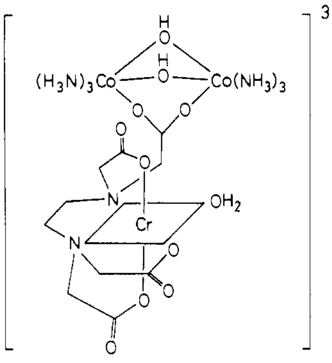
factors may be canceled out by the positively charged $Co(NH_3)_5^{3+}$ moiety for the uninegative entering ligand to approach. Also, incorporation of OAc^-, N_3^-, and NCS^- is thermodynamically not unfavorable compared to the case of EDTA and HEDTRA complexes.

Recently complex **3** was prepared, and the slow ligand substitution reactions with OAc^- and NCS^- were demonstrated.[12]



3

Comparing this result with the reactivity of **2**, we conclude that a carboxylate or a carbonyl oxygen atom in the pendant group must remain free for the labilization of the chromium(III) center.

The $[H^+]$ dependence of the rate of the reaction of **2** with OAc^- can be compared with that of the reaction of the Cr(III)–EDTA complex with OAc^-. In the case of **2**, reactions are clearly formulated as eq 3 and 4, and there is no so-called proton ambiguity encountered in the reaction of the Cr(III)–EDTA complex.[1,4] k'_{an} is of the same order of magnitude as k_{an}, and this trend is the same as for the Cr(III)–EDTA reaction.

In conclusion, the reactions of **2** have shown that the contribution of the steric factor of the pendant group is surprisingly small and the nucleophilic assistance of the ligand substitution by the pendant group is more important.

Registry No. $[(NH_3)_5Co\{(edta)Cr(H_2O)\}]^{2+}$, 61813-16-9; OAc^-, 71-50-1; N_3^-, 14343-69-2; NCS^-, 302-04-5.

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Reactions of Coordinated Molecules. 45. Identification of Another Isomer of (Ferra β-diketonato)difluoroboron Complexes

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During our study of the chemistry of metalla β-diketones and their corresponding enolate anions, we isolated a class of neutral (metalla β-diketonato)B(X)(Y) complexes in which the metalla β-diketonate anion coordinates as a bidentate, chelating ligand to the boron atom.[2-4] Solution infrared spectral data of the (ferra β-diketonato)difluoroboron complexes, $[(\eta\text{-}C_5H_5)(OC)Fe(\overline{RCO})(\underline{R'CO})]BF_2$, indicated the presence of two isomers in solution.[4] One isomer exhibits a carbonyl stretching band in the range 1960–1975 cm^{-1}, while the other isomer shows a carbonyl stretching band in the region 2000–2020 cm^{-1}. The relative amounts of these isomers (which undergo interconversion) are affected by changes in solvent polarity.

A structural determination of a (ferra β-diketonato)BF_2 complex in which R = Me and R′ = *i*-Pr revealed a boat-shaped conformation for the ferra chelate ring.[5] The carbonyl ligand now occupies the axial position at the Fe atom in greatest proximity to the axial fluorine substituent at the boron atom. The C_5H_5 ligand occupies an equatorial site at the Fe atom. For this isomer, the carbonyl C–O stretching frequency is observed at 2005 cm^{-1} in KBr. The structure of the second isomer (which has the lower C–O stretching frequency) was assumed to be the alternate boat isomer having an axial C_5H_5 substituent at the Fe atom, although the possibility of a chair conformation for this isomer could not be excluded.

We now report the preparation and structural characterization of the complex $[(\eta\text{-}C_5H_5)(OC)Fe(Me_3C\overline{CO})_2]BF_2$. This complex has a single C–O stretching band in solution at 1962 cm^{-1} and in the solid state (KBr) at 1956 cm^{-1}. The molecular structure reveals a boat-shaped conformation for the ferra chelate ring in which the C_5H_5 ligand now occupies the axial position. This observation unambiguously establishes the identity of the second geometrical isomer of this class of compound. The two boat isomers apparently interconvert by a "flipping" of the Fe and B atoms through an excited state having a planar six-membered ring. Structural characterization of the solution and solid-state conformations of (ferra β-diketonato)BF_2 complexes is relevant to a more complete understanding of the interligand C–C coupling reactions and Diels–Alder cycloaddition chemistry of these molecules.[6-10]

Experimental Section

All preparative chemistry was performed with standard inert-atmosphere techniques and solvent preparation as specified elsewhere.[4] Infrared and ^1H NMR spectra were obtained also as reported earlier.[4] Microanalysis was performed either by Galbraith Laboratories or by MicAnal Ltd.

Preparation of $(\eta\text{-}C_5H_5)(OC)_2FeC(O)CMe_3$ (1). Complex **1** was prepared according to a procedure similar to that used to prepare $(\eta\text{-}C_5H_5)(OC)_2FeC(O)CHMe_2$[11] and was isolated as amber crystals (61%): mp 70.5–71.5 °C; IR (C_6H_{12}) ν(CO) 2005 (s), 1960 (s) cm^{-1}; ^1H NMR $(CDCl_3)$ δ 1.08 (s, 9, Me_3C), 4.90 (s, 5, C_5H_5). Anal. Calcd for $C_{12}H_{14}FeO_3$: C, 55.00; H, 5.38. Found: C, 55.01; H, 5.49.

Preparation of $[(\eta\text{-}C_5H_5)(OC)Fe(Me_3C\overline{CO})_2]BF_2$ (2). To a stirred amber solution of 4.20 g (11.35 mmol) of **1** in 170 mL of ether at −78 °C was added dropwise 8.36 mL of a 1.9 M solution of *tert*-butyllithium over a 5-min period. The reaction solution was warmed to ca. −20 °C over a 30-min period, during which time the color changed to orange-brown. The solvent was removed at reduced pressure. The residue was dissolved in 150 mL of CH_2Cl_2, and then this solution was cooled to −78 °C. Boron trifluoride gas was bubbled through this solution at a moderate rate for 2 min. The reaction mixture was then warmed to room temperature. The solvent was removed at reduced pressure, and the residue was chromatographed on a Florisil/ether column. Crystallization from ether solution afforded 4.09 g (71%) of **2** as orange crystals: mp 140–142 °C; IR (hexane) ν(CO) 1962 cm^{-1}; ^1H NMR $(CDCl_3)$ δ 1.17 (s, 18, Me_3C), 4.76 (s, 5, C_5H_5). Anal. Calcd for $C_{16}H_{23}BF_2FeO_3$: C, 52.21; H, 6.32. Found: C, 51.94; H, 6.15.

X-ray Crystallographic Measurements. Amber crystals of **2** were obtained by crystallization from ether/pentane solution at −20 °C. Precession photography indicated $2/m$ Laue symmetry and systematic absences appropriate for the space group $P2_1/c$. Most parameters pertaining to data collection and structure solution and refinement are listed in Table I. Intensity data were collected on a four-circle automated

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Table I. Crystallographic Data for Complex **2**

formula	$C_{16}H_{23}BF_2FeO_3$
mol wt	367.84
cryst system	monoclinic
space group	$P2_1/c$
a	13.015 (2) Å
b	10.685 (2) Å
c	13.176 (3) Å
β	91.16 (1)°
V	1832 Å^3
Z	4
D_{calcd}	1.334 g cm^{-3}
cryst size	0.8 × 0.6 × 0.6 mm
μ(Mo Kα)	8.48 cm^{-1}
X radiation	λ = 0.7101 Å (Mo Kα) Nb filter
hkl space explored	$\pm h,+k,+l$ and $\pm h,-k,-l$
2θ range	0–55°
no. of reflns measd	9630
no. of unique data	4188
no. of unique data used	3498 (2σ cutoff)
scan type	θ–2θ
scan mode	0.03° steps; 1 s/step
bkgd time	20 s
abs cor	8 × 8 × 8 Gaussian grid
transmission factors	
max	0.6616
min	0.6265
av	0.6504
no. of stds used	5
intensity decay	8.5% (341 h of exposure to X-rays)
no. of variables refined	222
R	0.047
R_w[a]	0.058

[a] $R_w = [[\sum w(|F_o| - |F_c|)^2]/\sum w|F_o|^2]^{1/2}$ where w is $1/\sigma(F_o)^2$.

Table II. Refined Atomic Positional Parameters after Rounding (with Esd's) for Complex **2**

atom	x	y	z
Fe	0.20915 (3)	0.45706 (3)	0.69670 (3)
F(1)	0.2474 (3)	0.4765 (2)	0.3651 (1)
F(2)	0.1102 (2)	0.4017 (2)	0.4465 (2)
O(1)	0.2004 (2)	0.5764 (2)	0.5099 (1)
O(2)	0.2766 (2)	0.3694 (2)	0.5118 (1)
O(3)	0.3722 (2)	0.5503 (2)	0.8285 (2)
B	0.2058 (5)	0.4550 (4)	0.4544 (3)
C(1)	0.2067 (2)	0.5922 (2)	0.6061 (2)
C(2)	0.2920 (2)	0.3665 (2)	0.6080 (2)
C(3)	0.3101 (2)	0.5133 (3)	0.7725 (2)
C(4)	0.3829 (2)	0.2794 (3)	0.6314 (2)
C(5)	0.2097 (2)	0.7327 (2)	0.6285 (2)
C(8)	0.0496 (2)	0.4828 (4)	0.7200 (4)
C(9)	0.0993 (3)	0.4704 (4)	0.8133 (3)
C(10)	0.1452 (3)	0.3523 (5)	0.8158 (4)
C(11)	0.1250 (3)	0.2924 (4)	0.7270 (4)
C(12)	0.0653 (3)	0.3755 (5)	0.6650 (3)
C(41)	0.3767 (4)	0.1639 (4)	0.5645 (4)
C(42)	0.3922 (2)	0.2398 (4)	0.7416 (3)
C(43)	0.4804 (3)	0.3536 (5)	0.6069 (4)
C(51)	0.3203 (3)	0.7731 (3)	0.6058 (4)
C(52)	0.1844 (4)	0.7671 (3)	0.7367 (3)
C(53)	0.1329 (4)	0.8013 (3)	0.5584 (3)

Picker diffractometer. A sharpened Patterson function revealed the position of the Fe atom, which formed the basis for a diference synthesis from which the remaining atoms were located. Specific references to the control software, the solution and refinement methods, and the crystallographic software utilized have been reported previously.[5] A list of refined atomic positional parameters (after rounding) is provided in Table II. All hydrogen atoms were included in the final computational model. The maximum and minimum residual electron densities in the final difference map were 0.41 e Å^{-3} (located near Fe) and −0.34 e Å^{-3} [located near F(2)], respectively. Values of selected bond distances and angles of complex **2** are provided in Table III.

Results and Discussion

When the iron pivaloyl complex **1** is treated with *tert*-butyllithium, the ferra β-diketonato anion $[(\eta\text{-}C_5H_5)(OC)Fe(Me_3CCO)_2]^-$ is formed. Subsequent treatment of this anion with excess BF_3 in CH_2Cl_2 solution affords the neutral (ferra dipivaloylmethanato)BF_2 complex **2**. Complex **2** has only one C–O stretching band in its IR spectra taken both in solution phase (1962 cm^{-1}) and in KBr (1956 cm^{-1}). Because this compound exists solely as the (ferra β-diketonato)BF_2 isomer of unknown structure, it was chosen for a structural determination.

Table III. Values of Selected Interatomic Distances and Angles (with Esd's) for Complex **2**

	Interatomic Distances, Å		
Fe–C(1)	1.874 (3)	O(2)–B	1.494 (5)
Fe–C(2)	1.875 (3)	C(1)–C(5)	1.531 (4)
Fe–C(3)	1.742 (3)	C(2)–C(4)	1.542 (4)
F(1)–B	1.325 (5)	C(4)–C(41)	1.518 (5)
F(2)–B	1.371 (7)	C(4)–C(42)	1.514 (5)
O(1)–C(1)	1.279 (3)	C(4)–C(43)	1.525 (5)
O(2)–C(2)	1.279 (3)	C(5)–C(51)	1.538 (5)
O(3)–C(3)	1.152 (4)	C(5)–C(52)	1.516 (5)
O(1)–B	1.491 (5)	C(5)–C(53)	1.533 (5)
	Interatomic Angles, deg		
Fe–C(1)–O(1)	122.0 (2)	O(1)–B–O(2)	108.6 (3)
Fe–C(2)–O(2)	121.6 (2)	F(1)–B–F(2)	113.0 (4)
Fe–C(3)–O(3)	175.1 (3)	O(1)–B–F(1)	108.1 (3)
Fe–C(1)–C(5)	129.3 (2)	O(1)–B–F(2)	110.3 (4)
Fe–C(2)–C(4)	129.8 (2)	O(2)–B–F(1)	107.3 (4)
C(1)–Fe–C(2)	90.15 (11)	O(2)–B–F(2)	109.5 (3)
C(1)–Fe–C(3)	95.89 (13)	C(1)–C(5)–C(51)	104.9 (2)
C(2)–Fe–C(3)	95.68 (13)	C(1)–C(5)–C(52)	114.4 (2)
O(1)–C(1)–C(5)	108.7 (2)	C(1)–C(5)–C(53)	109.8 (2)
O(2)–C(2)–C(4)	108.6 (2)	C(2)–C(4)–C(41)	109.6 (3)
C(1)–O(1)–B	126.7 (2)	C(2)–C(4)–C(42)	113.7 (3)
C(2)–O(2)–B	126.8 (3)	C(2)–C(4)–C(43)	106.4 (3)

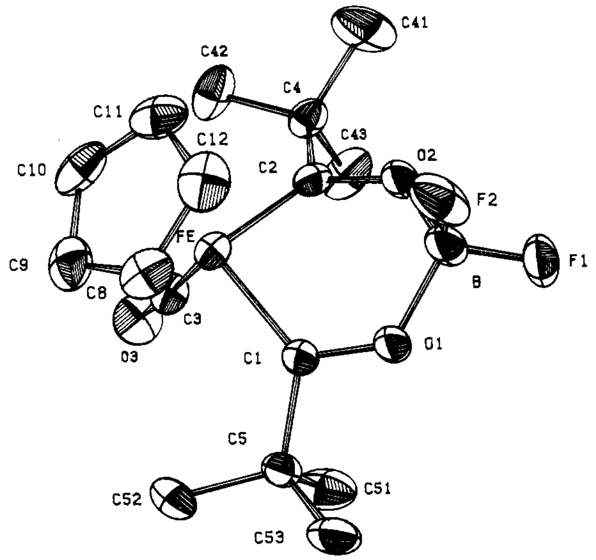
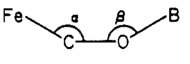


Figure 1. ORTEP view of complex **2** (thermal elliposids at 30% probability).

Figure 1 shows an ORTEP view of complex **2** along with the atomic numbering scheme. Of principal structural interest is the observation that complex **2** does exist as the alternate boat-shaped isomer of that reported previously for $[(\eta\text{-}C_5H_5)(OC)Fe(MeCO)(i\text{-}PrCO)]BF_2$ (**3**).[5] The IR spectrum of **3** in KBr shows a ν(CO) band at 2005 cm^{-1}. In complex **2**, the C_5H_5 ligand occupies the axial site at the Fe atom in greatest proximity to the axial F(2) substituent at the boron atom. Presumably, the location of the C_5H_5 ligand of **2** in an axial site rather than an equatorial site (as observed in **3**) greatly reduces the steric repulsion between the C_5H_5 ligand and the *tert*-butyl substituents of the ferra chelate ring.

The interatomic distances and angles of the complexes **2** and **3** do not differ considerably; however, there are significant differences between the geometries of the boat-shaped ferra chelate rings of these molecules that might reflect differences in intramolecular steric interactions. This boat conformation is shown schematically as **4** (side view). From the structures of **2** and **3**,



4

the following important comparisons can be made: (1) The Fe atom of **2** is displaced 0.19 Å further from the acyl [C(1), O(1), C(2), O(2)] plane than is the Fe atom of **3**. This result might reflect a steric repulsion between the bulky ring substituents of **2** and the ligands on the Fe atom greater than there is within **3**. (2) The values of the dihedral angles α and β of **2** are respectively 2.0 and 12°, larger than the corresponding angles in **3**. This result might indicate a steric repulsion between the axial F(2) atom and the axial C_5H_5 ligand of **2** greater than there is between the axial F(2) atom and the axial CO ligand of **3**.

Conclusion

The structure of a $[(\eta\text{-}C_5H_5)(OC)(\text{ferra }\beta\text{-diketonato})]BF_2$ complex that exhibits a carbonyl ligand stretching vibration at 2005 cm^{-1} reveals a boat-shaped ferra chelate ring having the C_5H_5 ligand in an axial site at the Fe atom. The alternate boat-shaped isomer having the CO ligand of the Fe atom in an axial site has been characterized previously. This isomer exhibits a carbonyl ligand stretching vibration at ca. 1960 cm^{-1}. Solution-phase and solid-state IR data now readily permit the determination of the identity and relative abundance of each boat-shaped isomer in this class of molecule for any combination of substituents on the ferra chelate ring.

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Registry No. **1**, 59125-00-7; **2**, 98778-63-3; boron trifluoride, 7637-07-2.

Supplementary Material Available: Lists of final atomic positional and thermal parameters before rounding, interatomic distances and angles, selected least-squares planes data, and final observed and calculated structure factors for complex **2** (28 pages). Ordering information is given on any current masthead page.

Contribution from the Laboratoire de Synthèse, Structure
et Réactivité de Molécules Phosphorées, UA 454,
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First Example of Prototropism in Iminobis(phosphines) Induced by Phosphorus Alkylation

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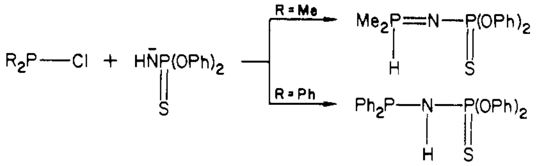
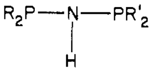
There are a few examples of tautomeric equilibrium in R_2PNHR systems. Depending on the nature of the R groups and on the temperature, the equilibrium is partially or totally shifted either to the aminophosphine form A or to the iminophosphorane form B.[2-8]

The versatility of such a tautomerism has been illustrated by the attempted synthesis of ((dimethylphosphoranyl)amino)diphenoxyphosphine sulfide or ((diphenylphosphino)amino)diphenoxyphosphine sulfide:[2]



We report here a surprising prototropic rearrangement induced by alkylation of a phosphorus atom of iminobis(phosphines) **1** and **2** by triphenylcarbenium hexafluorophosphate or methyl trifluoromethanesulfonate. This type of reaction has permitted us to obtain unknown phosphoranimine–phosphonium salts which are potentially useful as synthetic reagents.



$R_2P{-}N(H){-}PR'_2$

1, R=R'=Ph[9]
2, R=Ph, R'=*t*-Bu

Experimental Section

All experiments were performed under an atmosphere of dry argon or nitrogen. Dry and oxygen-free solvents were used at all times. $(C_6H_5)_2PCH_2P(C_6H_5)_2$, $(C_6H_5)_3C^+PF_6^-$, and $MeSO_3CF_3$ are commercially available and were used without further purification. Melting points are uncorrected. ^1H NMR spectra were recorded on a Varian T-60 or Bruker WM 250 spectrometer. ^1H chemical shifts are reported in ppm relative to Me_4Si as internal standard. ^{31}P NMR spectra were obtained on a Perkin-Elmer R 32 spectrometer at 36.4 MHz or Bruker WM 250 at 101.21 MHz. Downfield shifts are expressed with a positive sign, in ppm, relative to external 85% H_3PO_4. Infrared spectra were recorded on a Beckman IR 10 spectrometer, using polystyrene film for calibration. Mass spectra were obtained on a Ribermag R 10-10 E instrument.

Synthesis of $(t\text{-Bu})_2PNHPPH_2$ (2). Diphenylchlorophosphine (0.6 mL, 3.11 mmol) was added dropwise to a mixture of $(t\text{-Bu})_2PNH_2$ (0.5 g, 3.11 mmol) and triethylamine (0.43 mL, 3.11 mmol) in ether (2 mL) maintained at −70 °C. The reaction mixture was then stirred for 2 h at room temperature. After filtration and evaporation of the solvent under reduced pressure, the residue was recrystallized from toluene to give iminobis(phosphine) **2** as white crystals, mp 61 °C (0.8 g, 75% yield). IR (KBr): 980 (P–N) cm^{-1}. Anal. Calcd for $C_{20}H_{29}NP_2$: C, 69.54; H, 8.46; N, 4.06; P, 17.94. Found: C, 69.70; H, 8.40; N, 3.99; P, 17.78.

Reaction of 1 with Triphenylcarbenium Hexafluorophosphate. Triphenylcarbenium hexafluorophosphate (0.492 g, 1.27 mmol) in CH_2Cl_2 (4 mL) was added to a solution of iminobis(phosphine) **1** (0.490 g, 1.27 mmol) in CH_2Cl_2 (4 mL). After complete decoloration of the resulting mixture, the solvent was removed. Recrystallization of the residue from CH_3CN gave **3** as a white crystalline solid, mp 163–165 °C (0.835 g, 85% yield). IR (KBr): 1225 (P═N), 835 (P—N) cm^{-1}. Mass spectrum: *m/e* 628 (M^+). Anal. Calcd for $C_{43}H_{36}F_6NP_3$: C, 66.75; H, 4.69; N, 1.81; P, 12.01. Found: C, 66.38; H, 4.70; N, 1.79; P, 11.86.

Reaction of 1 with Methyl Trifluoromethanesulfonate. A mixture of **1** (0.492 g, 1.27 mmol) and methyl trifluoromethanesulfonate (0.208 g, 1.27 mmol) in CH_2Cl_2 (4 mL) was stirred for 1 h at room temperature. Evaporation of the solvent afforded **4** as an oil. IR (KBr): 1265 (P═N), 850 (P—N) cm^{-1}. Attempted crystallizations failed. However, a correct elemental analysis was obtained. Anal. Calcd for $C_{26}H_{24}F_3NO_3P_2S$: C, 56.83; H, 4.40; N, 2.55; P, 11.28. Found: C, 57.03; H, 4.52; N, 2.47; P, 11.02.

Reaction of 2 with Triphenylcarbenium Hexafluorophosphate. A so-

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