nonvolatile reagent and a volatile fluorinating agent which form a volatile and nonvolatile product, CrO_2F_2 and $MoOF_4$ or WOF_4, respectively, purification is greatly simplified. In addition, this provides a straightforward route to the oxide tetrafluorides of molybdenum and tungsten, which can be obtained pure via sublimation. The heating of a sample of CrO_3 mixed with WOF_4 to 120 °C leads to formation of chromyl fluoride. This accounts for a yield greater than 100% based on the reaction producing 1 mol of CrO_2F_2 per mol of WF_6.

In line with the reported relative reactivities of the two hexafluorides,[26] MoF_6 produced chromyl fluoride more readily than did WF_6.

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Registry No. CrO_2F_2, 7788-96-7; CrO_3, 1333-82-0; ClF, 7790-89-8; COF_2, 353-50-4; MoF_6, 7783-77-9; $MoOF_4$, 14459-59-7; WF_6, 7783-82-6; WOF_4, 13520-79-1.

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Contribution No. 2396 from the Central Research and Development Department, Experimental Station, E. I. du Pont de Nemours and Company, Wilmington, Delaware 19898

β-Diketonate Complexes of Iron(II)

S. D. Ittel

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The preparation of transition metal β-diketonate complexes has typically been accomplished by direct reaction of the β-diketones with metal salts in the presence of base or by other similar reactions. In addition to these reactions which do not involve any change in the oxidation state of the metal,[1] there are examples of preparations where a derivative of a metal in a lower oxidation state has been prepared by reduction from a higher oxidation state by the diketone.[2] The reaction of 2,4-pentanedione with $Mo(C_2H_4)(DPPE)_2$ [DPPE = bis-1,2-(diphenylphosphino)ethane)] represents the first oxidative addition of a β-diketone to a transition metal.[3] The resultant 7-coordinate Mo(II) is the only reported hydrido complex containing both β-diketonate and tertiary phosphorus ligands. The more common, analogous alkyl complexes are known for iron,[4] cobalt,[5] nickel,[6,7] and platinum.[8] The molybdenum complex is also isolated from the aluminum alkyl reduction of $Mo^{III}(acac)_3$ (acac = 2,4-pentanedionato). The alkyl complexes of the other metals are typically isolated as intermediates or impurities in similar reductions.

The treatment of $Fe(acac)_3$ with $AlEt_3$ or $AlEt_2(OEt)$ in the presence of DPPE at 0 °C, in ether under an inert atmosphere, has been shown[9] to afford $Fe(DPPE)_2(C_2H_4)$. We have found that if the reaction is carried out at −78 °C and then allowed to warm to room temperature, the primary product isolated is $Fe(DPPE)_2H_2$. It has been reported[10] that when the reduction is carried out using AlR_3 where R is larger than ethyl, the only product isolated is the dihydride, presumably as a result of thermal decomposition of an unstable iron dialkyl. It may be assumed that the product of the low-temperature reduction is $Fe(DPPE)_2Et_2$, which decomposes upon warming to yield the dihydride and ethylene.

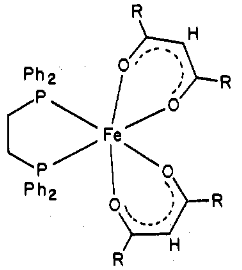
If the reduction is carried out at 0 °C with less aluminum alkyl, it is possible to isolate the paramagnetic compound $Fe^{II}(DPPE)(acac)_2$ (I). This is not a by-product as in the Mo reaction but is an intermediate and may be further reduced by addition of more aluminum alkyl.

The same product is isolated from the reaction of the β-diketone with Fe^0 in refluxing toluene according to the reaction

$$2Fe(DPPE)_2C_2H_4 + 2Hacac \rightarrow Fe(DPPE)(acac)_2 + Fe(DPPE)_2H_2 + DPPE + 2C_2H_4 \qquad (1)$$

This reaction, formally a disproportionation, affords an alternative to the 7-coordination observed in the molybdenum system; both iron(II) species are 6-coordinate, 18-electron systems, and both the diketonate and the hydride are coordinated. The golden diketonate complex is easily separated from the reaction mixture and recrystallized from tetrahydrofuran.

The oxidative addition reaction can be repeated with other β-diketones to produce complexes of the type



	Diketonate abbreviation
I, R = Me	acac
II, R = Ph	DBM
III, R = CF_3	$acacF_6$

Some idea as to the mechanism of reaction 1 can be obtained from the reaction of β-diketones with Fe^0 phosphite complexes.[11-13] When hexafluoro-2,4-pentanedione is reacted with FeL_5 where L = $P(OMe)_3$, an initial yellow product of the stoichiometry $[FeL_5H]^+[C_5F_6O_2H]^-$ can be isolated; the characteristic ^{31}P NMR spectrum of this material is identical with that of an authentic sample of FeL_5H^+.[11,14] This unstable compound reacts further to produce a red uncharacterized complex having coordinated β-diketonate. The initial hydride formation is to be expected because β-diketones are stronger 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 $(\eta^5\text{-}C_5H_5)(\text{arene})Fe^+$, 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:

$$FeC_5H_5^+ + Ar \rightarrow FeC_5H_5Ar^+ \quad (1)$$

These reactions provide additional illustrations of the ap-