material Available: A listing of the anisotropic thermal parameters and structure factor amplitudes (12 pages). Ordering information is given on any current masthead page.

Kinetics of the Protodestannylation of Vinyltrialkyltins and Substituted Vinyltrialkyltins

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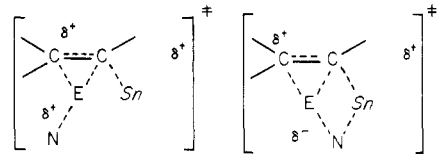
Results of a kinetic study of the protodestannylation of a number of vinyltrialkyltins and substituted vinyltrialkyltins by hydrogen chloride in methanol–water are reported. The relative rate constants are consistent with a steric sequence and open transition state. Substitution of a methyl group or phenyl group on the β-carbon leads to rate enhancement but in lesser magnitude than in the iodostannylation reaction. The effect of the concentration of water in methanol has been studied. Triphenylvinyltin underwent reaction with 2,4-dinitrobenzenesulfenyl chloride with the result that a tin–phenyl bond was cleaved.

Introduction

Electrophilic substitution involving cleavage of a carbon–metal bond has been studied in a number of systems. The favorite metal leaving groups have been those of group 4 and mercury while the carbon substrates have included alkyl, aryl, allyl, allenyl, and vinyl. Electrophilic agents have been bromine, iodine, mercuric halides, and the proton.[1] The order of substrate reactivity when the metal is tin has been shown to be allyl > allenyl > phenyl > vinyl > alkyl.[2,3]

Mechanistically the reaction can be described as S_E2 (S_E2' when the substrate is allyl[2] or a combination when the substrate is allenyl[3]), and the major point of discussion is the structure of the transition state. Since each electrophile carries with it one or more atoms with unshared pairs of electrons, the possibility exists for these atoms to provide nucleophilic assistance to the departing metal. Concomitant is the question of where the transition state lies on the reaction coordinate. An early transition state would presumably not involve significant nucleophilic assistance since not much charge is localized on the metal while a later transition state could involve nucleophilic assistance provided either by the attacking agent or by the solvent. Baekelmans et al.[4] and Abraham et al.[5] have described the two limiting cases as an open transition state (I) and a closed transition state (II).[6] It should be noted that the open transition state (I) does not preclude nucleophilic assistance from an appropriate solvent.[2]



I II

In vinylmetallic, allylmetallic, and allenylmetallic systems, the situation is more complicated in that the electrophile probably attacks the π electrons of the double bond. This suggests that the β-carbon of the vinylmetallic system will develop some positive charge in the transition state as the bond to the α-carbon is being formed.[6] Thus the electrophile may be coordinated to both carbons of the vinyl group. In studies of this system, Nesmeyanov et al.[7] and Beletskaya and Reutov[8] favor closed three-center and four-center transition states to account for retention of configuration in halo- and protodemercuration of vinylmercurials in dioxane, methanol, and DMF. Baekelmans et al.[4] suggests an open transition state for iododemetalation of a series of vinyltin compounds in methanol. Their conclusion was based primarily on a large positive salt effect. Also Gupta and Majee[9] report quantum mechanical calculations by the Del Re method which

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