Journal of Organometallic Chemistry, 428 (1992) 99–105
Elsevier Sequoia S.A., Lausanne
JOM 22448

Phosphine induced cyclopentadienyl ring slippage catalyzes CO insertion into a methyl rhenium compound to produce an acetyl rhenium compound *

Charles P. Casey, Ross A. Widenhoefer and Joseph M. O'Connor
Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706 (USA)

(Received September 10, 1991)

Abstract

The carbonylation of (η^5-C_5H_5)Re(NO)(PMe$_3$)(CH$_3$) (1) to form (η^5-C_5H_5)Re(NO)(PMe$_3$)(COCH$_3$) (4) under 4.95 atm CO at 90°C is accelerated by a factor of > 25 in the presence of 0.28 *M* PMe$_3$. Kinetic studies established a third order rate law: Rate = k_3 [1] [PMe$_3$][*p*(CO)], where $k_3 = (7.52 \pm 0.36) \times 10^{-5}$ M^{-1} atm^{-1} s^{-1} at 90°C. Kinetic and phosphine exchange studies are in agreement with a mechanism initiated by phosphine induced ring slippage.

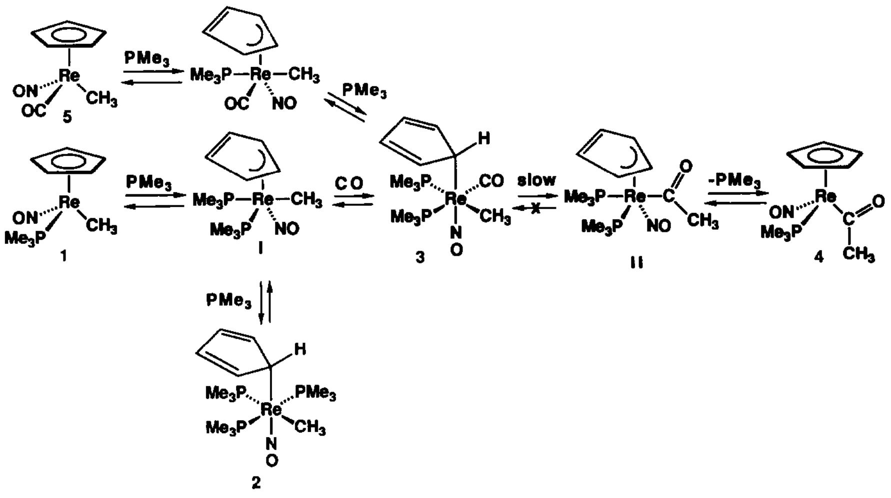
Introduction

The ability of a metal complex to develop an open coordination site is of central importance in the design of any catalytic system. This requirement is almost exclusively fulfilled through ligand dissociation. However, it is possible for coordinatively saturated metals not possessing a labile ligand to generate open sites via ring slippage of η^5-cyclopentadienyl ligands [1]. In catalysis, ring slippage has been invoked in the photolytic activation of carbon–hydrogen bonds of coordinatively saturated iridium [2] and zirconium [3] cyclopentadienyl complexes.

It is known that PMe$_3$ reacts reversibly with (η^5-C_5H_5)Re(NO)(CH$_3$)(PMe$_3$) (1) to form (η^1-C_5H_5)Re(NO)(CH$_3$)(PMe$_3$)$_3$ (2) presumably via the ring-slipped intermediate (η^3-C_5H_5)Re(NO)(CH$_3$)(PMe$_3$)$_2$ (I) [4]. The forward reaction may be viewed as the generation of the reactive η^3-Cp intermediate I by phosphine induced ring slippage, followed by trapping of the intermediate by a second phosphine to afford the η^1-Cp complex 2.

Correspondence to: Dr. C.P. Casey, Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706, USA.

* Dedicated to Professor Akio Yamomoto upon his retirement from the Tokyo Institute of Technology and in recognition of his central role in fostering excellent relations between chemists in Japan and the USA.



Scheme 1

In this context, it appeared plausible that a second, independently unreactive ligand could be incorporated into this $\eta^5 \rightarrow \eta^3 \rightarrow \eta^1$ cycle, in effect exploiting the phosphine generated η^3-Cp intermediate I. Specifically, we sought to determine whether PMe_3 would catalyze insertion of CO into $(\eta^5\text{-}C_5H_5)Re(NO)(CH_3)(PMe_3)$ (**1**). This could occur by addition of CO to η^3-Cp intermediate I to produce $(\eta^1\text{-}C_5H_5)Re(NO)(CO)(CH_3)(PMe_3)_2$ (**3**) followed by migration of methyl to CO aided by $\eta^1 \rightarrow \eta^3$ ring slippage (Scheme 1). The resulting η^3-Cp intermediate II could then expel PMe_3 with concurrent $\eta^3 \rightarrow \eta^5$ ring slippage to produce the acyl complex $(\eta^5\text{-}C_5H_5)Re(NO)(PMe_3)(COCH_3)$ (**4**). Here we report that PMe_3 does, in fact, catalyze insertion of CO into **1**.

Results

Migratory insertion of CO into a metal alkyl bond is an intramolecular process that requires prior coordination of CO [5]. In some cases, migratory insertion occurs by a first order process that generates a coordinatively unsaturated intermediate that is subsequently trapped by an incoming ligand. In other cases, the incoming ligand or a solvent molecule assists in the migratory insertion [6]. Since $(\eta^5\text{-}C_5H_5)Re(NO)(CH_3)(PMe_3)$ (**1**) has no coordinated CO, it is not surprising that CO insertion to produce $(\eta^5\text{-}C_5H_5)Re(NO)(PMe_3)(COCH_3)$ (**4**) occurred very slowly. When a 0.05 *M* solution of **1** was heated under CO (4.95 atm) at 90°C carbonylation proceeded slowly ($t_{1/2} = 68.8$ h) to produce **4** in low yield (20% by ^{1}H NMR). However, when the reaction was carried out in the presence of 0.28 *M* PMe_3, the reaction rate increased more than 25-fold ($t_{1/2} = 2.6$ h) and the yield of **4** improved to greater than 40%. The slow carbonylation of **1** in the absence of added PMe_3 is probably due to catalysis by the small observed concentration of free PMe_3 (~ 0.004 *M*) resulting from partial decomposition of **1** during the reaction; a small ($\sim 10\%$) amount of $(\eta^5\text{-}C_5H_5)Re(CO)(NO)(CH_3)$ (**5**) was also observed. Since these two experiments clearly established that PMe_3 catalyzes the

Table 1

PMe_3 dependence of rate of carbonylation of **1** at 90°C

$[PMe_3]$	p(CO) (atm) [b]	$(10^5)\ k_{obs}\ (s^{-1})$	% yield of **4**
– [a]	4.95	0.28 ± 0.06	20
0.063	4.95	1.89 ± 0.05	42
0.173	4.95	4.81 ± 0.08	46
0.277	4.95	7.24 ± 0.10	42

[a] No phosphine added. Decomposition led to ~ 0.004 *M* free PMe_3. [b] Calculated from amount of CO condensed at 77 K.

carbonylation of **1**, a more detailed kinetic study was undertaken to probe the mechanism of this unusual catalysis.

To determine the dependence of rate on PMe_3 concentration, the pseudo first order rate constants for the conversion of **1** to **4** at 90°C under constant CO pressure (4.95 atm) were measured as a function of the concentration of PMe_3. For each reaction, good first order rate plots for disappearance of **1** were obtained (Table 1). A plot of pseudo first order rate constants against $[PMe_3]$ established a first order rate dependence on $[PMe_3]$ (Fig. 1). Under constant CO pressure, a second order rate law was followed: rate $= k_2$ [**1**] $[PMe_3]$. The pseudo second order rate constant at 4.95 atm CO was calculated to be $k_2 = (2.51 \pm 0.05) \times 10^{-4}\ M^{-1}\ s^{-1}$.

To determine the dependence of rate on CO pressure, the pseudo first order rate constants for the conversion of **1** to **4** at 90°C in the presence of ~ 0.18 *M* PMe_3 were measured as a function of CO pressure. The data obtained in these experiments were inherently less accurate since errors in estimating the absolute CO pressure are ~ 10% for lower CO pressures. In addition, since it proved difficult to obtain identical concentrations of PMe_3, it was necessary to compare pseudo second order rate constants to correct for the slightly different PMe_3 concentrations (Table 2). A plot of pseudo second order rate constants against CO pressure established a first order rate dependence on the CO pressure (Fig. 2).

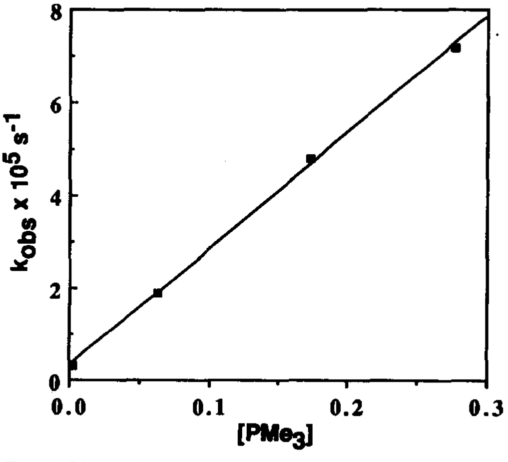


Fig. 1. PMe_3 dependence of the rate of conversion of **1** to **4** under 4.95 atm CO at 90°C.

Table 2

CO dependence of rate of carbonylation of **1** at 90°C

$[PMe_3]$	$p(CO)$ (atm) [a]	$(10^5)\ k_{obs}\ (s^{-1})$	$(10^4)\ k_2\ (M^{-1}\ s^{-1})$
0.230	1.47	0.76 ± 0.02	0.33
0.180	3.07	2.95 ± 0.05	1.63
0.173	4.95	4.81 ± 0.08	2.78
0.166	6.15	6.58 ± 0.15	3.96

[a] Calculated from amount of CO condensed at 77 K.

Overall, a third order rate law was followed: rate $= k_3$ [**1**] $[PMe_3][p(CO)]$. The third order rate constant was calculated to be $k_3 = (7.52 \pm 0.36) \times 10^{-5}\ M^{-1}\ atm^{-1}\ s^{-1}$.

The rates of phosphine exchange with both starting material **1** and carbonylation product **4** were found to be much faster than that of conversion of **1** to **4**. When a solution of **1** and $P(CD_3)_3$ (~ 0.17 *M*) under 4.95 atm CO at 90°C was monitored by ^1H NMR, phosphine was observed to exchange with **1** at a rate > 25 times faster than the rate of disappearance of **1** to form **4**. Similarly, when a solution of **4** and $P(CD_3)_3$ (~ 0.17 *M*) under 4.95 atm CO at 100°C was monitored by ^1H NMR, phosphine was observed to exchange with **4** at a rate > 7 times faster than the rate of conversion of **1** to **4** under these conditions and > 40 times faster than the rate of decomposition of **4**.

During the course of all of the phosphine catalyzed carbonylations of **1**, a nearly constant amount of the previously reported $(\eta^1\text{-}C_5H_5)Re(NO)(CO)(CH_3)(PMe_3)_2$ (**3**) ($\sim 5\%$) [7] was observed by ^1H NMR (δ 5.86, t, $J(PH) = 1.65$ Hz, Cp) until the reaction was nearly complete.

Discussion

The mechanism shown in Scheme 1 is consistent with all of our observations on the phosphine catalyzed carbonylation of **1**. The first step in the mechanism

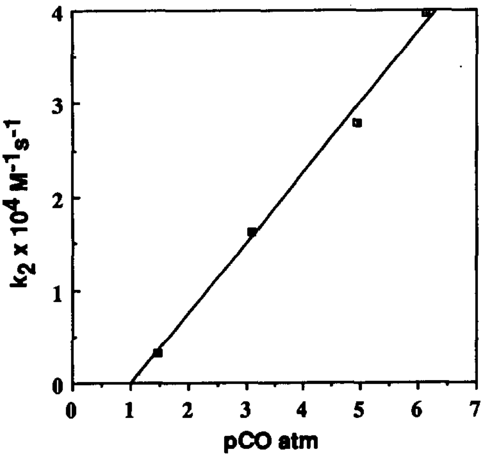


Fig. 2. CO pressure dependence of the rate of conversion of **1** to **4** in the presence of ~ 0.18 *M* PMe_3 at 90°C.

involves reversible addition of PMe_3 to **1** to produce η^3-Cp intermediate I. The rapid exchange of $P(CD_3)_3$ with **1**, and the observation that higher concentrations of PMe_3 than those employed here (8 *M*) lead to formation of (η^1-C_5H_5)Re(NO)(CH_3)(PMe_3)$_3$ (**2**) at 22°C are consistent with the formation of intermediate I. The second step in the mechanism involves addition of CO to η^3-Cp intermediate I which produces (η^1-C_5H_5)Re(NO)(CO)(CH_3)(PMe_3)$_2$ (**3**). Small amounts of **3** were observed during the carbonylation reaction; previously, the reversible formation of **3** from (η^5-C_5H_5)Re(NO)(CO)(CH_3) (**5**) and PMe_3 had been observed [7]. We propose that the rate determining step in the carbonylation of **1** is migration of methyl to the coordinated CO of η^1-Cp intermediate **3** which produces η^3-Cp intermediate II. The third order kinetic rate law requires that the composition of the transition state include the elements of **1**, PMe_3, and CO and is consistent with the proposed rate determining step. Finally, the reaction is completed by rapid dissociation of PMe_3 from η^3-Cp intermediate II which produces the observed carbonylation product **4** and regenerates the phosphine catalyst. The rapid exchange of $P(CD_3)_3$ with **4** is consistent with the reversibility of the loss of PMe_3 from η^3-Cp intermediate II.

The efficiency of the phosphine catalysis of the carbonylation of **1** is the direct result of the high nucleophilicity of PMe_3. Unlike CO, PMe_3 is nucleophilic enough to induce the difficult $\eta^5 \rightarrow \eta^3$-Cp ring slippage. Once the η^3-Cp intermediate has been accessed, either CO or PMe_3 is able to trap the reactive and indiscriminate η^3-Cp intermediate. Methyl migration can then occur in the resulting η^1-Cp intermediate.

In conclusion, we have presented the first example of a phosphine catalyzed CO insertion and have demonstrated the viability of induced cyclopentadienyl ring slippage in catalysis. We are now looking for additional examples of catalysis utilizing PMe_3 induced ring slippage.

Experimental

(η^5-C_5H_5)Re(NO)(PMe_3)($COCH_3$) (4). Previously, **4** was prepared in low yield from the thermolysis of (η^1-C_5H_5)Re(NO)(CH_3)(PMe_3)$_3$ (**2**) [4]. A higher yield procedure is reported here. A benzene solution of **1** (100 mg, 0.27 mmol) and PMe_3 (1 mmol, 0.15 *M*) under CO (8.3 mmol, 5 atm) was heated at 120°C for 10 h in a sealed tube. Volatile material was evaporated under vacuum and the residue was chromatographed (silica gel, acetone). The second yellow band to elute was collected and recrystallized from boiling hexane to give **4** (35 mg, 32%) as a yellow powder.

For **4**: m.p. 95–96°C(dec). ^1H NMR (benzene-d_6, 200 MHz): δ 4.84 (s, 5H), 2.89 (s, 3H), 1.10 (d, J(PH) = 10.2 Hz, 9H). $^{31}P\{^1H\}$ NMR (benzene-d_6, 125.8 MHz): δ −25.43. IR (CH_2Cl_2): 1644, 1548 cm^{-1}. HRMS (26 eV): calc. for $ReC_{10}H_{17}NO_2P$ 401.0553, found 401.0521.

Kinetic stability of 4. When a C_6D_6 solution of **4** (0.035 *M*) and PMe_3 (0.15 *M*) under 4.95 atm CO was heated at 90°C in a sealed tube, **4** gradually decomposed. After 14 h, 30% of **4** had decomposed. The decomposition of **4** did not follow first order kinetics: a plot of ln(**4**) *vs.* time showed initial rapid decomposition of **4** followed by a slower rate of decomposition. The decomposition of **4** did not produce detectable concentrations of either (η^5-C_5H_5)Re(NO)(CH_3)(PMe_3) (**1**) or (η^1-C_5H_5)Re(NO)(CO)(CH_3)(PMe_3)$_2$ (**3**).

PMe_3 dependence of the rate of conversion of 1 to 4. On a high vacuum line, C_6D_6 (0.34 mL) and CO (0.34 mmol) were condensed into a resealable 2.0 mL high pressure NMR tube containing **1** (0.016 mmol, 0.04 *M*) and hexamethylbenzene (4.4×10^{-3} mmol) as internal standard. The tube was sealed at the temperature of liquid nitrogen and heated to 90°C, where the pressure of CO was calculated to be 4.95 atm. The reaction was monitored periodically by ^1H NMR; concentrations were determined by integrating the cyclopentadienyl resonances of **1** (δ 4.62) and **4** (δ 4.83) relative to the hexamethylbenzene resonance (δ 2.12). The pseudo first order rate constant for the conversion of **1** to **4** was obtained by plotting ln(**1**) against time. For this reaction in the absence of added PMe_3, partial decomposition led to solutions containing small amounts (0.004 *M*) of PMe_3. Pseudo first order rate constants were determined for reactions carried out in the presence of added PMe_3 (0.063, 0.173, and 0.277 *M*) all under 4.95 atm CO (Table 1). The pseudo first order rate constants measured under constant 4.95 atm CO pressure showed a linear dependence on PMe_3 concentration (Fig. 1).

CO dependence of the rate of conversion of 1 to 4. The CO pressure dependence (1.47 to 6.15 atm) of the reaction of **1** (0.04 *M*) with CO in the presence of 0.16 to 0.23 *M* PMe_3 was determined in a similar manner (Table 2). The pseudo second order rate constants k_2 (taking into account PMe_3 concentrations) displayed a linear dependence on CO pressure (Fig. 2).

$P(CD_3)_3$ exchange with 1. A C_6D_6 solution of **1** (0.037 *M*) and $P(CD_3)_3$ ($\sim$ 0.17 *M*) containing hexamethylbenzene (2.41×10^{-3} mmol) as internal standard was heated at 90°C under 4.95 atm CO in a sealed tube. The rate of phosphine exchange was monitored by following the appearance of free PMe_3 (δ 0.79, $J = 2.5$ Hz) and the disappearance of the coordinated PMe_3 resonance of **1** (δ 1.10, $J = 9.6$ Hz) by ^1H NMR. Early in the reaction, little change was seen in the intensity of the Cp and Me resonances of **1**. The pseudo first order rate of phosphine exchange with **1** (1.22×10^{-3} s^{-1}) was $\sim$ 25 times faster than the pseudo first order rate of conversion of **1** to **4** (4.71×10^{-5} s^{-1}) under these conditions.

$P(CD_3)_3$ exchange with 4. A C_6D_6 solution of **4** (0.035 *M*) and $P(CD_3)_3$ ($\sim$ 0.17 *M*) containing hexamethylbenzene (2.41×10^{-3} mmol) as internal standard was heated at 100°C under 4.95 atm CO in a sealed tube. The rate of phosphine exchange was monitored by following the appearance of free PMe_3 (δ 0.79, $J = 2.5$ Hz) and the disappearance of the coordinated PMe_3 resonance of **4** (δ 1.10, $J = 10.0$ Hz) by ^1H NMR. Early in the reaction, little change was seen in the intensity of the Cp and COMe resonances of **4**. The pseudo first order rate of phosphine exchange with **4** (3.19×10^{-4} s^{-1}) was > 40 times faster than decomposition of **4** and $\sim$ 7 times faster than the conversion of **1** to **4** under similar conditions. After 3.8 h ($\sim$ 6 half lives for $P(CD_3)_3$ exchange), **4** had undergone about 19% decomposition.

Acknowledgments

Financial support from the National Science Foundation and from the Department of Energy, Division of Basic Energy Sciences, is gratefully acknowledged.

References

1 C.P. Casey and J.M. O'Connor, Chem. Rev., 87 (1987) 307.
2 A.J. Lees and D.E. Marx, Inorg. Chem., 27 (1988) 1121.
3 R.D. Sanner and F.D. Miller, Organometallics, 7 (1988) 818.
4 C.P. Casey, J.M. O'Connor and K.J. Haller, J. Am. Chem. Soc., 107 (1985) 1241.
5 A. Yamamoto, Organotransition Metal Chemistry–Fundamental Concepts and Applications, Chapter 6, Wiley–Interscience, New York, 1986.
6 M.J. Wax and R.G. Bergman, J. Am. Chem. Soc., 103 (1981) 7028.
7 C.P. Casey and W.D. Jones, J. Am. Chem. Soc., 102 (1980) 6154.