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Synthesis of organometallic compounds containing bonds between different metals: peculiarities of the mechanism[†]

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The possibility synthesizing compounds of the type $(\eta^5-C_5H_5)M(CO)_3M'Cl$ ($M = Mo, W$; $M' = Mg, Zn, Cd$) by direct metal interaction with chlorides of cyclopentadienyltricarbonylmolybdenum and tungsten was demonstrated. In the case of magnesium derivatives of the type $[(\eta^5-C_5H_5)M(CO)_3]_2Mg$ were observed also. The kinetics of magnesium, zinc and cadmium oxidation by Ph_3SnCl, $(\eta^5-C_5H_5)Mo(CO)_3Cl$ and $(\eta^5-C_5H_5)W(CO)_3Cl$ in tetrahydrofuran and *N,N*-dimethylformamide was investigated. Rate constants and activation energy were determined. For the process of oxidation a Langmuir–Hinshelwood scheme was proposed. The kinetic data obtained make it possible to calculate the equilibrium constants, enthalpy and entropy of adsorption of the oxidant and coordinating solvent on metal surface. Copyright © 2000 John Wiley & Sons, Ltd.

Keywords: organometallic compounds; magnesium; zinc; cadmium; kinetics; adsorption; mechanism; oxidation

INTRODUCTION

The oxidation of magnesium, zinc and cadmium by hydrocarbon halides is used extensively for preparation of the corresponding organometallic compounds. However, this method is rarely used for obtaining organic compounds containing a bond between different metals. The first report concerning oxidation of magnesium by triphenyltin chloride (**I**) to give bis(triphenyltin)magnesium was made by Tamborsky and co-workers.[1] The same interaction of zinc with **I** leads to formation of Ph_4Sn, metallic tin and phenylzinc chloride.[2] A number of polynuclear organometallic compounds have been obtained by reaction of R_nEX_m ($E = Si$, Ge, Sn; n, $m = 1–3$) with rare-earth elements.[3–5] There have been some examples of the formation of organobimetallic compounds by oxidation of magnesium[6] and mercury[7,8] with halides of cyclopentadienylcarbonylmetal derivatives. The kinetics and mechanism of these processes have not been investigated.

Here we report that the compounds containing M–M′ bonds (where M = Sn, Mo, W; M′ = Mg, Zn, Cd) can be obtained by oxidation of metallic magnesium by Ph_3SnCl, and of magnesium, zinc and cadmium by $CpMo(CO)_3Cl$ (**II**) and $CpW(CO)_3Cl$ (**III**) ($Cp = \eta^5-C_5H_5$) in tetrahydrofuran (THF) and *N,N*-dimethylformamide (DMFA). The kinetics of these processes is described and some thermodynamic parameters of the adsorption of the reagents on metal surface are presented.

EXPERIMENTAL

All operations were carried out in an argon atmosphere or in vacuum. Organic solvents were purified and dried according to the literature.[9] Pure solvents were used for preparation of organobimetallic compounds. The kinetic measurements involved mixtures of coordinating solvent (THF or DMFA) with benzene.

Compounds **I**, $Ph_3SnSnPh_3$(**IV**),[10] **II**[11] and **III**[12] were synthesized by the respective techniques (see the references indicated). The content of the basic substance in the compounds received was not less than 99%. The purity of **I–III** was estimated by elemental analysis and from melting points:

I: Found: C 55.4, H 3.8, Sn 30.6, Cl 9.4; (Calcd: C

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56.0, H 3.9, Sn 30.8, Cl 9.3%). M.p. 105.5 °C (lit.[10] m.p. 105–106 °C)

II: Found: C 34.0, H 2.0, Mo 34.4, Cl 12.5; (Calcd: C 34.2, H 1.8, Mo 34.2, Cl 12.6%). M.p. 144.5 °C dec. (lit.[11] m.p. 145 °C dec.)

III: Found: C 26.3, H 1.3, W 49.6, Cl 9.5; (Calcd: C 26.1, H 1.3, W 49.9, Cl 9.6%). M.p. 159 °C dec. (lit.[12] m.p. 160 °C dec.).

Compound **IV** was analysed by iodine titration, elemental analysis and melting point. Found: C 61.4, H 4.4, Sn 33.8; (Calcd: C 61.7, H 4.3, Sn 34.0%). M.p. 238 °C (lit.[10] m.p. 238 °C)

Magnesium, zinc and cadmium used for kinetics were taken as wires (diameter 0.5 mm) with purity 99.9%. Rieke magnesium was synthesized by a common method[13] involving interaction of magnesium chloride with metallic potassium in THF. Kinetic measurements were carried out by a resistometric method[14] modified for use of an argon atmosphere.

The quantity of $(Ph_3Sn)_2Mg$ was determined after treatment of the reaction mixture with 1,4-dioxan (to separate $MgCl_2$ as a precipitate[15] according to the Schlenk equilibrium), by evaluating the volume of ethylene generated after reaction with 1,2-dibromoethane.[16] The gas was analysed qualitatively and quantitatively by GC (Tsvet-104 chromatograph; column 1000 mm × 5 mm with activated charcoal; temperature of column and catarometer 110 °C; helium flow rate 40 ml min^{-1}; retention time 250 s).

Reaction of $CpM(CO)_3Cl$ (M = Mo,W) with magnesium

A solution of 0.42 g $CpMo(CO)_3Cl$ (or 0.553 g $CpW(CO)_3Cl$) in 5 ml of THF at 20 °C was added to 0.144 g of magnesium turnings. The reaction finished within 6 h. The brown solution and fine light precipitate were separated from unreacted magnesium. The precipitate was separated from solution by decantation and washed with THF.

(a) The brown solution was evaporated, then hydrolysed with degassed water, which led to the formation of a yellow precipitate which was separated by filtration and purified by sublimation. We obtained 0.27 g of $CpMo(CO)_3H$ (yield 75%) from the $CpMo(CO)_3Cl$, and 0.29 g of $CpW(CO)_3H$ (yield 58%) from the $CpW(CO)_3Cl$. The melting points of the hydrides corresponded to literature data.[17]

(b) The precipitate was hydrolysed with degassed water, which led to the formation of a yellow precipitate, which was separated by filtration and purified by sublimation. We obtained 0.03 g of $CpMo(CO)_3H$ (yield 9%) from the $CpMo(CO)_3Cl$ and 0.06 g of $CpW(CO)_3H$ (yield 12%) from the $CpW(CO)_3Cl$. The melting points of hydrides corresponded to literature data.[17]

(c) The brown solution was treated with 0.422 g $HgCl_2$, then the reaction mixture was evaporated. The yellow residue was extracted with acetone and recrystallized from ethanol. This resulted in formation of 0.6 g of yellow $CpMo(CO)_3HgCl$ crystals (yield 84%) in the case of $CpMo(CO)_3Cl$ and 0.61 g of $CpW(CO)_3HgCl$ (yield 78%) in the case of $CpW(CO)_3Cl$.

Reaction of $CpM(CO)_3Cl$ (M = Mo,W) with zinc

A solution of 0.42 g $CpMo(CO)_3Cl$ [or 0.553 g $CpW(CO)_3Cl$] in 5 ml of DMFA at 20 °C was added to 0.39 g of zinc turnings. The reaction finished within three days. The brown solution was filtrated from unreacted metal and treated with 0.422 g $HgCl_2$, then the reaction mixture was evaporated. The yellow residue was extracted with acetone and recrystallized from ethanol, resulting in formation of 0.69 g of yellow crystals of $CpMo(CO)_3HgCl$ (yield 96%) in the case of $CpMo(CO)_3Cl$ and 0.66 g of $CpW(CO)_3HgCl$ (yield 85%) in the case of $CpW(CO)_3Cl$.

Reaction of $CpM(CO)_3Cl$ (M = Mo,W) with cadmium

The solution of 0.42 g $CpMo(CO)_3Cl$ [or 0.553 g $CpW(CO)_3Cl$] in 5 ml of DMFA at 20 °C was added to 0.73 g of cadmium turnings. The reaction finished within three days. The brown solution was filtered from the unreacted metal and treated with 0.422 g $HgCl_2$, then the reaction mixture was evaporated. A yellow residue was extracted with acetone and recrystallized from ethanol, resulting in formation of 0.67 g of yellow crystals of $CpMo(CO)_3HgCl$ (yield 95%) in the case of $CpMo(CO)_3Cl$ and 0.62 g of $CpW(CO)_3HgCl$ (yield 80%) in the case of $CpW(CO)_3Cl$.

The melting points and IR spectra of the mercury derivatives corresponded to the literature data.[18] All yields were calculated with respect to the initial quantity of $CpMo(CO)_3Cl$ or $CpW(CO)_3Cl$.

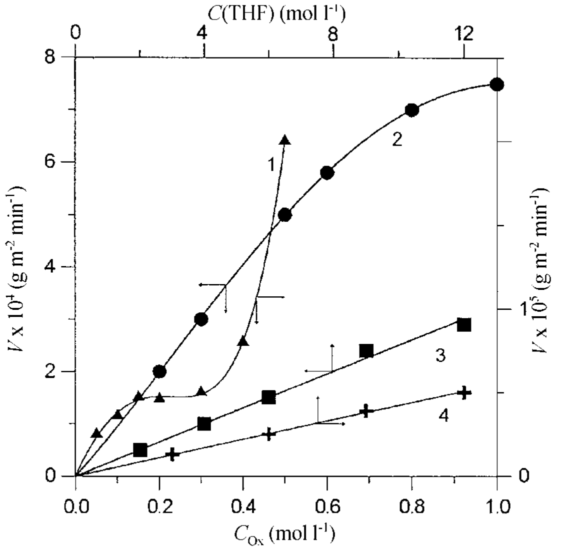


Figure 1 Magnesium oxidation rate in (1, 4) Ph_3SnCl–THF–benzene and (2, 3) $CpMo(CO)_3Cl$–THF–benzene systems. Curve 1, C(THF) = 12 mol l^{-1}, 303 K; curve 2, C(THF) = 12 mol l^{-1}, 293 K; curve 3, $C(CpMo(CO)_3Cl)$ = 0.3 mol l^{-1}, 293 K; curve 4, $C(Ph_3SnCl)$ = 0.1 mol l^{-1}, 303 K.

RESULTS AND DISCUSSION

The rate of magnesium oxidation by **I** is maximal in THF. The linear dependence of the process rate on THF concentration (Fig. 1) provides evidence that the adsorption equilibrium constant of this ligand on a magnesium surface is close to zero. The influence of the oxidant concentration upon reaction rate (Fig. 1) is analogous to that of alkyl and aryl halides.[19,20] The dependence of the magnesium oxidation rate upon the Ph_3SnCl concentration has two points of inflection. In the range $0\ \text{mol l}^{-1} < C_{Ox} < 0.3\ \text{mol l}^{-1}$ it corresponds to the Langmuir isotherm. Therefore, the oxidation of magnesium in benzene in the presence of THF is carried out according to a scheme by which the molecule **I** adsorbed on magnesium surface is attacked by a molecule of ligand from the bulk of the solution.[21] Thus in the case of constant ligand concentration the rate of the process is expressed by Eqn [1], where $k_1 = k'K_LC_L$, C_L and C_{Ox} are the concentrations of the ligand and oxidant respectively, K_L and K_{Ox} are the adsorption constants of the ligand and oxidant, $k' = kS_0$, k is the rate constant of the process and S_0 is the concentration of the adsorption centres on the metal surface.

$$V = \frac{k_1K_{Ox}C_{Ox}}{1 + K_{Ox}C_{Ox}} \qquad [1]$$

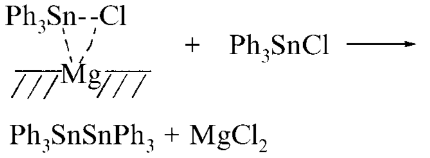
The transformation of Eqn [1] in coordinates $1/V$, $1/C$ allows calculation of the equilibrium constant of adsorption of **I** on the magnesium surface. Given these values at different temperatures, it was possible to calculate the adsorption enthalpy and entropy. The data obtained are given in Table 1.

Curve 1 on Fig. 1 has two points of inflection. One possible explanation is that at low oxidant concentration (less than 0.3 mol l^{-1}) a molecule of oxidant adsorbed on a magnesium surface reacts with the metal, forming an analogue of a Grignard reagent which reacts further with excess of **I** (Eqns [2] and [3]).

$$\underset{\mathbf{I}}{Ph_3SnCl} + Mg \longrightarrow Ph_3SnMgCl \qquad [2]$$

$$Ph_3SnMgCl + \underset{\mathbf{I}}{Ph_3SnCl} \longrightarrow \underset{\mathbf{IV}}{Ph_3SnSnPh_3} + MgCl_2 \qquad [3]$$

Raising the oxidant concentration increases the probability of **IV** formation by means of attack of the molecule of **I** adsorbed on an active centre on the magnesium surface by an analogous molecule from the bulk of the solution (Eqn [4]).



[4]

This process is described by Eqn [5].

$$V = \frac{k_2K_{Ox}C_{Ox}^2}{1 + K_{Ox}C_{Ox}} \qquad [5]$$

The rate of magnesium oxidation will be expressed by Eqn [6], which is the sum of Eqns [1] and [5].

$$V = \frac{k_1K_{Ox}C_{Ox} + k_2K_{Ox}C_{Ox}^2}{1 + K_{Ox}C_{Ox}} \qquad [6]$$

Coefficients k_1 and k_2 were determined by the least-squares method with respect to K_{Ox} obtained from the solution of Eqn [1]. Equation [6] gives a good approximation to experimental data (Fig. 2).

The compound **IV** formed in reactions [3] and [4] precipitates partially from a reaction mixture as a voluminous white deposit. Further reaction of **IV** with magnesium in THF at 20 °C leads to the formation of bis(triphenyltin)magnesium (**V**).[1]

Table 1 Effective rate constants and energies of activation, equilibrium constants, enthalpy and entropy of adsorption of organometallic halides and ligands on a metal surface

T (K)	K_{ox}	K_L	$-\Delta H_{ads}^{Ox}$ (kJ mol^{-1})	$-\Delta S_{ads}^{Ox}$ (J mol^{-1} K^{-1})	$-\Delta H_{ads}^{L}$ (kJ mol^{-1})	$-\Delta S_{ads}^{L}$ (J mol^{-1} K^{-1})	*k* (g m^{-2} min^{-1})	E_a (kJ mol^{-1})
Mg–Ph_3SnCl–THF								
303	0.44		26 ± 1	94 ± 1				59 ± 8
313	0.31							
323	0.23							
Mg–$CpMo(CO)_3Cl$–DMFA								
293	2.4	0.049	30 ± 2	92 ± 4	33 ± 1	138 ± 4	2.2×10^{-4}	67 ± 4
303	1.5	0.031					4.9×10^{-4}	
313	1.1	0.020					13×10^{-4}	
Mg–$CpW(CO)_3Cl$–DMFA								
293	1.4	0.049	30 ± 1	100 ± 4	33 ± 1	138 ± 4	2.1×10^{-4}	80 ± 4
298	1.2	0.037					3.8×10^{-4}	
303	1.0	0.031					6.2×10^{-4}	
Zn–$CpMo(CO)_3Cl$–DMFA								
283	5.3	1.17	29 ± 4	88 ± 5	21 ± 1	71 ± 4	4.0×10^{-2}	43 ± 4
293	4.2	0.85					7.1×10^{-2}	
303	2.3	0.65					14×10^{-2}	
Cd–$CpMo(CO)_3Cl$–DMFA								
288	26.8	0.75	42 ± 1	121 ± 4	22 ± 2	79 ± 5	2.4×10^{-2}	79 ± 5
293	19.6	0.66					4.6×10^{-2}	
298	14.4	0.55					7.7×10^{-2}	

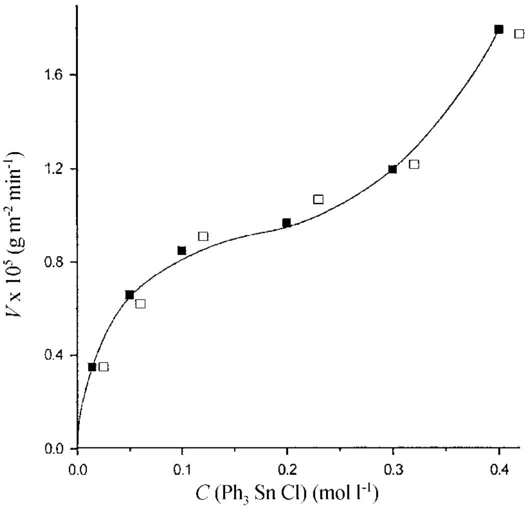


Figure 2 Magnesium oxidation rate in Ph_3SnCl–THF–benzene system. C(THF) = 12 mol l^{-1}, 313 K. ■, Experimental data; □, calculated data.

Analysis of the reaction mixture at the moment when **V** begins to form has shown that the yield of hexaphenylditin is 0.26 mol per mol of the initial compound **I**. The yield of **V** in the reaction products after the process ends (24 h after mixing the reagents) is 0.425 mol per mol of **I** introduced to the reaction.

It should be noted that the addition of $MgCl_2$, $MgBr_2$ or MgI_2 in amounts from 0.2 to 1 mol per mol of organotin compound, to an initial mixture of **IV** with magnesium in THF, did not lead to oxidation of the metal during at least 200 h at 20 °C. On the other hand, the interaction of **IV** with magnesium could be stimulated by the introduction of 1,2-dibromoethane (1 mol per mol of **IV**) to the initial reaction mixture. The final product of reaction is the compound **V**, of which the yield is about 0.42 mol per mol of initial **IV** (Eqn [7]). The interaction of hexaphenylditin with Rieke magnesium[13] in THF is also accompanied by formation of **V** in 24% yield. This confirms the fact that activated magnesium is capable of cleaving the Sn–Sn bond of hexaphenylditin,

$$\underset{\textbf{IV}}{Ph_3SnSnPh_3} + Mg \longrightarrow \underset{\textbf{V}}{Ph_3SnMgSnPh_3} \qquad [7]$$

The interaction of magnesium with **II** and **III** was investigated in order to synthesize organopolymetallic compounds by direct metal oxidation. The reaction proceeds in THF and DMFA.

Exothermic reaction of **II** or **III** with an excess of magnesium turnings in THF at 20 °C is finished within 6 h after mixing the reagents. At the end of the process the reaction mixture consists of a brown solution and light precipitate. The loss of magnesium weight shows that 1 mol of metal per mol of initial oxidant has entered the reaction. The solution at the end of the process contains the elements in the proportion Mo Mg Cl = 1:1.05:1.09 (or W Mg Cl=1:1.1:1.2); in the precipitates the element ratio is Mo(W) Mg = 2:1.

Analysis of a reaction mixture after the end of the process and some reactions of the compounds obtained (Scheme 1, below) have shown that the solution contains $CpM(CO)_3MgCl$, and that a precipitate is $[CpM(CO)_3]_2Mg$ (M = Mo, W). A deposit of $[CpM(CO)_3]_2Mg$ was separated from a solution by decantation with subsequent repeated washing with THF. The compounds obtained are white powders that begin to decompose without melting at 160 and 185 °C for M = Mo and W respectively. These observations are in agreement with known literature data.[6,22,23]

Contrary to reaction [3], derivatives of the type $[CpM(CO)_3]_2$ (M = Mo, W) are not found during the interaction of **II** or **III** with magnesium. Therefore the most probable route to $[CpM(CO)_3]_2Mg$ formation is via reaction [8] and the equilibrium [9]

$$\underset{\textbf{II, III}}{CpM(CO)_3Cl} + Mg \longrightarrow CpM(CO)_3MgCl \qquad [8]$$

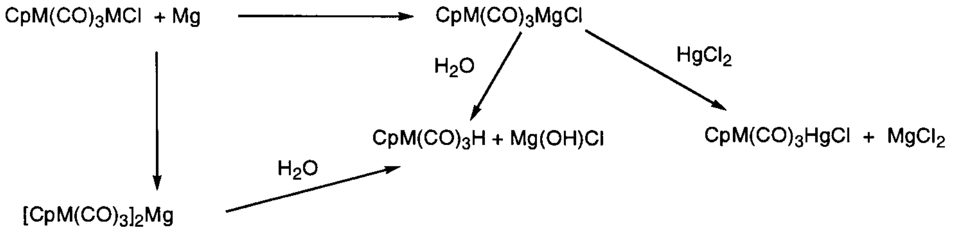
$$2\ CpM(CO)_3MgCl \rightleftharpoons [CpM(CO)_3]_2Mg + MgCl_2 \qquad [9]$$

The addition of the $MgCl_2$ solution in THF to the insoluble compound $[CpM(CO)_3]_2Mg$ (M = Mo, W) causes dissolution of a precipitate and formation of a Grignard reagent analogue. Attempts to separate the latter in an individual form failed. Evacuating the reaction mixture in vacuum gives only a dark oil.

In order to prove of the nature of the compounds obtained a number of reactions were carried out (Scheme 1).

The organopolymetallic compounds are not found in products of reaction of **II** or **III** with magnesium in DMFA, probably because of their interaction with the solvent.[17]

The dependence of the reaction rate of magnesium with **II** or **III** on THF concentration is close to linear (Fig. 1), which is further evidence of a low value of the adsorption equilibrium constant of the



Scheme 1

ligand on a magnesium surface. The dependence $V=f(C_{\mathrm{Ox}})$ is quite a good approximation of the Langmuir isotherm over the whole interval of oxidant concentration (Fig. 1). This fact provides the evidence that a reaction analogous to [4] does not occur in the case of **II** and **III**. The oxidation of magnesium by compound **II** or **III** in THF can be described by the same model as in the case of **I** ($0 \text{ mol l}^{-1} < C_{\mathrm{Ox}} < 0.3 \text{ mol l}^{-1}$).

In DMFA the dependence of magnesium oxidation rate on ligand or oxidant concentration is a curve with saturation for both **II** and **III** (Fig. 3). To discover the character of the adsorption of the reagents, the dependence curves $V/V_{\mathrm{MAX}} = f(C_{\mathrm{Ox}})$ (Fig. 4) were constructed. Since the curves at various initial ligand concentrations do not coincide, it is possible to conclude that the adsorption of reagents occurs on reaction centres of the surface that are of an identical native. In this case the process can be described by the Langmuir–Hinshelwood scheme[21] (Eqns [10]–[12], where Ox is the oxidant, L is a ligand, S is an active centre of the metal surface, and OxS and LS are adsorbed molecules of oxidant and ligand respectively.

$$\mathrm{Ox} + \mathrm{S} \overset{K_{\mathrm{Ox}}}{\rightleftharpoons} \mathrm{OxS} \qquad [10]$$

$$\mathrm{L} + \mathrm{S} \overset{K_{\mathrm{L}}}{\rightleftharpoons} \mathrm{LS} \qquad [11]$$

$$\mathrm{OxS} + \mathrm{LS} \xrightarrow{k} \text{products} \qquad [12]$$

The reaction rate can be expressed by Eqn [13], where $k' = kS_0^{\,2}$; S_0 = concentration of the active

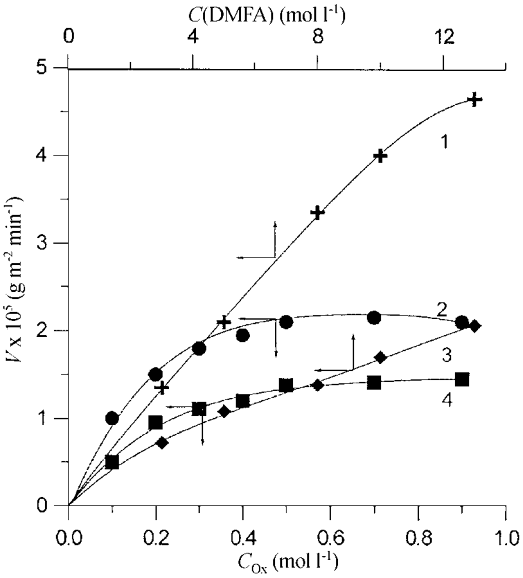


Figure 3 Magnesium oxidation rate in (1, 2) $\mathrm{CpMo(CO)_3Cl}$–DMFA–benzene and (3, 4) $\mathrm{CpW(CO)_3Cl}$–DMFA–benzene systems. Curve 1, $C(\mathrm{CpMo(CO)_3Cl}) = 0.3 \text{ mol l}^{-1}$, 313 K; curve 2, $C(\mathrm{DMFA}) = 13 \text{ mol l}^{-1}$, 293 K; curve 3, $C(\mathrm{CpW(CO)_3Cl}) = 0.5 \text{ mol l}^{-1}$, 293 K; curve 4, $C(\mathrm{DMFA}) = 13 \text{ mol l}^{-1}$, 293 K.

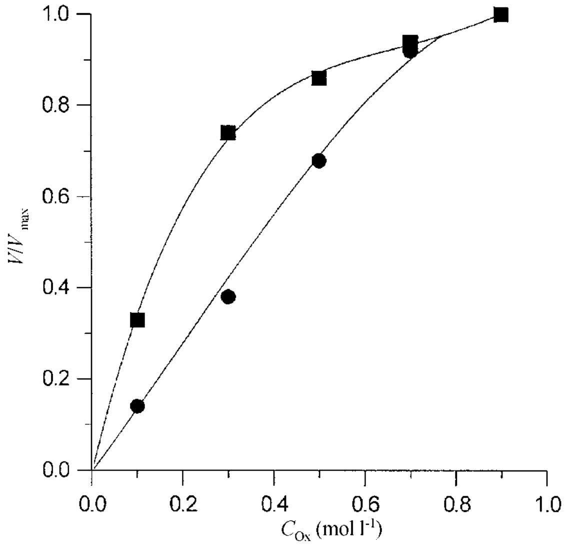


Figure 4 Dependence $V/V_{\mathrm{max}} = f(C_{\mathrm{Ox}})$ for magnesium oxidation in the $\mathrm{CpW(CO)_3Cl}$–DMFA–benzene system at 293 K. ■, $C(\mathrm{DMFA}) = 8 \text{ mol l}^{-1}$; ● $C(\mathrm{DMFA}) = 13 \text{ mol l}^{-1}$.

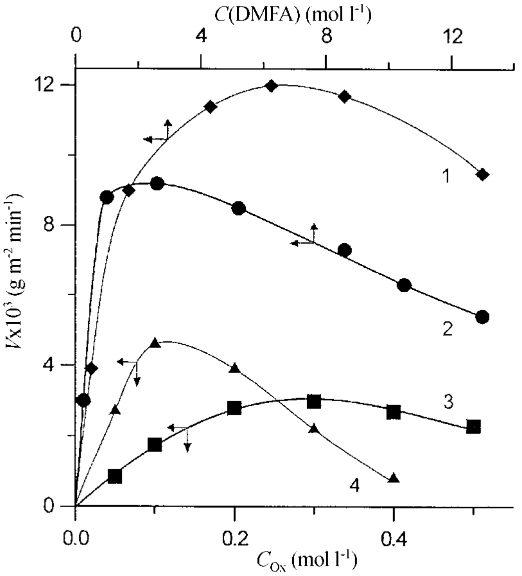


Figure 5 Metal oxidation rate in (2, 3) Zn–CpMo(CO)$_3$Cl–DMFA–benzene and (1,4) Cd–CpMo(CO)$_3$Cl–DMFA–benzene systems at 293 K. Curve 1, C(CpMo(CO)$_3$Cl) = 0.2 mol l^{-1}; curve 2, C(CpMo(CO)$_3$Cl) = 0.3 mol l^{-1}; curve 3, C(DMFA) = 0.25 mol l^{-1}; curve 4, C(DMFA) = 0.5 mol l^{-1}.

centres on a surface; k = rate constant; K_{Ox} and K_L = equilibrium constants of adsorption of an oxidant and ligand respectively.

$$V = k' \frac{C_{Ox} C_L K_{Ox} K_L}{(1 + K_{Ox} C_{Ox} + K_L C_L)^2} \qquad [13]$$

The transformation of experimental curves to the coordinates $(C_{Ox}/V)^{1/2} = f(C_{Ox})$ at C_L = constant and $(C_L/V)^{1/2} = f(C_L)$ at C_{Ox} = constant, with the subsequent joint solution of the equations obtained, has allowed calculation of effective rate constants and equilibrium constants of adsorption. From their temperature dependence, the effective energies of activation, enthalpy and entropy of adsorption for both reagents on a magnesium surface were calculated (Table 1).

The interaction of zinc and cadmium with compound **II** or **III** in DMFA is complete in approximately three days and results in formation of a yellow–brown solution. The equilibrium similar to [9] in the case of Zn and Cd is completely shifted to the left.[24,25] Therefore only compounds of the type CpM(CO)$_3$M′Cl (where M = Mo, W; M′ = Zn, Cd) are formed in the reaction of CpM(CO)$_3$Cl with Zn or Cd in DMFA. Yields were 96% (M = Mo M′ = Zn), 95% (M = Mo M′ = Cd), 85% (M = W M′ = Zn) and 80% (M = W M′ = Cd). We were unable to isolate these compounds in the individual state as in the case of magnesium. However, addition of the toluene solution of the 2,2′-bipyridine (2,2′-bipy) to the reaction mixture after the end of the zinc oxidation with compounds **II** and **III** gives complexes CpM(CO)$_3$ZnCl·2,2′-bipy as yellow precipitates of which the melting points and IR spectra correspond to literature data.[26] Also, the interaction of the solutions of CpM(CO)$_3$M′Cl obtained with HgCl$_2$ leads to the respective mercury derivatives in quantitative yields (Eqn [14]; M = Mo, W; M′ = Zn,Cd).

$$\mathrm{CpM(CO)_3M'Cl + HgCl_2 \longrightarrow CpM(CO)_3MHgCl + M'Cl_2} \qquad [14]$$

The dependence of the interaction rate in the CpMo(CO)$_3$Cl–Zn(Cd)–DMFA–benzene system upon concentration of both oxidant and ligand is shown in Fig. 5. In each case a curve with a maximum is obtained. The process of oxidation is well described by the Langmuir–Hinshelwood model with the adsorption of reagents on identical centres of a surface[21] (Eqns [10]–[13]). Calculated thermodynamic and kinetic parameters are given in Table 1.

CONCLUSIONS

Compounds containing bonds between Group 2 metals and Sn, Mo or W were obtained by reaction of the metals (Mg, Zn and Cd) with organometallic halides such as Ph$_3$SnCl, Cp(CO)$_3$MoCl or Cp(CO)$_3$WCl in coordinating solvents. The probable mechanisms of these processes have been proposed on the basis of kinetic measurements. Effective rate constants and the energy of activation, equilibrium constants, enthalpy and entropy of adsorption of organometallic halides and ligands on a metal surface have been determined.

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