Organometallics **2003,** *22,* 2284−2290

Solvent-Free Organometallic Migratory Insertion Reactions

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Received March 10, 2003

Migratory insertion reactions of organometallic complexes have been shown to occur in the absence of solvent and, more significantly, between solid reagents. Reaction between $(\eta^5\text{-}C_5H_5)M(CO)_3Me$ (M = Mo, W) or $(\eta^5\text{-}C_5H_5)Fe(CO)_2Me$ and PPh_3 (no solvent) took place at temperatures between 40 and 90 °C and gave the products $(\eta^5\text{-}C_5H_5)M(CO)_2(PPh_3)COMe$ and $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)COMe$ in moderate to good yield (60−99%). The Mo and W complexes reacted in the solid state when $T < 80$ °C. The decarbonylation of $(\eta^5\text{-}C_5H_5)Mo(CO)_2(PPh_3)COMe$ to yield $(\eta^5\text{-}C_5H_5)Mo(CO)_2(PPh_3)Me$ also occurred in the solid state (120 °C). Reaction of $(\eta^5\text{-}C_5H_5)Mo(CO)_3Me$ with a range of ligands, L (L = PPh_3, $P(p\text{-}MeOC_6H_4)_3$, PCy_3, PEt_3, $AsPh_3$, $POPh_3$, $P(OEt)_3$; 1:1 reagent ratio, 90 °C, 15 min), in the absence of solvent gave $(\eta^5\text{-}C_5H_5)Mo(CO)_2(L)COMe$ (7−100% yield) and, on extended reaction, $(\eta^5\text{-}C_5H_5)Mo(CO)_2(L)Me$ in varying yields. A kinetic study of the solid-state reaction between $(\eta^5\text{-}C_5H_5)Mo(CO)_3Me$ and PPh_3 yielded rate constants, e.g. $k = 5.18 \times 10^{-5}\ s^{-1}$ (Mo:P = 1:10; 50 °C), which compares with the literature solution data in toluene ($k = (0.8-2.5) \times 10^{-5}\ s^{-1}$, 50 °C) using similar metal to ligand ratios. The data are consistent with a pseudo-first-order reaction in the presence of PPh_3. Diffusional effects on the reaction rate are detected at low temperature and low PPh_3 ratios.

Introduction

Environmental concerns in synthetic chemistry have led to a reconsideration of reaction methodologies. This has resulted in investigations into atom economy,[1] the use of supercritical CO_2,[2] ionic liquids,[3] and other procedures to reduce the disposal problems associated with most chemical reactions. One obvious route to reduce waste entails generation of chemicals from reagents in the *absence* of solvents.[4]

While an obvious approach to chemical synthesis, there are many problems associated with this approach, the chief of which is the role of diffusion/interaction between reactants. Further, it is never clear that the reactions in the solid state will generate the same products as those found in the presence of solvents.

Some years ago we discovered that organometallic complexes, of the type $CpML_4$, undergo cis−trans ligand isomerization reactions in the solid state.[5] Little is known about reactivity patterns of organometallic complexes in the solid state, and we have now commenced a systematic examination of this type of reaction.[6] Our emphasis is on synthetic organometallic chemistry in the solid state, and the study interfaces with investigations of surface organometallic chemistry[7] and its relationship to catalysis.[8] Further, recent reports have indicated that the reaction of gases with solid organometallic compounds can lead to gas uptake (addition) reactions and that these studies may lead to the use of organometallic complexes as gas sensors.[9]

The reactions of $(\eta^5\text{-}C_5H_5)M(CO)_3Me$ (M = Mo, W) and $(\eta^5\text{-}C_5H_5)Fe(CO)_2Me$ with nucleophilic ligands, L, represent some of the earliest reactions reported in organometallic chemistry in the early 1950s.[10] Initial studies were dedicated to determining the mechanism of the reaction between $(\eta^5\text{-}C_5H_5)M(CO)_3Me$ (M = Mo, W), $(\eta^5\text{-}C_5H_5)Fe(CO)_2Me$, and other reactants with nucleophlilic ligands, L.[11] These reactions generated products of the

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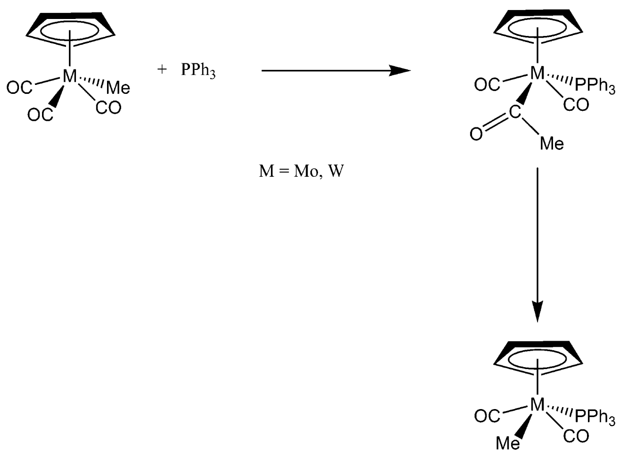
10.1021/om0301738 CCC: $25.00
Publication on Web 04/26/2003

Scheme 1. Migratory Insertion and Decarbonylation Reaction



type $(\eta^5\text{-}C_5H_5)M(CO)_2(L)COMe$ and $(\eta^5\text{-}C_5H_5)Fe(CO)(L)$-COMe (L = wide range of two-electron-donor ligands). A secondary reaction, decarbonylation of CO from the acyl product, was sometimes observed. The reaction (for the case of Mo and W) is summarized in Scheme 1.

Remarkably, no attempt appears to have been made to systematically investigate the reaction sequence of Scheme 1 in the absence of solvents. Only odd reports of reactions performed in the absence of solvent,[11f,12] e.g. that of $(\eta^5\text{-}C_5H_5)Mo(CO)_3Et$ with CO to give $(\eta^5\text{-}C_5H_5)Mo(CO)_3COEt$ and $[(\eta^5\text{-}C_5H_4Et)Mo(CO)_3]_2$, have appeared in the literature.[12a] A reported reaction on the influence of Lewis acids (e.g. $AlBr_3$) on the insertion reaction of $(\eta^5\text{-}C_5H_5)M(CO)_3Me$ to give $(\eta^5\text{-}C_5H_5)Mo$-$[C(OAlBrBr_2)Me](CO)_2$ (Br attached to CO also bonds to Mo) has been attempted in the solid state. While a related reaction between $Mn(CO)_5Me$ and $AlBr_3$ in the solid state was successful, extensive decomposition was noted for the Mo complex.[13]

Herein we report on a solid-state investigation of the migratory insertion reaction.[14] In particular we report on the CO insertion/methyl migration reaction of $(\eta^5\text{-}C_5H_5)M(CO)_3Me$ (M = Mo, W) and $(\eta^5\text{-}C_5H_5)Fe(CO)_2Me$ with phosphines, phosphites, $AsPh_3$, and CO in the absence of solvents. While reactions in neat PPh_3 (i.e. in the molten state) are known,[15] reactions with solid PPh_3 have not previously been described.

Experimental Section

The starting materials $(\eta^5\text{-}C_5H_5)M(CO)_3Me$ (M = Mo, W) were synthesized by minor variations of literature procedures.[10] $(\eta^5\text{-}C_5H_5)Fe(CO)_2Cl$, prepared by a literature procedure,[10,16] was reacted with MeMgI to give $(\eta^5\text{-}C_5H_5)Fe(CO)_2Me$. The complexes were characterized by IR and NMR spectroscopy (Table 1).

IR spectra were recorded on a Bruker Vector FTIR spectrometer, typically in CH_2Cl_2 (KBr cells), and NMR spectra on a Bruker AC 200 spectrometer ($CDCl_3$). High-pressure reactions were performed in a home-built autoclave (100 mL capacity).

Solventless Reaction of $(\eta^5\text{-}C_5H_5)Mo(CO)_3Me$ and L (L = PPh_3, $P(p\text{-}C_6H_4OMe)_3$, PCy_3, PEt_3, $AsPh_3$, $POPh_3$, $P(OEt)_3$). Reaction of a range of ligands, L, with $(\eta^5\text{-}C_5H_5)$-$Mo(CO)_3Me$ was performed in the absence of solvent. The ligand, L (L = PPh_3, $P(p\text{-}MeOC_6H_4)_3$, PCy_3, PEt_3, $AsPh_3$, $POPh_3$, $P(OEt)_3$; 0.08 mM), and $(\eta^5\text{-}C_5H_5)Mo(CO)_3Me$ (0.08 mM) were dissolved in dry CH_2Cl_2 (5 mL). The solvent was then removed in vacuo to give a bright yellow solid (or liquid). NMR spectra revealed no conversion to the insertion product by this procedure. About 14 mg of the mixture was loaded, under nitrogen, into an NMR tube and placed in an oil bath (90 °C). At this temperature the $(\eta^5\text{-}C_5H_5)Mo(CO)_3Me$ is a liquid (mp 81 °C) and the reaction thus takes place in the liquid phase. The mixture was allowed to react for 15 min, the tube removed from the oil bath, $CDCl_3$ added to the product, and the solution analyzed by solution IR and ^1H NMR spectroscopy. The results are shown in Table 2. Reactions were performed in the presence of ambient light and in the dark (foil-enclosed tubes), and no difference in the degree of reaction was noted.

Solventless Reaction of $(\eta^5\text{-}C_5H_5)Mo(CO)_3Me$ and PPh_3. $(\eta^5\text{-}C_5H_5)Mo(CO)_3Me$ (27.4 mg, 0.11 mM) and PPh_3 (1× to 25× excess; see Table 2) was completely dissolved in dry CH_2Cl_2 (3 mL). A bright yellow solid was collected after the removal of the CH_2Cl_2 in vacuo. About 15 mg of the mixture was loaded, under nitrogen, into an NMR tube and placed into an oil bath at a preset temperature (40−70 °C). The reaction, which occurs in the solid state, was then monitored with time. At the end of a requisite time period, the NMR tube was removed from the oil bath, $CDCl_3$ was added to the tube, and the NMR spectrum was recorded. At the end of a reaction (typically 100% conversion) the product was isolated and characterized by IR as well as ^1H and, in some instances, ^{31}P NMR spectroscopy. Both $(\eta^5\text{-}C_5H_5)Mo(CO)_2(PPh_3)COMe$ and $(\eta^5\text{-}C_5H_5)$-$Mo(CO)_2(PPh_3)Me$ were detected, the relative amounts varying with the reaction conditions.

When the reaction was performed at $T > 80$ °C, the PPh_3 and $(\eta^5\text{-}C_5H_5)Mo(CO)_3Me$ both melted and a yellow liquid formed that solidified rapidly at the reaction temperature (5 min) as product formed.

Solventless Reaction of $(\eta^5\text{-}C_5H_5)W(CO)_3Me$ and PPh_3. $(\eta^5\text{-}C_5H_5)W(CO)_3Me$ (34.8 mg, 0.1 mM) and PPh_3 (1:1 and 1:10 ratios) were completely dissolved in dry CH_2Cl_2 (3 mL). A bright yellow solid was collected after the removal of the CH_2Cl_2 in vacuo. The procedure used to study the solid-state reaction is the same as that described for the Mo reaction above.

Reaction of $(\eta^5\text{-}C_5H_5)Mo(CO)_3Me$ with CO. $(\eta^5\text{-}C_5H_5)$-$Mo(CO)_3Me$ (20 mg) was loaded into a sample vial and placed in a steel autoclave. The autoclave was purged with argon, after which a CO pressure of 10 bar was introduced. The autoclave was then placed into an oil bath at 70 °C (and 80 °C) and the reaction allowed to proceed for 15 h. A brown solid was collected at the end of the reaction and characterized as $(\eta^5\text{-}C_5H_5)Mo(CO)_3COMe$ (Table 1). A trace amount of decomposition product was observed. This result is to be contrasted with the high-pressure reactions *in solution* that gave mainly $Mo(CO)_6$.[17]

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Table 1. Spectroscopic Data for the Reactants and Products

complex	IR[a] ν_{CO}/cm^{-1}	IR[a] ν_{CO}(acetyl)/cm^{-1}	^{1}H NMR[b] C_5H_5	^{1}H NMR[b] Me	^{1}H NMR[b] CH_3CO	^{1}H NMR[b] other	ref
$(\eta^5\text{-}C_5H_5)Mo(CO)_3Me$	2018 (s), 1927 (s)		5.30	0.37 (s)			10
$(\eta^5\text{-}C_5H_5)W(CO)_3Me$	2018 (s), 1927 (s)		5.30	0.37 (s)			10
$(\eta^5\text{-}C_5H_5)Fe(CO)_2Me$	2006 (s), 1945 (s)		4.75	0.16 (s)			10
$(\eta^5\text{-}C_5H_5)Mo(CO)_2(PPh_3)COMe$	1938 (s), 1852 (vs)	1597 (w)	5.00		2.61	7.43 (m)	11c
$(\eta^5\text{-}C_5H_5)Mo(CO)_2(PEt_3)COMe$	1930 (s), 1844 (vs)	1598 (m)	5.14		2.56	1.13 (m), 1.84 (m)	12c
$(\eta^5\text{-}C_5H_5)Mo(CO)_2(PCy_3)COMe$	1928 (s), 1835 (s)	1600 (w)	5.18		2.58	1.26−2.03 (m)	18
$(\eta^5\text{-}C_5H_5)Mo(CO)_2[P(OPh)_3]COMe$	1949 (s), 1876 (s)	1593 (s)	4.82		2.36	7.29 (m)	11i
$(\eta^5\text{-}C_5H_5)Mo(CO)_2(P(OEt)_3)COMe$	1946 (s), 1862 (vs)	1609 (m)	5.22		2.56	1.30 (t), 3.94 (q)	11i
$(\eta^5\text{-}C_5H_5)Mo(CO)_2\,(P(p\text{-}MeOPh)_3)COMe$	1936 (s), 1841 (vs)	1594 (m)	5.00		2.61	6.89−7.25 (m)	18
$(\eta^5\text{-}C_5H_5)Mo(CO)_2(AsPh_3)COMe$	1937 (s), 1851 (vs)	1580 (w)	5.05		2.65	7.39 (m)	
$(\eta^5\text{-}C_5H_5)Mo(CO)_3COMe$	2006 (s), 1946 (s)	1665 (s)	5.29		2.17		
$(\eta^5\text{-}C_5H_5)W(CO)_2(PPh_3)COMe$	1938 (s), 1853 (vs)	1600 (w)	5.00[c]		2.61	7.43 (m)	11c
$(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)COMe$	1913 (vs)	1601 (s)	4.74		2.32	7.3−7.6 (m)	13
$(\eta^5\text{-}C_5H_5)Mo(CO)_2(PPh_3)Me$	1934 (s), 1896 (s), 1848 (vs)		4.75	0.40 (d)		7.40 (m)	11d
$(\eta^5\text{-}C_5H_5)Mo(CO)_2[P(OPh)_3]Me$			4.79[d] 4.55[e]	0.30 0.31		7.31−7.34 (m)	16
$(\eta^5{-}C_5H_5)Fe(CO)_2COMe$	1994 (s), 1951 (s)	1770 (s)	4.52	-	2.02		11a

[a] In CH_2Cl_2. [b] In $CDCl_3$, relative to TMS. Abbreviations: s = singlet, d = doublet, q = quintet, m = multiplet. [c] Occurs as doublet. [d] Cis isomer. [e] Trans isomer.

Table 2. Experimental Data for the Reaction between $(\eta^5\text{-}C_5H_5)M(CO)_nMe$ and Ligand (M = Fe, $n = 2$; M = Mo, W, $n = 3$)

reactants	reaction conditions	major product	yield[a,b]
$(\eta^5\text{-}C_5H_5)Mo(CO)_3Me + PPh_3$	solid−solid, 40 °C, 36 h	$(\eta^5\text{-}C_5H_5)Mo(CO)_2PPh_3COMe$	99
	solid−solid, 50 °C, 5 h		92
	solid−solid, 60 °C, 1 h		92
	solid−solid, 70 °C, 30 min		98
	solvent free, 80 °C, 30 min		99
	solvent free, 80 °C, 2 h		83:7
	solvent free, 90 °C, 15 min		90:10
$(\eta^5\text{-}C_5H_5)Mo(CO)_3Me + PCy_3$	solvent free, 90 °C, 15 min	$(\eta^5\text{-}C_5H_5)Mo(CO)_2(PCy_3)COMe$	25:25
$(\eta^5\text{-}C_5H_5)Mo(CO)_3Me + PEt_3$	solvent free, 90 °C, 2 min	$(\eta^5\text{-}C_5H_5)Mo(CO)_2(PEt_3)COMe$	100
$(\eta^5\text{-}C_5H_5)Mo(CO)_3Me + P(OEt)_3$	solvent free, 90 °C, 15 min	$(\eta^5\text{-}C_5H_5)Mo(CO)_2P(OEt)_3COMe$	80:5
$(\eta^5\text{-}C_5H_5)Mo(CO)_3Me + P(p\text{-}MeOPh)_3$	solvent free, 90 °C, 15 min	$(\eta^5\text{-}C_5H_5)Mo(CO)_2[P(p\text{-}MeOPh)_3]COMe$	80:5
$(\eta^5\text{-}C_5H_5)Mo(CO)_3Me + P(OPh)_3$	solvent free, 90 °C, 15 min	$(\eta^5\text{-}C_5H_5)Mo(CO)_2(P(OPh)_3)COMe$	80:10:10[c]
$(\eta^5\text{-}C_5H_5)Mo(CO)_3Me + AsPh_3$	solvent free, 90 °C, 15 min	$\eta^5\text{-}C_5H_5)Mo(CO)_2(AsPh_3)COMe$	10:2
$(\eta^5\text{-}C_5H_5)Mo(CO)_3Me + CO$	solvent free, 80 °C, 15 h, 10 bar of CO	$(\eta^5\text{-}C_5H_5)Mo(CO)_3COMe$	100
$(\eta^5\text{-}C_5H_5)W(CO)_3Me + PPh_3$	solid−solid, 40 °C, 48 h	$(\eta^5\text{-}C_5H_5)W(CO)_2(PPh_3)COMe$	60
	solid−solid, 50 °C, 5 h		72
	solid−solid, 60 °C, 1 h		75
	solid−solid, 70 °C, 30 min		78
$(\eta^5\text{-}C_5H_5)W(CO)_3Me + PPh_3$ (1:10)	solid−solid, 70 °C, 1 h		100
$(\eta^5\text{-}C_5H_5)Fe(CO)_2Me + PPh_3$	solvent free, 80 °C, 1 h	$(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)COMe$	30
$(\eta^5\text{-}C_5H_5)Fe(CO)_2Me + PPh_3$	solvent free, 80 °C, 15 h		80
$(\eta^5\text{-}C_5H_5)Fe(CO)_2Me + CO$	solvent free, 80 °C, 24 h, 10 bar of CO	$(\eta^5\text{-}C_5H_5)Fe(CO)_2COMe$	*d*
$(\eta^5\text{-}C_5H_5)Fe(CO)_2Me + CO$	solid−gas, 40 °C, 24 h, 5 bar	$(\eta^5\text{-}C_5H_5)Fe(CO)_2COMe$	trace[e]

[a] As determined from ^{1}H NMR spectra. [b] Ratio of acetyl and decarbonylation products. [c] Cis and trans isomers were both observed (10%), see text. [d] Sublimed product collected in the autoclave. [e] As determined by IR spectroscopy.

Reaction of $(\eta^5\text{-}C_5H_5)Fe(CO)_2Me$ with CO. The procedure used is the same as that described for $(\eta^5\text{-}C_5H_5)Mo(CO)_3Me$ above. The mixture was allowed to react for 24 h (80 °C, 10 bar of CO). A product was collected from the lid of the autoclave. TLC and IR and ^{1}H NMR spectral analyses confirmed the formation of $(\eta^5\text{-}C_5H_5)Fe(CO)_2COMe$ (Table 1). Under milder conditions (40 or 50 °C; 5 bar of CO, 24 h) only trace amounts of the product was detected by IR spectroscopy.

Solventless Reaction between $(\eta^5\text{-}C_5H_5)Fe(CO)_2Me$ and PPh_3. The reaction was performed as for the Mo complexes (80 °C) above to yield an orange-yellow product that was characterized as $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)COMe$ (1 h, 30% yield; 15 h, 80% yield; Table 1).

Decarbonylation Reactions of $(\eta^5\text{-}C_5H_5)Mo(CO)_2(PPh_3)COMe$. $(\eta^5\text{-}C_5H_5)Mo(CO)_3Me$ (0.274 g; 1.1 mmol) and PPh_3 (0.264 g, 1.0 mmol) were reacted at 90 °C for 30 min, and the product $(\eta^5\text{-}C_5H_5)Mo(CO)_2(PPh_3)COMe$ (obtained in quantitative yield) was recrystallized from 1:10 CH_2Cl_2−hexane. $(\eta^5\text{-}C_5H_5)Mo(CO)_2(PPh_3)COMe$ (100 mg, 0.19 mmol) was loaded into a flask and heated at 120 °C for 14 h to give 75% conversion to the decarbonylated product. The reaction was terminated and the product isolated by column chromatography (silica gel; 1:10 CH_2Cl_2−hexane). At 80 °C, <5% conversion was noted, even after 16 h. A reaction was also performed using a 0.25:1 mixture of $(\eta^5\text{-}C_5H_5)Mo(CO)_2(PPh_3)COMe$ and $(\eta^5\text{-}C_5H_5)Mo(CO)_3Me$ (90 °C, 2 h) to give $(\eta^5\text{-}C_5H_5)Mo(CO)_2(PPh_3)Me$ (5% yield; reaction products characterized by IR and NMR spectroscopy).

Results and Discussion

Reaction between $(\eta^5\text{-}C_5H_5)M(CO)_3Me$ and L (L = PPh_3, $P(p\text{-}C_6H_4OMe)_3$, PCy_3, PEt_3, $AsPh_3$, $POPh_3$, $P(OEt)_3$). Initially, reactions using 1:1 reactant ratios were performed at 90 °C (i) to evaluate the generality

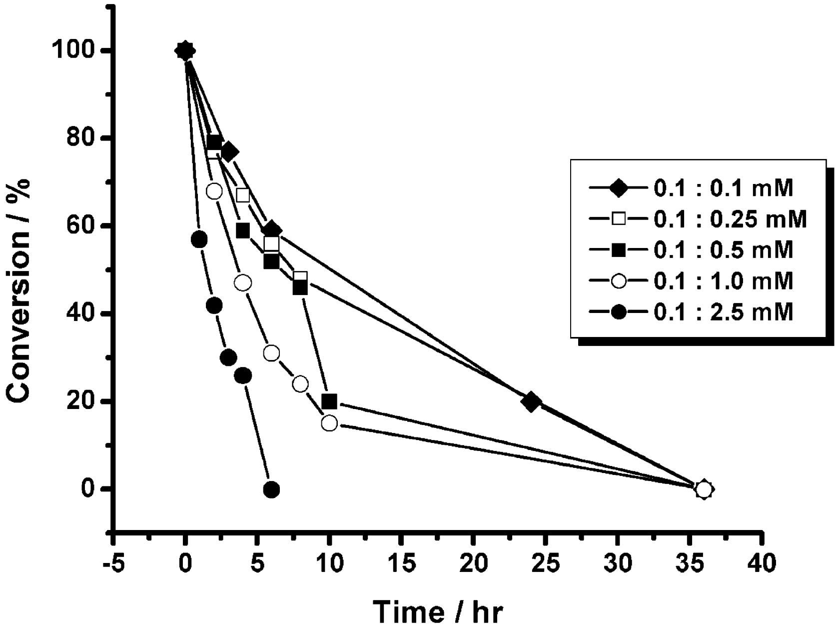

Figure 1. Plot of conversion against time for the reaction of (η^5-C_5H_5)Mo(CO)$_3$Me with PPh_3 at different Mo:P ratios (40 °C).

of the reaction and (ii) to limit the extent of the reaction. At this temperature reaction is expected to occur in the liquid/molten phase, as many of the ligands are liquids at $T > 90$ °C and the starting material is a liquid at this temperature (mp 81 °C). The data reveal conversion of (η^5-C_5H_5)Mo(CO)$_3$Me to (η^5-C_5H_5)Mo(CO)$_2$(L)COMe with the conversion dependent on L (Table 2). Only the trans isomer appears to have been formed.[11g] The crude rate data (total conversion after 15 min) reveals that the reaction rate decreases in the order $PEt_3 > P(OPh)_3 > PPh_3 \approx P(p\text{-}C_6H_4OMe)_3 \approx P(OEt)_3) > PCy_3 > AsPh_3$, in keeping with results obtained from solution studies.

Products derived from the decarbonylation reaction were generally observed in the reaction product (2−20%). They are formed in secondary reactions. Thus, reaction with $AsPh_3$ after 15 min gave 10% (η^5-C_5H_5)Mo(CO)$_2$($AsPh_3$)COMe and 2% (η^5-C_5H_5)Mo(CO)$_2$($AsPh_3$)Me, while after 30 min about 12% of *both* products were observed. However, the reaction is not a straightforward one, as noted for the reactions with PPh_3 (see below).

As yet, no information is available on the stereochemistry of the reaction, although in general only the trans decarbonylated products are observed. Even in the case where cis and trans isomers are observed (for (η^5-C_5H_5)Mo(CO)$_2$(P(OPh)$_3$)Me) the isomer ratio (1:1) generated could relate to isomerization *during* the NMR characterization procedure, since the ratio is the same as that reported in solution.[18]

Reaction between (η^5-C_5H_5)Mo(CO)$_3$Me and PPh_3. At $T < 70$ °C the reaction with PPh_3 was found to occur in the solid state (PPh_3 melts at ca. 80 °C). This reaction thus provides a facile system to investigate a solid-state organometallic migratory insertion reaction. To limit diffusional factors, thorough mixing of the reactants was achieved prior to reaction. Kinetic data were generated (i) by varying the molar reactant ratios (0.1:(0.1−2.5)) and (ii) by varying the reaction temperature (40−70 °C). The reaction was found to go to completion at 40 °C (ca. 36 h), indicating that no equilibrium is set up between the reactants and products.

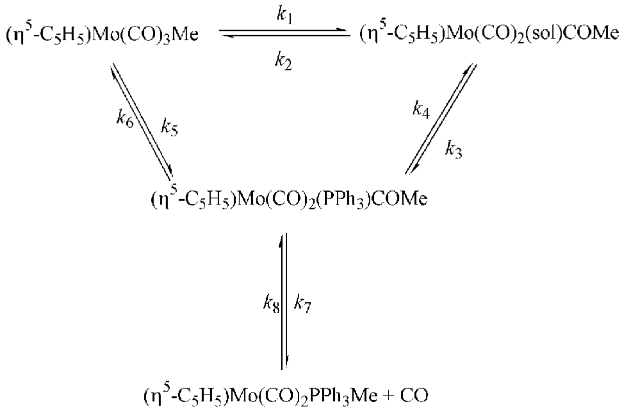

Figure 2. Reaction mechanism for the interaction of (η^5-C_5H_5)Mo(CO)$_3$Me with PPh_3 (based on ref 11a).

The rate of reaction as a function of PPh_3 molar ratio (40 °C) is shown in Figure 1. The reaction rate is clearly dependent on [PPh_3].

The mechanism of the migratory insertion reaction for the reaction *in solution* has been well studied,[11] and a comprehensive mechanism to explain most of the experimental data accumulated to date is shown in Figure 2. It will be noted that the proposed *general* mechanism allows for the formation of an intermediate, (η^5-C_5H_5)Mo(CO)$_2$(sol)COMe (sol = solvent molecule), prior to addition of a ligand.[11a] The reaction has been found to depend on both L and the solvent (tetrahydrofuran, substituted tetrahydrofurans, toluene etc.[11a,e]). Depending on the values of the rate constants, both first-order and second-order kinetics have been measured. For example, reaction with PPh_3 (in toluene) gives the rate equation[11a]

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[18] Faller, J. W.; Anderson, A. S. *J. Am. Chem. Soc.* **1970**, *92*, 5852.

$$\mathrm{d}[(\eta^5\text{-}C_5H_5)Mo(CO)_3Me]/\mathrm{d}t = (k_1 + k_5[PPh_3])[(\eta^5\text{-}C_5H_5)Mo(CO)_3Me]$$

and $k_{obs} = k_1 + k_5[L]$ with $k_1 = 0$.

If $[(\eta^5\text{-}C_5H_5)Mo(CO)_3Me]$ is kept constant, then

$$\mathrm{d}[(\eta^5\text{-}C_5H_5)Mo(CO)_3Me]/\mathrm{d}t = k'[PPh_3]$$

An attempt was made to evaluate the solid-state kinetic data *assuming* first-order kinetics. A typical plot is shown in Figure 3 (1:10 ratio, correlation factor 0.998). Similar plots were observed at the other Mo to P ratios (even the 1:1 ratio!), and k values are given in Table 3. Attempts to fit the data to other reaction orders were not successful.

The reaction was also carried out at different temperatures, at both the 1:1 and 1:10 ratios. Data for the reaction at a 1:10 ratio is shown in Figure 4, and the k values are listed in Table 3. The study in the solid state yielded rate constants, e.g. $k' = 5.18 \times 10^{-5}$ s^{-1} (Mo:P = 1:10; 50 °C), which can be compared with the literature data in toluene ($k = 0.8-2.5 \times 10^{-5}$ s^{-1}, 50 °C)[11a] under similar reaction conditions. (Note: the amount of ligand used has different units in the solid and solution states.)

The evaluation of solid-state rate data is fraught with difficulties,[19] and in this reaction diffusional issues are expected to dominate the rates of reactions. This is revealed by the attempts to extract activation energy data from the Arrhenius plots (Figure 5). Curvature can be seen suggesting two activation energies, one energy relating to diffusion and the other to the chemical reaction. At the higher PPh_3 ratio the curvature decreases (especially in the low-temperature regime).

Clearly as either the Mo:P ratio or the temperature increases, diffusional constraints will be restricted, as observed in Figure 5. Attempts to extract activation energies (E_a) from the data give limiting values: E_a(reaction) < 75 kJ mol^{-1} and E_a(diffusion) > 120 kJ mol^{-1}.

Conversion of $(\eta^5\text{-}C_5H_5)Mo(CO)_2(PPh_3)COMe$ to $(\eta^5\text{-}C_5H_5)Mo(CO)_2(PPh_3)Me$. A competing reaction in the solution state that occurs after migratory insertion is the CO decarbonylation reaction. In the solid state this reaction also occurs *after* the insertion migration reaction. The decarbonylation of purified (i.e. crystallized) $(\eta^5\text{-}C_5H_5)Mo(CO)_2(PPh_3)COMe$ in the solid state was monitored by carrying out the reaction in NMR tubes. Surprisingly, no product is formed when the reaction is carried out at 80 °C. This finding is at variance with the formation of insertion product (≈10%) during the ligand migratory insertion reaction, at 90 °C, described above. Further, the reaction in solution (acetonitrile) is also reported to be rapid.[20]One possibility is that the decarbonylation actually occurs in the molten/liquid phase at 90 °C.

To test this possibility, a 0.25:1 mixture of $(\eta^5\text{-}C_5H_5)Mo(CO)_2(PPh_3)COMe$ and $(\eta^5\text{-}C_5H_5)Mo(CO)_3Me$ was reacted at 90 °C, a temperature at which $(\eta^5\text{-}C_5H_5)Mo(CO)_3Me$ has melted. In this instance the reaction did generate $(\eta^5\text{-}C_5H_5)Mo(CO)_2(PPh_3)Me$ (5%, 30 min), consistent with the proposal.

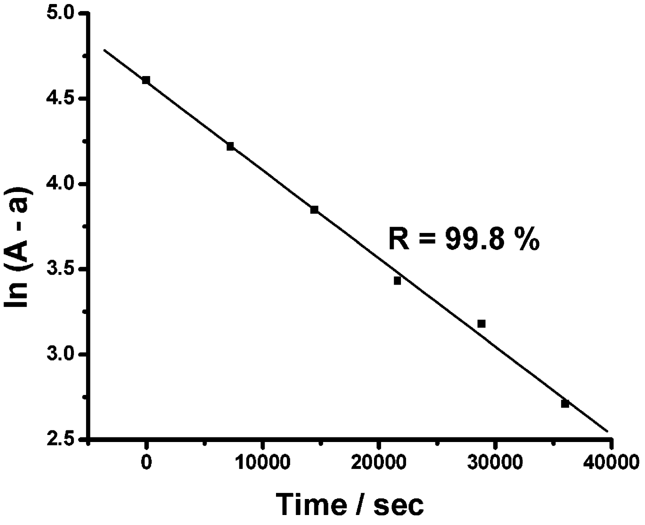

Figure 3. First-order plot of the reaction between $(\eta^5\text{-}C_5H_5)Mo(CO)_3Me$ with PPh_3 (1:10 ratio, 40 °C).

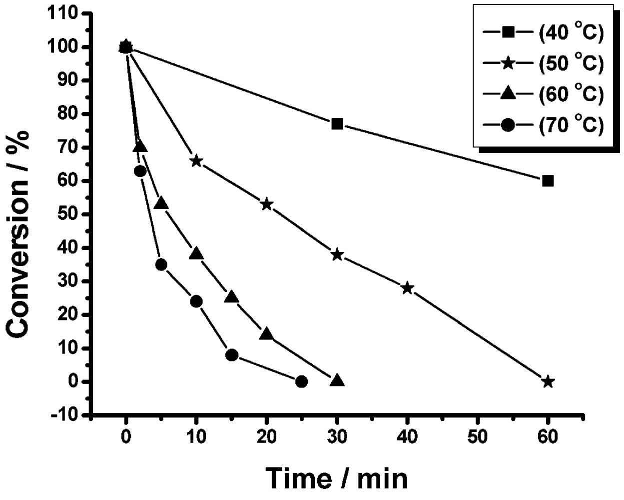

Figure 4. Plot of conversion against time for the reaction of $(\eta^5\text{-}C_5H_5)Mo(CO)_3Me$ with PPh_3 at different temperatures (1:10 reactant ratio).

Table 3. Rate Constant Data for the Reactions of $(\eta^5\text{-}C_5H_5)M(CO)_3Me$ with PPh_3

M	temp/°C	concn/mM	k/s^{-1}
Mo	40	0.10:0.10	1.81×10^5
		0.10:0.25	2.49×10^5
		0.10:0.50	3.89×10^5
		0.10:1.00	5.18×10^5
		0.10:2.50	9.28×10^5
	50	0.10:0.10	2.60×10^4
	60	0.10:0.10	1.30×10^3
	70	0.10:0.10	2.14×10^3
	50	0.10:1.00	5.18×10^4
	60	0.10:1.00	1.52×10^3
	70	0.10:1.00	2.61×10^3
W	60	0.10:0.10	1.11×10^3

At higher temperatures (120 °C) a solid-state decarbonylation reaction *does occur* and $(\eta^5\text{-}C_5H_5)M(CO)_2(PPh_3)Me$ is formed (45%, 4 h; 75%, 14 h). This is expected to be a first-order reaction.

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[19] (a) Galwey, A. K.; Brown, M. E. *Thermochim. Acta* **2002**, *386*, 91. (b) Bezjak, A.; Kurajica, S.; Sipusic, J. *Thermochim. Acta* **2002**, *386*, 81.

[20] (a) Barnett, K. W.; Pollmann, T. G.; Solomon, T. W. *J. Organomet. Chem.* **1972**, *36*, C23. (b) Barnett, K. W. *Inorg. Chem.* **1969**, *8*, 2009.

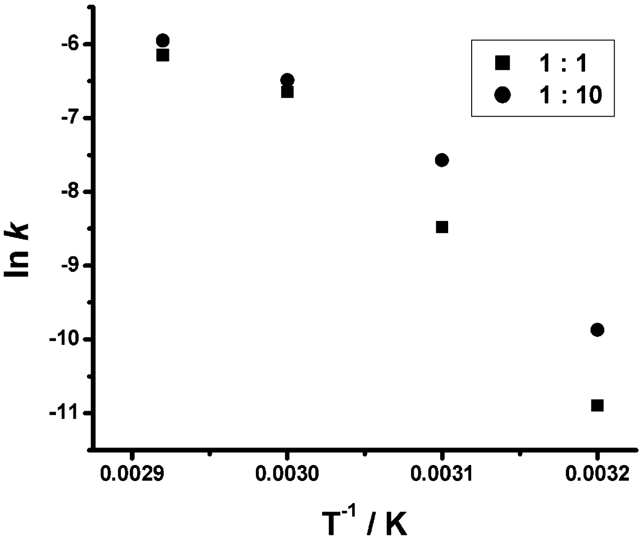

Figure 5. Arrhenius plot for the reaction of (η^5-C_5H_5)-Mo(CO)$_3$Me with PPh_3 (1:10 and 1:1 reactant ratios).

This large temperature difference between the solid state and solution reactions suggests strong solvent effects on the decarbonylation reaction, a result not apparent from earlier studies.[20]

Reaction between (η^5-C_5H_5)W(CO)$_3$Me and PPh_3. This reaction occurred at 40 °C to give the required product, (η^5-C_5H_5)W(CO)$_2$(PPh_3)COMe, in good yield (1:1 reactant ratio; 60%; 48 h). The reported reaction in solution gives poor conversions over extended time periods (refluxing acetonitrile, 48 h). Reactions (1:1 ratio) were also carried out at higher temperatures (Table 2), and the data reveal that the reaction does not go to completion (ca. 72−78% yield). No (η^5-C_5H_5)-W(CO)$_2$ (PPh_3)Me was formed under the reaction conditions. Not unexpectedly, reaction with a mixture of (η^5-C_5H_5)W(CO)$_3$Me and PPh_3 in a 1:10 ratio (70 °C, 1 h) gave 100% conversion, and under these conditions a small amount (5%) of (η^5-C_5H_5)W(CO)$_2$(PPh_3)Me was also formed.

A comparison of rate data between Mo and W complexes (1:10 ratio with PPh_3) at 60 °C is shown in Figure 6. The Mo complex reacts faster than the W complex at all temperatures studied, and although consistent with solution studies,[11c] the rates in the solid state are more similar than the rates obtained from solution studies.

The remarkably low reaction temperatures required to achieve the substitution reactions at W in the solid state suggests that solvent effects must be responsible for the poor reactions reported in the solution phase. The solid-state data are in keeping with reaction rates that are related to the Mo−C and W−C bond strengths in the complexes.[21] Could this methodology provide a general approach to overcoming the sluggish behavior of third-row transition metals?

Other Examples. The generality of the reaction type has briefly been explored, and the preliminary results indicate that the reaction is quite general.

(a) Reaction between (η^5-C_5H_5)Mo(CO)$_3$Me and CO. This reaction took place in an autoclave at 70 and 80 °C (15 h, 10 bar of CO), and (η^5-C_5H_5)Mo(CO)$_3$COMe was produced in quantitative yield under mild thermal conditions (Table 2). Earlier reports suggest that this is a difficult reaction to induce in a solvent.[17]

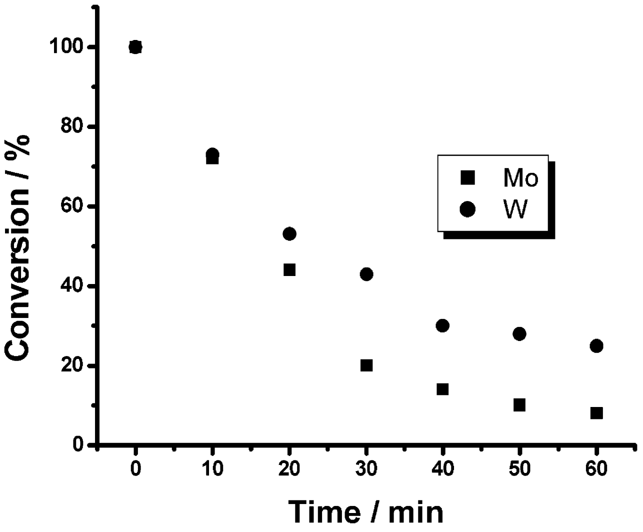

Figure 6. Comparison of reaction rates for (η^5-C_5H_5)-M(CO)$_3$Me (M = Mo, W) with PPh_3 (1:1 ratio; 60 °C).

(b) Reaction between (η^5-C_5H_5)Fe(CO)$_2$Me and L (L = PPh_3, CO). Reactions between (η^5-C_5H_5)Fe(CO)$_2$-Me and L in the solution state have been investigated by numerous workers over the years.[13,17] The solid-state reaction between (η^5-C_5H_5)Fe(CO)$_2$Me and PPh_3 occurs more slowly than that between (η^5-C_5H_5)Mo(CO)$_3$Me and PPh_3 (80 °C; 80%, 15 h versus 99%, 30 min; Table 2), in line with solution data. The reaction between CO and (η^5-C_5H_5)Fe(CO)$_2$Me, in an autoclave, was also attempted.[17] As the reactant is a waxy solid, it is assumed that the reaction takes place in the molten state in the autoclave. The reaction was performed at temperatures between 40 and 80 °C (24 h, 5−10 bar of CO). While the reaction occurred to give (η^5-C_5H_5)-Fe(CO)$_2$COMe, difficulty was experienced in evaluating the reaction conversion because of product/reactant sublimation. The reaction has not been pursued further at this time.

Reaction Mechanism. As mentioned above, the extraction of thermodynamic and mechanistic information from kinetic data obtained in solid-state reactions is nontrivial.[19] The migratory insertion has similarities to inorganic addition reactions of the type A + B → C, and analyses of a variant of this reaction type (spinel formation) has revealed the importance of diffusion in these reactions.[22]

Reaction is initiated when reactants are in contact with each other. In the ideal situation reactants A and B (in our case A = PPh_3 and B = (η^5-C_5H_5)Mo(CO)$_3$-Me)), would be precipitated in pairs, viz. ABABABAB... More likely, however, the precipitation will yield domains of A and B, viz. AAABBABBBBBAAAA... Reaction between A and B molecules in close proximity will be determined by the migratory insertion chemical reaction. However, as the reaction proceeds, product formation creates a barrier to further reaction, leading to a decrease in reaction rate, viz. AAABBABBBB-

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[21] Mancuso, C.; Halpern, J. *J. Organomet. Chem.* **1992**, *428*, C8.

[22] (a) Brown, W. E.; Dollimore, D.; Galwey, A. K. In *Comprehensive Chemical Kinetics*; Bamford, C. H., Tipper, C. F. H., Eds.; Elsevier: Amsterdam, 1980; Vol. 22, Chapter 5. (b) Tolkatchev, V. A. *Reactivity of Molecular Solids*; Boldyreva, E., Boldyrev, V., Eds.; Wiley: Chichester, U.K., 1999; Chapter 5.

BAAAA... → AA(AB)(BA)BBBB(BA)AAA..., where (AB) = (BA) = $(\eta^5\text{-}C_5H_5)M(CO)_2(PPh_3)COMe$.

Only if A and/or B are mobile will further reaction occur. The kinetic analysis must thus describe both the chemical reaction and diffusional components of the reaction.

In the migratory insertion reaction, premixing of reactants is expected to lead to a reasonably good contact between reagents. Our studies to date have entailed reaction with amorphous materials, and *particle size effects* are not expected to be a dominant effect in the reaction. However, the premixing is not expected to remove domain effects. Since grinding of reactants leads to reaction, reactions carried out by merely mixing reagents have given limited data and thus to date we have not been able to separate out the diffusional effects from the chemical reaction.

It is not clear at this stage whether the Mo complex and/or the ligand are mobile. Both are bulky, and both have similar melting points. The reaction also requires the correct orientation of the reagents. Since reaction with the 1:1 mixture of PPh_3 and $(\eta^5\text{-}C_5H_5)Mo(CO)_3Me$ occurs at 40 °C, it is apparent that the diffusional and orientational barriers for the reaction cannot be large.

Conclusion

This study reveals that migratory insertion of organometallic compounds can occur between a solid organometallic complex and a ligand that exists in the *solid, liquid, or gas phase without the intervention of a solvent.* Well-known examples have been chosen to highlight this reaction type and, where possible, to compare data with equivalent solution state studies.

In the studies reported above, the products are the same as those found in solution studies. The rates of reaction are similar in the solid and solution phases, and this would suggest that the mechanisms (involving reactant interaction) are similar in the different phases. Single-crystal studies on some of the above reactions may provide further detail to generate more precise stereochemical information, especially on the decarbonylation reactions.

Reaction between a solid and a liquid ligand is more facile than between two solids, and indeed the reaction between $(\eta^5\text{-}C_5H_5)Mo(CO)_3Me$ and PPh_3 (70−90 °C; PPh_3 is a solid at the lower temperature and a liquid at the higher temperature) shows this. It is possible that the reaction at the lower temperatures actually occurs at the microscopic level in a “liquid” phase, but this possibility needs further study.

When the two solid reagents are in close proximity to each other, reaction can occur. The actual manner in which this interaction occurs is still not known and will require further study. The reactions between $(\eta^5\text{-}C_5H_5)Mo(CO)_3Me$ or $(\eta^5\text{-}C_5H_5)Fe(CO)_2Me$ and CO most certainly also occur in the solid phase. Modification of the ligands attached to the metals will provide for a variation of channel widths in the solid and, consequently, on the ability to control CO diffusion to the metal center. Experiments to evaluate this possibility are in progress.

Acknowledgment. We wish to thank the NRF (Project #2053379), THRIP, and the University of the Witwatersrand for financial support.

OM0301738