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

Stereochemistry of Migratory Carbonyl Insertion with Respect to Iron(II). Trans Effect of η^1-Acyl

C. R. JABLONSKI* and YU-PIN WANG

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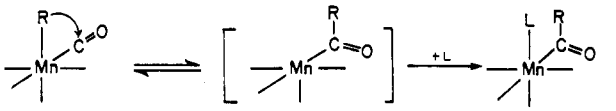
Lewis base promoted migratory carbonyl insertion reactions of *fac*-[(diars)Fe(CO)$_3$Me]$^+$ proceed readily at 0 °C to give good yields of [(diars)Fe(CO)$_2$(C(O)Me)L]$^+$ (diars = *o*-phenylenebis(dimethylarsine), L = Lewis base). For L = ^{13}CO and a number of phosphines (L = P(OMe)$_3$, P(OPh)$_3$, PhP(OMe)$_2$, Ph$_2$PMe) a single kinetic product is obtained with a *trans*-L–Fe–C(O)Me geometry. More basic phosphines (L = PMe$_3$, PhPMe$_2$, P(*t*-C$_4$H$_9$)$_3$, P(C$_6$H$_{11}$)$_3$) show less stereoselectivity. Decarbonylation of specifically labeled *fac*-[(diars)Fe(CO)$_2$(^{13}CO)(C(O)Me)]$^+$ occurs with loss of a CO trans to acyl due to the strong trans effect of η^1-C(O)Me.

Introduction

Detailed studies[1-3] of Lewis base promoted migratory carbonyl insertion reactions using octahedral Mn(I) as a probe are congruent with a rate-determining alkyl migration onto a cis-bound carbon monoxide to give a coordinatively unsaturated static square-pyramidal intermediate[4] which subsequently[5] coordinates a sixth ligand in the incipient vacant site (cf. Scheme I). Analysis of the octahedral kinetic acyl products shows that the stereochemistry at manganese is, in all cases[6-9] studied thus far, cis with respect to L–Mn–C(O)R as required by Scheme I. Examination of the reverse reaction for L = CO in a molecule containing a suitable stereochemical signpost is consistent with the loss of a CO cis to acyl as required by the principle of microscopic reversibility.[7a,8,10,11]

Unfortunately, no clear general pattern of stereochemistry at the metal center emerges when the results obtained from a larger sample of d^6 octahedral examples are considered. In this connection, while Pañkowski and Bigorgne[12] report that *trans,cis*-(PMe$_3$)$_2$M(CO)$_2$MeI (M = Ru, Fe) gives cis acyl kinetic products on carbonylation with ^{13}CO via a CO migration, Mawby has quite clearly demonstrated that L$_2$Ru(CO)$_2$XMe (L = PhPMe$_2$, PhAsMe$_2$; X = Cl, Br, I)[13] and (PhAsMe$_2$)IrCl$_2$(CO)$_2$Et[14] give trans kinetic acyl products. Interestingly, a recent kinetic study[15] of *trans,cis*-(PMe$_3$)$_2$Fe(CO)$_2$MeI carbonylation concurs with Pañkowski's original conclusion[16] that the major acyl product, *trans,trans*-(PMe$_3$)$_2$Fe(CO)$_2$(C(O)Me)I, which has a *cis*-acyl–Fe–CO geometry, forms *directly* via the methyl migration mechanism of Scheme I.

Scheme I



In this paper we report the results of a study of the Lewis base promoted migratory carbonyl insertion reactions of *fac*-methyl(*o*-phenylenebis(dimethylarsine))tricarbonyliron tetrafluoroborate[17] (**1**) designed to test the stereochemistry at octahedral d^6 iron.

Experimental Section

Nuclear magnetic resonance (^{1}H, ^{13}C, and ^{31}P) spectra were recorded on a Bruker WP-80 spectrometer fitted with a B-VT 1000 temperature controller. Samples were prepared in degassed solvents in nitrogen-filled NMR tubes capped with a tight-fitting rubber septum. Infrared spectra were recorded on a Perkin-Elmer Model 283 spectrometer. All preparative reactions were carried out in Schlenkware under a atmosphere of dry prepurified nitrogen with use of the general techniques described by Shriver.[18] Methylene chloride was freshly distilled from P_4O_{10} under a nitrogen atmosphere. Diethyl ether was freshly distilled from a blue solution of sodium/benzophenone ketyl under nitrogen. P(OMe)$_3$, PhP(OMe)$_2$, Ph$_2$P(OMe), PhPMe$_2$, Ph$_2$PMe, P(*t*-C$_4$H$_9$)$_3$, and P(C$_6$H$_{11}$)$_3$ were purchased from Strem Chemicals and were used without further purification. PMe$_3$ was prepared by thermolysis of its silver iodide adduct at 160 °C according to the established procedure.[19] *fac*-[(diars)Fe(CO)$_3$Me]$^+$BF$_4^-$ (diars = *o*-phenylenebis(dimethylarsine)) was prepared as described previously.[17] Enriched (90%) ^{13}CO was purchased from Monsanto Research Corp. and used as received. Analyses were determined by Canadian Microanalytical Service, Vancouver, B.C.

General Preparation of the Acyl Complexes. Preparation of [(diars)Fe(CO)$_2$L(C(O)Me)]$^+$BF$_4^-$, L = Phosphine. A 2–5-fold excess of the phosphine, L, was slowly added at 0 °C to a solution prepared by dissolving 0.50 g (0.95 mmol) of *fac*-[(diars)Fe(CO)$_3$Me]$^+$BF$_4^-$[17] in 5 mL of methylene chloride. The reaction mixture was stirred at 0 °C for 3 h and the product precipitated by adding ether. The resulting pale yellow gummy solid was triturated with several portions of dry ether to remove excess phosphine. The crude product was purified by chromatography on a small (0.8 cm × 2 cm) column of Florisil, with elution by methylene chloride followed by recrystallization from methylene chloride/ether. Traces of solvent and volatile phosphines were removed in vacuo at 25–45 °C. Isolated yields varied

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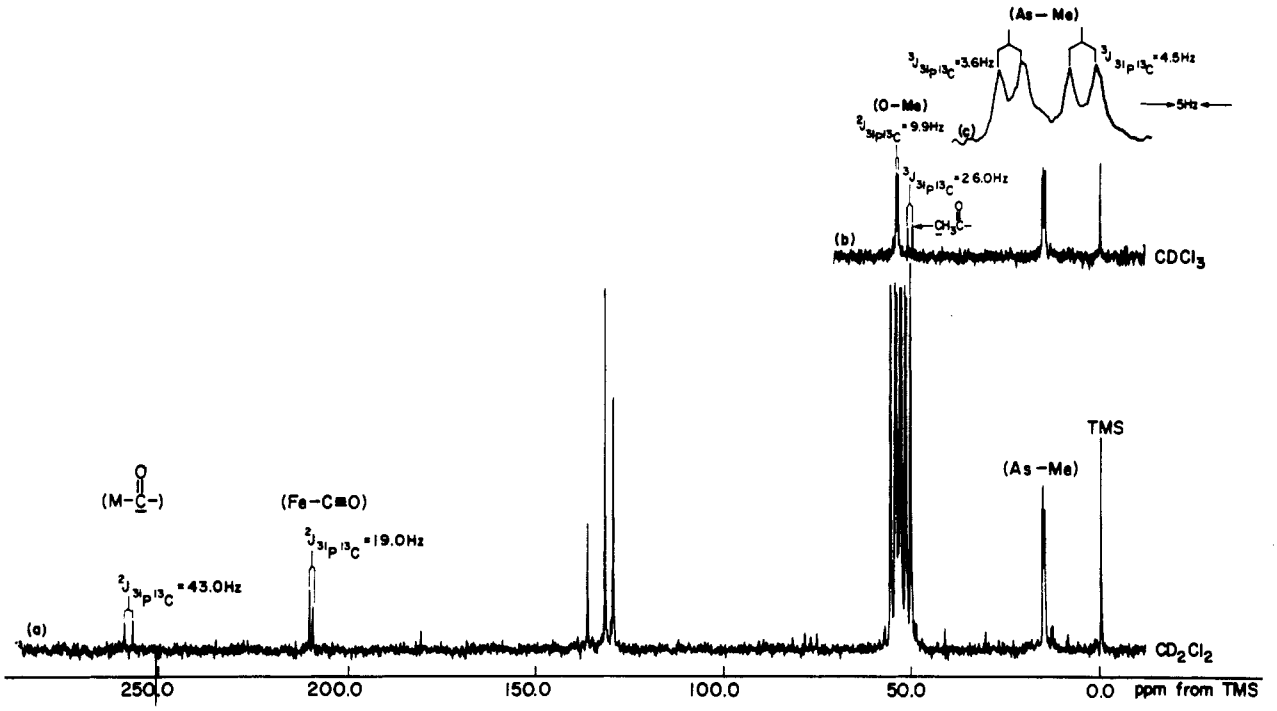

Figure 1. $^{13}C\{^1H\}$ NMR spectrum (20.1 MHz) of **2a** (L = $P(OMe)_3$) (a) in CD_2Cl_2 and (b) in $CDCl_3$.

from 60 to 70% except for the cases L = Ph_3P, $P(t\text{-}C_4H_9)_3$, and $P(C_6H_{11})_3$, where very low conversions (<10% by ^1H NMR) frustrated isolation.

Preparation of *fac*-[(diars)Fe(CO)$_2$(^{13}CO)(C(O)Me)]$^+$BF$_4^-$. A solution of 300 mg of *fac*-[(diars)Fe(CO)$_3$Me]$^+$BF$_4^-$ in 2 mL of methylene chloride was prepared in a three-neck 125-mL round-bottom flask fitted with a magnetic stirrer and a rubber septum inlet. The flask was connected to a vacuum line, frozen, evacuated and then charged with 1.5 atm (at 25 °C) of 90% enriched ^{13}CO. After 1 h of stirring at room temperature the product was precipitated by injecting 10 mL of ether through the septum. The resulting off-white solid was collected and purified by several recrystallizations from methylene chloride/ether to give a total yield of 195 mg of *fac*-[(diars)Fe(CO)$_2$(^{13}CO)(C(O)Me)]$^+$BF$_4^-$.

Decarbonylation of *fac*-[(diars)Fe(CO)$_2$(^{13}CO)(C(O)Me)]$^+$BF$_4^-$. A methylene chloride solution of *fac*-[(diars)Fe(CO)$_2$(^{13}CO)(C(O)Me)]$^+$BF$_4^-$ was refluxed under a nitrogen purge for a total of 10 h. Removal of solvent at reduced pressure gave an off-white solid, which was recrystallized from methylene chloride/ether. Comparison of infrared (CH_2Cl_2) and ^{13}C NMR ($CDCl_3$) spectra showed the product to be identical with an authentic sample of unlabeled *fac*-[(diars)Fe(CO)$_3$Me]$^+$BF$_4^-$.[17]

Determination of the Acyl Kinetic Product Distribution. Samples containing 5 mg of *fac*-[(diars)Fe(CO)$_3$Me]$^+$BF$_4^-$ in 0.4 mL of CD_2Cl_2 were prepared under N_2 in 5-mm NMR tubes fitted with a rubber septum cap. Excess phosphine (ca. 5–10-fold excess) was introduced by syringe at −78 °C and the sample transferred to the NMR probe equilibrated at 0 °C. Reaction progress was monitored by recording ^1H spectra at appropriate time intervals. The acyl product distribution as determined by the number and intensity of acyl methyl resonances in the 2.5–2.7 ppm region was compared at early stages in the reaction (<20% conversion) after equilibration at 0 °C for 5–10 h (100% conversion in most cases) and, in some instances, after extended equilibration at room temperature. Peak assignments were made by comparison with the ^1H NMR spectra obtained from isolated samples of the acyl prepared according to the procedure described above.

Results

Characterization of the Isolated Acyl Products. The cationic methyl complex *fac*-[(diars)Fe(CO)$_3$Me]$^+$BF$_4^-$ (**1**) reacts with excess phosphine (L = **a**–**g**; cf. Scheme II) to give good isolated yields of the cationic carbon monoxide inserted product [(diars)Fe(CO$_2$)L(C(O)Me)]$^+$. In the case of the very bulky phosphines Ph_3P, $P(t\text{-}C_4H_9)_3$, and $P(C_6H_{11})_3$, all with very large cone angles[20] (145, 182, and 170°, respectively), low equilibrium conversions prevented product isolation.

Table I. Physical Data for [(diars)Fe(CO)$_2$(C(O)CH$_3$)L]$^+$

	calcd		found		
compd	% C	% H	% C	% H	mp,[a] °C
2a-BF$_4$	28.70	3.26	28.83	3.10	>97 dec with gas evolution
2b-BF$_4$	45.86	4.09	44.98	4.08	>101 dec
2c-BF$_4$	37.86	4.33	37.70	4.32	>134 dec
2d-BF$_4$	43.59	4.34	43.40	4.27	>140 dec
2e-BF$_4$	44.55	4.43	44.45	4.52	>75 dec
2f-BF$_4$	39.68	4.54	39.20	4.66	>135 dec
2g-BF$_4$	33.81	4.67	33.55	4.60	>144 dec

[a] Sealed, N_2-filled capillary.

Table II. Infrared Spectra for [(diars)Fe(CO)$_2$(C(O)CH$_3$)L]$^+$ in CH_2Cl_2[a]

compd	$\nu_{C\equiv O}$, cm^{-1} [b]	ν_{acyl}, cm^{-1} [b]	compd	$\nu_{C\equiv O}$, cm^{-1} [b]	ν_{acyl}, cm^{-1} [b]
2a	1987, 2027	1640	2e	1982, 2020	1649
2b	1994, 2030	1654	2f	1983, 2025	1648
2c	1988, 2022	1640	2g + 3g	1976, 2012	1638, 1626
2d	1985, 2020	1644			

[a] All compounds showed strong BF_4^- absorptions at 1050–1060 cm^{-1}. [b] ±3 cm^{-1}.

The composition of the isolated acyl products was established from analytical (cf. Table I) and spectroscopic data. Infrared spectra in methylene chloride showed strong absorptions at 1638-1654 cm^{-1} (cf. Table II) characteristic of ν_{CO} for η^1 M–C(O)Me.[1-3,6-10,16] All of the isolated acyl complexes exhibited two strong carbonyl stretching bands, indicating a mutually cis pair of CO groups.

Analysis of infrared, ^1H NMR, and $^{13}C\{^1H\}$ NMR spectra of the isolated acyls indicates that, although four isomeric acyls are possible, the majority of Lewis bases examined (cf. Scheme II, **a**–**e** and **i**) lead to a single isolable product with cis,trans geometry **2** (cf. Scheme II). The case for L = $P(OMe)_3$ is exemplary. Of the three isomeric acyls (**2**–**4**) consistent with

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Scheme II

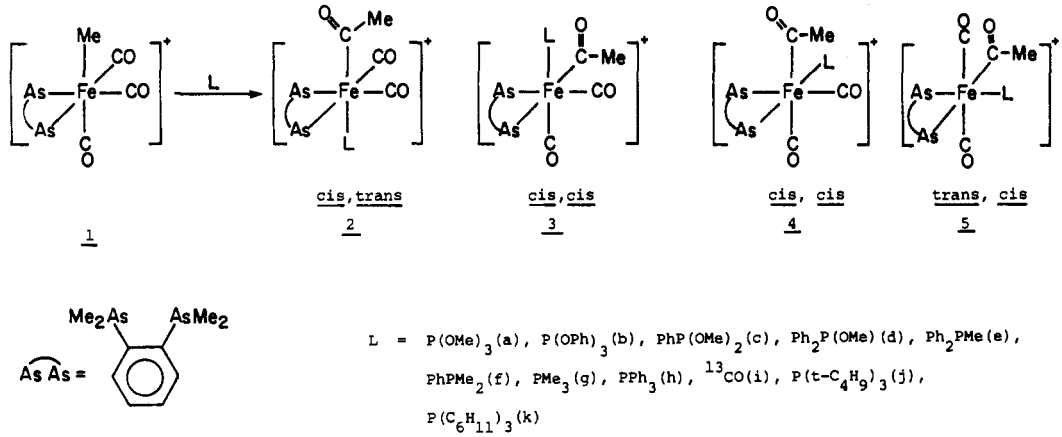


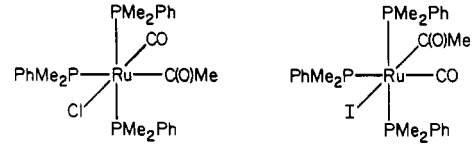
Table III. 80-MHz[a] ^{1}H and 32.4-MHz[b] ^{31}P NMR Spectra of $[(diars)Fe(CO)_2(C(O)CH_3)L]^+$

compd	solvent	As-CH_3	PCH_3	$C(O)CH_3$	P-OCH_3	P-Ph, P-OPh	As-Ph	^{31}P shift[b]	Δ[c]
2a	CD_2Cl_2 (^{1}H)	1.71 (s)	...	2.53 (d, J = 1.0)	3.70 (d, J = 11.0)	...	7.87 (m)	151.48	+11.5
	$CDCl_3$ (^{31}P)	1.72 (s)							
2b	$CDCl_3$	1.87 (s)	...	2.60 (d, J = 0.7)	...	6.83 (m)	7.85 (m)	143.63	+15.9
		2.16 (s)				7.15 (m)			
2c	$CDCl_3$	1.73 (s)	...	2.51 (s)	3.79 (d, J = 10.7)	7.67-7.8 (m)		176.51	+17.5
		1.88 (s)							
2d	$CDCl_3$	1.72 (s)	...	2.57 (s)	3.26 (d, J = 11.5)	7.3-7.9 (m)		145.76	+30.2
		1.82 (s)							
2e	$CDCl_3$	1.54 (s)	2.20 (d, J = 7)	2.66 (s)	...	7.34 (m)	8.0 (m)	29.71	+57.7
		1.75 (s)							
2f	CD_2Cl_2	1.61 (s)	1.58 (d, J = 7.6)	2.57 (s)	...	7.75 (m)		14.65	+61.1
		1.65 (s)							
3f or 4f	CD_2Cl_2	*d*	*d*	2.95 (s)	...	*d*			
2g	$CDCl_3$	1.77 (s)	1.44 (d, J = 8.1)	2.62 (s)	...	...	7.8 (m)	−11.73	+50.3
		1.86 (s)							
3g or 4g	$CDCl_3$	1.71 (s)	1.46 (d, J = 9.3)	2.77 (s)	...	...	7.8 (m)	13.27	+75.3
		1.82 (s)							
		1.93 (s)							
		2.03 (s)							
2h	acetone-d_6 (^{1}H)	1.52 (s)	...	2.73 (s)	...	*d*		59.7	
	$CDCl_3$ (^{31}P)	1.87 (s)							
2j	CD_2Cl_2	*d*	...	2.43 (s)[e]	...	*d*			
2k	CD_2Cl_2	*d*	...	2.58 (s)[e]	...	*d*			

[a] Chemical shifts for ^{1}H spectra are reported in ppm relative to internal Me_4Si; s = singlet, d = doublet, m = multiplet, and J = coupling constant in Hz. [b] ^{31}P chemical shifts in ppm relative to external 85% H_3PO_4. [c] Δ = complexation shift = δ(complex) − δ(free ligand). [d] Signals obscured or too weak to be measured. [e] Major kinetic product. At equilibrium acyl signals were observed at 2.81 and 2.24 for L = $P(C_4H_9)_3$ and 2.78, 2.58, and 2.22 for L = $P(C_6H_{11})_3$.

the presence of two terminal ν_{CO} observed at 1987 and 2024 cm^{-1}, only *cis,trans*-**2** contains a symmetry plane bisecting the chelating diarsine. Both the ^{1}H (cf. Table III) and the $^{13}C\{^1H\}$ (cf. Table IV and Figure 1) NMR spectra are compatible with such a plane. In particular Figure 1 shows three aromatic signals assignable to C(ipso), C(ortho), and C(meta) with no resolvable ^{31}P couplings,[21] two magnetically nonequivalent arsenic methyl signals with $^3J_{^{31}P^{13}C}$ = 3.6 and 4.5 Hz,[22] and a single CO resonance with $^2J_{^{31}P^{13}C}$ = 19 Hz. Confirmatory evidence for the cis,trans geometry **2a** for $[(diars)Fe(CO)_2(P(OMe)_3)(C(O)Me)]^+$ is provided by its ^{1}H NMR spectrum, which shows two nonequivalent arsenic methyl resonances (cf. Table III).

All the acyl complexes with cis,trans geometry **2** showed (cf. Table IV) $^2J_{^{31}P^{13}C}$(*trans*-P–Fe–*C*(O)Me) > $^2J_{^{31}P^{13}C}$(*cis*-P–Fe–C≡O) in keeping with the usual[23] but not inviolable[4b] diagnostic. A case in point is the Ru(II) complex **6**,[13] where



$^2J_{^{31}P^{13}C}$(*trans*-P–Ru–*C*(O)Me) = 82.0 Hz, while $^2J_{^{31}P^{13}C}$(*cis*-P–Ru–*C*(O)Me) = 11.0 Hz and $^2J_{^{31}P^{13}C}$(*cis*-P–Ru–CO) = 11.0 and 13.0 Hz. Complex **7**[13] shows $^2J_{^{31}P^{13}C}$(*trans*-P–Ru–CO) = 87.2 Hz while $^2J_{^{31}P^{13}C}$(*cis*-P–Ru–CO) = 13.6 Hz and $^2J_{^{31}P^{13}C}$(*cis*-P–Ru–*C*(O)Me) = 8.0 Hz.

We also detected a well-resolved ^3J coupling of ca. 14–26 Hz between the trans-lying ^{31}P and the acyl methyl resonance

(21) Related alkyl complexes containing a phosphite moiety trans to diars show nonequivalent ipso carbons and a small coupling ($^3J_{^{31}P^{13}C} \simeq$ 4–5 Hz) assigned to the *trans*-C–As–Fe–P link: Jablonski, C. R.; Wang, Y.-P., unpublished results.

(22) The assignment of the four observed arsenic methyl signals (cf. Figure 1 and Table IV) for **2a** as a pair of doublets and the CO resonances as a doublet due to coupling with ^{31}P was confirmed by the constancy of the measured couplings at 62.83 MHz.

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Table IV. 20.1-MHz $^{13}C\{^1H\}$ NMR[a] Spectra for [(diars)Fe(CO)$_2$(C(CO)CH$_3$)L]$^+$

compd	solvent	As-CH$_3$	P-CH$_3$	C(O)CH$_3$	P-O-CH$_3$	P-Ph	As-Ph	Fe-C≡O	C(O)CH$_3$
2a	$CDCl_3$	15.30 (d, ^3J = 4.5)[b] 15.78 (d, ^3J = 3.6)		51.40 (d, ^3J = 26.0)	54.9 (d, ^2J = 9.9)	...	131.26 (C_2, C_5) 133.59 (C_3, C_4) 138.32 (C_1, C_6)	211.11 (d, ^2J = 19.0)[b]	259.20 (d, ^2J = 43.0)
2b	$CDCl_3$	15.28[d] 15.06[d]	...	50.78 (d, ^3J = 27.9)	...	126.20 130.51 120.10 (d, J = 2.9) 151.31 (d, J = 13.2)	130.51 (C_2, C_6) 132.85 (C_3, C_4) 136.36 (C_1, C_6)	209.2 (d, ^2J = 16.2)	256.8 (d, ^2J = 49.0)
2c	$CDCl_3$	14.41 (d, ^3J = 2.9) 15.53 (d, ^3J = 4.4)	...	51.43 (d, ^3J = 27.9)	58.02 (d, ^2J = 16.2)	128.61 129.27 130.79 132.63 133.66 (d, J = 41.2)	130.29 (C_2, C_5) 132.41 (C_3, C_4) 137.01 (C_1, C_6)	210.43 (d, ^2J = 14.7)	260.48 (d, ^2J = 36.7)
2d	$CDCl_3$	15.36[d] 16.40	...	50.56 (d, ^2J = 17.2)	55.3 (d, ^2J = 15.5)	129.45 129.88 130.74 131.51 132.10 132.79 133.30		211.40 (d, ^2J = 12.0)	258.09 (d, ^2J = 29.2)
2f	$CDCl_3$	15.22 (d, ^3J = 3.4) 16.45 (d, ^3J = 5.2)	18.8 (d, ^1J = 24.1)	51.24 (d, ^3J = 15.5)	...	131.20 130.18 129.75 136.57 (d, ^1J = 36.7)	137.75 (C_1, C_6) 130.69, 133.68 (C_2, C_5; C_3, C_4) 137.95 (C_1, C_6)	212.40 (d, ^2J = 10.3)	257.56 (d, ^2J = 25.2)
2g	$CDCl_3$	15.86 (d, ^3J = 5.2) 14.62 (d, ^3J = 3.4)	19.44 (d, ^1J = 25.8)	51.11 (d, ^3J = 13.8)	...	...	130.18, 132.59 (C_2, C_5; C_3, C_4) 136.93 (C_1, C_6)	211.96 (d, ^2J = 11)	260.15 (d, ^2J = 20)
3g or 4g	$CDCl_3$	16.42 17.79 19.33 19.60	15.43 (d, ^1J = 25.8)	52.55 (s)	...	...	130.2, 131.2 (C_2, C_5; C_3, C_4) 131.4 (C_1, C_6)	*c*	*c*

[a] Chemical shifts reported in ppm with respect to internal Me_4Si; s = singlet, d = doublet, J = coupling constant in Hz. [b] Coupling constants verified at 62.83 MHz: 15.30 ppm (d, ^3J = 4.88), 15.78 ppm (^3J = 3.70), 211.11 ppm (^2J = 18.8). [c] Signal obscured or too weak to be located with confidence. [d] No $^{31}P^{13}C$ coupling resolvable.

observed at ca. 50 ppm in all complexes of geometry **2** (cf. Table IV). In agreement the Ru(II) complex **6**[13] shows a corresponding ^3J(trans) $\simeq$ 27 Hz while ^3J(cis) = 0 with no observable ^{31}P coupling to the acyl methyl in **7**.

In the case of L = PMe_3 the product was isolated as a ca. 65/35 mixture of two isomeric acyls. The geometry of the major isomer was established as cis,trans by comparison of its ^{1}H and ^{13}C{^{1}H} NMR spectral parameters with other acyls prepared in this study (cf. Tables III and IV). The minor isomer showed four arsenic methyl resonances in both its ^{1}H and ^{13}C{^{1}H} NMR spectra consistent with the absence of a symmetry plane in either diastereomeric cis,cis isomer **3** or **4**. The behavior of L = $PhPMe_2$ was analogous. Low conversions for L = $P(t\text{-}C_4H_9)_3$ and $P(C_6H_{11})_3$ even in the presence of a large excess of phosphine prevented detailed stereochemical assignments; however, acyl methyl ^{1}H NMR signals similar to those observed for **2g** and **3g** or **4g** were apparent.

Stereochemistry of the Kinetic Products. Samples **2a–g** aged in chloroform or methylene chloride showed complicated ^{1}H NMR spectra. Several acyl signals at ca. 2–3 ppm due to an apparent slow equilibration among the isomers **2–5** were observed. Weak high-field signals tentatively assigned to the Fe–Me group of the decarbonylated species were also detected after the sample stood for extended periods at room temperature. It was, therefore, important to unequivocally establish the stereochemistry of the *kinetic* acyl product(s) in order to adequately define the stereochemistry of insertion with respect to iron. This was accomplished by using ^{1}H NMR to monitor the time dependence of the acyl product distribution. The analyses were carried out at 0 °C in the presence of excess phosphine in order to minimize the possibility of product equilibration.

Two stereochemical outcomes for the Lewis base promoted insertions of **1** were established. The phosphines **a–e** gave a *single* kinetic product identical with the isolated acyls of stereochemistry **2**. Equilibration of the solution at 25–80 °C (under CO pressure) for several hours led to the formation of several isomeric acyls, and in the case of L = Ph_2PMe and $P(OMe)_3$, the cis,trans isomer **2** was *not* the thermodynamic product. Solvents appears to have little effect on the stereospecificity observed for the reaction of phosphines **a–e**. The case of L = $P(OMe)_3$ was examined in several solvents (methylene chloride, chloroform, methanol, and acetone), and in each case **2a** was the only observable kinetic product.

Reaction with excess $PhPMe_2$ or PMe_3, however, produced two isomeric acyl kinetic products in constant ratio in methanol, methylene chloride, or chloroform at 0 °C. Concentration ranges from 0.036 to 1.81 mol/dm^3 in $PhPMe_2$ formed **2f**/(**3f** or **4f**) in a 4.5/1 ratio at 0 °C in methylene chloride-d_2. Although low overall conversion prevented a detailed analysis, $P(t\text{-}C_4H_9)_3$ and $P(C_6H_{11})_3$ displayed a similar pattern and at least two isomeric acyl products were observed. Figure 2 shows a comparison of the ^{1}H NMR spectra for L = Ph_2PMe, which gives a single acyl isomer, and L = $PhPMe_2$, which gives two isomeric acyl kinetic products.

A competition experiment was carried out in methylene chloride by allowing a 1/1 mixture of PMe_3/$P(OMe)_3$ (which show different kinetic product distributions) to compete for the reactive acyl intermediate expected from **1** on the basis of the mechanism shown in Scheme I. Analysis of the kinetic product distribution using ^{1}H NMR as described above indicated the formation in constant ratio of three acyl products identified by comparison of acyl chemical shifts as **2g**, **3g** or **4g**, and **2a**. Integration of the total Me_3P–Fe–C(O)Me/$(MeO)_3P$–Fe–C(O)Me signals gave a competition ratio of 2.7/1.

^{13}CO-Promoted Insertion. Previously we reported[17] that

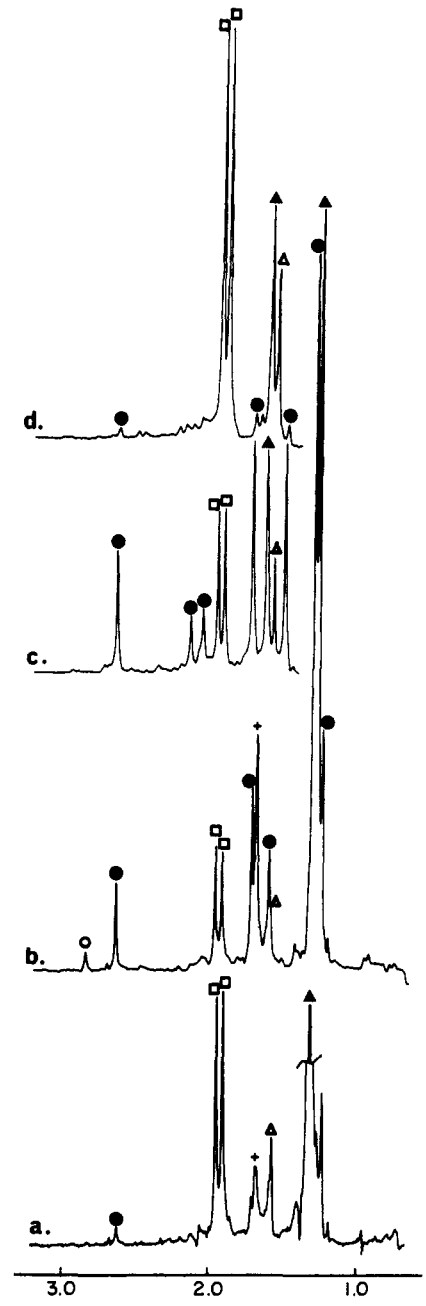
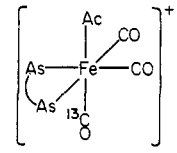


Figure 2. ^{1}H NMR determination of kinetic products: (a) initial spectrum (<3% conversion) **1** + $PPhMe_2$, ● = **2g**, □ = **1**, △ = water, + = impurity, ▲ = excess $PPhMe_2$; (b) ca. 38% conversion for **1** + $PPhMe_2$, ● = **2g**, ○ = **3g** or **4g**, □ = **1**, + = impurity, △ = water, ▲ = excess $PPhMe_2$; (c) ca. 36% conversion for **1** + PPh_2Me, ● = **2e**, □ = **1**, ▲ = excess PPh_2Me, △ = water; (d) initial spectrum (<2% conversion) **1** + PPh_2Me, ● = **2e**, □ = **1**, ▲ = excess PPh_2Me, △ = water.

carbonylation of **1** proceeds readily to give *fac*-[(diars)Fe-$(CO)_3$(C(O)Me)]$^+$. Infrared (ν_{CO} region) and ^{13}C NMR spectra of the product isolated with use of 90% enriched ^{13}CO are compared in Figures 3 and 4, respectively. Assumption that the label is trans to acyl and thus that C_s molecular symmetry is maintained in **2i** allows qualitative interpretation of the results.



2i

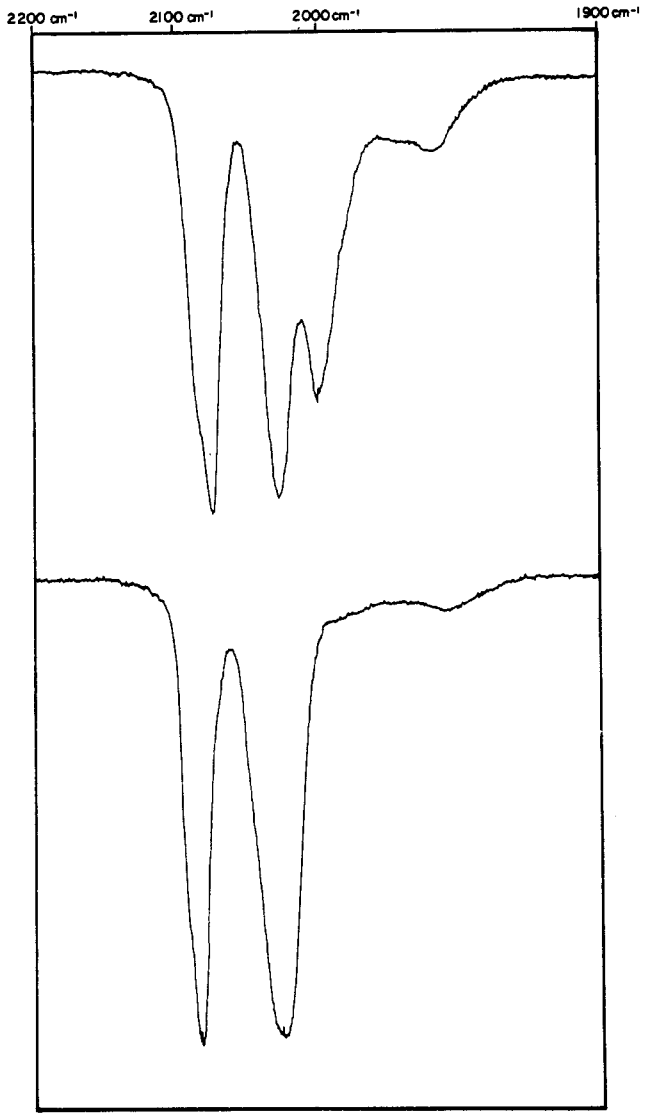


Figure 3. Bottom: Partial infrared spectrum of *fac*-[(diars)Fe(CO)$_3$(C(O)Me)]$^+$ in CH_2Cl_2. Top: Partial infrared spectrum of **2i** in CH_2Cl_2.

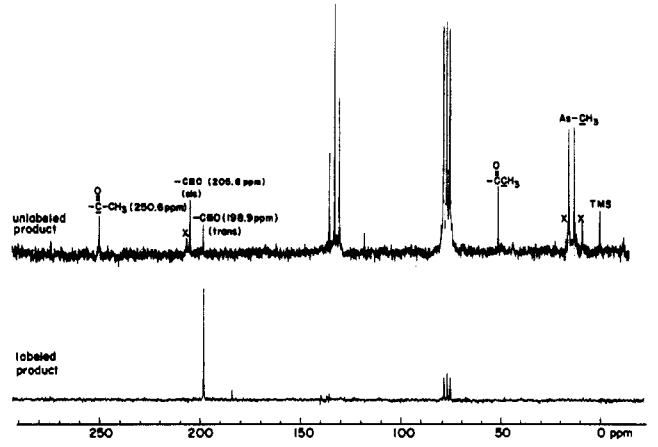


Figure 4. Top: $^{13}C\{^1H\}$ NMR spectrum of unlabeled *fac*-[(diars)Fe(CO)$_3$(C(O)Me)]$^+$ in $CDCl_3$. Bottom: $^{13}C\{^1H\}$ NMR spectrum of specifically labeled **2i**.

In agreement with the Teller–Redlich rule[24] the total isotope shift of ca. 45 cm^{-1} expected on substitution of ^{13}C for ^{12}C in carbon monoxide is distributed between $\nu_{CO}(A'_a)$ (Δ = 2084 − 2075 = 9 cm^{-1}) and $\nu_{CO}(A'_b)$ (Δ = 2025 − 1998 = 33 cm^{-1}) while $\nu_{CO}(A'')$, which involves neither a displacement of the label nor coupling with the A′ modes, shows no appreciable shift (Δ = 2025 − 2025 = 0). A cis- (with respect to acyl) labeled product (C_1 molecular symmetry) would, on the other hand, distribute the isotope shift among all three CO stretching frequencies on the assumption that they are coupled.

Nuclear magnetic resonance spectra confirm the stereochemical analysis. Figure 4 compares the $^{13}C\{^1H\}$ NMR spectra of the unlabeled and labeled acyl product. Clearly the ^{13}CO is introduced specifically into the 198.6-ppm site with no detectable scrambling. Comparison with the unlabeled analogue, which shows two nonequivalent CO sites at 205.6 and 198.9 ppm with relative intensities of ca. 2/1, respectively, shows that the label is trans to acyl.

Carbon monoxide promoted insertion (where the question of kinetic vs. thermodynamic product control does not apply since only *fac* product is observed) is thus intramolecular and proceeds with the same stereospecificity and relative stereochemistry as found for the majority of phosphine bases discussed above. Decarbonylation of **2i** proceeds readily in refluxing dichloromethane to give **1** with no detectable retention of the label (viz., ^{13}C NMR and IR analyses), indicating a stereospecific loss of the CO trans to acyl.

Discussion

The evidence presented in this paper clearly establishes the lability of the cationic Fe–Me complex **1** with respect to neutral Lewis base promoted migratory insertion. Although significant amounts of *cis*-L–Fe–(C(O)Me) product form for the highly basic trialkyl- and dialkylarylphosphines studied, the product stereochemistry under kinetic control is overwhelmingly *trans*-L–Fe–C(O)Me. Interpretation of the stereochemical results is possible on the basis of the reaction mechanism shown in Scheme III, which has been shown to apply to the majority of migratory carbonyl insertion reactions studied.[1-3,5,15] Preliminary results[25] indicate the same general mechanism applies to the reaction of **1** with neutral Lewis bases with the proviso that $k_2[L] >> k_{-1}$.

Scheme III

$$[(\text{diars})\text{Fe}(\text{CO})_3\text{Me}]^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [(\text{diars})\text{Fe}(\text{CO})_2(\text{C(O)Me})]^+$$
1 **8**

$$\xrightarrow{k_2[L]} [(\text{diars})\text{Fe}(\text{CO})_2\text{L}(\text{C(O)Me})]^+$$

However formed, the intermediate **8** must have an incipient vacant site trans to acyl in order to accommodate the observed stereochemistry. Rate-determining concerted migration of methyl and a cis-lying CO would lead to an approximate trigonal-bipyramidal intermediate with an equatorial acyl; cf. **9** (Scheme IV). The same intermediate *must* be reached by the reverse reaction, which proceeds via the loss of the unique CO in **2i** in agreement with the substantial trans-directing effect established for η^1-acyl relative to group 5 donors[13,14,26] or CO.[27] Thus the Ru(II) complex **6** readily exchanges[13] phosphine from the site trans to acyl but not (except under more forcing conditions) trans to phosphine in spite of the statistical advantage. Additional evidence derives from the observation that the Ir(III) complex **10** readily dissociates Cl$^-$ (trans to acyl) to give, in the presence of excess Br$^-$, the di-

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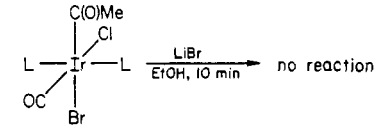
10 11

L = $PhPMe_2$



12

L = $PhPMe_2$

bromo complex **11** while its isomer **12** (Cl trans to CO) does not.[27] Clearly, then, the trans effect of acyl is larger than the trans effect of diars in dissociative reactions of **2i**.

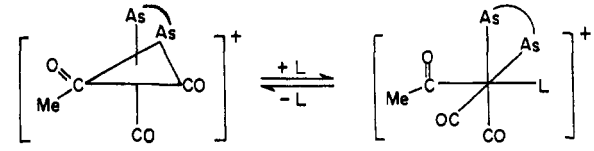
While the current data are insufficient to establish the origin of the trans effect attributed to acyl, it is apparent that η^1-acyl can be viewed as a strong σ-bonding ligand.[28] As such the arguments of Langford and Gray[29a] as well as Drago and Zumdahl[29b] which describe a σ trans effect in terms of a transition-state stabilization and a (less important) ground-state destabilization (trans influence) would seem to apply. Alternatively, arguments based on π bonding, although probably of less importance in the cationic Fe(II) complexes of the present study than in more electron-rich systems, lead to the same conclusion. The CO groups cis to acyl are in fact trans to the poorly π-accepting diars and are thus rendered nonlabile relative to the CO group trans to acyl, which, in principle at least, has π-acceptor capabilities.

In the case of decarbonylation of **2i**, the principle of microscopic reversibility quite clearly also requires[30-32] that preferential loss of CO trans to the labilizing η^1-acyl in the decarbonylation of **2i** produce an intermediate which not only is identical with the one formed during the insertion of **1** but also discriminates in favor of nucleophilic attack by L at a site trans to acyl (cf. Scheme IV). Less basic ligands (CO, phosphites, diarylalkylphosphines) thus react with **9** to give acyls to stereochemistry **2** while highly basic trialkylphosphines[33] react with less stereoselectivity to give mixtures of **2** and **3** or **4**.

Some relaxation of intermediate **9** toward a square pyramid with apical acyl might be anticipated in view of crystallographic data[34-36] for Rh(III) analogues and, on the assumption that η^1-acyl is a strong σ donor,[28] molecular orbital calculations of ligand site preference in five-coordinate d^6 species.[37,38] However, any such distortions would only enhance the observed stereoselectivity.

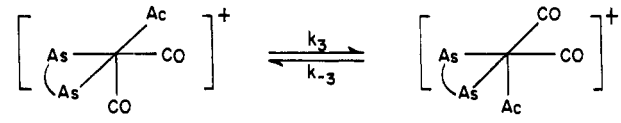
Alternatively it might be expected that the increased basicity of the trialkylphosphines compared to that of the other bases

Scheme IV



9 2

Scheme V



13 14

k_4 [L] k_5[L]

3 2

examined in this study combined with the cationic nature of the substrate **1** would facilitate a direct S_N2 insertion.[39,40] Concurrent uni- (first order in **1**) and bimolecular (first order in **1**, first order in L) paths could lead to the observed *cis,trans*-**2** and *cis,cis*-(**3** or **4**) products, respectively. Our observation of clean first-order kinetics[25] and constant product ratios in the presence of varying concentrations of excess $PhPMe_2$ make this hypothesis untenable.

A further mechanistic possibility involves the capture of a stereochemically labile square-pyramidal intermediate **13** formed by methyl migration of **1** (cf. Scheme V). As k_4[L] approaches k_3, significant amounts of **13** would be trapped as *cis,cis*-**3** before rearrangement to the more stable intermediate **14**. The argument requires a sharp increase of the bimolecular rate constant k_4 with increasing ligand basicity as might be intuitively expected for $P(OR)_3$ vs. PR_3. However, evidence from direct measurements[41] as well as competition ratios[42,43] establishes that bimolecular rate constants for the capture of five-coordinate d^6 fragments are rather insensitive to the nature of the nucleophile. With the assumption that a first-order reaction applies[25] these expectations are verified for the intermediate produced from **1**. Competition of equimolar concentrations of PMe_3 and $P(OMe)_3$ for the intermediate **8** showed only a slight preference (2.7/1) for the more basic ligand. Thus Scheme V seems unlikely at this point, and we conclude that the stereochemical results are best interpreted assuming a stereodirected nucleophilic attack on a pseudo-trigonal-bipyramidal complex (**9**) (or square-pyramidal intermediate with apical acyl descendant from **9**) controlled by the strong trans effect of η^1-acyl.

Finally we note that **2i** decarbonylates under very mild conditions (refluxing methylene chloride) compared to those for its neutral isoelectronic and isostructural Mn(I) analogue *fac*-[(diars)$Mn(CO)_3(C(O)Me)$],[4b] which required extended reflux in toluene. Apparently the cationic nature of **2i** sufficiently increases formal positive charge on iron to weaken the bond to CO and markedly facilitate decarbonylation. Molecular orbital calculations[5] as well as independent observations of oxidative activation of the reaction **15** → **16**,[44]

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rapid alkyl-acyl interconversion of the cationic Rh(III) complexes **17** → **18**,[34] and the facile acyl formation of **1** observed in this study indicate that the formal charge on the metal also plays an important role in methyl migration.

$$\underset{\mathbf{15}}{C_5H_5Fe(CO)_2R} \xrightarrow[CO]{EtOH,\ CuCl_2,} \underset{\mathbf{16}}{RC(O)Et}$$

$$\underset{\mathbf{17}}{[Rh(PhPMe_2)_3(Me)(CO)Cl]^+} \rightarrow \underset{\mathbf{18}}{[Rh(PhPMe_2)_3(C(O)Me)Cl]^+}$$

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Registry No. **1**, 78764-24-6; **2a**, 82963-54-0; **2b**, 82963-56-2; **2c**, 82963-58-4; **2d**, 82963-60-8; **2e**, 82963-62-0; **2f**, 82963-64-2; **2g**, 82963-66-4; **2h**, 82963-68-6; **2i**, 82963-70-0; **2j**, 82963-72-2; **2k**, 82963-74-4; **3f**, 83023-49-8; **3g**, 83023-47-6; **4f**, 83023-53-4; **4g**, 83023-51-2.

Contribution from the Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada T6G 2G2

Steric Control of the Site Preference in Five-Coordinate Iron Carbonyl Derivatives: Molecular Structures of (η^2-Diethyl fumarate)(triphenylphosphine)tricarbonyliron, $Fe(CO)_3(PPh_3)$(DEF), and (η^2-Diethyl maleate)(triphenylphosphine)tricarbonyliron, $Fe(CO)_3(PPh_3)$(DEM)

MATTHEW V. R. STAINER and JOSEF TAKATS*

Received October 15, 1981

The structures of $Fe(CO)_3(PPh_3)$(DEF) and $Fe(CO)_3(PPH_3)$(DEM) (Ph = C_6H_5, DEF = diethyl fumarate, DEM = diethyl maleate) have been determined by single-crystal X-ray diffraction techniques. The crystals of $Fe(CO)_3(PPh_3)$(DEF) are monoclinic, space group $C2/c$, with unit cell constants a = 17.674 (4) Å, b = 16.551 (4) Å, c = 19.491 (6) Å, β = 91.98 (2)°, and Z = 8. $Fe(CO)_3(PPh_3)$(DEM) crystallizes in triclinic space group $P\bar{1}$ with unit cell constants a = 14.792 (21) Å, b = 10.420 (1) Å, c = 10.807 (2) Å, α = 112.41 (1)°, β = 65.89 (1)°, γ = 90.51 (1)°, and Z = 2. Full-matrix least-squares refinement of the structures with 3541 and 3119 unique reflections ($F_o^2 \geq 3(\sigma F_o))^2$) led to final discrepancy indexes of R = 0.056, R_w = 0.073 and R = 0.053, R_w = 0.064 for $Fe(CO)_3(PPh_3)$(DEF) and $Fe(CO)_3(PPh_3)$(DEM), respectively. Both molecular structures are based on the trigonal bipyramid with the olefin bonded in an equatorial position, as is expected from electronic considerations. The PPh_3 ligand occupies an axial site in the maleate complex, while in the fumarate derivative it coordinates in the electronically less favored equatorial site. The unexpected equatorial disposition of the phosphine ligand in $Fe(CO)_3(PPh_3)$(DEF) is assigned to the steric hindrance caused by the trans substituents of the DEF moiety at the axial sites of the trigonal bipyramid. The Fe–CO and Fe–C(olefin) distances appear to reflect the relative π acidity of the coordinated olefins. This is also borne out by the degree of deformation of the olefinic ligands. Noteworthy is the fact that, whereas in the DEF moiety both substituents are almost coplanar with the plane of the olefin, in the DEM ligand only one substituent is oriented in this fashion; the other is approximately perpendicular to this. The resulting asymmetric nature of this olefin is reflected in the M–C(olefin) distances; the bond to the carbon bearing the π-acceptor substituent is longer.

Introduction

The elucidation of the coordination geometry of five-coordinate transition-metal complexes and the distribution of ligands on the coordination sphere have formed the basis of several theoretical studies[1,2] and a multitude of physical, mainly X-ray diffraction, investigations.[3] It is now well established that, for d^8 metal complexes containing nominally monodentate ligands, the geometry is based overwhelmingly on the trigonal bipyramid. In a very broad treatment, Hoffmann and Rossi[1] have established the electronic site preference of ligands and their influence on the metal–ligand bond distances in five-coordinate molecules. However, these authors readily recognized that the geometry of metal complexes is influenced not only by electronic factors but by steric effects as well.

During our studies on the fluxional behavior of $Fe(CO)_4$(olefin) derivatives[4a] we prepared a series of complexes of the type $Fe(CO)_3(PR_3)$(olefin)[4b] (PR_3 = PPh_3, PMe_2Ph, $P(OMe)_3$; olefin = diethyl fumarate, diethyl maleate). Since the compounds contain significantly different ligands, their structures could in principle shed light on the relative importance of steric and electronic factors in determining the positioning of ligands on pentacoordinate, trigonal-bipyramidal molecules. Furthermore, infrared spectroscopy seemed to indicate that the fumarate and maleate complexes belonged to different isomeric classes, and this gave added impetus to determine the solid-state structure of a member of each class. Here we report the single-crystal X-ray structure determination of $Fe(CO)_3(PPh_3)$(DEF) and $Fe(CO)_3(PPh_3)$(DEM).

Experimental Section

(Diethyl fumarate)- and (diethyl maleate)(triphenylphosphine)-tricarbonyliron, $Fe(CO)_3(PPh_3)$(DEF) and $Fe(CO)_3(PPh_3)$(DEM), were prepared by prolonged photolysis of $Fe(CO)_4(PPh_3)$ in the presence of excess olefin. Chromatography on alumina followed by crystallization from CH_2Cl_2/pentane affords the pure complexes as yellow crystals suitable for single-crystal X-ray diffraction studies.[4b]

Crystals of the complexes were sealed in thin-walled glass capillaries and aligned on a Picker FACS-1 automated diffractometer. A summary of the data collection is given in Table I.

The intensity data were processed in the usual manner, but because of the regular crystal shapes and small linear absorption coefficients,

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