acids than NH_4^+ or methanol, which rapidly protonate the iron(0) phosphite complex.[11,14] It is not unreasonable that the complex, $Fe(DPPE)_2C_2H_4$, would be as basic as the phosphite complex and thus reaction 1 may very well proceed through an initial protonation.

Experimental Section

All solvents were dried and degassed by standard methods. The aluminum alkyl preparation was carried out using Schlenk techniques under nitrogen or argon; all other operations were carried out in a nitrogen-filled Vacuum Atmospheres drybox. Magnetic moments were measured in acetone at +40 °C by the Evans technique[15] at 60 MHz using solutions which were approximately 0.01 M.

Preparation of $Fe(DPPE)(acac)_2$ (I). Method I. A round-bottom flask equipped with a mechanical stirrer is charged with $Fe(acac)_3$ (21.2 g, 60 mmol), DPPE (23.8 g, 60 mmol), and ether (400 ml). The suspension is maintained around −5 °C under an inert atmosphere as a solution of triethylaluminum (54.7 ml 400 mmol) in ether (70 ml) is added dropwise over 30 min. The red suspension turns golden orange, and stirring is continued an additional 15 min. The mixture is transferred to a drybox, and the product is collected by vacuum filtration. The gold powder is washed with ether and then is taken up in a minimum of THF, filtered, and precipitated by very slow addition of ether. The golden yellow, highly crystalline product is collected by vacuum filtration; yield 29.4 g, 75%.

Method II. A toluene solution of $Fe(DPPE)_2C_2H_4$ (2.64 g, 3.0 mmol) and 2,4-pentanedione (0.30 g, 3.0 mmol) is brought to reflux. Just at reflux, the solution lightens from dark red to yellow. Cooling and addition of ether result in formation of long fibrous needles of $Fe(DPPE)(acac)_2$ which are collected by vacuum filtration. The filtrate contains a mixture of $Fe(DPPE)_2H_2$ and DPPE: yield 0.83 g, 85% of theory; $\mu_{EFF} = 5.10$; mp 193–194 °C; IR ν_{acac} 1575, 1531, 1517 cm^{-1}. Anal. Calcd for $FeP_2O_4C_{36}H_{38}$: P, 9.5; O, 9.8; C, 66.3; H, 5.87. Found: P, 9.7; O, 9.6; C, 65.9; H, 5.83.

Preparation of $Fe(DPPE)(DBM)_2$ (II). This compound is prepared by method II above, reacting $Fe(DPPE)_2C_2H_4$ and dibenzoylmethane in refluxing toluene. The solution darkens from red to purple. Cooling and standing result in a brownish-purple product which gives purple crystals when recrystallized from toluene–ether: yield 0.88 g, 65% of theory; mp 187–189 °C; IR ν_{DBM} 1600, 1572, 1538, 1522 cm^{-1}; $\mu_{EFF} = 5.08$. Anal. Calcd for $FeP_2O_4C_{56}H_{46}$: P, 6.9; O, 7.1; C, 74.7; H, 5.15. Found: P, 6.3; O, 7.2; C, 73.5; H, 5.32.

Preparation of $Fe(DPPE)(acacF_6)_2$ (III). Hexafluoro-2,4-pentanedione is reacted with $Fe(DPPE)_2C_2H_4$ in toluene to give an immediate color change without heating as is necessary in the above preparations. Addition of pentane precipitates $Fe(DPPE)H_2$ and DPPE. The solution is then reduced in volume and cooled, resulting in a deep red crystalline product, identified as $Fe(DPPE)(acacF_6)_2$: yield 1.04 g, 80% of theory; mp 119 °C; ν_{acacF_6} 1038, 1597, 1551, 1523 cm^{-1}; $\mu_{EFF} = 5.01$. Anal. Calcd for $FeP_2C_{36}H_{26}O_4F_{12}$: Fe, 6.4; F, 26.3; C, 49.8; H, 3.02. Found: Fe, 6.2; F, 27.9; C, 49.9; H, 3.17.

Preparation of $\{Fe[P(OMe)_3]_5H\}\{acacF_6\}$. A solution of $Fe[P(OMe)_3]_5$ in THF is reacted with a slight excess of hexafluoro-2,4-pentanedione at room temperature. The solution is stripped to an oil and washed with pentane. Addition of ether results in a dark red purple solution from which yellow crystals are precipitated by addition of hexane, followed by reduction in volume under vacuum. The yellow material is unstable and must be stored at low temperature and free of solvent or it will turn violet; the material decomposes above room temperature. Analysis was carried out within an hour of the preparation but the operation, necessarily carried out at room temperature, caused noticeable decomposition before completion. Anal. Calcd for $FeP_5O_{17}C_{20}H_{47}F_6$: P, 17.5; C, 27.2; H, 5.35; F, 12.9. Found: P, 19.4; C, 26.7; H, 5.28; F, 14.0.

Registry No. I, 61827-21-2; II, 61827-22-3; III, 61827-23-4; $\{Fe[P(OMe)_3]_5H\}\{acacF_6\}$, 61827-24-5; $Fe(acac)_3$, 14024-18-1; $Fe(DPPE)_2C_2H_4$, 36222-39-6; $Fe[P(OMe)_3]_5$, 26673-06-3.

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Contribution from the Departments of Chemistry,
University of Cincinnati, Cincinnati, Ohio 45221,
and Case Western Reserve University, Cleveland, Ohio 44106

Gas-Phase Formation of Ionic Sandwich Complexes of Iron

Philip H. Hemberger[1a] and Robert C. Dunbar*[1b]

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Recent gas-phase studies of the ion–molecule reactions of ferrocene and related compounds have reported the formation of "triple-decker" cationic complexes,[2,3] charge-transfer reactions,[3] the proton affinity of ferrocene,[3] and the binding energies of 30 n-donor ligands to the cyclopentadienyl nickel cation.[4] This report describes the observation of a facile and apparently general route to the gas-phase production of ligand-exchange derivatives of ferrocene of the form $(\eta^5\text{-}C_5H_5)(arene)Fe^+$, via direct association of the aromatic ligand with the cyclopentadienyliron cation, $(\eta^5\text{-}C_5H_5)Fe^+$. These complexes have been previously synthesized in solution under Friedel-Crafts conditions.[5] Neutral heterocyclic iron sandwich compounds are also known.[6]

Experimental Section

The experiments were performed with a standard Varian Associates ICR-9 ion cyclotron resonance (ICR) spectrometer operated in the normal drift mode[7] at an ionizing energy of 20 eV. Ferrocene and the aromatic compounds were used as supplied. No indication of impurities was found in the ICR single resonance mass spectra. All liquids were thoroughly degassed by several freeze–pump–thaw cycles. Typical operating pressures were in the 10^{-6} Torr range as measured directly from the Vac Ion pump current. Pressures monitored with a Bayard-Alpert gauge were generally an order of magnitude greater. In each experiment the partial pressures of ferrocene and the aromatic compound were maintained at a 1:1 ratio.

Only two ions were observed in the single resonance mass spectrum of ferrocene at 20 eV: $Fe(C_5H_5)_2^+$ (100) and $Fe(C_5H_5)^+$ (10).[8] Appearance potentials and relative abundances agree with other mass spectroscopic results.[9]

Results and Discussion

In mixtures of ferrocene and an arene, products with *m*/*e* values corresponding to the formula $FeC_5H_5Ar^+$ were observed where Ar = C_6H_6, $C_6H_5CH_3$, $C_6H_5NO_2$, $C_{10}H_8$, $C_6H_5OCH_3$, and C_5H_5N. Ion cyclotron double resonance,[10] supported by appearance potential measurements, shows that the reaction proceeds as:

$$FeC_5H_5^+ + Ar \rightarrow FeC_5H_5Ar^+ \tag{1}$$

These reactions provide additional illustrations of the apparently ready formation of ion–molecule products in organometallic systems at low pressure by direct association and stabilization without neutral product formation,[11] in contrast to the well known low probability of such processes in hydrocarbon and related ion–molecule systems. The mechanism of stabilization of the association complex is presumably collisional rather than radiative, since the rate of ion–neutral collision at the pressures used is of the order of 100 s^{-1}, while the radiative deexcitation rate is probably[12] of the order of 1 s^{-1} or less. The long lifetime of such complex association ions is an interesting phenomenon worthy of further exploration, but beyond noting that the amount of stabilized product ion increased with increasing pressure, no quantitative characterization of this system was attempted.

Experiments performed with C_6H_5Cl gave rise to a product with *m/e* 198 corresponding to $Fe(C_5H_5)(C_6H_5)^{+}\cdot$. Double resonance experiments indicated the reaction:

$$FeC_5H_5^+ + C_6H_5Cl \rightarrow Fe(C_5H_5)(C_6H_5)^{+}\cdot + Cl\cdot \qquad (2)$$

A reaction analogous to (2) was found in solution under Friedel-Crafts conditions using C_6H_5Br, whereas the reaction of ferrocene with C_6H_5Cl under identical solution conditions produced $Fe(C_5H_5)(C_6H_5Cl)^+$ and $Fe(C_5H_5)(C_6H_5C_6H_5)^+$.[5a] The solution results were presumed to occur through dehalogenation after ligand exchange in the π complex.

ICR data do not yield structural information. However, a sandwich structure obeying the 18-electron rule can be drawn for each complex assuming, in the naphthalene case, that six of the ten π electrons are delocalized into the metal; these complexes are formally isoelectronic with ferrocene. In view of the method of formation of these species, and the close formal analogy with ferrocene, it seems entirely reasonable to assume a $(\eta^5\text{-}C_5H_5)(\eta^6\text{-Ar})Fe^+$ sandwich structure.

The pyridinecyclopentadienyliron cation need not necessarily have the π-bonded sandwich structure since the high basicity of the lone pair electrons of the nitrogen atom may result in σ bonding to the iron atom. Experiments performed with a mixture of ferrocene and CH_3NH_2 showed a product with *m/e* 152 corresponding to $Fe(C_5H_5)NH_2CH_3^+$ at pressures approaching 1×10^{-4} Torr. The very low intensity of this ion inhibited meaningful double resonance experiments. It may be inferred from the greater ease of formation of the pyridine complex compared to the methyl amine complex that the pyridinecyclopentadienyl complex is likely to exist as a π-bonded system.

Most of the species described here, while novel as gas-phase ions, are known species in solution. However, there has been a conspicuous failure to prepare arenecyclopentadienyliron complexes in which strongly electron withdrawing substituents such as NO_2 are attached to the arene. In view of the fact that the $Fe(C_5H_5)(C_6H_5NO_2)^+$ ion has been found in this investigation there appears to be no inherent reason why a suitably designed solution attack should not succeed.

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Registry No. $FeC_5H_5C_6H_6^+$, 51364-24-0; $FeC_5H_5C_6H_5CH_3^+$, 32760-28-4; $FeC_5H_5C_6H_5NO_2^+$, 61827-25-6; $FeC_5H_5C_{10}H_8^+$, 46466-61-9; $FeC_5H_5C_6H_5OCH_3^+$, 32758-64-8; $FeC_5H_5C_5H_5N^+$, 61827-26-7; $FeC_5H_5^+$, 61827-27-8.

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Contribution from the Department of Chemistry,
Faculty of Science, Shizuoka University,
Oya, Shizuoka 422, Japan

Diastereoisomers of Bis(1,10-phenanthroline) and Bis(2,2′-bipyridine)chromium(III) Complexes Containing L-(+)-Tartrate Ion

Akira Tatehata

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Circular dichroism (CD) spectra of cobalt(III) complexes containing optically active chelate ligands have been studied extensively. However, there have been few studies on the analogous chromium(III) complexes containing optically active chelate ligands. Information regarding the spectroscopic properties of chromium(III) complexes in the chiral environment can be useful for comparison of the two systems. We have previously reported on separation and characterization of the configurationally optically active isomers of $[Co(tart)(phen\ or\ bpy)_2]^+$, where tart is the dianion of L-(+)- or D-(−)-tartaric acid, and phen and bpy are 1,10-phenanthroline and 2,2′-bipyridine, respectively.[1,2] It has been shown that use of an SP-Sephadex column is effective for the separation of the diastereoisomers of this type and that the interactions between SP-Sephadex and the tartrate side in the complexes distinguishes one diastereoisomer from the other in the elution process. An extension of this investigation to chromium(III) complexes has been carried out. We present here the absorption (AB) and the CD spectra and the optical rotatory dispersion (ORD) curves of L-tartratobis(phen or bpy)-chromium(III) complexes having the coordination chromphore CrO_2N_4, which is identical to that for oxalatobis(phen or bpy)chromium(III) complexes.[3,4] The AB and CD spectra of these tartrato complexes are discussed in comparison with those of the corresponding oxalato complexes.

Experimental Section

Preparation and Separation. (1) Δ- and Λ-[Cr(L-tart)(phen)$_2$]ClO$_4$. To 1.0 g (1.8 mmol) of $[CrCl_2(phen)_2]Cl\cdot 2H_2O$[5] dissolved in 30 ml of water, 0.46 g (2.0 mmol) of sodium L-tartrate dihydrate (Na_2(L-tart)$\cdot 2H_2O$) was added. The mixture was heated on a boiling water bath for 2 h. The reaction mixture was evaporated almost to dryness in a rotary evaporator under reduced pressure. Thirty milliliters of ethanol–ether (1:1) mixture was added, and then the reaction product was filtered off. About 0.5 g of the reaction product dissolved in 5 ml of 0.2 M $Na_2[Sb_2(\text{L-tart})_2]$ aqueous solution as the eluent was filtered in order to remove the unreacted $[CrCl_2(phen)_2]Cl\cdot 2H_2O$, and the filtrate was subjected to column (2.7 × 50 cm) chromatography on SP-Sephadex C-25, with 0.2 M $Na_2[Sb_2(\text{L-tart})_2]$. The first band and the second one (in the order of elution) were separately collected, and their effluent was concentrated in a rotary evaporator under reduced pressure at room temperature. After filtering off the precipitate of the eluting agent by adding ethanol, the filtrate was