Stereospecific, Sequential Carbonyl Insertion and Extrusion Reactions. Preparation and Characterization of $[Fe(diars)(L_\alpha)(CO)_2(CH_3)]^+$ and $[Fe(diars)(L_\alpha)(L_\beta)(CO)(C(O)CH_3)]^+$ Complexes

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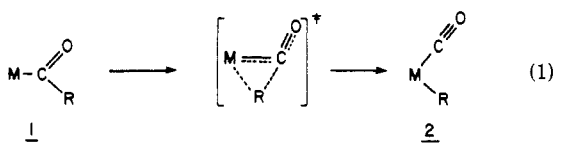
A series of σ-alkyl octahedral Fe(II) complexes, **9**, of the form $[Fe(diars)(CO)_2(L_\alpha)(CH_3)]^+$ (diars = *o*-phenylenebis(dimethylarsine)) was stereospecifically prepared by thermal extrusion of carbon monoxide from the corresponding acyl derivatives. Migratory carbon monoxide insertion of **9** in the presence of a second phosphorus ligand, L_β, afforded the isosteric acyl complexes $[Fe(diars)(CO)(L_\alpha)(L_\beta)(C(O)CH_3)]^+$ (**15**). The strong trans-labilizing effect of σ-acyl is proposed to account for the stereochemistry observed. Equilibrium constants for **9** ⇌ **15** are a function of the total steric demand of L_α and L_β. Diastereotopic phosphine substituents (L_α or L_β = L = PR'_2R'') were detected with use of ^1H NMR spectroscopy, which indicates that the chiral Fe atom is configurationally stable on the 80- and 300-MHz ^1H NMR time scales.

Introduction

Photochemical-, thermal, or reagent-induced extrusion of carbon monoxide from η^1-acyl complexes according to eq 1 represents a general synthetic entry for the preparation of σ-alkyl complexes. Carbon monoxide extrusion



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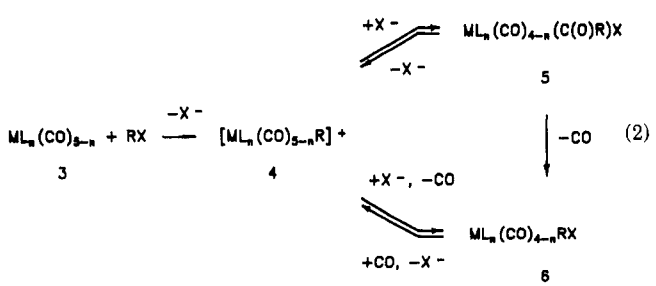
is also of importance in that it represents the critical step in the application of Wilkinson's catalyst as a decarbonylation agent for the stoichiometric synthesis of organic aldehydes and acyl halides.[2] Use of η^1-acyl complexes as σ-alkyl synthons is especially appropriate in cases where direct preparation by oxidative addition or substitution of the requisite alkyl derivative fails,[3-5] R is chiral,[6] or the appropriate substrate complex is unavailable.[7]

Oxidative addition of alkyl halides to coordinatively saturated, phosphine-substituted d^8 MD_5 complexes **3** (M = Fe, Ru, Os) is a well-established route for the preparation of octahedral alkyl complexes (cf. eq 2). For n = 1 the neutral alkyl **6** is obtained[8] directly. In the absence of a labile ligand[9-12] the frequently unobserved intermediate[13] **4** undergoes preferential CO insertion for n = 2 to form the neutral η^1-acyl **5**,[14-16] which can be converted to an alkyl complex via subsequent CO extrusion. Further flexibility in the synthetic applications of eq 2 is provided by the ability to divert the coordinatively saturated acyl **5** (X = halide) to produce either alkyl **4** or **6** depending on whether X or CO is lost. Decarbonylation[17,18] agents or halide "sinks" have been used to effect selective[7,16,19,20] CO extrusions.



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Although the transition-metal basicity of **3** parallels the degree of phosphine substitution n, extension of the direct synthesis of the alkyl series **4**, **6** to $n \geq 3$ has seen only limited success. Karsch[21] and Muetterties[22] report that the isoleptic n = 5 (L = $P(CH_3)_3$, $P(OCH_3)_3$) substrates **3** form the corresponding cationic alkyls **4**. Only one example of the oxidative additon **3** → **4** has been reported for n = 4.[23] Direct synthesis of the carbonyl-substituted alkyls **4** and **6** (n = 3) via eq (2) has, to our knowledge, not been accomplished presumably due to synthetic difficulties associated with the preparation of the appropriate parent d^8 complexes **3**.[24,25]

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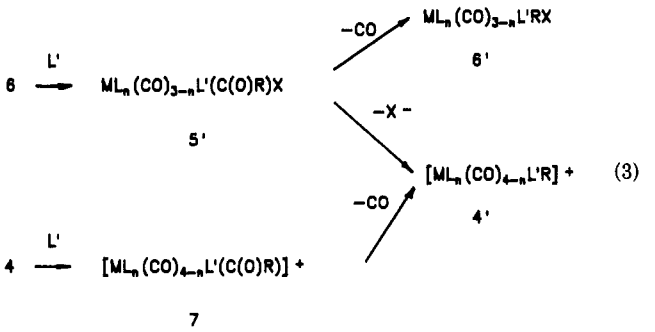
Table I. Physical Properties of $[Fe(diars)(CO)_2(L_\alpha)(CH_3)]^+BF_4^-$

L_α, compd	formula	anal. calcd (found)	mp, °C[a]	reacn temp, °C[b]	time, h[b]	ν_{CO}, cm^{-1} [c]	FAB MS, m/e (%)[d]
$P(OCH_3)_3$, **9a**	$C_{16}H_{28}As_2BF_4FeO_5P$	C, 30.80; H, 4.52 (C, 30.51; H, 4.46)	132	110	12	2027.0 1974.3	537 (100) 481 (38.9) 466 (35.1)
$PPh(OCH_3)_2$, **9b**	$C_{21}H_{30}As_2BF_4FeO_4P$	C, 37.65; H, 4.51 (C, 37.64;, H, 4.35)	156	100	72	2028.2 1975.8	583 (29.1) 527 (40.2) 512 (39.2)
$PPh_2(OCH_3)$, **9c**	$C_{26}H_{32}As_2BF_4FeO_3P$	C, 39.54; H, 4.74 (C, 39.47; H, 4.88)	148	100	24	2021.9 1970.4	629 (70.4) 573 (46.3) 558 (23.8)
$P(CH_3)_3$, **9d**	$C_{16}H_{28}As_2BF_4FeO_2P$	C, 43.61; H, 4.50 (C, 43.22; H, 4.44)	163	150	4	2018.8 1964.9	489 (100) 433 (65.8) 418 (35.0)
$PPh(CH_3)_2$, **9e**	$C_{21}H_{30}As_2BF_4FeO_2P$	C, 33.37; H, 4.90 (C, 33.39; H, 4.76)	170	100	24	2016.6 1964.2	551 (81.0) 495 (62.8) 480 (42.9)
PPh_2CH_3, **9f**	$C_{26}H_{32}As_2BF_4FeO_2P$	C, 44.61; H, 4.61 (C, 44.20; H, 4.51)	190	100	20	2016.9 1964	613 (23.4) 557 (8.5) 542 (7.6)
ETPB, **9g**	$C_{19}H_{30}As_2BF_4FeO_5P$	C, 34.48; H, 4.57 (C, 34.61; H, 4.56)	110	100	24	2042.3 1990.4	575 (84.2) 519 (44.9) 504 (49.9)

[a] Sealed tube, N_2 atmosphere. [b] Solid-state conditions. [c] In CH_2Cl_2, ±1 cm^{-1}.[29] All compounds showed strong ν_{BF_4} bands at 1050–1060 cm^{-1}. [d] M^+, $M^+ - 2CO$, $M^+ - (2CO + CH_3)$; 100% = m/e 357 ($M^+ - L - 2CO$) unless otherwise indicated.

The substituted alkyl derivatives **4** and **6** ($n = 3$) are potentially accessible via alkylation[26,27] of the corresponding neutral halide or from a sequence of coupled phosphine-promoted CO insertion/extrusion reactions represented by eq 3. The latter strategy has been successfully applied in a variety of cases.[7,28-30] Clearly, the formation of an acyl intermediate is not required since direct substitution of X^- or CO affords the identical product. Mechanistic results are mixed in this regard, and exclusive direct substitution,[31] intermediate acyl formation,[7,8,32,33] or mixed reaction pathways[16,28] appear to operate. Exclusive substitution[23] also occurs in cases where no *cis*-(alkyl, CO) pairs are present as in *trans*-$[Fe(P(CH_3)_3)_4(CO)(CH_3)]^+$.



The fact that thermal decarbonylation of $Mn(CO)_5(C^{13}(O)CH_3)$ gives exclusively *cis*-$Mn(CO)_4(C^{13}O)(CH_3)$[34,35] provides compelling evidence that carbonyl extrusion *can* proceed stereoselectively in d^6-octahedral systems. Other examples are also well established for substituted Mn(I),[36] Fe(II),[7,30,37-39] and Ru(II)[7,37] derivatives. Preparative applications of the reported stereoselectivity are infrequent since the stereochemical outcome in many cases is mediated by competing trans effects of the ligand sphere. Further complications result from the forcing conditions often required for preparative carbon monoxide extrusions, which result in thermodynamic rather than kinetic control of product stereochemistry.

In this paper we report the extension of the series of octahedral Fe(II) alkyl complexes[29,30] **4** to $n = 3$ via the stereospecific, sequential carbonyl insertion/extrusion sequence of eq 3, in which the number of phosphine ligands increases by one for each cycle. The reaction involves (vide infra) the carbonyl insertion/extrusion sequence **4** → **7** → **4'** rather than the direct substitution **4** → **4'**.

Results and Discussion

Synthesis and Characterization of the $[Fe(diars)(CO)_2(L_\alpha)(CH_3)]^+$ Complexes (9). The previously described[33,40] *cis,trans*-$[Fe(diars)(CO)_2(L_\alpha)(C(O)CH_3)]^+$ acyl complexes[41] (**8a–g**) are thermally labile. In contrast to the results found for the neutral ruthenium acyls **5** (M

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(41) Stereodescriptors for the derivatives $Fe(diars)(CO)_2AB$ indicate the relative position of the ligand pairs CO, CO and A, B, respectively (A = L_α, B = R for **8a–g**). Thus, the cis,cis isomer has the stereochemistry **11** or **13** while the cis,trans isomer is specified as **12**.

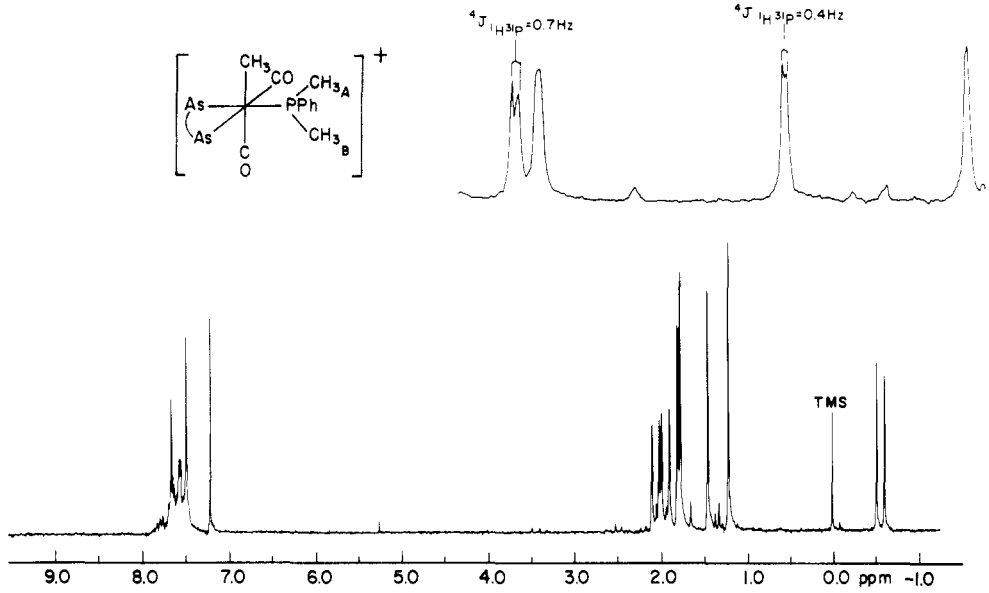

Figure 1. 80-MHz ^1H NMR spectrum of **9e** in $CDCl_3$. The inset shows an expansion of the 1.2–1.9 ppm region.

= Ru, n = 3), which dissociate phosphine rapidly on the NMR time scale,[32] the most labile ligand in the cationic iron complexes **7** (n = 3) under the conditions of this study appears to be carbon monoxide. Thus, heating solid **8a–g** at 100–150 °C under dynamic vacuum for several hours results in clean decarbonylation to form the corresponding cationic methyl derivatives **9a–g** (cf. eq 4a). This difference is apparently not related to the presence of the chelating ligand in the iron case, since $[Fe(P(CH_3)_3)_2(CO)_2L(C(O)CH_3)]^+$ (L = phosphine) is also reported to show facile decarbonylation.[28] The extent of reaction was followed by monitoring the characteristic[33] acyl stretching frequency at ca. 1650 cm^{-1}. Table I summarizes the reaction times and temperatures used to prepare the complexes. Formulation of **9** as the simple decarbonylation product of **8** is supported by analytical and mass spectroscopic data (cf. Table I).

$$[Fe(diars)(CO)_2L_\alpha(C(O)CH_3)]^+ \xrightarrow{\text{solid}} [Fe(diars)(CO)_2L_\alpha CH_3]^+ \quad (4a)$$

8a–g → 9a–g

$$[Fe(diars)(CO)_2L_\alpha(C(O)CH_3)]^+ \xrightarrow{\text{solution}} 9a\text{–}g + fac\text{-}[Fe(diars)(CO)_3CH_3]^+ \quad (4b)$$

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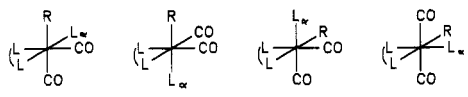
a, $P(OCH_3)_3$; **b**, $PhP(OCH_3)_2$; **c**, $Ph_2P(OCH_3)$; **d**, $P(CH_3)_3$; **e**, $PhP(CH_3)_2$; **f**, Ph_2PCH_3; **g**, ETPB

In most cases the conversion is quantitative and the off-white to yellow decarbonylation products are readily purified by slow diffusion of ether onto methylene chloride solutions of the crude product. The alkyl complexes **9** are air stable in the solid state but decompose slowly in solution unless an inert atmosphere is maintained.

Decarbonylation may also be carried out in solution by heating in toluene/methylene chloride mixtures at 70 °C. Solution decarbonylation proceeds more slowly to give the same alkyl product, **9**, contaminated with a small amount (5–20%) of *fac*-$[Fe(diars)(CO)_3(CH_3)]^+$ (**10**) formed by phosphine dissociation with concomitant CO extrusion.[33] Formation of **10** during solution decarbonylation can be blocked by adding the appropriate phosphine ligand L_α; however, additional side reactions due to sequential CO insertions are then encountered.

Decarbonylation of the *cis,trans*-$[Fe(diars)(CO)_2(L_\alpha)(C(O)CH_3)]$ acyl complexes proceeds stereospecifically under conditions favoring kinetic control. ^1H NMR analysis of incompletely decarbonylated samples established *cis,cis*-$[Fe(diars)(CO)_2L(CH_3)]^+$ (stereochemistry **11**) as the kinetic product of thermal decarbonylation.[42] Isomerization occurs during the latter stages of the reaction or upon prolonged standing. Acyl **8d** (L = $P(CH_3)_3$), which was available only as a 1:2 mixture of the cis,trans (stereochemistry **12**, R = $C(O)CH_3$, L_α = $P(CH_3)_3$) and cis,cis (stereochemistry **11** or **13**, R = $C(O)CH_3$) isomers,[33] proved considerably more resistant to decarbonylation; however, ^1H NMR material balance measurements indicated that CO extrusion remained stereospecific. Thus, solid-state decarbonylation of isomeric **8d** at 110 °C in vacuo afforded quantitative conversion of the cis,trans-acyl isomer (stereochemistry **12**, R = $C(O)CH_3$, L_α = $P(CH_3)_3$) to the corresponding alkyl while, under identical conditions, the cis,cis-alkyl isomer remained completely unreactive. Hence, the relative ease of CO extrusion is **12** > **11** or **13**. Of the oxidative decarbonylation agents $(CH_3)_3NO$[17,18] and C_6H_5IO,[43] only the former proved suitable. In the case of **8a**, decarbonylations proceeded smoothly at room temperature in the presence of $(CH_3)_3NO$; however, a more tedious workup coupled with the lack of any measurable improvement in yield mitigated against its broader use.

Chart I



11 12 13 14

Structure and Stereochemistry of $[Fe(diars)(CO)_2(L_\alpha)(CH_3)]^+$ (9a–g). Both ^1H and ^{13}C NMR spectroscopy confirmed the formation of an $Fe–CH_3$ group (cf. Tables II and III). A high-field doublet ($\delta(CH_3)$ = ca. –0.5 ppm, $^3J_{PH}$ = ca. 7 Hz; $\delta(CH_3)$ = ca. –10.0 ppm, $^2J_{CP}$ = ca. 15–20 Hz) was unequivocally assigned to the $Fe–CH_3$ moiety. Four geometric isomers, illustrated by structures **11–14** (cf. chart I) for the case under consideration, are possible for octahedral complexes of the general form $[M(L\frown L)ABC_2]$, where $L\frown L$ is a symmetrical bidentate ligand. The cis,cis isomers **11** and **13** are chiral. All of the alkyl

(42) A full mechanistic study of these decarbonylation reactions is underway and will be published elsewhere.

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Table II. $^1H^a$ and $^{31}P^b$ NMR Data for $[Fe(diars)(CO)_2(L_\alpha)(CH_3)]^+BF_4^-$

L_α, compd	$\delta(C_6H_4)$	δ(PPh)	δ(POR)	$\delta(P(CH_3))$	$\delta(As(CH_3))$	$\delta(FeCH_3)$	δ(P)
$P(OCH_3)_3$, **9a**	7.7 (m)		3.88 (d, 11.2)		1.70 1.68 1.77 (d, 1.2) 1.74 (d, 0.7)	−0.56 (d, 6.5)	161.5
$PPh(OCH_3)_2$, **9b**	7.7 (m)	7.7 (m)	3.92 (d, 11.0) 3.99 (d, 11.5)		1.66 1.71 1.75 (d, 0.7) 1.80 (d, 1.0)	−0.64 (d, 6.8)	188.7
$PPh_2(OCH_3)$, **9c**	7.7 (m)	7.6 (m)	3.57 (d, 1.7)		1.65 1.72 1.78 1.86 (d, 0.7)	−0.64 (d, 6.8)	164.1
$P(CH_3)_3$, **9d**[c]	7.8 (m)			1.70 (d, 9.7)	1.73 1.78 (d, 0.4) 1.80 1.82 (d, 0.5)	−0.54 (d, 7.5)	20.0
$PPh(CH_3)_2$, **9e**	7.6 (m)			1.98 (d, 9.5) 2.06 (d, 8.8)	1.23 1.47 1.79 1.82 (d, 0.5)	−0.57 (d, 7.6)	27.1
PPh_2CH_3, **9f**	7.7 (m)	7.7 (m)		2.05 (d, 8.8)	0.90 1.35 1.83 1.90	−0.60 (d, 7.3)	42.4
ETPB, **9g**	7.8 (m)		4.48 (d, 5.0, α) 1.28 (q, −, δ) 0.89 (t, −, γ)		1.75 1.79[d] 1.83 (d, 1.1)	−0.49 (d, 6.5)	155.4

[a] In $CDCl_3$, 80 MHz; chemical shifts are in ppm relative to internal TMS. Multiplicities and J values (in Hz) are given in parentheses. [b] In $CDCl_3$, 32.4 MHz; chemical shifts are in ppm relative to external 85% H_3PO_4. [c] In CD_2Cl_2. [d] Degenerate signal assigned to two $AsCH_3$ groups.

Table III. ^{13}C Data[a] for $[Fe(diars)(CO)_2(L_\alpha)(CH_3)]^+BF_4^-$

L_α, compd	δ(CO)	$\delta(C_6H_4)$[e]	δ(POR)	$\delta(PCH_3)$	$\delta(AsCH_3)$	$\delta(FeCH_3)$
$P(OCH_3)_3$, **9a**[b]	212.6 (d, 35.3) 206.1 (d, 25.0)	137.3, 138.8 (d, 4.5) 130.79 131.04	55.1 (d, 8.8) (d, 8.8)		15.7 15.4 9.2 9.0	−12.6 (d, 22.1)
$PPh(OCH_3)_2$, **9b**	216.7 (d, 31.8) 206.3 (d, 21.8)	137.1, 138.1 (d, 4.9) 130.8 132.6	56.8 (d, 12.6) 56.45 (d, 10.8)		15.6 15.3 9.0 8.1	−11.0 (d, 18.6)
$PPh_2(OCH_3)$, **9c**	213.5 (d, 26.7) 207.6 (d, 17.9)	136.8, 139.0 (d, 4.9) 130.8[d] 132.7[d]	57.0 (d, 13.0)		8.6 8.4 15.1[c]	−7.7 (d, 16.3)
$P(CH_3)_3$, **9d**	214.0 (d, 25.8) 206.6 (d, 18.9)	136.8, 139.0 (d, 5.2) 132.7, 132.4 130.6		18.8 (d, 31.0)	8.6[c] 15.5 15.2	−11.6
$PPh(CH_3)_2$, **9e**	213.8 (d, 26.0) 206.9 (d, 16.3)	136.7, 139.3 (d, 65) 130.6 130.0		19.3 15.4 (d, 34.2)	7.0 8.7 14.6 15.5	−10.8 (d, 14.7)
PPh_2CH_3, **9f**	214.3 (d, 27.5) 208.1 (d, 17.2)	136.2, 139.2 131.1[d] 130.7[d]		16.0 (d, 46.4)	6.2 15.5[c] 18.6	−9.1 (d, 13.8)
ETPB, **9g**	210.4 (d, 36.1) 203.8 (d, 24.1)	136.8, 138.1 (d, 4)	76.2 (d, 6.9, α) 35.5 (d, 32.7, β) 22.4 (−, −, γ) 6.6 (−, −, δ)		8.4 8.9 15.3 14.9	−14.3 (d, 22.4)

[a] In $CDCl_3$, 20.1 MHz; chemical shifts are in ppm relative to internal TMS. Multiplicities and J values (in Hz) are given in parentheses. [b] In CD_2Cl_2, 75.5 MHz. [c] Degenerate signal assigned to two $AsCH_3$ groups. [d] Assignment ambiguous. [e] Ipso, ortho, and meta signals are given on separate lines.

complexes **9** examined in this study showed two IR-active ν_{CO} bands (cf. Table I) consistent with stereochemistry **11**, **12**, or **13**. In all cases but **9g**, ^1H NMR spectra showed four nonisochronous arsine methyl groups (cf. Table I and Figure 1) consistent only with the cis,cis geometry **11** or **13**.

On the basis of spectroscopic evidence alone it is difficult to unequivocally establish which of the two possible cis,cis geometries **11** and **13** is correct. The most valuable evidence is derived from ^{13}C NMR spectra. Two nonisochronous diars σ-C_6H_4 ipso carbon resonances, *one* of which shows a resolvable coupling to ^{31}P, are observed. Although

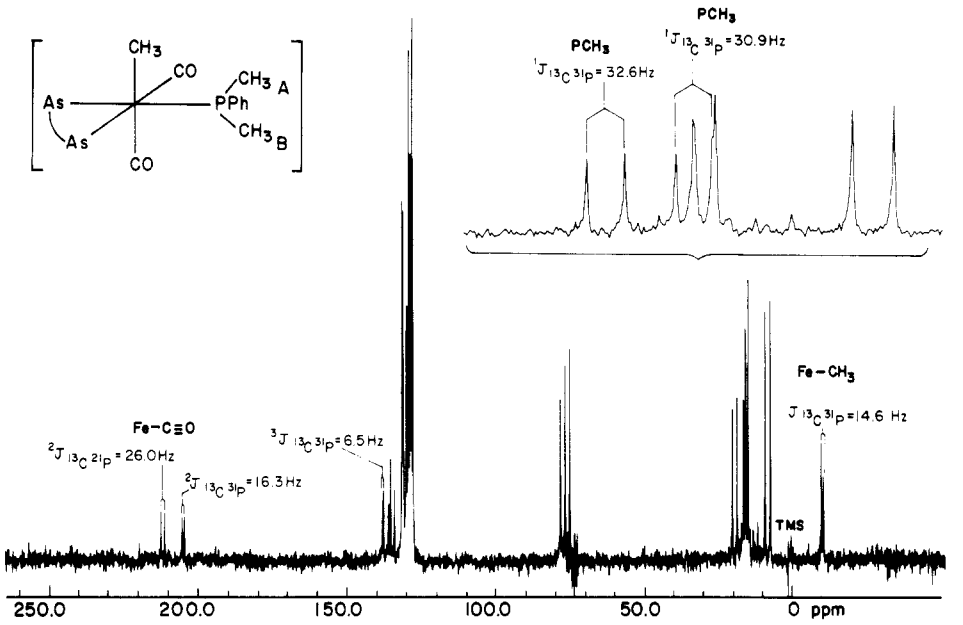

Figure 2. 20.1-MHz $^{13}C\{^1H\}$ NMR spectrum of **9e** in $CDCl_3$.

both cis,cis isomers lack a symmetry plane bisecting the diars ligand and must therefore have nonequivalent C_{ipso}, isomer **11** with a cis and trans P–Fe–As–C link appears more consistent with the phosphorus coupling evidence.

In support of these arguments $^2J_{PC}$ couplings (cf. Table III and Figure 2) for the two nonisochronous carbonyl groups are consistent with a mutual cis geometry as in **11** with respect to the P-donor ligand L_α. The observed $^2J_{PC}$ couplings are substantively different but are less than the range of 39–50 Hz reported for trans $^2J_{PC}$.[44] We assign[45-47] the smaller phosphorus coupling to the carbonyl group trans to the methyl group (larger trans influence) and the larger phosphorus coupling to the carbonyl trans to arsenic (smaller trans influence). Alternatively it might be argued that stereochemistry **13** shows a small phosphorus coupling to one C_{ipso} because of the difference in trans influence of methyl compared to that of carbon monoxide and that different cis and trans $^2J_{PC}$ values follow from geometric considerations. The former argument appears correct since the methyl complex **9b** was shown to have stereochemistry **11** by crystallography.[30]

While the R′ groups in **9** (L = PR'_2R) are enantiotopic for stereochemistry **12** or **14**, they become diastereotopic for the chiral complexes **11** and **13**. Subject to the restriction that Fe retain its stereochemical integrity on the NMR time scale, the R′ groups in **11** and **13** must be nonisochronous. Examination of Tables II and III shows that the $P(OCH_3)_2$ and $P(CH_3)_2$ groups of **9b** and **9e** are indeed nonequivalent (cf. also figures 1 and 2). Distinct signals are resolved at temperatures up to 70 °C in CD_2Cl_2[48] indicating that as found for other related cases,[7] the chiral Fe center is configurationally stable.

Reactions of $[Fe(diars)(CO)_2(L_\alpha)(CH_3)]^+$ (9a–g). The methyl complexes **9** react readily with phosphines in methylene chloride solution at ambient temperature according to eq 5 to afford the bis(phosphine)-substituted acyl complexes **15**. The phosphine-promoted migratory CO insertion of **9** (L_α = phosphine) was considerably more sluggish than that for the parent methyl complex **10**.[29]

$$9a\text{–}g \underset{-L_\beta}{\overset{+L_\beta}{\rightleftharpoons}} [Fe(diars)(CO)L_\alpha L_\beta(C(O)CH_3)]^+ \qquad (5)$$

15 a–g,a; a–g,g

Formulation of the product isolated as the acyl **15** is supported in each case by analytical, IR, and MS data (cf. Table IV). All the acyl products showed a single δ_{CO} absorption at ca. 1960–1990 cm^{-1} with a tendency toward decreasing frequency with increasing σ-donor properties of the phosphine ligands L_α and L_β. The acyl stretching frequency was relatively insensitive to the nature of L_α and L_β. Fast atom bombardment (FAB) mass spectra generally showed a very weak molecular ion; however, prominent fragments corresponding to the even-electron ions $M^+ - L_\alpha$ and $M^+ - L_\beta$ were always present. Characteristic AB ($L_\alpha = L_\beta$) or AX ($L_\alpha \neq L_\beta$) patterns were observed in the $^{31}P\{^1H\}$ NMR spectra of the bis(phosphine)-substituted acyls **15** (cf. Table II).

Equation 5 is reversible, and in most cases a large excess of L_β was required to drive the equilibrium in the direction of the CO-inserted product **15**. Although bis(phosphine)-substituted acyls could be detected by using ^1H NMR or IR spectra in the presence of excess L_β for an extensive range of L_α and L_β, it did not prove possible to isolate and fully characterize all the complexes shown in Table IV. In some cases, particularly those with bulk L_α and/or L_β, isolation of the acyl product **15** was successful only when crystallization was carried out in the presence of excess L_β. The isolable acyls **15** are moderately stable in the solid state and can be dried in vacuo at 40 °C for short periods; however, they are generally unstable with respect to dissociation of L_β in solution.

Although complex mixtures containing several mono- and bis(phosphine) acyl and methyl isomers formed on standing in solution for extended periods, shorter reaction times resulted in stereospecific or highly stereoselective acyl formation. ^1H NMR analyses of the crude reaction mixtures under conditions favoring kinetic control indicated the formation of a single acyl isomer. Reversing the order of introduction of the phosphine ligands L_α and L_β led to the formation of isomeric acyl products. For ex-

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(48) ^1H NMR spectra of **9b** and **9e** in CD_2Cl_2 were examined at elevated temperatures in sealed tubes.

Table IV. Physical Properties and IR and MS Data for [Fe(diars)(CO)(L_α)(L_β)(C(O)CH_3)]$^+BF_4^-$[a]

L_α, L_β; compd	formula	anal. calcd. (found)	mp, °C[b]	ν_{CO}, cm^{-1}[c]	ν_{acyl}, cm^{-1}[c]	FAB MS, m/e (%)[d]
$P(OCH_3)_3$, ETPB; **15ag**	$C_{21}H_{39}As_2BF_4FeO_8P_2$	C, 33.62; H, 5.00 (C, 33.75; H, 5.04)	90	1982	1609	699 (4.0) 671 (20.0) 575 (16.8) 537 (79.7)
$PPh(OCH_3)_2$, ETPB; **15bg**	$C_{27}H_{41}As_2BF_4FeO_7P_2$	C, 39.98; H, 4.97 (C, 39.07; H, 5.27)	73	1980	1601	717 (20.8) 575 (8.8) 583 (65.4)
$PPh_2(OCH_3)$, ETPB; **15cg**	$C_{32}H_{43}As_2BF_4FeO_6P_2$	C, 43.77; H, 4.94 (C, 43.39; H, 5.47)	105	1972	1602	791 (0) 763 (0) 575 (18.1) 629 (27.3)
$P(CH_3)_3$, ETPB; **15dg**	$C_{22}H_{39}As_2BF_4FeO_5P_2$	C, 35.81; H, 5.33 (C, 35.28; H, 5.56)	106	1970	1603	651 (0) 623 (21.2) 575 (10.4) 489 (38.1)
$PPh(CH_3)_2$, ETPB; **15eg**	$C_{27}H_{41}As_2BF_4FeO_5P_2$	C, 40.53; H, 5.17 (C, 39.53; H, 5.27)	102	1968	1605	713 (0.4) 685 (22.0) 575 (14.7) 551 (25.1)
PPh_2CH_3, ETPB; **15fg**	$C_{32}H_{43}As_2BF_4FeO_5P_2$		97	1962	1595	775 (0) 747 (0) 575 (16.6) 613 (25.9)
ETPB, ETPB; **15gg**	$C_{25}H_{41}As_2BF_4FeO_8P_2$	C, 36.44; H, 5.02 (C, 35.28; H, 4.81)	118	1995	1612	737 (0) 709 (12.7) 575 (57.9) 575 (57.9)
$P(OCH_3)_3$, $P(OCH_3)_3$; **15aa**	$C_{19}H_{37}As_2BF_4FeO_8P_2$	C, 30.512; H, 4.99 (C, 30.61; H, 5.14)	132	1968	1595	661 (2.1) 633 (21.2) 537 (60.1) 537 (60.1)
$PPh(OCH_3)_2$, $P(OCH_3)_3$; **15ba**	$C_{24}H_{39}As_2BF_4FeO_7P_2$	C, 36.30; H, 4.95 (C, 36.38; H, 4.94)	132	1978	1603	707 (0) 679 (14.6) 537 (6.9) 583 (78.1)
$PPh_2(OCH_3)$, $P(OCH_3)_3$; **15ca**	$C_{29}H_{41}As_2BF_4FeO_6P_2$	C, 41.46; H, 4.92 (C, 40.95; H, 4.96)	123	1966	1597	753 (0) 725 (0) 537 (7.0) 629 (41.1)
$P(CH_3)_3$, $P(OCH_3)_3$; **15da**	$C_{19}H_{37}As_2BF_4FeO_5P_2$	C, 32.60; H, 5.33 (C, 32.11; H, 5.18)	65	1962	1596	
$PPh(CH_3)_2$, $P(OCH_3)_3$; **15ea**	$C_{24}H_{39}As_2BF_4FeO_5P_2$		82	1967	1599	675 (0) 647 (6.3) 537 (17.8) 551 (60.0)
ETPB, $P(OCH_3)_3$; **15ga**	$C_{22}H_{39}As_2BF_4FeO_8P_2$	C, 33.62; H, 5.00 (C, 32.25; H, 4.55)	90	1989	1607	699 (0.5) 671 (19.4) 537 (12.4) 537 (12.4) 575 (44.5)
PPh_2CH_3, $P(OCH_3)_3$; **15fa**				1954	1597	753 (0) 725 (0) 537 (7.0) 629 (41.1)
ETPB, $PPh(OCH_3)_2$; **15gb**				1990	1606	745 (0) 717 (6.1) 583 (12.5) 575 (37.6)
$P(OCH_3)_3$, $PPh(OCH_3)_2$; **15ab**				1972	1605	707 (0) 679 (6.3) 583 (4.4) 537 (100)
$PPh(OCH_3)_2$, $PPh(OCH_3)_2$; **15bb**				1970	1592	
$P(CH_3)_3$, $PPh(OCH_3)_2$; **15db**				1958	1590	
ETPB, $P(CH_3)_3$; **15gd**				1976	1600	
$P(OCH_3)_3$, $P(CH_3)_3$; **15ad**				1962	1602	

[a] Cf. structure **19**. [b] Sealed tube, N_2 atmosphere. [c] In CH_2Cl_2, ±1 cm^{-1}. All compounds showed strong ν_{BF_4} bands at 1050–1060 cm^{-1}. [d] M^+, $M^+ - CO$, $M^+ - L_\beta$, $M^+ - L_\alpha$; 100% = m/e 357 ($M^+ - L - 2CO$) unless otherwise indicated.

ample phosphine site-exchanged isomers of **15** resulted from the treatment of **9a** with ETPB (**15ag**) and **9g** with $P(OCH_3)_3$ (**15ga**). Similarly, reaction of **9b** with ETPB or $P(OCH_3)_3$ gave exclusively **15bg** and **15ba**, respectively,

Table V. ^1H and ^{31}P NMR Data for [Fe(diars)(CO)(L_α)(L_β)(C(O)CH_3)]$^+BF_4^-$ [a]

L_α, L_β; compd	δ(C_6H_4), δ(PPh)	δ(POR)	δ(PCH_3)	δ($AsCH_3$)	δ(acyl)	δ(P_2),[b] δ(P_1)	other (^1H)
$P(OCH_3)_3$, ETPB; **15ag**	7.7 (m), –	3.92 (d, 10.9) 4.13 (d, 4.7)		1.81 1.75 1.56 1.57	2.48	150.9 (51.1), 161.6 (51.1)	1.21 (q, 7.9) 0.85 (t, 7.9)
$PPh(OCH_3)_2$, ETPB; **15bg**[c]	7.8 (m), 7.8 (m)	4.08 (d, 4.7)		1.53 1.62 1.77 1.83	2.39	150.0 (41.0), 186.6 (41.0)	
$PPh_2(OCH_3)$, ETPB; **15cg**[c]	7.6 (m), 7.6 (m)	3.82 (d, 4.4)		1.82 1.69 1.56	2.12	148.8 (41.0), 159.1 (41.0)	
$P(CH_3)_3$, ETPB; **15dg**[c]	7.8 (m), –	4.14 (d, 4.7)	1.69 (d, 9.1)	1.83 1.61 1.58	2.52	148.6 (37.5), 15.1 (37.5)	
$PPh(CH_3)_2$, ETPB; **15eg**[c]	7.6 (m), 7.6 (m)	4.13 (d, 4.4)	2.08 (d, 9.1) 1.86 (d, 8.2)	1.58 1.54 1.91 1.83	2.16	149.2 (36.0), 24.3 (36.0)	
PPh_2CH_3, ETPB; **15fg**[c]	7.6 (m), 7.6 (m)	3.91 (d, –)	2.22 (d, 8.5)	1.49 1.58 1.86	2.02	148.4 (37.4), 3.49 (37.4)	
ETPB, ETPB; **15gg**	7.7 (m), –	4.99 (d, 5.0) 4.40 (d, 4.4)		1.82 1.77 1.60	2.52	149.5 (53.2), 158.3 (53.2)[c]	1.52 (m) 2.20 (m)
$P(OCH_3)_3$, $P(OCH_3)_3$; **15aa**[d]	7.6 (m), –	3.89 (d, 10.7) 3.66 (d, 10.0)		1.46 1.49 1.70 1.73	2.45	155.3 (54.9), 161.5 (54.9)[e]	
$PPh(OCH_3)_2$, $P(OCH_3)_3$; **15ba**[d]	7.7 (m), 7.7 (m)	3.49 (d, 10.5) 3.84 (d, 11.0) 4.00 (d, 10.3)		1.50 1.61 1.70 1.88	2.29	154.3 (41.4), 186.6 (41.4)	
$PPh_2(OCH_3)$, $P(OCH_3)_3$; **15ca**[c,d]	7.6 (m), 7.6 (m)	3.26 (d, 10.3) 3.37 (d, 12)		1.48 1.64 1.68 1.88	2.03	151.8 (41.5), 158.8 (41.5)	
$P(CH_3)_3$, $P(OCH_3)_3$; **15da**[c,d]	7.7 (m), –	3.74 (d, 10.3)	1.69 (d, 9.5)	1.58 1.79 1.86	2.51	154.7 (36.3), 15.4 (36.6)	
$PPh(CH_3)_2$, $P(OCH_3)_3$; **15ea**[c,d]	7.7 (m), 7.7 (m)	3.50 (d, 10.9)	1.91 (d, 9.4) 2.01 (d, 7.3)	1.47 1.57 1.69 1.90	2.35	153.4 (36.6), 23.4 (36.6)	
PPh_2CH_3, $P(OCH_3)_3$; **15fa**[c,d]						151.6 (33.0), 34.0 (33.0)	
ETPB, $P(OCH_3)_3$; **15ga**[c,d]	7.7 (m), –	4.42 (d, 4.6) 3.68 (d, 10.3)		1.52 1.56 1.74 1.76	2.50	154.5 (44.3), 159.0 (44.3)	
$P(OCH_3)_3$, $PPh(OCH_3)_2$; **15ab**	7.7 (m), 7.7 (m)			1.54 1.61 1.75 1.87	2.47	182.4 (42.7), 160.0 (42.7)	

[a] Cf. structure **19**; ^1H NMR spectra recorded at 80 MHz in CD_2Cl_2 or $CDCl_3$, with chemical shifts in ppm with respect to internal TMS; ^{31}P spectra recorded at 32.4 MHz in CD_2Cl_2, with chemical shifts in ppm with respect to external 85% H_3PO_4. Multiplicities and J values (in Hz) are given in parentheses. [b] AB or AX pattern, $^2J_{PP}$ obtained from computer-simulated spectra. [c] Spectrum recorded in the presence of excess L_β. [d] Spectrum recorded at 0 °C. [e] Assignments ambiguous.

while **9g** and **9a** reacted with $PPh(OCH_3)_2$ to afford **15gb** and **15ab**. These results underscore the stereospecificity of the kinetically controlled, phosphine-promoted CO insertion observed in this work.

Stereochemistry of the [Fe(diars)(CO)(L_α)(L_β)(C(O)CH_3)]$^+$ Complexes (15). As described above, migratory insertion of the methyl complexes **9** according to eq 5 resulted in the formation of the single isomeric acyl **15**. Since permuting the order of introduction of L_α and L_β results in geometric site exchange of L_α and L_β in the acyl product, the observed stereospecifically *cannot* be the result of simple approach to thermodynamic equilibrium and must therefore be kinetic in origin. Of the six possible geometric isomers **16–21** (cf. Chart II), **16** and **17** are eliminated as possible products since permutation of L_α and L_β would give enantiomers and two diastereomers were observed depending on the order of introduction of L_α and L_β. Further, $^{31}P\{^1H\}$ NMR spectra show distinctive AB patterns when $L_\alpha = L_\beta$ as in compounds **15aa** and **15gg** (cf. Table II).

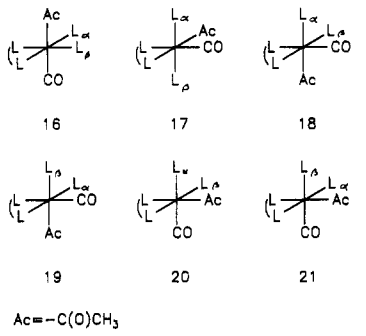
Critical information regarding the stereochemistry of the acyls **15** is derived from the product formed by treating

Table VI. ^{13}C NMR Data for [Fe(diars)(CO)(L_α)(L_β)(C(O)CH_3)]$^+BF_4^-$[a]

L_α, L_β; compd	$\delta(C(O)CH_3)$	δ(CO)	δ(POC) L_α	δ(POC) L_β	$\delta(C(O)CH_3)$
$P(OCH_3)_3$, $P(OCH_3)_3$; **15aa**	268.8 (dd, 44.7, 29.2)	215.1 (dd, 34.3, 22.4)	54.0 (d, 11)	54.4 (d, 11)	50.8 (dd, 24.0, 1.7)
$PPh(OCH_3)_2$, $P(OCH_3)_3$; **15ba**	268.4 (dd, 46.4, 25.8)	214.3, (dd, 29.3, 22.3)	56.7 (d, 13.0) 56.4 (d, 13.7)	52.6 (d, 12)	48.8 (dd, 23.9, 3.6)
$P(CH_3)_3$, $P(OCH_3)_3$; **15da**			53.9 (d, 10.3)		50.5 (d, 25.8)
$PPh(CH_3)_2$, $P(OCH_3)_3$; **15ea**[b]	272.1 (dd, 22.7, 51.3)	216.2 (t, 22.8)			
$P(OCH_3)_3$, $PPh(OCH_3)_2$; **15ab**	269.4 (dd, 41.3, 30.9)	215.0 (dd, 33.6, 18.0)	54.3 (d, 8.6)	57.4 (d, 17.2)	50.9 (d, 18.9)

[a] Cf. structure **19**; 20.1-MHz $^{13}C\{^1H\}$ NMR spectra recorded in $CDCl_3$, with chemical shifts in ppm with respect to internal TMS and T = 0 °C. Multiplicities and J values (in Hz) are given in parentheses. [b] Spectrum recorded in the presence of excess L_β.

Chart II



9a with 10–15 psig of carbon monoxide. The reaction does not proceed to completion and is reversed on release of CO pressure. ^1H NMR analysis of the equilibrium product mixture at 22.5 °C under a CO atmosphere indicated the formation of a 4.8/1 mixture of two acyl products. Comparison of the spectrum with that of an authentic sample[33] showed that **8a** (stereochemistry **18**, L_α = $P(OCH_3)_3$, L_β = CO) was *not* formed. The ^1H NMR spectrum of the major component showed four As–CH_3 signals; hence, isomer **21** (L_α = $P(OCH_3)_3$, L_β = CO), which has a symmetry plane, is effectively eliminated, leaving **19** and **20** (L_α = $P(OCH_3)_3$, L_β = CO). Evidence supporting structure **19** (L_α = $P(OCH_3)_3$, L_β = CO) was obtained from the ^{13}C NMR spectrum, which like that for **9a**, showed a resolvable phosphorus coupling for only *one* of the two ipso *o*-phenylene ring carbons. $^2J_{PC}$ values were consistent with a *cis*-P–Fe–C link (cf. Experimental Section). The stereochemistry of the major acyl product obtained can be accounted for by assuming that the promoting ligand L_β enters trans with respect to the acyl.

Labelling experiments with ^{13}CO showed no detectible CO site exchange for the carbonylation of **9a** → **8a** (stereochemistry **19**, L_α = $P(OCH_3)_3$, L_β = ^{13}CO). Figure 3 shows the results obtained when a solution of **9a** was treated with 1 atm of ^{13}CO. Incorporation of the label occurs *only* at the 203.0 ppm carbonyl site of **19**, which shows the smaller phosphorus coupling ($^2J_{PC}$ = 17.5 Hz vs 32.4 Hz for δ_{CO} = 210.0 ppm) due to the strong trans influence of σ-acyl. The larger phosphorus coupling (32.4 Hz) compares favorably with that found for the minor isomer (stereochemistry **21**, L_α = $P(OCH_3)_3$, L_β = CO), identified by its single ^{13}C resonance (δ_{CO} = 207.2 ppm, $^2J_{PC}$ = 39.3 Hz) corresponding to the presence of mutually trans carbonyl groups. The larger phosphorus coupling can be understood in terms of the relatively weak trans influence of CO.

In the absence of crystallographic evidence it is difficult to unambiguously assign the stereochemistry of the acyl complexes **15** as **19** or **20**; however, FAB MS data strongly support the former. Table VII summarizes the appropriate results. For the three isomeric pairs **15** which have L_α and

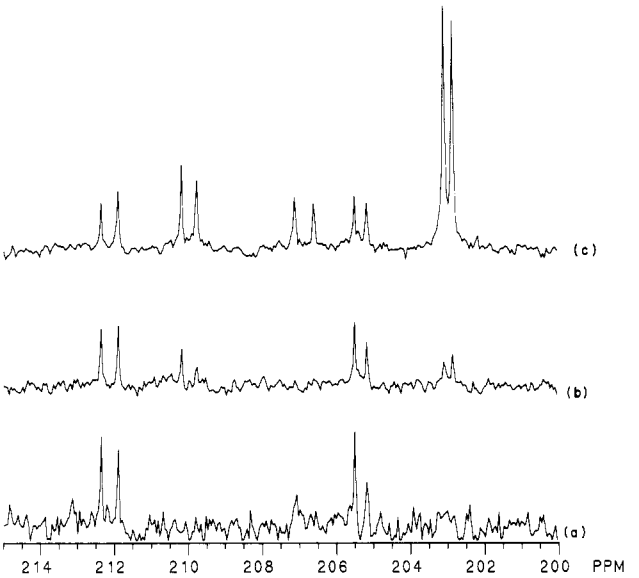


Figure 3. 75.5-MHz ^{13}C NMR spectrum of **9a** + CO in $CDCl_3$: (a) carbonyl region of **9a**; (b) carbonyl region of **9a** + CO; (c) carbonyl region of **9a** + ^{13}CO.

Table VII. Comparison of FAB MS Data for [Fe(diars)(CO)(L_α)(L_β)(C(O)CH_3)]$^+BF_4^-$[a]

fragment	rel abund **15ab**	**15ba**	**15bg**	**15gb**	**15ag**	**15ga**
$M^+ - L_\beta$[a]	114.0	78.1	65.4	37.6	80.7	41.5
$M^+ - L_\alpha$	5.2	6.9	8.8	12.5	12.4	16.8

[a] Relative abundance calculated by assuming $Fe(diars)CH_3^{\bullet+}$ (m/e = 337) = 100%.

L_β exchanged, fragmentation proceeds predominantly by cleavage of L_β, the ligand introduced in the insertion step (eq 5), rather than by cleavage of L_α. Since the acyl group is known to be strongly trans labilizing[32,39,49–53] in octahedral mononuclear d^6 complexes, we propose that L_β occupies the coordination site trans to σ-$C(O)CH_3$. Microscopic reversibility then dictates that L_β must enter trans to σ-$C(O)CH_3$, and the stereochemistry is therefore fixed as **19**.

Thermodynamic Measurements. At equilibrium the insertion (eq 5) is incomplete and, except for **15gg** and **15ag**, an excess of L_β is required to drive the reaction toward completion. Equilibrium constants were measured

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Table VIII. Equilibrium Constants for Eq 5

L_α, L_β; compd	K_{eq} (0 °C),[a] L mol^{-1}	$\theta(L_\alpha)$,[b] deg	$\theta(L_\beta)$,[b] deg	$pK_a(L_\alpha)$[c]	$pK_a(L_\beta)$[c]
$PPh_2(OCH_3)$, ETPB; **15cg**	3.4×10^4 [d]	132	101	2.69	1.74
$P(CH_3)_3$, ETPB; **15dg**	6.3×10^4 [d]	118	101	8.65	1.74
$PPh(CH_3)_2$, ETPB; **15eg**	1.00×10^5 [d]	122	101	6.50	1.74
PPh_2CH_3, ETPB; **15fg**	8.8×10^3	136	101	4.57	1.74
$P(OCH_3)_3$, $P(OCH_3)_3$; **15aa**	6.4×10^3	107	107	2.60	2.60
$PPh(OCH_3)_2$, $P(OCH_3)_3$; **15ba**	3.3×10^2	115	107	2.64	2.60
$PPh_2(OCH_3)$, $P(OCH_3)_3$; **15ca**	6.8×10	132	107	2.69	2.60
$P(CH_3)_3$, $P(OCH_3)_3$; **15da**	2.9×10^2	118	107	8.65	2.60
$PPh(CH_3)_2$, $P(OCH_3)_3$; **15ea**	9.1×10	122	107	6.50	2.60
ETPB, $PPh(OCH_3)_2$; **15gb**	4.9×10^4 [d]	101	115	1.74	2.64
$P(CH_3)_3$, $PPh(OCH_3)_2$; **15db**	3.4×10	118	115	8.65	2.64

[a] Measured by ^{31}P NMR spectroscopy in $CDCl_3$. Reported values taken as the average of two samples with varying $[L_\beta L_b]$. [b] Cone angles taken from Tolman.[55] [c] pK_a values taken from Giering et al.[54] [d] Extrapolated from K_{eq} data measured at 305, 313, 323, and 333 K.

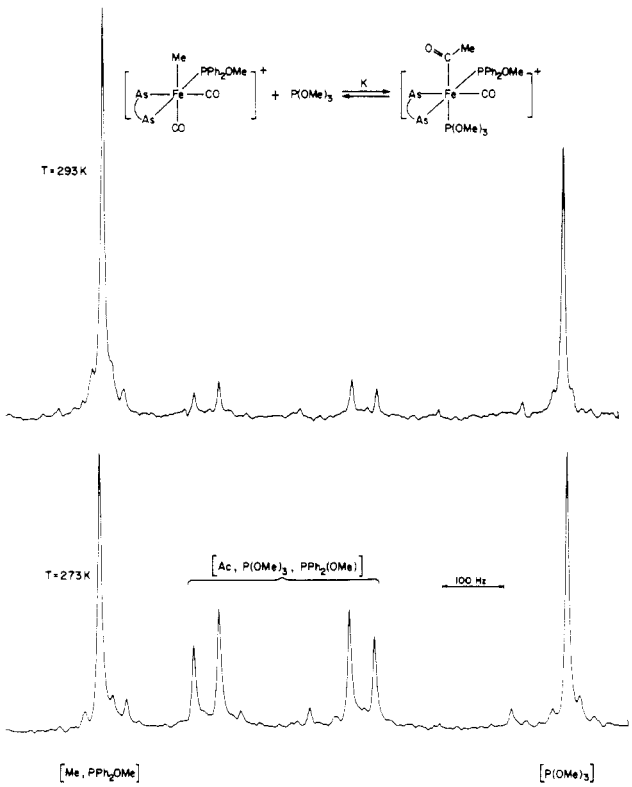

Figure 4. 32.4-MHz ^{31}P NMR spectrum of **9c** + $P(OCH_3)_3$ = **15ca** in $CDCl_3$.

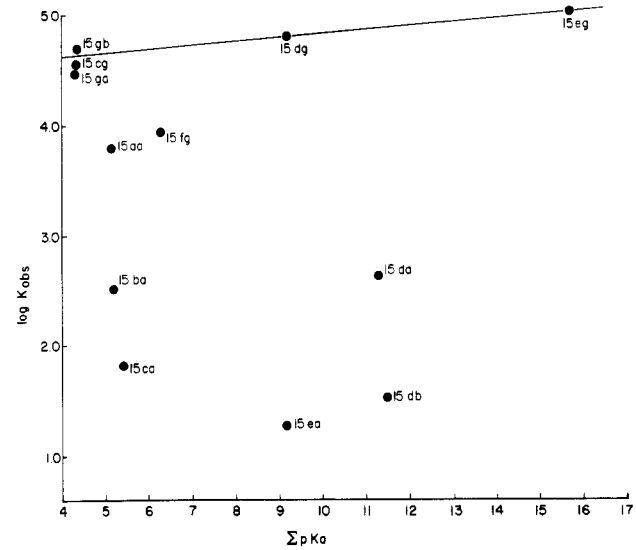

Figure 5. Electronic profile for eq 5.

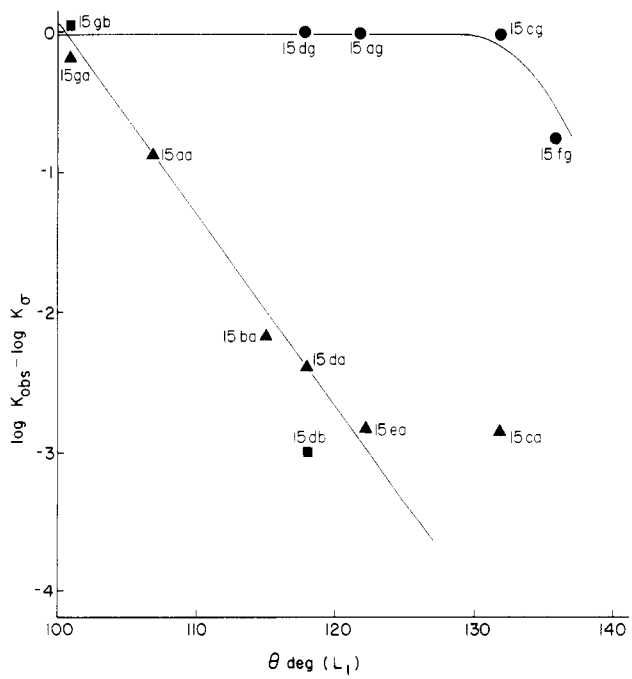

Figure 6. Steric profile for eq 5.

by using ^{31}P NMR spectroscopy, which clearly distinguished between the methyl complexes **9** and the corresponding acyl complexes **15** (cf. Figure 4). The results, shown in Table VIII, demonstrate that the measured K_{eq} values depend on the nature of the phosphine ligands L_α and L_β. Analysis of the data by the method of Prock and Giering[54] reveals that the ligand sphere influences the magnitude of K_{eq} predominantly through steric rather than electronic effects.

Our analysis is based on the assumption that σ electronic effects of L_α and L_β will be additive for the acyl series **15**. Figure 5 shows a plot of log K_{eq} vs $\sum pK_a(L_\alpha L_\beta)$. The electronic profile for eq 5 was determined with use of **15dg** and **15eg** since ETPB is a ligand of exceptionally small steric demand and both $P(CH_3)_3$ and $PPh(CH_3)_2$ are class II σ-donor ligands of similar cone angles.[55] Acyls **15cg**, **15ga**, and **15gb** correlate well, indicating that steric effects are minimal for systems that contain the very small bicyclic ETPB ligand. The slope of the line drawn in Figure 5 suggests that the electronic effects of the ligand sphere only weakly perturb K_{eq}.

Provided that the electronic profile is well established, deviations from the line drawn through **15dg** and **15eg** are

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related to steric factors. A plot of $\log K_{obs} - \log K_\sigma$ vs the steric demand of the ligand sphere for the series $[Fe(diars)(CO)(L_\alpha)(L_\beta)(C(O)CH_3)]^+$ (L_β = ETPB, $P(OCH_3)_3$, $PPh(OCH_3)_2$) approximated by the ligand cone angle θ_{L_α} is shown in Figure 6. Two distinct patterns emerge from the analysis: (i) acyl complexes **15** not containing the bicyclic phosphite ETPB show a steady, sharp decrease of K_{eq} with increasing steric demand of the ligand sphere; (ii) the remaining bis(phosphine)-substituted acyl complexes show a sharp break in the plot consistent with the presence of an apparent steric threshold[54] (θ_{st} = ca. 132°).[56] Steric hindrance of eq 5 follows from a consideration of the increased steric congestion of **15** vs that of **9**. The apparent steric threshold found when L_α or L_β is ETPB shows that the steric demands of the rigid, bicyclic phosphite are considerably less than that of the more flexible $P(OCH_3)_3$ and $PPh(OCH_3)_2$ ligands. A sharp decline in K_{eq} with increasing steric demand occurs when the volume element available to the remaining phosphine, L_α or L_β, is exceeded.

Summary

Carbon monoxide extrusion from the acyls **8** (stereochemistry **12**, R = $C(O)CH_3$) proceeds stereospecifically under conditions favoring kinetic control to give the methyl complexes **9** with stereochemistry **11** (R = CH_3). The chiral Fe center in **11** is stable on the NMR time scale. Stereochemistry **19** is established for the reaction products afforded under preparative conditions from the carbonyl insertion reaction of **9** (eq 5). The isostructural acyl series **15** obtained is consistent with the high trans-directing ability of σ-acyl previously established[32,39,49-53] for related acyl complexes prepared by carbonyl insertion. FAB MS fragmentation patterns corroborate the anticipated high trans-labilizing effect of σ-acyl in these complexes and establish that L_β is trans to σ-acyl. Preparative applications of the stereodirected CO insertion are limited to some degree by steric interactions that effectively determine the position of the CO insertion equilibrium.

Experimental Section

Reagents and Methods. All manipulations were performed under an atmosphere of dry, oxygen-free nitrogen with use of standard Schlenk techniques.[57] Nitrogen gas was purified by passing through a series of columns containing BTS catalyst (BASF), granular P_4O_{10}, and finally activated 3A molecular sieves. The phosphorus compounds $P(OCH_3)_3$, $PPh(OCH_3)_2$, $PPh_2(OCH_3)$, $P(CH_3)_3$, $PPh(CH_3)_2$, PPh_2CH_3, and ETPB (4-ethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane) were purchased from Strem Chemicals and used as received. Diars[58] (*o*-phenylenebis(dimethylarsine)), and $[Fe(diars)(CO)_2(L_\alpha)(C(O)CH_3)]^+$ (**8a–g**) were prepared[33] by using the established literature procedures.

Infrared spectra were measured in KBr solution cells (0.1 mm) with a Perkin-Elmer Model 283 instrument. NMR spectra were obtained on a Bruker WP-80 or a General Electric GN-300 instrument. Chemical analysis were performed by Canadian Microanalytical Service, Vancouver, BC, Canada.

Equilibrium Constant Measurements. K_{eq} values for eq 5 were measured by using $^{31}P\{^1H\}$ NMR spectroscopy. Standard solutions of the methyl complex **9** (ca. 18 mM mL^{-1}) were prepared under a nitrogen atmosphere in a 5- or 10-mL volumetric flask fitted with a septum cap. Two 2-mL aliquots were withdrawn via syringe and transferred to 10-mm NMR tubes fitted with septum caps. Different amounts, generally 0.2–2 equiv of phosphine L_β, were then added via syringe and the samples equilibrated at 273 or 293 K for 3 days. Finally $[Cr(acac)_3]$, ca. 15 mg, was added as a relaxation agent and the sample transferred to a temperature-equilibrated NMR probe. Equilibrium concentrations of **9**, L_β, and **15** were determined from normalized peak heights and/or integration. The equilibrium constant was calculated from the expression $K = c(a + c)/C_{Fe}ab$, where a, b, and c are peak heights or integrals of **9**, L_β, and **15**, respectively, and C_{Fe} is the formal concentration of **9** used. Agreement between runs with varying [L] was generally on the order of ±10%.

Preparation of the $[Fe(diars)(CO)_2(L_\alpha)(CH_3)]^+$ Complexes (9a–g). The phosphine-substituted acyl complexes **8a–g** were thermally decarbonylated by direct heating of the solid under a dynamic vacuum. Typically, ca. 500 mg of the acyl **8** was placed in a Schlenk flask, which was evacuated and heated in a oil bath at 0.1 mmHg. The temperatures and times used are tabulated in Table I. Initially the acyl melts to give a froth as CO is liberated. Continued heating results in the formation of a solid, which was cooled, dissolved in methylene chloride, and filtered through a small column (0.5 × 3 cm) of Florisil. The resulting yellow solution was concentrated to ca. 1 mL under a stream of nitrogen and precipitated by the addition of 5 mL of ether. In some cases the crude product is oily, but repeated trituration with fresh portions of ether gradually gave the product as an off-white to yellow solid. Yields were generally >80%. In some cases well-formed crystals can be grown by slow diffusion of ether into a methylene chloride solution of the crude solid obtained as described above.

Oxidative Decarbonylation. A 227-mg sample of **8a** was stirred at room temperature with 1 equiv of $(CH_3)_3NO{\cdot}2H_2O$ in methylene chloride for 24 h. The resulting cloudy suspension was filtered through Celite, concentrated to ca. 1 mL, and precipitated by adding ether to give 74 mg of an off-white powder identified as **9a** by ^1H NMR spectroscopy. Similar treatment of **8a** with iodosobenzene resulted in decomposition. No **9a** was detected by ^1H NMR spectroscopy.

Preparation of the $[Fe(diars)(CO)(L_\alpha)(L_\beta)(C(O)CH_3)]^+$ Complexes (15). The isolable derivatives were prepared by addition of a 4–30-fold excess of the ligand L_β (L_β = $P(OCH_3)_3$, ETPB) to a methylene chloride solution of ca. 200 mg of **9a–g** in 10 mL of methylene chloride at 0 °C. After 2 h the solution was allowed to reach ambient temperature. Stirring was continued overnight. Removal of volatiles at 0.1 mmHg left a sticky residue, which was redissolved in methylene chloride and the solution filtered. The clear, yellow solution was concentrated under a nitrogen stream and the crude product precipitated by the addition of ether. It is critical to precipitate the product rapidly, especially for bulky L_β, which dissociate phosphine readily. The crude product can be further purified by washing with ether at 0 °C and can be dried at 40 °C/0.1 mmHg. Attempts to recrystallize the acyl product from methylene chloride/ether were unsuccessful and in general led to deterioration of the sample.

Product isolation is frustrated when both L_α and L_β are bulky. Although most combinations of ligands gave the bis(phosphine)-substituted, spectroscopically detectible, acyl product **15** according to eq 5, it did not prove possible to isolate analytical solids in all cases. The data presented for complexes **15fa**, **15gb**, **15ab**, **15bb**, **15db**, **15gd**, and **15ad** were obtained either from samples prepared in situ by adding a large excess of L_β to **9** according to eq 5 or by precipitation from solutions containing excess L_β.

Carbonylation of 9a. A 5-mm NMR tube fitted with a screw cap/septum was charged with 29.4 mg of **9a** and 0.5 mL of CD_2Cl_2. The solution was briefly purged with carbon monoxide and the tube pressurized to 10–15 psig. ^1H NMR analysis indicated partial conversion to two isomers of **8a**. ^1H NMR (22 °C, 300 MHz, CD_2Cl_2): major isomer (stereochemistry **21**, L_α = $P(OCH_3)_3$, L_β = CO), 7.8 ppm (m, C_6H_4), 4.02 ppm (d, J = 11 Hz, $P(OCH_3)$), 2.47 ppm (s, $C(O)CH_3$), 1.88, 1.83, 1.79, 1.60 ppm (s, $AsCH_3$); minor isomer (stereochemistry **21**, L_α = $P(OCH_3)_3$, L_β = CO), 7.8 ppm (m, C_6H_4), 3.99 ppm (d, J = 11 Hz, $P(OCH_3)$), 2.71 ppm (s, $C(O)CH_3$), 1.86, 1.76 ppm (s, $AsCH_3$). ^{13}C NMR (22 °C, CD_2Cl_2): major isomer, 257.7 ppm (d, J = 29.0 Hz, $C(O)CH_3$), 210.4 ppm (d, J = 32.4 Hz, CO), 203.4 ppm (d, J = 17.5 Hz, CO), 55.4 ppm (d, J = 8.7 Hz, $P(OCH_3)$), 50.2 ppm (s, $C(O)CH_3$), 15.4, 14.8, 13.2,

(56) Since electronic effects for eq 5 appear to be small (cf. Figure 5), plots of K_{eq} vs $\sum\theta$ for the series L_β = $P(OCH_3)_3$ show the same qualitative behavior.

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13.0 ppm (s, $AsCH_3$); minor isomer, 258.2 ppm (d, J = 41.4 Hz, $C(O)CH_3$), 207.2 ppm (d, J = 39.3 Hz, CO), 55.7 ppm (d, J = 9.5 Hz, $P(OCH_3)$), 51.6 ppm (s, $C(O)CH_3$), 13.4, 12.6 ppm (s, $AsCH_3$).

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Registry No. **8a**, 124379-93-7; **8b**, 124379-94-8; **8c**, 124379-95-9; **8d**, 124379-96-0; **8e**, 124399-61-7; **8f**, 124379-97-1; **8g**, 124379-98-2; **9a**, 124380-00-3; **9b**, 124380-02-5; **9c**, 124380-04-7; **9d**, 124380-06-9; **9e**, 124380-08-1; **9f**, 124380-10-5; **9g**, 124380-40-1; **15ag**, 124380-12-7; **15bg**, 124602-43-3; **15cg**, 124649-43-0; **15dg**, 124380-16-1; **15eg**, 124380-18-3; **15fg**, 124380-38-7; **15gg**, 124380-20-7; **15aa**, 124380-22-9; **15ba**, 124440-11-5; **15ca**, 124380-24-1; **15da**, 124380-26-3; **15ea**, 124380-28-5; **15ga**, 124440-05-7; **15fa**, 124380-30-9; **15gb**, 124649-43-0; **15ab**, 124380-32-1; **15bb**, 124380-34-3; **15db**, 124380-36-5; **15gd**, 124440-07-9; **15ad**, 124440-09-1; $P(OCH_3)_3$, 121-45-9; $PhP(OCH_3)_2$, 2946-61-4; $Ph_2P(OCH_3)$, 4020-99-9; $P(CH_3)_3$, 594-09-2; $PhP(CH_3)_2$, 672-66-2; Ph_2PCH_3, 1486-28-8; ETPB, 824-11-3; $(CH_3)_3NO$, 1184-78-7; iodosobenzene, 536-80-1.

Qualitative Molecular Orbital Studies of d^6 $M(alkyne)_2L_2$ and $M(alkyne)_3L$ Complexes

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Qualitative molecular orbital arguments, supported by calculations at the extended Hückel level, are used in the analysis of the structure and bonding of d^6 $M(alkyne)_2L_2$ and $M(alkyne)_3L$ complexes. In the former stoichiometry, the observed staggering is ascribed to an interaction between the alkyne $\pi_\perp$ orbitals and vacant orbitals on the metal. However, other structures with the alkynes coplanar are relatively low in energy by comparison, for a filled $d\pi$–$p\pi$ conflict is avoided by the presence of a low-energy π-back-bond between orbitals that are formally vacant on the separated fragments. The tris(alkyne) stoichiometry has been discussed by others before; here a comparison is made between the observed C_{3v} structure and a structure with one of the alkynes rotated by 90°. The former is more stable because a filled $\pi_\perp$ orbital on the alkyne interacts with a combination on the other alkynes to create a rigorously nonbonding set. Such a masking is not available in the rotated structure. Both stoichiometries have marked asymmetries between the two ends of the alkyne ligand, as observed experimentally through bond distances or spectroscopic parameters. These can be explained in terms of corresponding asymmetries in the bonding to the two carbons.

Introduction

Alkynes are the only organic ligands in transition-metal chemistry that can, in principle, donate a variable number of electrons to a metal center without a change in the number of bound atoms. There are alkyne complexes known for almost all of the transition metals, and a firm consensus about their bonding to a metal, particularly a formally "electron deficient" metal, has been established.[1] Such bonding schemes are very important in the chemistry of mono(alkyne) complexes, and the literature contains examples of the reversible interconversion of four- and two-electron bonding modes on the coordination of an additional ligand[2] or the addition of two electrons to a metal center.[3] Poly(alkyne) complexes, for which possible conflicts and cooperation among the alkynes in π-donation and acceptance add an additional dimension of interest, form an important subgroup in the alkyne literature, with examples spanning almost the whole transition series. Among the studied poly(alkyne) stoichiometries are d^{10} $M(alkyne)_2$ (M = Pt[4]), d^4 $M(alkyne)_2(O)X$ (M = Re[5]), $M(alkyne)_2(\eta^5$-cyclopentadienyl)X (M = Mo, W[6]), $M(alkyne)_2(\eta^5$-cyclopentadienyl)L (M = V, Nb, Ta[7]), d^4 $M(alkyne)_2L_2X_2$ (M = Mo, W[8]), and d^6 $M(alkyne)_2L_4$ (M = W[9]).

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