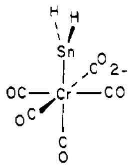
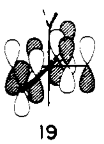
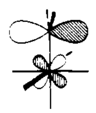
namely, $[(Me_3Si)_2CH]_2PFe(CO)_4$.[20] The alkyl groups at phosphorus are very bulky. Their experimental results nicely agree with our contention that in a trigonal isomer 3a″ may lie lower than 4a′. The ESR spectrum of their compound shows no observable hyperfine coupling to ^{31}P or ^{1}H. Furthermore, narrow lines are observed in the ^{31}P, ^{13}C, and ^{1}H NMR spectra for the ligand portion of their molecule. This is not consistent with placing the odd electron in 4a′—an orbital that would be heavily weighted on phosphorus. The Mössbauer spectrum suggests that the extra electron does not reside at the metal. Finally, the CO stretching frequencies are lowered by $\sim 100\ cm^{-1}$ from analogues. This is compatible with 3a″ being singly occupied. As we pointed out earlier, since 3a″ is carbonyl π^* based, one would expect the equatorial bond length and stretching frequencies to be increased upon occupation. An optimal case for the occupation of 3a″ rather than 4a′ would be one where the equatorial carbonyls of **3** were replaced by isoelectronic NO^+ ligands. The more electronegative nitrogen lowers the energy of π^* significantly. This means that a_2 (see Figure 1) will go down in energy greatly. Our calculations on **17** confirm this. In fact, at all reasonable values of θ, 3a″ lies lower than 4a′. One minimum is then found for pyramidalization (θ = 147°). Another complex where we have found a similar pattern is $(H_2Sn)Cr(CO)_5^{2-}$ (**18**). **19** is found to lie lower in energy than **20**. Several complexes with two electrons less are known.[21] Low-temperature electrochemical reduction studies on them would be very interesting. We again calculate that in the carbon analogue of **18** there is a reversal of level ordering. The level **20** is calculated to lie lower than **19**. One-electron reduction of $(R_2C)M(CO)_5$ (M = Cr, Mo, W) complexes yields a species that has been investigated by ESR.[22] In agreement with our results the unpaired electron resides in **20** rather than **19**.



18



19



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Appendix

All calculations were performed with use of the extended Hückel method.[23] The H_{ii}'s and orbital exponents listed in Table I were taken from other work.[24] The modified Wolfsberg–Helmholz formula[25] was used. All Fe–C, Cr–C, C–O, M–Sn, Fe–N, N–O, Sn–H, and C–H distances were set at 1.78, 1.84, 1.14, 2.54, 1.70, 1.17, 1.70, and 1.09 Å, respectively. The M–C–O and Fe–N–O angles were held at 180°.

Registry No. $(H_2Sn)Fe(CO)_4^{2-}$, 78939-73-8.

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Contribution from the Department of Chemistry, Memorial University of Newfoundland,
St. John's, Newfoundland, Canada A1B 3X7

Preparation and Properties of Some Low-Spin Octahedral [*o*-Phenylenebis(dimethylarsine)]iron(II) Alkyl and η^1-Acyl Complexes. Carbonyl Insertion/Extrusion Reactions

C. R. JABLONSKI

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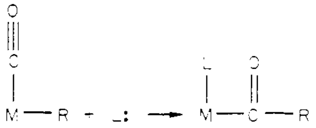
Reaction of CH_3OSO_2F with $(DIARS)Fe(CO)_3$ (DIARS = *o*-phenylenebis(dimethylarsine)) results in simple oxidative addition to give $[(DIARS)Fe(CO)_3CH_3]^+$. With CH_3I or CF_3I initial oxidative addition is followed by iodide-promoted migratory carbonyl insertion to form iodo η^1-acyl or η^1-perfluoroacyl complexes. The acyl $(DIARS)Fe(CO)_2(COCH_3)I$ does not readily decarbonylate even under forcing conditions. Halide abstraction of the η^1-acyl produces a coordinatively unsaturated intermediate, which extrudes CO to give *fac*-$[(DIARS)Fe(CO)_3CH_3]^+$. The cationic CO extrusion product readily undergoes migratory CO insertion in the presence of both neutral and anionic Lewis bases.

Introduction

An understanding of the factors determining stability/reactivity patterns of metal–carbon σ bonds is fundamental for meaningful extensions of most catalytic cycles involving transition metals. Carbonyl insertion,[1,2] eq 1, wherein a coordinated CO molecule formally "inserts" into a metal–carbon σ bond provides for the formation of value added oxygenated products in the hydroformylation process,[3a] the catalytic carbonylation of methanol,[3b] and the chain propagation steps



$$M(CO)\text{—}R + L: \longrightarrow M(L)\text{—}C(=O)\text{—}R \qquad (1)$$

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in the Fischer–Tropsch[3c] reaction, which converts coal-derived synthesis gas to liquid hydrocarbons. Carbonylation is proposed to occur on simple mononuclear five-coordinate complexes (Co(I), Rh(I), Ir(I)) for the former two reactions, but the situation is less clear in the Fischer–Tropsch reaction.

Although CO fixation using cluster catalysts has been suggested to require simultaneous coordination of both C and O in the initiation steps,[3c] propagation via migratory carbonyl insertion[4] is thought to occur on a single coordination site. Even the $Ru_3(CO)_{12}$-catalyzed hydrogenation of CO to methanol appears to proceed[3d,e] via an active mononuclear species. Consideration of recent reports of successful reduction of Fe–CO to methane,[5] effective homogeneous catalysis of the water-gas shift reaction using iron carbonyls,[6] and current Fe-based heterogeneous Fischer–Tropsch technology suggests that a further examination of reaction 1, M = Fe, is warranted. In this paper we report our initial results concerning the preparation and carbonyl migratory insertion reactions on some simple low-spin octahedral Fe(II) complexes containing an Fe–C σ bond.

Experimental Section

General Comments. All reactions were carried out under an atmosphere of prepurified nitrogen with use of the techniques described by Shriver.[7] Melting points were taken on a Thomas-Hoover apparatus using sealed nitrogen-filled capillary tubes and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer Model 280 spectrometer. Nuclear magnetic resonance spectra were obtained on a Bruker WP-80 spectrometer fitted with a BVT 1000 temperature controller. Chemical shifts are reported in ppm with respect to internal tetramethylsilane. Mass spectra were recorded on a Perkin-Elmer RMU 6E spectrometer. Analyses were performed by the Canadian Microanalytical Service Ltd., Vancouver, B.C.

DIARS (*o*-phenylenebis(dimethylarsine)) was purchased from Strem Chemicals and used without further purification or prepared from cacodylic acid according to the literature method[8] and distilled at 78–84 °C (0.1 mmHg) before use. Silver salts (Alfa) and $Fe(CO)_5$ (Strem) were used without further purification.

(DIARS)Fe(CO)$_3$. The following procedure consistently gives substantially increased yields compared to the literature method.[9] A Carius tube (20 mm i.d. × 26 cm) is charged with 2.5 mL (1.21×10^{-2} mol) of *o*-phenylenebis(dimethylarsine) and 1.5 mL (1.12×10^{-2} mol) of $Fe(CO)_5$. The contents are degassed with use of three freeze/pump/thaw cycles and sealed under vacuum (0.1 mmHg). The tube was wrapped in foil and heated in an oil bath at 180 °C for 7 h. The temperature is critical since heating beyond 190 °C will cause decomposition while lower temperatures decrease yields. After standing overnight at room temperature, the tube was frozen in liquid nitrogen and opened (*caution*! CO pressure). The solid residue was crushed and washed under N_2 with ether (4×5 mL) to remove unreacted DIARS and taken up in CH_2Cl_2, and the solution was filtered under N_2 through a pad of Celite. Removal of solvent gave the product as a lemon yellow, very air-sensitive crystal, yield 2.35 g (98%). The product as received is contaminated with (DIARS)Fe(CO)$_4$ (ν_{CO} (cyclohexane) 2048 (s), 1981 (s), 1944 (vs) cm^{-1}), which can be removed by careful chromatography under N_2 on Florisil eluting with 1:10 benzene/hexane. (DIARS)Fe(CO)$_3$ does not store well and gradually darkens even under N_2 in the cold, giving a product insoluble in hexane or CH_2Cl_2.

(DIARS)Fe(CO)$_2$(COCH$_3$)I. To a N_2-saturated solution of 4.80 g of (DIARS)Fe(CO)$_3$ in 10 mL of CH_2Cl_2 contained in a Schlenk tube was added 10 mL of freshly distilled CH_3I. The reaction mixture was stored in the dark at 0 °C for 48 h to give an intense orange solution. Removal of solvent at water aspirator pressure gave the crude product in quantitative yield as an orange-brown air-stable solid containing an approximate 1:1 mixture of cis,cis and cis,trans isomers. Pure yellow cis,trans isomer (mp 165–166 °C) may be isolated by equilibrating the crude product from above at 25 °C in $CHCl_3$ for 3 h. The solution thus obtained is rich in cis,trans isomer, which can be purified by chromatography on silica gel eluting with 3:1 chloroform/hexane followed by several recrystallizations from CH_2Cl_2/hexane.

Anal. Calcd for $As_2C_{14}H_{19}FeO_3I$: C, 29.61; H, 3.37; O, 8.46. Found: C, 29.45; H, 3.23; O, 9.02. Mass spectrum (*m/e*): 568 (M$^+$), 553 (M$^+$ – CH$_3$), 540 (M$^+$ – CO), 525 (M$^+$ – COCH$_3$), 512 (M^3 – 2CO), 497 ((M$^+$ – CO) – Ac), 484 (M$^+$ – 3CO), 469 ((M$^+$ – 2CO) – Ac), 454 ((M$^+$ – 2CO – Ac) – CH$_3$), 398 (M$^+$ – CH$_3$COI), 370 ((M$^+$ – CH$_3$COI) – CO), 362 (M$^+$ – AsMe$_2$I), 342 ((M$^+$ –CH$_3$COI) – 2CO), 286 (DIARS$^+$), 271 (DIARS$^+$ – CH$_3$), 256 (DIARS – 2CH$_3$), 241 (DIARS – 3CH$_3$), 226 (DIARS – 4CH$_3$).

Pure cis,cis isomer may be prepared by reacting (DIARS)Fe(CO)$_3$ with excess neat CH_3I at 0 °C for 24 h. Removal of volatiles at 0 °C in vacuo followed by recrystallization from octane at 100 °C gives the cis,cis product as brown-orange needles (mp 141–143 °C with gas evolution).

Anal. Calcd for $As_2C_{14}H_{19}FeO_3I$: C, 29.61; H, 3.37. Found: C, 29.28; H, 3.23. The mass spectrum is identical with that of the cis,trans isomer.

Reaction of CH$_3$I and (DIARS)Fe(CO)$_3$ in Flow Reactor. A solution of 100 mg of (DIARS)Fe(CO)$_3$ in 10 mL of CH_3I was suspended on a medium-porosity glass frit held at 0 °C. A steady flow of nitrogen was passed through the solution for 12 h. Removal of solvent at 0 °C left an orange-brown solid, which showed a ^1H NMR spectrum identical with that of the *cis,cis*-(DIARS)Fe(CO)$_2$(COCH$_3$)I isomer described above.

[(DIARS)Fe(CO)$_3$CH$_3$]$^+$BF$_4^-$. A 100-mL flask fitted with a nitrogen inlet, pressure-equalized dropping funnel, and magnetic stirrer was charged with 1.34 g of an isomeric mixture of (DIARS)Fe(CO)$_2$(COCH$_3$)I and 10 mL of acetone, which had been dried over activated molecular sieves. The orange solution was degassed and cooled to 0 °C in an ice bath. Then a solution prepared by dissolving 0.46 g of $AgBF_4$ in 10 mL of dry acetone was added dropwise with stirring. A yellow precipitate of AgI formed instantly, and the addition was continued until the yellow just disappeared and no further turbidity developed. The resulting colorless solution was filtered through a pad of Celite, and the volatiles were removed in vacuo. The resulting gummy solid was triturated with several portions of dry ether and collected to give a pale yellow solid. Recrystallization from CH_2Cl_2/ether gave 0.93 g (74%) of pale yellow crystals (mp 192 °C dec). Anal. Calcd for $C_{14}H_{19}As_2O_3FeBF_4$: C, 31.85; H, 3.60. Found: C, 31.89; H, 3.47. Raman (ν_{CO}): 2090 (s), 2046 (s), 2017 (vs) cm^{-1}.

The PF_6^- salt was prepared from $AgPF_6$ and (DIARS)Fe(CO)$_2$AcI by following the same procedure (mp >210 °C dec). Anal. Calcd for $C_{14}H_{19}As_2O_3FePF_6$: C, 28.70; H, 3.26. Found: C, 28.83; H, 3.10. The infrared spectrum was identical with that of the BF_4^- salt except for PF_6^- absorptions. The ^1H NMR spectra (CD_2Cl_2) is identical with that of the BF_4^- salt.

Oxidative Addition of CH$_3$OSO$_2$F to (DIARS)Fe(CO)$_3$. To 307 mg (0.72 mmol) of freshly chromatographed (DIARS)Fe(CO)$_3$ in an N_2-filled Schlenk tube fitted with a stirbar was added 5 mL of freshly distilled CH_3OSO_2F (Cationics). The initial clear red-orange solution was stirred at room temperature for 4.5 h to give a cloudy yellow suspension. Removal of volatiles in vacuo left a yellow gummy hygroscopic solid, which was triturated with several portions of dry ether and extracted into methylene chloride. Then the solution was filtered through a pad of Celite. Evacuation at 0.1 mmHg overnight at room temperature to remove volatiles gave the crude product (308 mg) as a yellow glass. The infrared spectrum (CH_2Cl_2) showed two strong ν_{CO} bands identical with those of [(DIARS)Fe(CO)$_3$CH$_3$]$^+$BF$_4^-$ or -PF$_6^-$ prepared as described above. ^1H NMR analysis, however, showed the presence of ca. 35% *mer* isomer. Anal. Calcd for $C_{14}H_{19}As_2O_6FeSF$: C, 31.11; H, 3.52. Found: C, 30.55; H, 3.41.

The OSO_2F^- salt resisted crystallization from a variety of solvents but was successfully purified as the PF_6^- salt. This was prepared by passing a 10% aqueous methanolic solution of the crude OSO_2F^- salt through an anion-exchange column (Dowex-1-X8) prepared in the PF_6^- form. Crystallization of the ion-exchanged product from CH_2Cl_2/ether gave a pale yellow crystal containing 18% *mer*- and 82% *fac*-[(DIARS)Fe(CO)$_3$CH$_3$]$^+$PF$_6^-$ by ^1H NMR analysis (cf.

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(4) There are, however, alternative mechanisms for chain propagation. Cf.: Bradley, J. S.; Ansell, G. B.; Hill, E. W. *J. Am. Chem. Soc.* **1979**, *101*, 7417 and ref 3c.

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Table II). The infrared spectrum (Nujol) of this isomeric mixture was, however, identical with that of the pure *fac* isomer previously prepared as described above.

Attempt To Observe Intermediates in CH_3I Oxidative Addition. Ten microliters of CH_3I (freshly distilled) was added to an NMR tube charged with 4 mg of (DIARS)Fe(CO)$_3$ and 0.35 mL of CD_2Cl_2 at −78 °C. ^{1}H NMR spectra were collected as the sample was allowed to warm in the NMR probe. No reaction occurred until 305 K at which point slow oxidative addition/insertion proceeded to give a mixture of both cis,cis and cis,trans acetyl iodo complexes. No other signals assignable to intermediates or other products were evident.

Low-Temperature Halide Abstraction of (DIARS)Fe(CO)$_2$AcI. To a stirred acetone-d_6 solution of (DIARS)Fe(CO)$_2$AcI immersed in a −78 °C bath was added dropwise a solution of $AgPF_6$ in acetone-d_6. Addition was continued until no further turbidity developed. The reaction mixture was allowed to stand for 15 min at −78 °C, and the supernatant was transferred to a precooled NMR tube.

^{1}H NMR spectra recorded at 240 K showed clear formation of *fac*-[(DIARS)Fe(CO)$_3$CH$_3$]$^+$. No other signals were evident.

[(DIARS)Fe(CO)$_3$C(O)CH$_3$]$^+$BF$_4^-$. A solution of 250 mg of [(DIARS)Fe(CO)$_3$CH$_3$]$^+$BF$_4^-$ in 5 mL of CH_2Cl_2 was prepared in a 100-mL flask fitted with a magnetic stirrer and rubber septum. The flask was flushed with carbon monoxide and then pressurized to 1.5 atm. After 2 h, 10 mL of ether was added to precipitate the product as a yellow oil. Trituration with 3–10-mL portions of ether followed by drying in vacuo gave 224 mg of pale yellow solid, which was crystallized from CH_2Cl_2/ether to give colorless needles (mp >187 °C dec). Anal. Calcd for $C_{15}H_{19}As_2O_4FeBF_4$: C, 32.40; H, 3.42. Found: C, 32.29; H, 3.34.

Attempted Decarbonylation of (DIARS)Fe(CO)$_2$AcI. (a) A solution of 5 mg of (DIARS)Fe(CO)$_2$AcI (90% cis,trans, 10% cis,cis) in 0.35 mL of toluene-d_8 was prepared in an NMR tube and three times freeze/thaw degassed. Heating to 368 K in the NMR probe resulted in fairly rapid geometric isomerization, and the proportion of cis,cis product increased to ca. 25–30%. Continued heating to 383 K resulted in decomposition. No new signals other than those assignable to isomeric (DIARS)Fe(CO)$_2$AcI could be clearly assigned.

(b) A 200-mg sample of (DIARS)Fe(CO)$_2$AcI (50% cis,trans, 50% cis,cis) was placed in a sublimator and heated to 120 °C in vacuo (0.50 mmHg) for seveal hours. An air-sensitive yellow-orange solid sublimed onto a water-cooled probe, leaving an insoluble brown solid. The sublimate was identified as (DIARS)Fe(CO)$_3$ by its IR spectrum in cyclohexane.

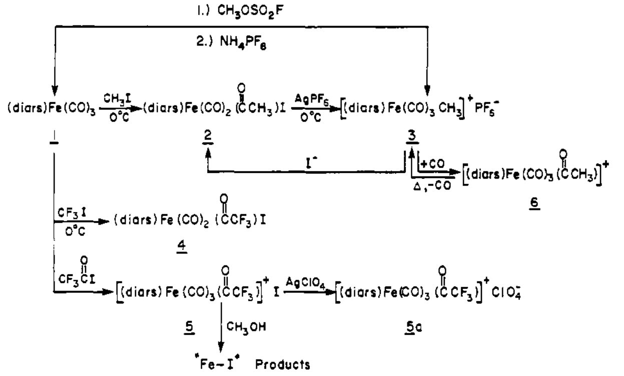
Oxidative Addition of CF_3I to (DIARS)Fe(CO)$_3$. A solution of 700 mg of (DIARS)Fe(CO)$_3$ in 5 mL of CH_2Cl_2 was allowed to react in the dark with excess freshly distilled CF_3I at 0 °C for 48 h. Removal of volatiles left a dark red solid, which was chromatographed on silica gel. Elution with 1:1 cyclohexane/chloroform separated a yellow and a slower moving orange band. The yellow band (mp 185–186 °C) was identified as *cis,trans*-(DIARS)Fe(CO)$_2$(C(O)CF$_3$)I. Anal. Calcd for $C_{14}H_{16}FeAs_2O_3F_3I$: C, 27.03; H, 2.57. Found: C, 27.22; H, 2.36. Mass spectrum (*m/e*): 662 (M$^+$), 594 (M$^+$ − CO), 566 (M$^+$ − 2CO), 553 (M$^+$ − CF$_3$), 548 (M$^+$ − 3CO), 525 ((M$^+$ − CF$_3$) − CO), 497 ((M$^+$ − CF$_3$) − 2CO), 488 (?), 469 ((M$^+$ − CF$_3$) − 3CO), 362 (?), 286 (DIARS$^+$), 271 (DIARS − CH$_3$), 256 (DIARS − 2CH$_3$), 241 (DIARS − 3CH$_3$), 226 (DIARS − 4CH$_3$).

The orange band (mp 151–157 °C) was found to be *cis,cis*-(DIARS)Fe(CO)$_2$(C(O)CF$_3$)I. Anal. Calcd for $C_{14}H_{16}FeAs_2O_3Fe_3I$: C, 27.03, H, 2.57. Found: C, 27.30; H, 2.37. The mass spectrum was identical with that of the cis,trans isomer.

The same products were also isolated from the reaction of excess CF_3I and (DIARS)Fe(CO)$_3$ in CH_2Cl_2 containing 3 mol % hydroquinone or galvinoxyl radical inhibitors.

Oxidative Addition of $CF_3C(O)I$ to (DIARS)Fe(CO)$_3$. Excess $CF_3C(O)I$, prepared[10] from trifluoroacetic anhydride, was distilled onto solid (DIARS)Fe(CO)$_3$ at −78 °C to produce a flocculent white precipitate. The reaction mixture was allowed to warm to 0 °C. After 1.0 h, volatiles were removed in vacuo and the white precipitate was washed with 3 × 5 mL of benzene followed by 3 × 5 mL of ether. The product was crystallized from acetone/ether to give an off-white powder (mp >125 °C dec) identified as *mer*-[(DIARS)Fe(CO)$_3$(C(O)CF$_3$)]$^+$I$^-$. Anal. Calcd for $C_{15}H_{16}FeO_4As_2F_3I$: C, 27.77; H, 2.46. Found: C, 27.64; H, 2.21.

Scheme I



Treatment of an acetone solution of the iodide product with an acetone solution of $AgClO_4$ gave a yellow precipitate of AgI. The suspension was filtered through Celite and concentrated in a nitrogen stream. Addition of ether gave colorless needles (mp 155–157 °C dec) of the ClO$_4^-$ salt. Anal. Calcd for $C_{15}H_{16}FeAs_2O_8F_3Cl$: C, 28.92; H, 2.57. Found: C, 29.36; H, 2.38.

Results

Preparation and Characterization of the Fe–R and Fe–C(O)–R Complexes. Only a very few alkyliron complexes have been reported that do not contain the η^5-C$_5$H$_5$ ligand.[11-13] Our synthetic approach follows the oxidative addition route reported by Pankowski and Bigorgne[12] substituting the bidentate ligand *o*-phenylenebis(dimethylarsine), DIARS, for PMe$_3$. Our choice of DIARS rests on its ability to stabilize low-spin octahedral Fe(II)[14] as well as its minimal steric requirements.[15]

Tricarbonyl[*o*-phenylenebis(dimethylarsine)]iron(0) proved extremely reactive with respect to oxidative addition. Treatment with CH_3I at 0 °C gave orange solutions within 0.5 h of mixing. Rather unexpectively, these solutions did not contain the anticipated Fe(CH$_3$)I compound,[12] giving instead a quantitative yield of carbonyl "inserted" product, Fe(C(O)CH$_3$)I; cf. Scheme I. The η^1-acyl product **2** presumably results from oxidative addition/insertion as observed by Pankowski[12] and others.[16]

Four isomers excluding enantiomers are possible for the octahedral complex **2**. Combination of vibrational and NMR (^{1}H and/or ^{13}C) spectroscopy readily distinguishes the cis,trans (**2a**) isomer from the trans,cis (**2b**) or the diastereomeric cis,cis pair (**2c**, **2d**). Observation of Figure 1a clearly shows that the kinetic product of oxidative addition of CH_3I at 0 °C leads *stereospecifically* to a *single* cis,cis isomer (**2c** or **2d**), which requires *four* magnetically nonequivalent arsine methyl groups. Geometric rearrangement occurs readily at 307 K, giving at equilibrium at 25:25:60 mix of cis,cis (**2c** or **2d**):cis,cis (**2d** or **2c**):cis,trans (**2a**) isomers. The thermodynamically favored cis,trans isomer **2a** was separated by chromatography followed by fractional crystallization, and its ^{1}H NMR spectrum shows

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(15) Attempts to oxidatively add RI to P$_2$Fe(CO)$_3$, where P = PPh$_2$Me or Ph$_2$P(CH$_2$)$_2$PPh$_2$, are unsuccessful: Button, T.; Jablonski, C. R. unpublished results.[12]

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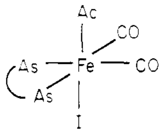
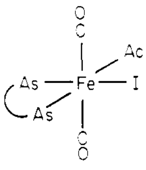
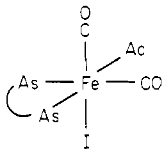


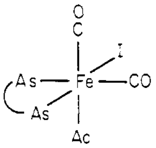
2a



2b



2c



2d

two magnetically nonequivalent arsine methyl groups (cf. Figure 1c).

That the thermodynamic product is cis,trans (**2a**) and not trans,cis (**2b**) is evident from the observation of *two* infrared-active carbonyl stretching modes in cyclohexane solution (cf. Table I).

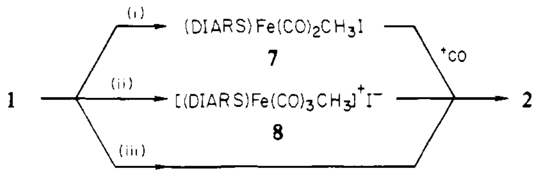
Quite apart from the related $P_2M(CO)_2(C(O)CH_3)X$ (P = phosphine, X = halide) complexes of Fe(II)[12] or Ru(II),[17] the DIARS acyls **2** resist thermal decarbonylation. Thermolysis at 368 K in toluene resulted in initial isomerization followed by decomposition. Heating solid **2** in vacuo also results in decomposition; however small amounts of (DIARS)$Fe(CO)_3$ were isolated. Attempts to chemically abstract carbon monoxide using $[Rh(PPh_3)_2Cl]_2$[18] also failed.

Quantitative extrusion of carbon monoxide to form alkyl complexes could be forced by halide abstraction using soluble silver salts with noncoordinating counterions[19] (cf. Scheme I). Interestingly, isomeric mixtures of **2** (predominantly **2a** and **2c** or **2d**) gave *only* the *fac* isomer of **3** even when the reaction was carried out at low (195 K) temperature.

The *fac* geometry for **3** follows from its ^1H and ^{13}C NMR spectra (cf. Figure 2), which show *two* magnetically nonequivalent arsine methyl and carbonyl groups. The ^{13}C NMR spectrum is more revealing in this respect since the lack of observed splitting of the C_1, C_2 and C_3, C_6 *o*-phenylene resonances clearly shows the presence of a symmetry plane bisecting the chelating ligand thus fixing the stereochemistry as *fac* not *mer*. The cis,cis acyl complex **2c** (and others in this series, **4**), which does not contain a bisecting σ plane shows four signals for the magnetically nonequivalent carbons C_1, C_2, C_3, and C_6. The solution IR spectrum (cf. Table I) of *fac*-**3** shows only two resolvable CO stretching modes. Analysis of integrated intensities allows assignment as the $A_1 + E$ modes for local symmetry C_{3v} or as three absorptions of approximately equal intensity[20,21] $2\ A' + A''$ for C_s symmetry with two of these being accidently degenerate.

The cationic $Fe-CH_3$ complex **3** was also prepared directly as a 65:35 *fac*/*mer* mixture, which does not readily isomerize in CH_2Cl_2 solution by oxidative addition of methyl fluorosulfonate according to Scheme I. Pure *mer*-**3** could not be separated but was conclusively identified by its ^1H NMR spectrum (cf. Table II), which clearly shows two $As-CH_3$ signals and a $Fe-CH_3$ signal *distinct* from *fac*-**3**. Addition of iodide to these *fac*/*mer* mixtures gave complete conversion to isomeric acyl iodide **2**. No other products were detectable via ^1H NMR.

Scheme II



Rather surprisingly in view of the reluctance of carbon monoxide to "insert" into metal perfluoroalkyl bonds[2,22-24] in general and specifically in the case of iron,[25] reaction of **1** with CF_3I appears to follow the same course as with CH_3I (cf. Scheme I). To our knowledge the isolation of **4** represents the first documented example of carbonyl "insertion" into a perfluoroalkyl bond. The reaction proceeds readily even at −78 °C as evidenced by the instantaneous deep red color produced upon contact of CF_3I and **1**. Chromatographic separation of the acyl products gave a *cis,trans*-**4a** (cf. **2a**) and a *cis,cis*-**4c** or **4d** (cf. **2c**, **2d**) isomer identified by their respective ^1H and ^{13}C NMR spectra as well as their IR spectra (cf. Tables I and II). The same acyl products were isolated when the reaction was carried out in the presence of radical scavengers.

Treatment of **1** with trifluoroacetyl iodide precipitates an off-white oxidative addition product characterized as the cationic acyl **5**. The stereochemistry appears to be exclusively *mer* as evidenced by its IR spectrum (Table I). Although the perchlorate salt prepared by reaction of the iodide with $AgClO_4$ is stable, methanolic solutions of **5** gradually develop an intense orange color indicating the formation of covalent iodides. We have not been able to characterize the product that could conceivably be the result of substitution of CO by I^- or less likely I^--promoted insertion to give a $Fe-C(O)C(O)-CF_3$ derivative.[26]

Lewis Base Induced Insertion Reactions. The isolated cationic methyl derivative **3** readily undergoes carbon monoxide "insertion" in the presence of halides or added CO to give the acyls **2** and **6**, respectively (cf. Scheme I). Isolated acyl iodide complexes obtained from *fac*-**3** are identical with samples prepared by reaction of **1** with CH_3I. *fac*-**3**/*mer*-**3** mixtures gave isomeric acyl iodide complexes (**2a** and **2c** or **2d**) when treated with LiI in methanol-d_4 solution at 273 K. Chloride, bromide, and thiocyanate ion showed similar reactions. The acyl products were not isolated in these cases but showed ^1H NMR spectra consistent with their assigned structures.

Infrared as well as ^{13}C and ^1H NMR spectra are in accord with a *fac* geometry for the acyl **6**; however the terminus of the incoming CO group (assuming the intramolecular insertion) was not determined. Carbonyl "insertion" is reversible in this case, and *fac*-**3** can be regenerated by warming solutions of **6** under a N_2 purge.

The stereochemistry of the kinetic products of halide- and pseudohalide-induced insertion to give neutral acyls is a function of both solvent and ligand. Figure 3 shows sequential ^1H NMR spectra for the iodide-promoted reaction $\mathbf{3} \rightarrow \mathbf{2}$ in methanol-d_4 at 273 K. Under the conditions of the experiment, further equilibrium of the acyl iodide isomers is a slow process. Analysis of the spectra of Figure 3 shows two isomeric kinetic products (**2a** and **2c** or **2d**) formed in constant ratio. Results

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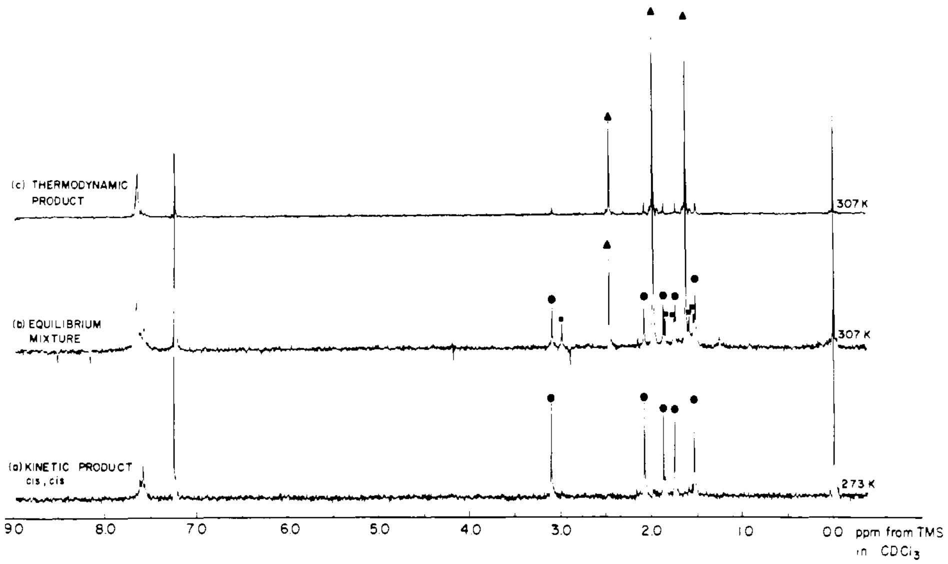


Figure 1. ^{1}H NMR spectra, 80 MHz: (a) kinetic product of the oxidative additions of CH_3I to $(DIARS)Fe(CO)_3$; (b) equilibrium product distribution at 307 K in $CDCl_3$; (c) isolated cis,trans thermodynamic product.

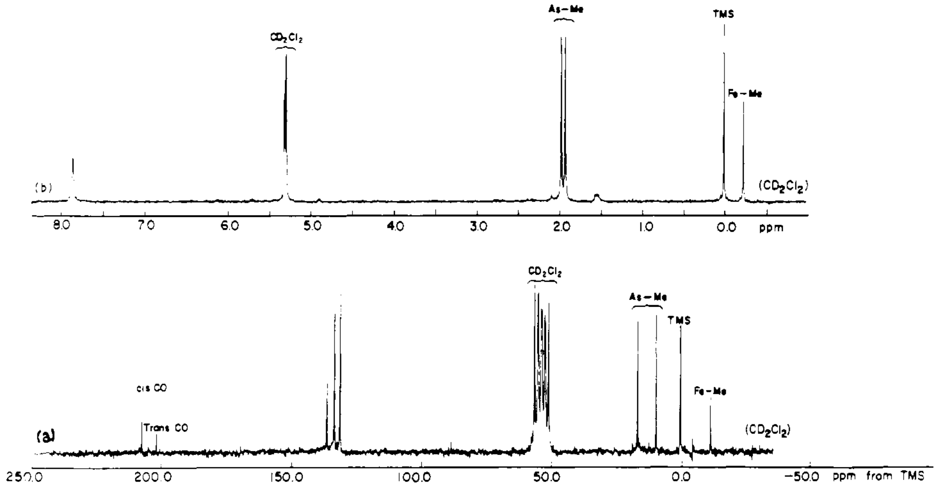


Figure 2. NMR spectra of *fac*-**3** in CD_2Cl_2: (a) ^{13}C, 20.1 MHz; (b) ^{1}H, 80 MHz.

Table I. Infrared Spectra (cm^{-1}) of the *o*-Phenylenebis(dimethylarsine) Complexes

compd	ν_{CO} soln	ν_{CO} Nujol mull	other[a]
$(DIARS)Fe(CO)_3$	1992 (vs)[b]		
	1924 (vs)		
	1909 (vs)		
cis,cis-$(DIARS)Fe(CO)_2AcI$	2011 (vs)[b]		1626 (m, br)[d] ($\nu_{CO,acetyl}$)
	1959 (vs)		
cis,trans-$(DIARS)Fe(CO)_2AcI$	2016 (vs)[b]		1620 (m, br) ($\nu_{CO,acetyl}$)
	1975 (vs)		1340 (m)[d] (–C(O)–CH_3, def)
fac-$[(DIARS)Fe(CO)_3CH_3]^+BF_4^-$	2082 (vs)[c]	2096 (vs)	1050 (s, br)[d] (BF_4^-)
	2018 (vs, br)	2046 (vs)	
		2024 (vs)	
fac-$[(DIARS)Fe(CO)_3Ac]^+BF_4^-$	2086 (vs)[c]	2095 (vs)	1664 (s, br)[d] ($\nu_{CO,acetyl}$)
	2026 (vs, br)	2030 (br)	1342 (m)[d] (–C(O)–CH_3, def)
			1050 (s, br) (BF_4^-)
cis,cis-$(DIARS)Fe(CO)_2(C(O)CF_3)I$	2031 (vs)[b]		1640 (s)[e] ($\nu_{CO,acyl}$)
	1978 (vs)		1236 (s), 1180 (s), 1132 (sh, s) 1126 (s) (ν_{C-F})
cis,trans-$(DIARS)Fe(CO)_2(C(O)CF_3)I$	2039 (vs)[b]		1625 (s)[e] ($\nu_{CO,acyl}$)
	2000 (vs)		1233 (s), 1175 (s), 1127 (s) (ν_{C-F})
$[(DIARS)Fe(CO)_3(C(O)CF_3)]^+ClO_4^-$	2105 (w)[c]	2116 (m)	1665 (s) ($\nu_{CO,acyl}$)
	2057 (sh)	2155 (vs)	1651 (sh) ($\nu_{CO,acyl}$)
	2045 (s)	2135 (vs)	1248 (s), 1187 (s), 1130 (s) (ν_{C-F})
			1090 (vs) ($\nu_{ClO_4^-}$)

[a] All complexes showed ligand bands at 434–439, 364–372, and 262–274 cm^{-1} (cf.: Lewis, J.; Nyholm, R. S.; Rodley, G. A. *J. Chem Soc.* 1965, 1483). [b] Cyclohexane solution. [c] CH_2Cl_2 solution. [d] Nujol mull. [e] KI pellet.

Table II. 80-MHz ^{1}H NMR Spectra[a]

no.	compd	solvent	Fe–CH$_3$	As–CH$_3$	–C(O)–CH$_3$	3,4-Ph
1	(DIARS)Fe(CO)$_3$	CD$_2$Cl$_2$		1.56 [s] (12)		7.61 [AA'BB' multiplet] (4)
2c 2d	*cis,cis*-(DIARS)Fe(CO)$_2$AcI	CDCl$_3$		1.54 [s] (3), 1.76 [s] (3), 1.89 [s] (3), 2.09 [s] (3)	3.12 [s] (3)	7.62 [m] (4)
	cis,cis-(DIARS)Fe(CO)$_2$AcI	CDCl$_3$		1.55 [s] (3), 1.59 [s] (3), 1.76 [s] (3), 1.86 [s] (3)	3.01 [s] (3)	7.61 [m]
2a	*cis,trans*-(DIARS)Fe(CO)$_2$AcI	CDCl$_3$		1.64 [s] (6), 1.99 [s] (6)	2.48 [s] (3)	7.67 [m] (4)
3	*fac*-[(DIARS)Fe(CO)$_3$CH$_3$]$^+$BF$_4^-$	CD$_2$Cl$_2$	−0.23 [s] (3)	1.94 [s] (6), 1.99 [s] (6)		7.96 [m] (4)
	mer-[(DIARS)Fe(CO)$_3$CH$_3$]$^+$OSO$_2$F$^-$	CD$_2$Cl$_2$	0.56 [s] (3)	1.97 [s] (6), 2.01 [s] (6)		7.96 [m] (4)
6	*fac*-[(DIARS)Fe(CO)$_3$Ac]$^+$BF$_4^-$	CDCl$_3$		1.94 [s] (6), 2.00 [s] (6)	2.67 [s] (3)	7.87 [m] (4)
4c or 4d	*cis,cis*-(DIARS)Fe(CO)$_2$(C(O)CF$_3$)I[b]	CDCl$_3$		1.65 [s] (3), 1.76 [s] (3), 2.02 [s] (3), 2.19 [s] (3)		7.64 [m] (4)
4a	*cis,trans*-(DIARS)Fe(CO)$_2$(C(O)CF$_3$)I[c]	CDCl$_3$		1.29 [s] (6), 2.08 [s] (6)		7.70 [m] (4)
5	*mer*-[(DIARS)Fe(CO)$_3$C(O)CF$_3$]$^+$ClO$_4^-$ [d]	CD$_2$Cl$_2$		2.04 [s] (6), 2.08 [s] (6)		7.83 [m] (4)

[a] Chemical shifts reported in ppm relative to internal Me$_4$Si; s = singlet, m = multiplet. Relative intensity is given in parentheses. [b] ^{19}F NMR: 33.64 (s) relative to internal CFCl$_3$; CDCl$_3$ solution. [c] ^{19}F NMR: 34.40 (s) relative to internal CFCl$_3$; CDCl$_3$ solution. [d] ^{19}F NMR: 52.54 (s) relative to internal CFCl$_3$; CD$_2$Cl$_2$ solution.

Table III. 20.1-MHz ^{13}C NMR Spectra[a]

no.	compd	solvent	Fe–CH$_3$	As–CH$_3$	–C(O)–*C*–		Fe–C≡O	–*C*(O)–C–
2c or 2d	*cis,cis*-(DIARS)Fe(CO)$_2$AcI	CDCl$_3$[c]		11.97 12.69 13.65 13.89	53.26	$\left.\begin{matrix}130.56\\130.32\end{matrix}\right\}(C_2, C_5)$ 131.11 (C$_3$, C$_4$) $\left.\begin{matrix}141.65\\141.81\end{matrix}\right\}(C_1, C_6)$	214.24 214.24	258.66
2a	*cis,trans*-(DIARS)Fe(CO)$_2$AcI	CDCl$_3$		12.62 16.05	50.86	130.16 (C$_2$, C$_5$) 131.96 (C$_3$, C$_4$) 139.42 (C$_1$, C$_6$)	214.72	266.46
3	*fac*-[(DIARS)Fe(CO)$_3$CH$_3$]$^+$BF$_4^-$	CD$_2$Cl$_2$	−11.88	9.49 17.56		131.54 133.77 136.59 (C$_1$, C$_6$)	202.06 (trans, CH$_3$) 207.70 (cis, CH$_3$)	
6	*fac*-[(DIARS)Fe(CO)$_3$Ac]$^+$BF$_4^-$	CDCl$_3$		12.91 15.64	51.37	130.9 133.25 135.90	198.90 (trans, Ac) 205.60 (cis, Ac)	250.61
4c or 4d	*cis,cis*-(DIARS)Fe(CO)$_2$(C(O)CF$_3$)I	CDCl$_3$		12.59 12.98 13.67 14.35	115.75[e]	$\left.\begin{matrix}130.24\\130.63\end{matrix}\right\}(C_2, C_5)$ 164.54 (C$_3$, C$_4$) $\left.\begin{matrix}140.72\\140.91\end{matrix}\right\}(C_1, C_6)$	212.11[d] 212.85	*d* 249.36[f]
4a	*cis,trans*-(DIARS)Fe(CO)$_2$(C(O)CF$_3$)I	CDCl$_3$		11.70 14.77	112.95[e]	129.26 130.88 138.34 (C$_1$, C$_6$)	211.42	256.67[f]
5	[(DIARS)Fe(CO)$_3$(C(O)CF$_3$)]$^+$ClO$_4^-$	acetone-*d*$_6$		13.85 14.27	*b*	132.06 (C$_3$, C$_4$) $\left.\begin{matrix}133.77\\133.93\end{matrix}\right\}(C_2, C_5)$ $\left.\begin{matrix}138.21\\138.90\end{matrix}\right\}(C_1, C_6)$	*b*	*b*

[a] Chemical shifts reported in ppm relative to internal Me$_4$Si, T = 308 K. [b] Signal too weak to be observed. [c] At 263 K. [d] At 62.83 MHz. [e] $J(^{13}C^{19}F)$ = 302.7 Hz. [f] $J(^{13}C^{19}F)$ = 31.7 Hz.

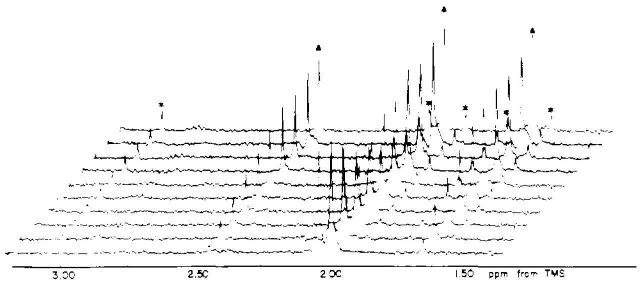


Figure 3. Sequential (500-s interval) ^{1}H NMR spectra of I$^-$-promoted carbonyl "insertion" of *fac*-**3** in methanol-*d*$_4$ at 273 K; [I$^-$] >> [**3**]: * = cis,cis; ▲ = cis,trans.

Table IV. Kinetic Products of Insertion at 273 K

fac-[(DIARS)Fe(CO)$_3$CH$_3$]$^+$ + X$^-$ → (DIARS)Fe(CO)$_2$(C(O)CH$_3$)X

		relative product distribution[a]			
X$^-$	solvent	cis,trans[b]	trans,cis[b]	cis,cis or cis,cis[b]	[X$^-$],[c] mol dm^{-3}
I$^-$ [d]	methanol-*d*$_4$	4.4	. . .	1	0.2–1
Br$^-$		2.1	. . .	1	0.14–0.23
Cl$^-$		1.1	. . .	1	
NCS$^-$		2.4	. . .	1	0.2
I$^-$	acetone-*d*$_6$	<0.5	0.4	1	0.2–0.5
NCS$^-$		0.52	. . .	1	
I$^-$	CD$_2$Cl$_2$[e]	0.05	. . .	1	≃0.04

[a] Product ratios ±5% (estimated) were constant within experimental error from 10 to 100% reaction. [b] Cf. structures **2a–d**. [c] Reactions run under pseudo-first-order conditions for X$^-$ ([X$^-$] ≫ [**3**]. [d] Either **3**-BF$_4^-$ or **3**-ClO$_4^-$ salts were used with no effect on product ratios. [e] In the presence of dibenzo-18-crown-6.

obtained with other halides and in other solvents are presented in Table IV.

Discussion

Oxidative Addition/Insertion Reactions. A number of mechanistic possiblities arise for the facile reactions of CH$_3$I with the coordinatively saturated d^8 complex **1** to give the acyl **2** (Scheme II). Initial oxidative addition could occur with expulsion of a carbon monoxide ligand (i) to give the d^6 six-coordinate iodoalkyl complex **7**. In this case oxidative addition would presumably occur on a coordinatively unsaturated d^8 fragment produced by loss of CO.[27] That such an event is not unlikely is evidenced by the lability of **1**, which spontaneously loses CO even in the solid state[28] and must be stored under a CO pressure or at very low temperature (cf. Experimental Section).

A second alternative (ii) involves nucleophilic displacement (S_N2) of I^- on CH_3I by **1** to produce the cationic alkyl **8**, which subsequently undergoes iodide-promoted migratory insertion. A last possibility (iii) involves a concerted oxidative addition/insertion, which we consider unlikely since it requires a 20-e transition state.

Our evidence strongly favors path ii. First, oxidative addition of CH_3I to **1** in a N_2-purged reactor, which would remove any *free* CO, still produced quantitative yields of the iodoacetyl-inserted product **2** (cf. Experimental Section). Second, the proposed intermediate **8** can be prepared via two independent routes and characterized (cf. Scheme I) when iodide in CH_3I is exchanged for a nonnucleophilic counterion (BF_4^-, PF_6^-, ClO_4^-, OSO_2F^-). Quantitative yields of *cis,cis*-**2** identical with that formed by oxidative addition result when the isolated intermediate is treated with LiI in low dielectric media (CH_2Cl_2) with use of a crown ether to solubilize the halide. Finally, although low-temperature (195 K) additon of CH_3I to **1** did not reveal an ^1H NMR observable intermediate, the oxidative addition of $CF_3C(O)I$ gave a white precipitate, which was characterized and assigned the structure **5**. In this case at least nucleophilic attack at carbon with displacement of I^- is evident.

Treatment of **1** with the more electrophilic CF_3I gives an extremely facile reaction. Condensation of CF_3I onto solid **1** at −78 °C results in an essentially instantaneous reaction as evidenced by the development of a deep red coloration. The analogous reaction with CH_3I is comparatively slow since the typically red color characteristic of Fe–I develops only relatively slowly at 0 °C. Although we have not investigated this aspect in detail, we presume that the CF_3I reaction also follows path ii. Of greatest interest in the perfluoroalkyl case is the iodide-promoted insertion step. Both experimental[2,23-25,29] and theoretical[22] evidence shows that strongly electron-withdrawing alkyls are less prone to undergo carbonyl migratory insertion presumably as a result of the strengthening of the metal–carbon σ bond.

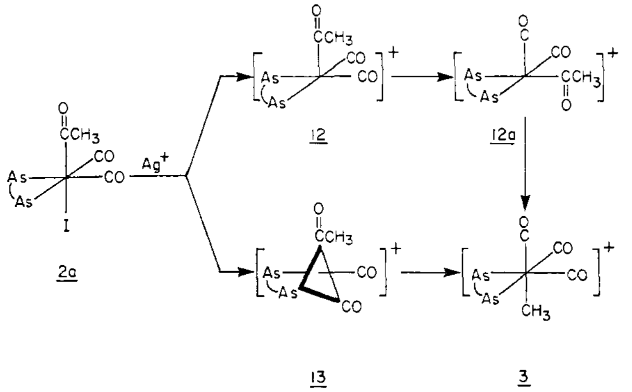
Comparison of reaction of CF_3I with the diarsine complex **1** and the parent $Fe(CO)_5$ reveals a striking difference in reactivity. Thus, on the assumption that both reactions proceed via initial nucleophilic attack at carbon with concomitant displacement of iodide, it is apparent that **9** *inserts* while **10** *substitutes*[25] CO when iodide enters the coordination sphere.

$$\underset{\mathbf{9}}{[(\mathrm{DIARS})\mathrm{Fe(CO)_3CF_3}]^+\mathrm{I}^-} \xrightarrow{273\ \mathrm{K}} \underset{\mathbf{4}}{(\mathrm{DIARS})\mathrm{Fe(CO)_2(C(O)CF_3)I}}$$

$$\underset{\mathbf{10}}{[\mathrm{Fe(CO)_5CF_3}]^+\mathrm{I}^-} \xrightarrow{340\ \mathrm{K}} \underset{\mathbf{11}}{\mathrm{Fe(CO)_4(CF_3)I}} + \mathrm{CO}$$

It is difficult to rationalize the facile iodide-promoted migratory insertion of the Fe–R_f derivative **9**. This is especially true when one considers the results of Hoffmann,[22] which suggest that poorer π acceptors than CO will hinder acyl formation when present in the reaction plane.

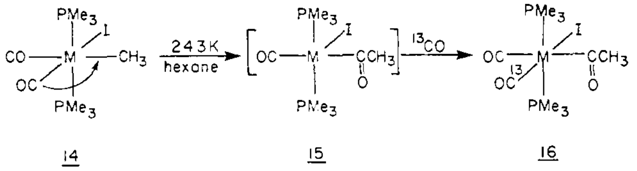
Scheme III



Ag+-Promoted CO Extrusion. As no evidence was found to support the formation of an η^2-acyl[30] intermediate in the Ag^+-induced halide abstractions of the isomeric iodoacyls **2** to provide *fac*-**3**, we assume the intermediacy of a coordinatively unsaturated five-coordinate species. The question of geometry of such an intermediate is difficult to answer for the d^6 case. Evidence favoring a trigonal bipyramid (tbp) or a square-based pyramid (sp) has been presented when five-coordinate structures are postulated both as intermediates and as stable entities.[22,31-34] However, the energy difference between the alternatives cannot be large, and generally speaking the potential energy surface encorporating both extreme geometries is fairly flat so that stereochemical lability is frequently observed.

The most revealing case considered in this paper is the conversion of *cis,trans*-**2** into *fac*-**3**. Scheme III shows the reaction path operating through the extreme sp intermediate, formed by loss of I^- without further rearrangement, and the tbp intermediate, which requires movement of As and CO towards the incipient vacant site. Subsequent rearrangement of the 16-e intermediate via alkyl, CO or a combination of alkyl and CO migration (the microscopic reverse of CO "insertion") leads to the observed alkyl.

Methyl migration[1,2,35] to give a static[36] square-pyramidal (sp) 16-e intermediate has been convincingly demonstrated as the mechanism of "CO insertion" and decarbonylation for Mn(I). However Pankowski[37] has recently reinterpreted earlier evidence[12] to suggest that CO migration is involved in the stereospecific ^{13}CO-promoted conversion of **14** to the acyl **16** via the static sp intermediate **15**.



M = Fe, Ru

Clearly, the initial sp intermediate of Scheme III lacks a vacant site cis to acyl and must rearrange before the alkyl can form. Migration of alkyl to the cis site on **12a** stereospecifically

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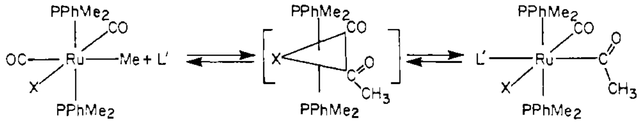
produces *fac*-**3**. In spite of the general preference of π acceptors for the basal site,[32] even a small concentration of **12a** will provide **3**. We also note here that **16** may be obtained from **14** via the more conventional methyl migration route *provided* that the sp intermediate is stereochemically labile.[22]

Alternatively the reaction can proceed through a trigonal-bipyramidal (tbp) intermediate (Scheme III). If acyl is equatorial, the question of alkyl or CO migration obviously does not apply since some movement of *both* groups is likely. Intermediate **13** can conceivably lead to *fac* or *mer* products depending on whether movement of $-CH_3$ is toward or away from the equatorial As. Mawby has recently presented strong evidence[17] derived from the stereochemistry of Lewis base induced insertion reactions on Ru(II) that supports a tbp intermediate. Unless we assume that the anticipated greater thermodynamic stability of 18-e *fac* complexes compared to their *mer* isomers[38] leads to a significantly lower energy barrier for the formation of *fac*-**3**, it is difficult to reconcile the stereospecificity with which **13** proceeds along the reaction coordinate. The possibility of rapid *mer*-**3** $\rightarrow$ *fac*-**3** isomerization is ruled out by the observation that *fac*/*mer* mixtures of **3** prepared by oxidative addition of CH_3OSO_2F to **1** are geometrically stable in solution.

Halide-Promoted Migratory Insertion Reactions. Although we cannot rule out the possibility of a second-order (first order in **3** and halide) or a solvent-assisted[1] reaction at this time,[39] halide-promoted migratory insertion can be considered to occur via the reverse of Scheme III. Many kinetic studies of Mn(I) systems have in fact found that the insertion rate is independent of incoming ligand and proceeds via a rate-determining formation of a coordinatively unsaturated 16-e acyl. Theoretical studies agree and show that interaction of nucleophile and OC–M–R substrate prior to acyl formation is in fact destabilizing.[22]

It is notable that the stereochemistry of the CO migratory insertions studied in this paper is strongly solvent and ligand dependent (Table IV). Thus far *all* insertions of Mn(I) have given products where the incoming ligand and acyl are mutually cis in agreement with a rigid sp intermediate formed by alkyl migration. Ru(II)[17] and Ir(III)[40] as well as the Fe(II) complexes studied in this paper appear to be quite different in this respect giving kinetic products with acyl trans to the incoming ligand. In the case of Ru(II) a tbp intermediate is assumed. Trans geometry in the acyl kinetic product **19** results from preferential attack trans to acyl. It should be pointed out that the mechanism described above may not be general since complex **14** (M = Ru) is reported to give a kinetic product **16** with cis L–M–C(O)CH_3 geometry.[37]



17 18 19

L′ = CO, PPhMe2

It is premature to further speculate on the mechanism of the halide-promoted insertions at this point, but it is apparent that attack of iodide in the equatorial plane of **13** can give three (**2a**, **2c**, and **2d**) of the four possible acetyl iodo isomers described in this study.

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Registry No. **1**, 56760-75-9; **2a**, 78764-22-4; **2c**, 78821-61-1; **2d**, 78821-62-2; *fac*-**3**, BF_4^- salt, 78764-24-6; *fac*-**3**, PF_6^- salt, 78764-25-7; *fac*-**3**, OSO_2F^- salt, 78764-26-8; *mer*-**3**, OSO_2F^- salt, 78821-64-4; *mer*-**3**, PF_6^- salt, 78821-65-5; **4a**, 78822-13-6; **4c** or **4d**, 78764-27-9; *mer*-**5**, I^- salt, 78764-28-0; *mer*-**5**, ClO_4^- salt, 78764-30-4; *fac*-**6**, BF_4^- salt, 78764-32-6; $Fe(CO)_5$, 13463-40-6; CH_3I, 74-88-4; CH_3OSO_2F, 421-20-5; CF_3I, 2314-97-8; $CF_3C(O)I$, 354-36-9; Br^-, 24959-67-9; Cl^-, 16887-00-6; NCS^-, 302-04-5.

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Contribution from the Department of Chemistry,
Bowling Green State University, Bowling Green, Ohio 43402

Chromium(III) Complexes Containing Macrocyclic Ligands

R. G. SWISHER, G. A. BROWN, R. C. SMIERCIAK, and E. L. BLINN*

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Five chromium(III) compounds, *cis*-[Cr([12]aneN_4)Cl_2]Cl·H_2O, *cis*-[Cr([12]aneN_4)$(NCS)_2$]NCS·$2H_2O$, *cis*- and *trans*-[Cr(1,4,7,11[14]aneN_4)Cl_2]Cl, and *trans*-[Cr([15]aneN_4)Cl_2]Cl·$2H_2O$ ([12]aneN_4 = 1,4,7,10-tetraazacyclododecane, 1,4,7,11[14]aneN_4 = 1,4,7,11-tetraazacyclotetradecane, [15]aneN_4 = 1,4,8,12-tetraazacyclopentadecane), were synthesized and characterized. For the chromium(III) complexes containing the 12-membered macrocycle, only the cis isomer was isolated, while for the chromium(III) complex containing the 15-membered ring, only the trans isomer was isolated. The chromium(III) complexes containing the unsymmetrical 14-membered ring, 1,4,7,11[14]aneN_4, were isolated in equal amounts of cis and trans forms. The ranking of the Dq^{xy} for various trans complexes is 1,4,8,11[14]aneN_4 > 1,4,7,10[14]aneN_4 > [15]aneN_4. [12]aneN_4 appears to be a relatively weak-field ligand. Conductivity and spectral data indicate that the first- and second-aquation rates for [Cr([12]aneN_4)Cl_2]Cl·H_2O are unusually fast.

Introduction

We have prepared cobalt(II), nickel(II), and copper(II) complexes that contain strained metal-to-nitrogen bonds.[1-7] Ligands include the 12-membered 1,4,7,10-tetraazacyclododecane ([12]aneN_4)[1-3] and 1,4,7,10-tetrabenzyl-1,4,7,10-tet-

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