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Preliminary communication

RATE-STRUCTURE CORRELATIONS FOR MIGRATORY CO INSERTION. STERIC ACCELERATION FOR THE OCTAHEDRAL IRON(II) CASE

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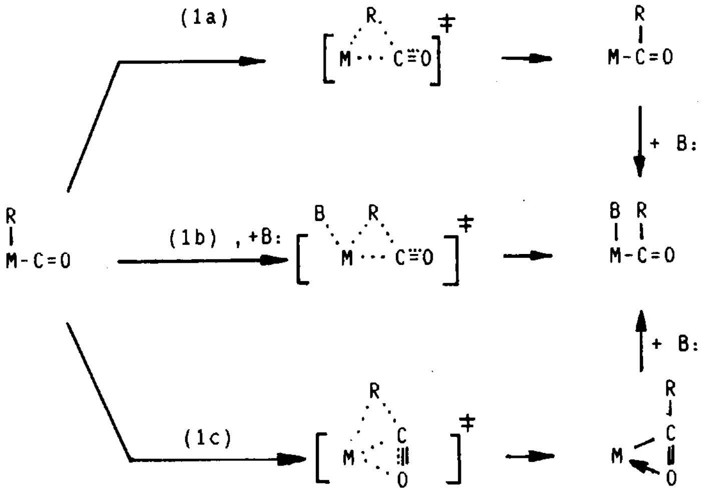
Summary

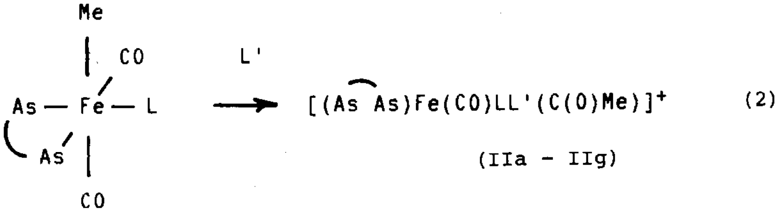
The kinetics of the migratory insertion reaction of *cis,cis*-[(diars)-Fe(CO)$_2$L(Me)]$^+$, (Ia—Ig), (L = $C_6H_{11}O_3P$ (ETPB), $P(OMe)_3$, $PhP(OMe)_2$, PMe_3, $PhPMe_2$, $Ph_2P(OMe)$ or Ph_2PMe) in the presence of excess L′ (L′ = $P(OMe)_3$ or i-C_3H_7NC) in methylene chlorine-d_2 to form [(diars)-Fe(CO)LL′(C(O)Me)]$^+$, (IIa—IIg), follow the rate law: Rate = k_{insert}[(I)]. The first order rate constant, k_{insert}, depends primarily on steric factors and shows an overall increase of a factor of 270 (at 290 K) as L varies from ETPB (cone angle 101°) to Ph_2PMe (cone angle 136°). The pronounced steric acceleration of insertion rate is in accord with a unimolecular rate determining insertion step which requires neither inter- nor intramolecular nucleophilic participation.

Previously [1] we proposed on the basis of kinetic and stereochemical evidence that the neutral Lewis base (B:) promoted migratory CO insertion on the d^6 octahedral complex *fac*-[(diars)Fe(CO)$_3$Me]$^+$ was essentially a unimolecular process. Kinetic analysis indicated a clean, first-order reaction with k_{insert} independent of both solvent nucleophilicity and base concentration consistent with the rate determining formation of the coordinatively unsaturated 16e^- acyl [(diars)Fe(CO)$_2$(C(O)Me)]$^+$ (cf. Scheme 1, eq. 1a). Although these results find recent experimental[2a—2d] and theoretical [2e] support, conflicting evidence derived from second order terms in the insertion rate law or from correlations of the insertion rate with solvent nucleophilicity exists [3a—3f] which imply substantial associative character for alkyl migrations onto carbon monoxide. In the latter case the transition state for alkyl migration presumably requires considerable bond formation either with solvent or with promoting base B: (cf. Scheme 1, eq. 1b).



SCHEME 1. As⌒As = o-(AsMe$_2$)$_2$C$_6$H$_4$; a, L = C$_6$H$_{11}$O$_3$P (ETPB); b, L = P(OMe)$_3$; c, L = PhP(OMe)$_2$; d, L = PMe$_3$; e, L = PhPMe$_2$; f, L = Ph$_2$P(OMe); g, L = Ph$_2$PMe; L = P(OMe)$_3$ or i-C$_3$H$_7$NC.

In cases where the insertion rate is independent of promoting base and where no correlation with solvent nucleophilicity is found, an associative transition state involving intramolecular dihapto coordination of the nascent acyl (Scheme 1, eq. 1c) cannot be discounted. [4] As the major kinetic product of migratory insertion of *fac*-[(diars)Fe(CO)$_3$Me]$^+$ was found to have a *trans*-B—Fe—(C(O)Me) link [5], we gave argued against participation of a putative dihapto acyl. In this work we provide further kinetic support of our original results [1] regarding the intimate mechanism of migratory CO insertion based on an unprecedented steric acceleration of the rate for eq. 2



[(As⌒As)Fe(CO)LL'(C(O)Me)]$^+$ (2)

(IIa - IIg)

(Ia - Ig)

The P-donor ligand substituted octahedral alkyl complexes (Ia—Ig) were stereospecifically prepared from *fac*-[(diars)Fe(CO)$_3$Me]$^+$ via a sequential migratory insertion-decarbonylation sequence [6a,b]. Owing to unfavourable equilibrium constants for the insertion step, the synthesis fails for sterically demanding P-donor ligands (e.g. PCy$_3$, PPh$_3$). The all-*cis* stereochemistry with the methyl group *cis* to both As atoms was fixed crystallographically [6a] in the case of Id and spectroscopically for the remaining isostructural derivatives. [7]. Two strong CO stretching frequencies and a selective, small three-bond ^{13}C^{31}P coupling to one of the *ipso* diars carbons found in the ^{13}C NMR spectrum of each case was considered sufficient to establish the all-*cis* geometry shown in structure I. As with the parent derivative [(diars)Fe(CO)$_3$Me]$^+$, the P-donor substituted derivatives (Ia—Ig) contain a *cis*-Me—Fe—CO link and are thus labile with respect to migratory insertion. [2b] ^{1}H NMR analysis of the reaction of the methyl complexes with a large (10—30 fold) excess of P(OMe)$_3$ in methylene chloride-d_2 indicated that the reaction proceeded cleanly according to eq. 2. Under these conditions acyl formation was complete for the methyl complexes Ia—Id but with phosphorus ligands of larger steric requirements Ie—Ig the reverse reaction became increasingly important and methyl $\rightleftharpoons$ acyl equilibria were observed even in the presence of a very large excess of trimethylphosphite. [8] The latter cases were successfully driven to completion using excess i-C$_3$H$_7$NC.

The rate of eq. 2 was determined in methylene chloride-d_2 with L′ (L′ = P(OMe)$_3$ or i-C$_3$H$_7$NC) as flooding reagent using ^{1}H NMR to monitor the decrease in intensity of the high field Fe—Me doublet (J ca. 6.5 Hz) at —0.47 to —0.67 ppm [9]. Good pseudo first-order behaviour was obtained over at least 2—3 half lives. Experiments at varying concentration of L′ determined that the insertion rate of Ia,Ib was independent of [P(OMe)$_3$] and thus confirmed the first order rate law: Rate = k_{obs}[I]. Further verification of a simple first order insertion as previously found [1] for I (L = CO) follows from the constancy of k_{obs} obtained for Ic,Id using either L′ = P(OMe)$_3$ or i-C$_3$H$_7$NC as promoting base.

TABLE 1

RATE CONSTANTS FOR $[(\widehat{\text{As\quad As}})\text{Fe(CO)}_2\text{L(Me)}]^+$ (IIa—IIg) (eq. 2) AT 290 K

	ETPB	P(OMe)$_3$	PhP(OMe)$_2$	PMe$_3$	PhPMe$_2$	Ph$_2$P(OMe)	Ph$_2$PMe
$k_{\text{obs}} \times 10^4$ s^{-1} [a]	0.30	0.96	2.1	5.9	9.1	10.7	80
	(±0.05)	(±0.1)	(±0.4)	(±1)	(±0.6)	(±0.7)	(±8)
Cone [b] angle	101	107	115	118	122	132	136
ν(CO) [c]	2042.3	2027.0	2028.0	2018.8	2016.6	2021.9	2016.9
	1990.4	1974.2	1975.8	1964.9	1964.2	1970.4	1964
Force [d] constant (mdyne/Å)	16.42	16.16	16.18	16.04	16.00	16.09	16.00
Electronic parameter [b]	2086.8	2079.5	2075.8	2064.1	2065.3	2072	2067

[a] Extrapolated to 290 K from plots of ln(k_{obs}) vs. $1/T$ using at least three rate constants determined in duplicate over a temperature range of ca. 20—30° C. Estimated error limits given in brackets. [b] Cone angles (ϕL) and electronic parameters taken from the data of Tolman [14]. [c] Infrared spectra were measured in CH$_2$Cl$_2$ and calibrated using DCl$_{(g)}$. The reported frequencies are considered accurate to within ± 1 cm^{-1}. [d] Calculated using the equations of Cotton and Kraihanzel [17].

The kinetic data presented in Table 1 clearly show that k_{obs}, which in this case is equivalent with the migratory insertion rate constant, k_{insert}, for eq. 2 is sensitive to changes in the ligand sphere. Presumably, both electronic and steric effects operate. There is little doubt that electronic effects are very important. Effective catalysis of alkyl migrations by oxidants [10] or coordination of Lewis acids to the migration terminus [11] delineates the importance of electronic effects on alkyl migrations in general. In an earlier study [12] we demonstrated that electronic effects are also important in the specific case of eq. 2 by showing that the replacement of Fe$^{\text{II}}$ by Mn$^{\text{I}}$ in complex I (L = CO) results in a sharp decrease in the insertion rate. These results are in collective agreement with a general migration mechanism [13] involving an intramolecular nucleophilic attack of alkyl on an electron-poor carbonyl and hence account for the sensitivity of the reaction to electronic factors.

The kinetic data of Table 1, however, show no apparent correlation of insertion rate with electronic effects alone as measured by the carbonyl stretching frequencies (or force constants) of the substrates Ia—Ig or by Tolman's electronic parameter for the appropriate ligand L [14]. On the basis of electronic effects alone ETPB, which shows the highest carbonyl stretching frequencies and presumably the lowest electron density on the carbon migration terminus, is predicted to have the largest k_{insert}. Exactly the opposite is observed. Clearly, the origin of the underlying structure-activity relationship must be sought elsewhere.

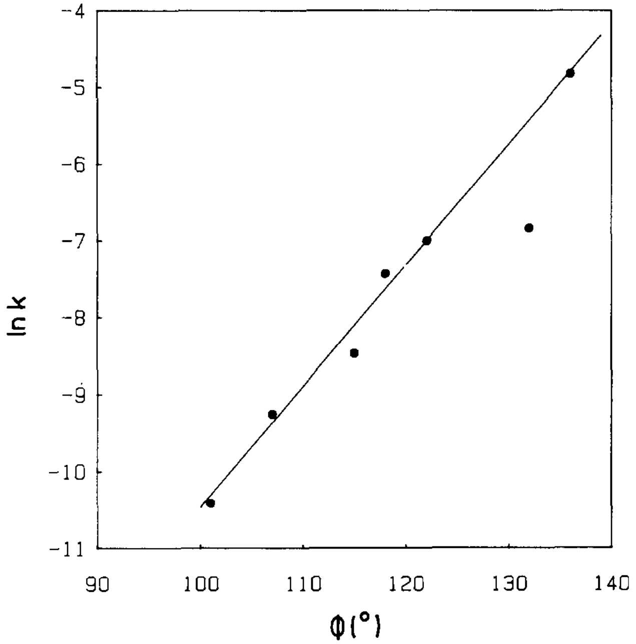


Fig. 1. Variation of $\ln(k_{insert})$ for eq. 2 with cone angle (ϕ) of the phosphine, L, in Ia—Ig.

Figure 1 shows a plot of $\ln(k_{insert})$ vs. the steric requirement of the ligand sphere as measured by Tolman's cone angle [14] of the phosphorus ligand L in the series Ia—Ig (cf. Table 1). The excellent correlation obtained demonstrates that, while electronic effects may well operate, steric effects appear to dominate. The steady increase in the insertion rate with increasing steric requirements of L indicates that the rate of migratory insertion according to eq. 2 is subject to a pronounced steric acceleration characteristic for dissociative reactions where the transition state is naturally less crowded than the ground state. [15]

Comparison of the data in Table 1 shows that the overall acceleration due primarily to steric factors found for eq. 2 is appreciable (k_{insert}(Ia, cone angle 101)/k_{insert}(Ig, cone angle 136) = ca. 270). Such significant effects are anticipated only for dissociative reactions in which the ground state substrate is sufficiently sterically congested so that a substantial reduction in the activation free energy is achieved on formation of a transition state with reduced coordination number. A crystallographic study of Id confirmed that distinct angular deviations from rigid octahedral geometry are required to accommodate the PMe_3 (cone angle 118°) ligand. [6a]

The kinetic results obtained in this study suggest that the insertion of the octahedral Fe^{II} complexes (I) according to eq. 2 is a simple unimolecular process and, taken together with the *trans*-acyl—Fe—L′ stereochemistry of the kinetic product [5], imply the formation of a coordinatively unsaturated monohapto acyl [16] of the type described by eq. 1a in Scheme 1. Neither solvent, L′, nor nascent acyl interact with the Fe atom prior to the transition state for insertion.

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References

1 C.R. Jablonski and Y.-P. Wang, Inorg. Chim. Acta, 69 (1983) 147.

2 (a) D.R. Saunders, M. Stephenson, and R.J. Mawby, J. Chem. Soc. (Dalton Trans.), (1984) 530; (b) D.R. Saunders, M. Stephenson, and R.J. Mawby, J. Chem. Soc. (Dalton Trans.), (1984) 1153; (c) G. Cardaci, G. Reichenbach, and G. Bellachioma, Inorg. Chem., 23 (1984) 2936; (d) T.C. Flood and K.D. Campbell, J. Am. Chem. Soc., 106 (1984) 2853; H. Berke and R. Hoffmann, ibid., 100 (1978) 7224.

3 (a) J.D. Cotton and R.D. Markwell, Organometallics, 4 (1985) 937; (b) J.D. Cotton and P.R. Dunstan, Inorg. Chim. Acta, 88 (1984) 223; (c) M. Wax and R.G. Bergman, J. Am. Chem. Soc., 103 (1981) 7028; (d) for leading references to the earlier literature appropriate to this point cf. A. Wojcicki, Adv. Organomet. Chem., 11 (1971) 87 and F. Calderazzo, Angew. Chem. Int. Ed. Engl., 16 (1977) 299.

4 Several Group VIIIb η^2-acyl complexes have been isolated. cf. W.R. Roper, G.E. Taylor, J.M. Naturs, and L.J. Wright, J. Organomet. Chem., 182 (1974) C46; W.R. Roper and L.J. Wright, ibid., 142 (1977) C1; U. Franke and E. Weiss, ibid., 165 (1979) 329.

5 C.R. Jablonski and Y.-P. Wang, Inorg. Chem., 21 (1982) 4037.

6 (a) C.R. Jablonski, Y.-P. Wang and N.J. Taylor, Inorg. Chim. Acta, 96 (1985) L17; (b) B. Gregory, C.R. Jablonski, and Y.-P. Wang, J. Organomet. Chem., 269 (1984) 75.

7 Satisfactory analyses and spectral data were obtained for all new compounds.

8 K_{eq} values extrapolated to 290 K were determined for eq. 2 by ^{31}P NMR in favourable cases IIb—IIf and were found to decrease with increasing total steric requirements of L and L′. In the worse case used (IId, L = $P(OMe)_3$), K_{eq} was determined to be ca. 200 dm^3/mol which leads to ca. 95% conversion in the presence of a 10-fold excess of L at the concentrations employed in the kinetic studies. The reaction of IIe with $P(OMe)_3$ was thermodynamically less favourable (K_{eq} at 290 K 50 dm^3/mol; ca. 83% conversion) hence kinetic data were obtained with L = i-C_3H_7 (nc) which proceeds to completion. Values of K_{eq} for eq. 2 with varying L and L′ will be presented elsewhere.

9 In a typical reaction 2—5 mg of the alkyl complex I was weighed under a nitrogen atmosphere into a standard 5 mm NMR tube fitted with a serum cap. A small amount of CD_2Cl_2 was added to dissolve the complex. The tube and contents were subsequently frozen and a known amount of $P(OMe)_3$ or i-C_3H_7NC was added through the septum cap via a micro syringe. Immediately before a kinetic run the tube was warmed briefly in an ice bath, diluted to a precalibrated mark with CD_2Cl_2, and quickly positioned in the NMR probe. Temperatures were calibrated using chemical shift measurements obtained from a standard methanol sample and were found to be constant to within ± 0.3 K. Spectra were recorded at computer determined time intervals and the digitized free induction decays were stored subsequent to further analysis. Rate constants, k_{obs}, were determined in duplicate from non-linear least squares computer fits of the first order expression $[I] = [I_0]\exp(-k_{obs}t)$ using at least 15 data points taken from intensity measurements on spectra recorded using a Bruker WP-80 spectrometer fitted with a B-VT-1000 temperature controller as the sum of twelve 8 K transients. An inverse gated homonuclear decoupling sequence was used to reduce interference from large signals resulting from excess L′. Reproducibility of individual rate constants was in general better than 5%. The k_{obs}(290 K) values reported in Table 1 are derived from plots of $\ln(k_{obs})$ vs. $1/T$.

10 (a) R.H. Magnuson, R. Meirowitz, S. Zulu, and W.P. Giering, Organometallics, 2 (1983) 460; (b) R.S. Bly, G.S. Silverman, M.M. Hossain, and K. Bly, Organometallics, 3 (1984) 642.

11 C.P. Horwitz and D.F. Shriver, Adv. Organometal. Chem., 23 (1984) 219.

12 C.R. Jablonski, Inorg. Chim. Acta, 112 (1986) C19.
13 D. Saddei, H.-J. Freund, and G. Hohlneicher, J. Organomet. Chem., 186 (1980) 63.
14 C.A. Tolman, Chem. Revs., 77 (1977) 313.
15 M.L. Tobe, Inorganic Reaction Mechanisms, T. Nelson and Sons, London, 1972, p. 63; F. Basolo and R.G. Pearson, Mechanisms of Inorganic Reactions, Wiley, New York, 1967, p. 162 and 387.
16 R.B. Hitam, R. Narayanaswamy, and A.J. Rest, J. Chem. Soc. (Dalton Trans.), (1983) 615.
17 F.A. Cotton and C.S. Kraihanzl, J. Am. Chem. Soc., 84 (1962) 4432.