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Microwave-Assisted Synthesis of Group 6 (Cr, Mo, W) Zerovalent Organometallic Carbonyl Compounds

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Summary: The microwave-assisted synthesis of a series of compounds of the form ML(CO)$_4$ (M = Cr, Mo, W; L = en, bipy, dppm, dppe), results in the reduction of reaction times and an increase in yields over previously published syntheses. Reaction times are reduced by a factor of 5 to over 500.

Introduction

In the past two decades, the use of microwave ovens in chemical synthesis and analysis has increasingly grown in importance. Many chemical reactions can be perfomed more rapidly under microwave irradiation than under conventional conditions; this was first demonstrated for organic synthesis in 1986[1,2] and for inorganic synthesis in 1989.[3] Microwave-assisted synthesis (MAS) is particularly interesting due to its ability to dramatically reduce reaction times, improve yield, and simplify procedures. While MAS has been applied predominantly to organic synthesis,[4] we show that this method lends itself especially well to organometallic syntheses which may involve extended reaction times (refluxes as long as days) at elevated temperatures.

While traditional organometallic synthesis often involves working with open systems (open either to air or to an inert atmosphere) and heating with thermostated baths or at solvent reflux temperatures, our MAS reactions are carried out in pressure-tight, microwave-transparent Teflon vessels and temperature is maintained through dielectric-loss heating. The accelerated rates realized in MAS are the result of the elevated temperature and higher pressure achieved in a closed system. Commercial microwave oven systems, unlike domestic microwave ovens, are equipped to monitor and control either the temperature or pressure (or both) of the reaction mixture; the ability to finely manipulate the reaction conditions provides powerful synthetic control to the chemist.

In this paper, we demonstrate the use of MAS in the synthesis of zerovalent substituted Cr, Mo, and W carbonyl compounds using 2,2′-bipyridine (bipy), ethylenediamine (en), bis(diphenylphosphino)methane (dppm), and bis(diphenylphosphino)ethane (dppe) as ligands. We describe simple microwave-assisted synthetic procedures that result in decreased reaction times and that are accompanied by product yields improved over those observed using traditional published procedures.

Although many variations of the syntheses presented here have been published since the late 1950s, none has so dramatically impacted the reaction time as has the MAS. All of the compounds selected for this study are used as starting materials for the synthesis of a wide variety of organometallic products, for kinetic studies, or for catalytic investigations. For example, the dppm and dppe ligands, as well as the larger analogues, have been used in numerous spatial studies[5,6] and ligand-exchange mechanistic studies.[7] The molybdenum compounds possess ligand-selective catalytic properties.[8]

Results and Discussion

Our results are summarized in Table 1 and consist of the reaction times of both the traditional synthesis (reflux at solvent boiling point) and the MAS, as well as the rate enhancement (the ratio of MAS time to reflux time) of each reaction. MAS reduces the overall reaction times by a factor of 8−576. The rate enhancements we observe are similar to those observed for organic microwave-assisted syntheses[9] and clearly show the time reduction attainable through MAS. Along with decreased reaction times, an increase in yield is generally observed, as is also shown in the table.

The temperatures at which the syntheses were performed are shown, which, with the exception of the synthesis of enMo(CO)$_4$, are performed at a higher temperature than the published procedures.

It has been noted in the literature that syntheses involving the use of the hexacarbonyls of Cr, Mo, and W are handicapped by the sublimation and deposition of the metal hexacarbonyl on the reflux condenser, and this deposit must be mechanically returned to the reaction flask.[10] The yields of microwave-assisted syntheses improve in part because, with the closed system, starting materials are constrained to the reaction vessel and are continually washed back into the reaction mixtures. With the closed system, higher pressures can be generated, leading to superheating of the solvents

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Table 1. MAS and Reflux Reaction Times, Yields, and Rate Enhancements

compd	synthetic method	time, min	temp, °C	yield, %	rate enhancement[a]
(bipy)Cr(CO)$_4$	MAS	5	180	68	24
	reflux	120	110	40	
(bipy)Mo(CO)$_4$	MAS	0.5	180	99	180
	reflux	90	110	88	
(bipy)W(CO)$_4$	MAS	10	180	75	12
	reflux	120	140	76	
(en)Cr(CO)$_4$	MAS	5	150	64	12
	reflux	60	120	34	
(en)Mo(CO)$_4$	MAS	0.5	150	62	30
	reflux	15	165	12	
(en)W(CO)$_4$	MAS	15	150	81	8
	reflux	120	120	16	
(dppm)Cr(CO)$_4$	MAS	5	180	55	9
	reflux	45	135	82	
(dppm)Mo(CO)$_4$	MAS	0.5	180	58	90
	reflux	45	115	75	
(dppm)W(CO)$_4$	MAS	5	180	62	576
	reflux	2880	165	51	
(dppe)Cr(CO)$_4$	MAS	0.5	180	86	270
	reflux	135	135	41	
(dppe)Mo(CO)$_4$	MAS	0.5	180	80	50
	reflux	25	120	68	
(dppe)W(CO)$_4$	MAS	2	180	64	90
	reflux	180	155	55	

[a] Ratio of reflux time to MAS time.

used in the syntheses; higher temperatures rapidly drive the reactions toward completion. The ability to reach these temperatures, the majority of them higher than the boiling point of the solvent, is one of the factors attributing to the reduced reaction times.

The choice of the dielectric solvent is critical in microwave-assisted organometallic synthesis. A complexing solvent is not desirable, nor is one whose dielectric constant is so small that the time required to heat the solvent makes the microwave synthesis no faster than the traditional synthesis. Nonpolar solvents, possessing no dipole moment, cannot be heated by direct microwave irradiation but can be indirectly heated by the addition of a polar solvent. Another consideration is the vapor pressure of the solvent at reaction temperature; the reaction vessels have pressure limits associated with them that must be carefully observed. The best solvent or solvent mixture for a given synthesis is generally determined empirically. Of the dielectric solvents explored in our study, solvent systems containing 2-methoxyethyl ether (diglyme) and *o*-dichlorobenzene reached the reaction temperature the fastest. Others, containing chlorobenzene or 1,1,1-trichloroethane, took as long as 20 min to reach the same temperature, negating in some cases the time savings over the reflux method. Diglyme was chosen to be the dielectric solvent in all of our syntheses because it was more easily removed during the workup than was *o*-dichlorobenzene. Heating times and temperatures were optimized experimentally.

We have demonstrated the speed and utility of MAS for the synthesis of a series of organometallic compounds. This work further broadens the scope of MAS in organometallic synthesis.

Experimental Section

Apparatus. All microwave-assisted syntheses were conducted using an MSP-1000 microwave sample preparation system (CEM Corp., Matthews, NC) and Teflon-lined digestion vessels (LDV). The LDV, illustrated in Figure 1, consisted of an Ultem poly(etherimide) outer body and a Teflon inner liner, Teflon cap, and safety rupture membrane. The cap had ports that allowed for the insertion of a fluoroptic temperature probe and for the connection of a pressure control line. During irradiation, the LDV was positioned on a turntable around a central vapor containment vessel inside the microwave cavity. A Teflon tube ($^{1}/_{8}$ in.) in the vent system connected the LDV to the vapor-containment vessel, while a Teflon tube ($^{1}/_{4}$ in.) in the center of that vessel led to the cavity exhaust duct. This provided expedient removal of solvent vapor from the oven cavity in the event of a ruptured membrane due to overpressurization. A microwave-transparent valve on the pressure control system allowed the LDV to be removed from the cavity immediately following irradiation.

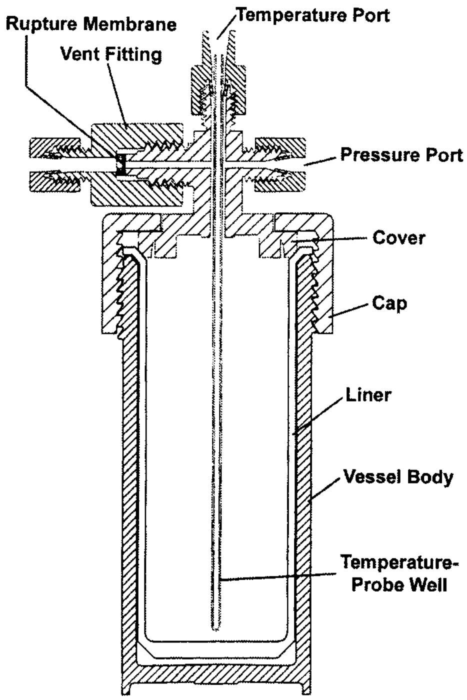

Figure 1. Lined digestion vessel (LDV) with temperature and pressure control (used by permission, CEM Corp.).

Synthetic Method. All reagents were of analytical grade or better. Chromium, molybdenum, and tungsten hexacarbonyls, 2,2′-bipyridyl, bis(diphenylphosphino)methane, bis(diphenylphosphino)ethane, and all solvents were purchased from Aldrich Chemical Co. and used as received. Ethylenediamine was distilled prior to each use.

The reagents for synthesis were placed into an LDV and purged with dry nitrogen gas for 15 min. In each MAS performed, both temperature and pressure were monitored; however, only temperature was regulated at a programmable set point. The maximum-pressure set point was set to 200 psi, the limit of the Teflon liners. The syntheses are modifications of previously published syntheses.[11−13] Reactions in which the published synthesis used a nonpolar solvent were modified by the addition of diglyme to indirectly heat the reaction mixture. All products were dried in vacuo and stored under dry nitrogen away from light. Reaction times and yields at set-point temperatures are summarized in Table 1.

The identity of the compounds was verified by ^{1}H NMR as solutions in CDCl$_3$ or DMSO-d_6 by comparison with the spectra of authentic compounds. Elemental analyses were performed by Desert Analytics (Tucson, AZ).

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Preparation of $M^0(2,2'\text{-bipyridyl})(CO)_4$ (M = Cr, Mo, W). A mixture of 0.5 g (2.3 mmol) of $Cr(CO)_6$ and a 10% excess (by mmol) of 2,2′-bipyridyl was suspended in 20 mL of toluene and 10 mL of diglyme in the LDV and heated at 180 °C for 5 min (M = Cr), 30 s (M = Mo), or 10 min (M = W). The reaction mixture was cooled to room temperature, and precipitation was completed with the addition of petroleum ether. The solid was recrystallized from acetone with water, collected by filtration, and dried in vacuo.

M = Cr: yield 0.50 g, 68%. Anal. Calcd for $C_{14}H_8N_2O_4Cr$: C, 52.51; H, 2.52. Found: C, 52.14; H, 2.35. M = Mo: yield 0.70 g, 99%. Anal. Calcd for $C_{14}H_8N_2O_4Mo$: C, 46.17; H, 2.21. Found: C, 45.92; H, 2.30. M = W: yield 0.47 g, 75%. Anal. Calcd for $C_{14}H_8N_2O_4W$: C, 37.20; H, 1.78. Found: C, 37.19; H, 1.78.

The syntheses were also performed as reported in the literature by refluxing 2,2′-bipyridyl and metal hexacarbonyl in toluene for 120 min (M = Cr), in toluene for 90 min (M = Mo), and in xylenes for 120 min (M = W).[11]

Preparation of $M^0(\text{ethylenediamine})(CO)_4$. A mixture of 0.35 g (1.6 mmol) of $Cr(CO)_6$ and a 100% excess of ethylenediamine (by millimoles) was combined in the LDV in 5 mL of diglyme. After heating the contents of the LDV at 150 °C for 5 min (M = Cr), 30 s (M = Mo), or 15 min (M = W), the reaction mixture was cooled to room temperature and the pale yellow solid was precipitated with ethanol and water. The solid was collected by filtration and dried and purified by sublimation in vacuo.

M = Cr: yield 0.23 g, 64%. Anal. Calcd for $C_6H_8N_2O_4Cr$: C, 32.15; H, 3.60. Found: C, 32.17; H, 3.51. M = Mo: yield 0.32 g, 62%. Anal. Calcd for $C_6H_8N_2O_4Mo$: C, 26.88; H, 3.01. Found: C, 26.65; H, 2.86. M = W: yield 0.41 g, 81%. Anal. Calcd for $C_6H_8N_2O_4W$: C, 20.24; H, 2.27. Found: C, 20.35; H, 2.16.

The syntheses were also performed as reported in the literature by heating ethylenediamine and the metal hexacarbonyl at 120 °C for 60 min (M = Cr), at 130 °C for 15 min (M = Mo), or at 120 °C for 120 min (M = W).[12]

Preparation of $M^0(\text{bis(diphenylphosphino)methane})(CO)_4$. A mixture of 0.21 g (0.95 mmol) of $Cr(CO)_6$ and a 10% excess of bis(diphenylphosphino)methane (by millimoles) was suspended in 3 mL of diglyme in the LDV. After the reaction mixture was heated at 180 °C for 5 min (M = Cr, W), or 30 s (M = Mo), the reaction mixture was cooled to room temperature. Methanol was added to precipitate the yellow product. The solid was collected by filtration and dried in vacuo.

M = Cr: yield 0.29 g, 55%. Anal. Calcd for $C_{29}H_{22}P_2O_4Cr$: C, 63.51; H, 4.04. Found: C, 63.45; H, 4.10. M = Mo: yield 0.34 g, 58%. Anal. Calcd for $C_{29}H_{22}P_2O_4Mo$: C, 58.80; H, 3.74. Found: C, 58.83; H, 3.90. M = W: yield 0.41 g, 62%. Anal. Calcd for $C_{29}H_{22}P_2O_4W$: C, 51.20; H, 3.26. Found: C, 50.84; H, 3.22.

The syntheses were also performed as reported in the literature by heating bis(diphenylphosphino)methane and the metal hexacarbonyl in diglyme at 135 °C for 3.5 h (M = Cr), 115 °C for 10 h (M = Mo), or 165 °C for 48 h (M = W).[13]

Preparation of $M^0(\text{bis(diphenylphosphino)ethane})(CO)_4$. A mixture of 0.21 g (0.93 mmol) of $Cr(CO)_6$ and a 10% excess (by millimoles) of bis(diphenylphosphino)ethane was suspended in 3 mL of diglyme in the LDV. After the reaction mixture was heated at 180 °C for 30 s (M = Cr, Mo) or 2 min (M = W), the reaction mixture was cooled to room temperature. Methanol was added to the reaction mixture to precipitate the pale yellow product. The solid was collected by filtration, recrystallized from a solution of methanol and water, and dried in vacuo. The microanalysis for the tungsten compound is low due to its light and air sensitivity.

M = Cr: yield 0.49 g, 86%. Anal. Calcd for $C_{30}H_{24}P_2O_4Cr$: C, 64.06; H, 4.30. Found: C, 63.95; H, 4.27. M = Mo: yield 0.31 g, 80%. Anal. Calcd for $C_{30}H_{24}P_2O_4Mo$: C, 59.42; H, 3.99. Found: C, 59.68; H, 4.04. M = W: yield 0.41 g, 64%. Anal. Calcd for $C_{30}H_{24}P_2O_4W$: C, 51.90; H, 3.48. Found: C, 51.00; H, 3.27.

The syntheses were also performed as reported in the literature by heating bis(diphenylphosphino)ethane and the metal hexacarbonyl in diglyme at 135 °C for 3 h (M = Cr), 115 °C for 25 min (M = Mo), or 155 °C for 4 h (M = W).[13]

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