Inorganica Chimica Acta, 112 (1986) L19–L22

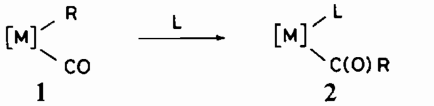
A Kinetic Study of the Trimethylphosphite Promoted Migratory CO Insertion of *fac*-Methyl-*o*-phenylenebis(dimethylarsine)tricarbonylmanganese: Evidence for Activation by Electron-poor 18e$^-$ Transition Metals

CHESTER R. JABLONSKI

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

Received May 27, 1985

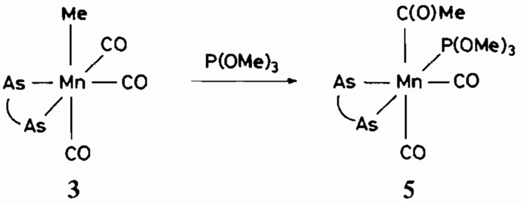
Several successful strategies currently exist for activating the migratory alkyl insertion reaction of transition metal bound carbon monoxide according to eqn. (1).



(1)

Chemical or electrochemical redox catalysis either by 1e$^-$ oxidation [1] or 1e$^-$ reduction [2] which produce reactive 17e$^-$ or 19e$^-$ intermediates respectively have been reported. Intermolecular [3–5] and more recently intramolecular [6] bifunctional electrophilic activation involving binding to the oxygen atom of a terminal carbonyl group are also documented. In this communication we present evidence based on kinetic studies of the iso-structural d^6 complexes *fac*-[(diars)Mn(CO)$_3$(Me)] [7], 3, and [*fac*-[(diars)Fe(CO)$_3$(Me)]$^+$ [8], 4, which extends the known activating groups to include electrophilic carbon-bonded 18e$^-$ metals.

Like the parent [Mn(CO)$_5$(Me)] [9, 10] and the phosphine substituted derivatives [(L$_n$)Mn(CO)$_{5-n}$(Me)] [11], the chelated diarsine manganese complex 3 reacts smoothly with P-donor ligands according to eqn. (2). Extended reaction with excess trimethylphosphite in refluxing chloroform affords a single isolable acyl isomer, 5.



(2)

As⌒As = o-(AsMe$_2$)$_2$C$_6$H$_4$

The all-*cis* geometry, 5, established on the basis of spectroscopic evidence* is consistent with the observation of two infrared-active carbonyl stretching frequencies and four nonequivalent As–Me resonances in the ^{1}H and ^{13}C NMR spectra. A small but distinct four-bond ^{1}H–^{31}P coupling found for two of the four As–Me sites favours the all-*cis* geometry with the phosphite *trans* to one As atom (J = *ca.* 0.5 Hz) and *cis* to the other (J = 0 Hz), *cf.* structure 5. Low temperature (200 K) ^{13}C NMR spectra which effectively selfdecouple ^{55}Mn (I = 1) and ^{13}C (I = ½) corroborate the assignment. A three-bond ^{13}C–^{31}P coupling of 7.9 Hz to one of the two nonequivalent diars C$_{ipso}$ is fully in accord with structure 5 but not the alternative all-*cis* isomer. Although it has been convincingly demonstrated that the methyl migration mechanism applies for [Mn(CO)$_5$(Me)] [10], it is evident in the present case either that a CO migration mechanism [12] operates or that 5 is not the kinetic product (*vide infra*).

Careful examination of ^{1}H NMR spectra in methylene chloride early in the reaction shows the presence of a weak transient signal at 2.55 ppm. Low maximum concentrations for the transient (0.1 mol fraction calculated on the basis of a three proton signal at *ca.* 10% conversion) precluded a definitive assignment. An inflection point coincident with the maximum concentration of the transient was observed in the ^{1}H NMR derived concentration/time profiles for the formation of 5. The transient may be tentatively formulated** as an isomeric kinetic [11, 13] acyl product [(diars)Mn(CO)$_2$(P(OMe)$_3$)(C(O)Me)], 5a, or as [(diars)Mn(CO)$_2$(C(O)Me)], 6, with either a 16e$^-$ monohapto structure similar to that detected in matrix isolation studies [14] and frequently presumed on the basis of kinetic [9, 15] and stereochemical evidence [10] in the case of [Mn(CO)$_5$(Me)] or a coordinatively saturated dihapto acyl structure found in other non-oxophilic d^6 cases [16]. The rate of phosphite promoted insertion of 3 according to eqn. (2) was determined by monitoring the decrease in the Mn–Me ^{1}H NMR signal

---

*Melting point 172–173 °C; *Anal.* Calc. for C$_{17}$H$_{28}$O$_6$As$_2$MnP: C, 36.19; H, 5.00. Found: C, 36.35; H, 5.08. IR(CH$_2$Cl$_2$): ν(CO) 1929, 1856; ν(acyl) 1547 cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$): 5.28 (m, 4, diars); 3.71 (d, J = 10.6 Hz, 9, P(OMe)$_3$); 2.26 (s, 3, acyl); 1.61 (s, 3, As–Me); 1.52 (s, 3, As–Me); 1.42 (d, J = 0.6 Hz, 3, As–Me); 1.29 (d, J = 0.5, 3, As–Me). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 200 K): 297.0 (d, J = 29.5, –$\underline{C}$(O)Me); 227.2 (d, J = 31.5, CO); 220.3 (d, J = 19.7, CO); 142.8 (d, J = 7.9, C$_6$H$_4$ *ipso*); 139.8 (s, C$_6$H$_4$ *ipso*); 130.0, 130.9 (s, C$_6$H$_4$ *ortho* and *meta*); 51.8 (d, J = 5.9, P(OMe)$_3$); 51.4 (s, –C(O)$\underline{Me}$); 14.4, 13.4, 11.7, 11.2 (s, AsMe).

**Further effort to establish the identity of this transient by trapping with stronger nucleophiles is in progress.

0020-1693/86/$3.50

at −1.21 ppm in deuterated methylene chloride at 333 K* in the presence of a large excess of phosphite ligand. Excellent pseudo first order behaviour was observed and all reactions were followed for at least three half-lives. The first order rate constants, k_{obs}, were determined from non-linear (least squares fits [17] of the first order expression $[3] = [3]_0\exp(-k_{obs}t)$ with the initial concentration $[3]_0$, and k_{obs} as parameters. The results are presented in Table I.

TABLE I. Kinetic Data for Eqn. (2) in Methylene Chloride at 333 K

$[3]^a$ (mol/l)	$[P(OMe)_3]^a$ (mol/l)	$k_{obs} \times 10^6$ $(s^{-1})^b$
7.42×10^{-3}	8.49×10^{-2}	5.47(0.42)
9.89×10^{-3}	1.42×10^{-1}	6.68(0.32)
1.98×10^{-2}	2.84×10^{-1}	9.08(0.30)
1.98×10^{-2}	5.68×10^{-1}	10.6(0.30)
1.98×10^{-2}	1.14	10.6(0.30)
1.98×10^{-2}	1.99	10.3(0.30)
2.83×10^{-3}	2.83×10^{-2}	3.60(0.82)
5.67×10^{-3}	5.66×10^{-2}	4.17(0.27)
8.50×10^{-3}	8.48×10^{-2}	5.46(0.18)
1.13×10^{-2}	1.41×10^{-2}	7.86(0.14)
2.26×10^{-2}	1.14×10^{-1}	7.91(0.18)
1.13×10^{-2}	2.82×10^{-1}	9.69(0.25)
2.26×10^{-2}	2.28×10^{-1}	9.34(0.23)
2.26×10^{-2}	5.66×10^{-1}	10.0(0.22)
2.26×10^{-2}	8.48×10^{-1}	10.6(0.27)
2.26×10^{-2}	1.70	10.8(0.25)

[a] +/− 5% estimated error. [b] Non linear iterative least squares fit for $[3] = [3]_0\exp(-k_{obs}t)$ using the Wentworth algorithm [17]. Relative concentrations of 3 were determined from internally referenced (Mn–Me/TMS) peak height or peak area data using an exponential apodization function with a time constant of 0.75–1.5 Hz on 24 or 48 transient 8 K free induction decays collected at 303 K with a total delay of 6 s between successive scans. [b] Standard deviations are shown in parentheses.

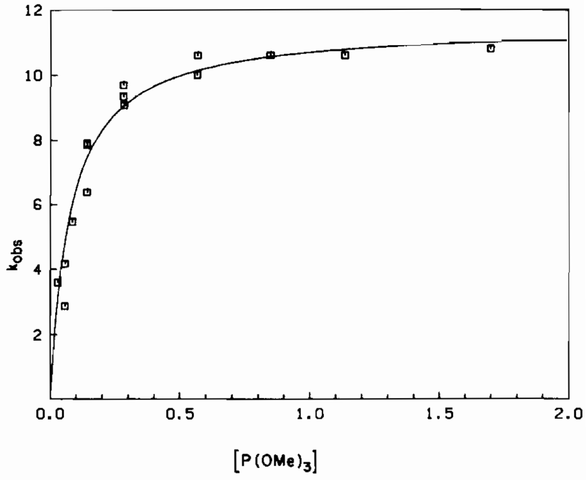


Fig. 1. Pseudo first order rate constants, k_{obs} ($\times 10^6$ s^{-1}), *vs.* $[P(OMe)_3]$ (mol/l) for eqn. (2).

Kinetic studies of the migratory insertion reaction of $[Mn(CO)_5Me]$ have shown that the rate law is highly dependent both on solvent and promoting base L: [15] with second order kinetics (Rate = $k[Mn][L:]$) or mixed first and second order (Rate = $k'[Mn] + k[Mn][L:]$) generally prevailing in low dielectric, low donicity media [18]. We find in the present case that plots of the pseudo first order rate constants k_{obs} *vs.* $[P(OMe)_3]$ tend towards a limiting value and therefore define a saturation kinetics regime (*cf.* Fig. 1) in accord with the formation of a reactive intermediate which either returns to reactant or is intercepted by the promoting base and converts to product [15] with similar overall rates.

It is well to note that examination of a restricted concentration range may well give the appearance of simple second order kinetics, particularly if return of the intermediate to reactant is appreciable. By comparison, the Fe(II) analog 4 shows clean, first-order kinetics (zero-order in promoting base) consonant with the formation of an intermediate having little tendency to return to reactant [8]. An iterative computer fit [17] of the pseudo first order rate data of Table I to the saturation kinetics expression (3) converged with $k_a = 1.15(0.2) \times 10^{-5}$ s^{-1} and $k_b = 7.76(0.43) \times 10^{-2}$ mol/l.

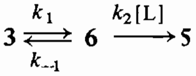
$$k_{obs} = k_a[L]/(k_b + [L]) \qquad (3)$$

The kinetic results permit several reaction schemes. Scheme 1 applies to the straight forward case where the transient observed is the $16e^-$ h^1 or $18e^-$ h^2 acyl 6 (*vide supra*). Application of the usual steady state approximation for the intermediate 6 provides the k_{obs} expression (3) with $k_a = k_1$ and $k_b = k_{-1}/k_2$. Scheme 2 applies to the case where the observed transient acyl is the kinetic product, 5a, formed via a single unobserved intermediate 6 (Scheme 2a) or a dissociative mechanism [13, 19] involving the successive formation of two unstable intermediates 6,6′ with different stereochemistry (Scheme 2b). Application of the steady state approximation for all the intermediates (5a, 6, 6′) gives the k_{obs} expression (3) with $k_a = k_1$ and $k_b = k_{-1}/k_2$ for mechanism 2a and $k_a = k_1$ and $k_b = k_{-1}/k'$, where $k' = k_2k_3k_4/$

---

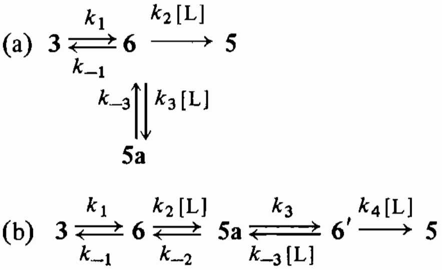
*In a typical run weighed amounts of 3 and at least a 10-fold excess of the flooding reagent, $P(OMe)_3$, were transferred to standard 5 mm NMR tubes and carefully diluted to a precalibrated mark. The contents were subjected to three freeze/thaw degassing cycles, sealed under an atmosphere of dry nitrogen, and equilibrated in a constant-temperature bath. The tubes were periodically withdrawn, quenched by cooling to 273 K, and their ^1H NMR spectra determined.

$(k_{-2}k_{-3} + k_{-2}k_4 + k_3k_4)$ for mechanism 2b. Following the rate of total acyl product appearance yields less precise but identical results within the limits of experimental error confirming the application of the Bodenstein assumption ([intermediates] $\ll$ [3] + [5]) used in the kinetic analysis.



$$3 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 6 \xrightarrow{k_2[\mathrm{L}]} 5$$

Scheme 1.



$$\text{(a)}\quad \begin{tikzcd} 3 \arrow[r, shift left, "k_1"] & 6 \arrow[l, shift left, "k_{-1}"] \arrow[r, "k_2{[\mathrm{L}]}"] \arrow[d, shift left, "k_3{[\mathrm{L}]}"] & 5 \\ & 5\mathrm{a} \arrow[u, shift left, "k_{-3}"] & \end{tikzcd}$$

$$\text{(b)}\quad 3 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 6 \underset{k_{-2}}{\overset{k_2[\mathrm{L}]}{\rightleftharpoons}} 5\mathrm{a} \underset{k_{-3}[\mathrm{L}]}{\overset{k_3}{\rightleftharpoons}} 6' \xrightarrow{k_4[\mathrm{L}]} 5$$

Scheme 2.

Comparison of the rate of migratory CO insertion (eqn. (1)) for the Mn(I) complex 3 with the isoelectronic and isostructural Fe(II) complex 4 [8] demonstrates that changes in the electrophilicity of the d^6 central metal can exert a very pronounced effect on the rate of reaction (1). A rate enhancement* of 1.82 × 10^4 is observed on going from Mn(I) to Fe(II). The rate enhancement obtained in this study which effectively results from an increase of one nuclear charge unit on going from Mn(I) to Fe(II) can be understood on the basis of a simple mechanistic model which views migratory CO insertion as an intramolecular nucleophilic attack of a donor alkyl (polarized as $M^{\delta+}$–$R^{\delta-}$) on an acceptor CO (polarized as $M^{\delta-}$–$C^{\delta+}$–O) [4, 20]. Clearly, whether attributable to a diminution of the antibonding pi CO orbital energy [4, 21] or, as recent extended Huckel calculations appear to suggest, to diminished repulsive interactions of the filled carbon sigma bonding FMOs of R^- and M–CO on approach to the transition state [21, 22], factors which serve to increase carbonyl carbon electrophilicity will facilitate the reaction according to eqn. (1). Since M–CO polarization is largely determined by the extent of backbonding, a convenient measure for the relative electrophilicity of Fe(II) and Mn(I) is provided by the CO stretching frequencies which establish the relative order 4 [8] (ν_{CO} (CH_2Cl_2) = 2082, 2018 cm^{-1}) $\gg$ 3 (ν_{CO} (CH_2Cl_2) = 1993, 1911, 1882 cm^{-1}).

These results support the interpretation that the oxidative and Lewis activation of migratory alkyl insertions are a common consequence of increased electrophilicity at the migration terminus. Very recent evidence indicates that alkyl migrations to carbenes can be similarly activated [23].

Acknowledgements

We thank the Natural Sciences and Engineering Research Council of Canada and Memorial University for financial support.

References

1 R. S. Bly, G. S. Silverman, M. M. Hossain and K. Bly, *Organometallics, 3,* 642 (1984); R. H. Magnuson, R. Meirowitz, S. Zulu and W. P. Giering, *Organometallics, 2,* 460 (1983); R. H. Magnuson, R. Meirowitz, S. Zulu and W. P. Giering, *J. Am. Chem. Soc., 104,* 5790 (1982); R. H. Magnuson, S. Zulu, W.-M. T'sai and W. P. Giering, *J. Am. Chem. Soc., 102,* 6888 (1980); E. K. G. Schmidt and M. J. Dogan, *J. Organomet. Chem., 234,* 73 (1982); M. P. Balem, M. Le Plouzennec and M. Louer, *Inorg. Chem., 21,* 2573 (1982); D. L. Reger and E. Mintz, *Organometallics, 3,* 1759 (1984); S. N. Anderson, C. W. Fong and M. D. Johnson, *J. Chem. Soc., Chem. Commun.,* 163 (1973); K. M. Nicholas and M. Rosenblum, *J. Am. Chem. Soc., 95,* 4449 (1973).

2 D. Miholova and A. A. Vlcek, *J. Organomet. Chem., 240,* 413 (1982).

3 J. P. Collman, R. G. Finke, J. N. Cawse and J. I. Brauman, *J. Am. Chem. Soc., 100,* 4766 (1978).

4 D. F. Shriver, in P. C. Ford (cd.), 'A.C.S. Symp. Ser.' Vol. 152, Am. Chem. Soc., Washington, D.C., 1981, Chap. 1; C. P. Horwitz and D. F. Shriver, *Adv. Organomet. Chem., 23,* 219 (1984).

5 S. J. LaCroce and A. R. Cutler, *J. Am. Chem. Soc., 104,* 2312 (1982).

6 S. J. Mclain, *J. Am. Chem. Soc., 105,* 6355 (1983).

7 C. S. Kraihanzel and P. K. Maples, *Organomet. Chem., 117,* 159 (1976).

8 C. R. Jablonski and Y.-P. Wang, *Inorg. Chim. Acta, 69,* 147 (1983); C. R. Jablonski and Y.-P. Wang, *Inorg. Chem., 21,* 4037 (1982); C. R. Jablonski, *Inorg. Chem., 20,* 3940 (1981).

9 E. J. Kuhlmann and J. J. Alexander, *Coord. Chem. Rev., 33,* 195 (1980).

10 T. C. Flood, J. E. Jensen and J. A. Statler, *J. Am. Chem. Soc., 103,* 4410 (1981).

11 C. S. Kraihanzel and P. K. Maples, *J. Organomet. Chem., 20,* 269 (1969); P. K. Maples and C. S. Kraihanzel, *J. Am. Chem. Soc., 90,* 6645 (1968).

12 M. Pankowski and M. J. Bigorgne, *J. Organomet. Chem., 251,* 333 (1983).

13 K. Noack, M. Ruch and F. Calderazzo, *Inorg. Chem., 7,* 345 (1968).

14 R. B. Hitam, T. Narayanaswamy and A. J. Rest, *J. Chem. Soc., Dalton Trans.,* 615 (1983).

15 F. Calderazzo, *Angew. Chem., Int. Ed. Engl., 16,* 299 (1977); A. Wojcicki, *Adv. Organomet. Chem., 11,* 87 (1973).

16 W. R. Roper and L. J. Wright, *J. Organomet. Chem., 142,* C1 (1977); W. R. Roper, G. E. Taylor, J. M. Naturs and L. J. Wright, *J. Organomet. Chem., 182,* C46 (1974); U.

---

*k_1(Fe(II))/k_1(Mn(I)) = 2.09 × 10^{-1} s^{-1}/1.15 × 10^{-5} s^{-1} where k_1 is the first order rate constant for migratory CO insertion at 333 K. The value for the Fe complex, 4, was extrapolated from the data of ref. 8.

Franke and E. Weiss, *J. Organomet. Chem., 165,* 329 (1979).

17 W. E. Wentworth, *J. Chem. Educ., 42,* 96; 162 (1965).

18 M. Green, R. I. Hancock and D. C. Wood, *J. Chem. Soc. A,* 2718 (1968); R. J. Mawby, F. Basolo and R. G. Pearson, *J. Am. Chem. Soc., 86,* 3994 (1964); B. L. Booth, R. N. Haszeldine and N. P. Woffenden, *J. Chem. Soc. A,* 1979 (1970).

19 G. Wright, R. W. Glyde and R. J. Mabwy, *J. Chem. Soc., Dalton Trans.,* 220 (1973).

20 D. Saddei, H.-J. Freund and G. J. Hohlneicher, *J. Organomet. Chem., 186,* 63 (1980); D. L. Thorn and T. H. Tulip, *J. Am. Chem. Soc., 103,* 5984 (1981); R. S. Threlkel and J. E. Bercaw, *J. Am. Chem. Soc., 103,* 2650 (1981).

21 A. Cameron, V. H. Smith and M. C. Baird, *Organometallics, 2,* 465 (1983).

22 H. Berke and R. Hoffmann, *J. Am. Chem. Soc., 100,* 7224 (1978).

23 J. C. Hayes, P. Jernakoff, G. A. Miller and N. Cooper, *J. Pure Appl. Chem., 56,* 25 (1984).