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Inorganic Grignard Reagents. Preparation and Their Application for the Synthesis of Highly Active Metals, Intermetallics, and Alloys

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$NiCl_2$, $FeCl_2$, $PdCl_2$, $PtCl_2$, $RuCl_3$, $RhCl_3$, and $IrCl_3$ react with *excess amounts* of "active magnesium" (Mg*) or diethylmagnesium (Et_2Mg) in THF generating soluble bimetallic species with the generalized formula $[M^1(MgCl)_m{\cdot}(MgCl_2)_p]$, $m = 1-3, p = 0-1$ ("inorganic Grignard reagents"). In the Ru− and Ir−Mg−Cl systems, it appears that two different metal Grignard reagents, $[Ru(MgCl)_2{\cdot}0.5MgCl_2]$ (**8a**) or $[IrMgCl{\cdot}MgCl_2]$ (**10a**) and $[M'(MgCl)_3]$, M′ = Ru (**8b**) or Ir (**10b**), can be prepared through application of Et_2Mg and Mg* respectively. Hydrolysis or alcoholysis of THF solutions containing the inorganic Grignard reagents deliver finely divided, X-ray amorphous metals M^1 (usually) hydrogen gas and the corresponding Mg salts. The inorganic Grignard reagents in THF react with metal chlorides M_2Cl_n in the molar ratio of $n{:}m$ with the precipitation of nanoparticulate intermetallics or alloys $M^1{}_nM^2{}_m$ according to equation $n[M^1(MgCl)_m{\cdot}(MgCl_2)_p] + mM^2Cl_n \rightarrow M^1{}_nM^2{}_m\downarrow + (mn + p)MgCl_2$. The isolated X-ray amorphous intermetallics or alloys were characterized by ^{57}Fe Mössbauer spectroscopy (where M^2 = Fe), DSC and high resolution TEM. Thermal annealing of the X-ray amorphous bimetallic solids leads in most cases to micro- or nanocrystalline intermetallics or alloys which can then be identified through X-ray powder diffraction. Thus the preparation of highly active, nanocrystalline metals, intermetallics, and alloys is possible through solution chemistry via a *controlled* two-step process.

Introduction

The first example of a crystalline compound containing a covalent transition metal−magnesium bond, as determined by X-ray crystallography, was reported by Felkin et al. in 1974.[1] The compound, $[CpFe(diphos)MgBr(THF)_3$ (Cp = η^5-C_5H_5; diphos = 1,2-diphenylphosphinoethane), was then and still can be described as an inorganic analogue of Grignard's reagents. This complex as well as the related nickel compound reported in 1972 $[CpNi(PPh_3)MgBr]$[2] was prepared by reacting the appropriate bromide precursor directly with an excess amount of magnesium in THF. Inorganic Grignard compounds containing molybdenum, $[Cp_2Mo(H)MgBr(OEt_2)MgBr(C_6H_{11})]_2$ and $[CpMo(H)MgBr(THF)_2]$, were successfully prepared from Cp_2MoH_2 and $C_6H_{11}MgBr$ and structurally characterized by Green et al. in 1974.[3] By reacting $[CpCo(C_2H_4)_2]$ and C_3H_5MgBr in THF, Jonas et al.[4] were able to synthesize in 1986 a compound revealing a covalent cobalt−magnesium bond, $[CpCo(\eta^3$-$C_3H_5)MgBr(THF)_2]$.

More recently, we have developed a new preparative route toward known and unprecedented Mg intermetallics and/or their hydrides through the reduction of metal halides or organometallic complexes with stoichiometrically *excess* amounts[5] of elemental magnesium, magnesium hydrides, or organomagnesium compounds in THF.[6] During our experimental work, we observed that with certain transition-metal halides, besides the desired solid-state intermetallic reaction products, dark-colored THF-solutions are generated revealing significant concentrations of the corresponding transition metal, Mg and halogen.[6a,7] Of particular interest is the production of metal−magnesium−chlorine systems with palladium or platinum. $PdCl_2$ and $PtCl_2$ react with diethyl magnesium (Et_2Mg) in a 1:2 molar ratio with

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[⊗] Abstract published in *Advance ACS Abstracts,* May 1, 1995.

(1) (a) Felkin, H.; Knowles, P. J.; Meunier, B.; Mitschler, A.; Ricard, L.; Weiss, R. *J. Chem. Soc., Chem. Commun.* **1974**, 44. (b) Felkin, H.; Knowles, P. J.; Meunier, B. *J. Organomet. Chem.* **1978**, *146*, 151.

(2) (a) Felkin, H.; Knowles, P. J. *J. Organomet. Chem.* **1972**, *37*, C14. (b) Felkin, H.; Swierczewski, G. *Tetrahedron Lett.* **1972**, 1433; *Tetrahedron* **1975**, *31*, 2735.

(3) (a) Green, M. L. H.; Moser, G. A.; Packer, I.; Petit, F.; Forder, R. A.; Prout, K. *J. Chem. Soc., Chem. Commun.* **1974**, 839. (b) Prout, K.; Forder, R. A. *Acta Crystallogr.* **1975**, *B31*, 852. (c) Davies, S. G.; Green, M. L. H.; Prout, K.; Coda, A.; Tazzoli, V. *J. Chem. Soc., Chem. Commun.* **1977**, 135. (d) Davies, S. G. Green, M. L. H. *J. Chem. Soc. Dalton Trans.* **1978**, 1510.

(4) Jonas, K.; Koepe, G.; Krüger, C. *Angew. Chem.* **1986**, *98*, 901; *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 923.

(5) With respect to the amount of magnesium reagent required for the reduction of a metal halide to the metallic stage.

(6) (a) Bogdanović, B.; Wilczok, U. (Studiengesellschaft Kohle mbH) Europ. Pat. Appl. 0469463 (1992); priority date July 31, 1990. (b) Aleandri, L. E.; Bogdanović, B.; Wilczok, U.; Noreus, D.; Block, G. *Z. Phys. Chem. (Munich)* **1994**, *185*, 131.

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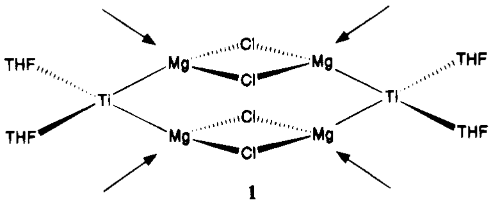
Table 1. Preparation of [$(NiMgCl)_2 \cdot MgCl_2$] (2) from $NiCl_2$ and Activated Mg Powder in THF

expt	$NiCl_2$:activator:Mg [molar ratio]	activator	$NiCl_2$ conversion [%][a]	yield of **2** (%)	mol H_2/mol Ni	composition of the solution
1	1:0.08:10	anthracene	96	20	1.54	$NiMg_6Cl_{9.5}$[b]
2	1:0.09:27	BrC_2H_4Br	92	48	1.42	$NiMg_{2.9}Cl_{4.6}$
3	1:–:3	Mg*	100	67	1.45	$NiMg_2Cl_{2.9}$
4	1:2:10	MgCl2, US	98	80–90	1.44–1.50	$NiMg_{3.8}C_{16.4}$[c]

[a] Based upon the amount of Cl^-(Br^-) titrimetrically analyzed in the THF solution. [b] 5.3 mol % of n-C_4H_9OH with respect to Mg. [c] 7 mol % of n-C_4H_9OH with respect to **2**.

elimination of ethyl as C_2H_4 and C_2H_6 in a 1:1 mixture to give, almost quantitatively, bimetallic systems with the composition [$M(MgCl)_2$] (M = Pd and Pt) in the form of dark-colored THF solutions (eqs 5 and 12)[6a].

These and other results detailed in section 1 suggested that these THF solutions contain soluble intermetallic species which may also be described as inorganic analogues of Grignard reagents, in other words, systems which have direct transition metal–magnesium bonds. Recently through X-ray absorption spectroscopy at the Ti K-edge of a related titanium magnesium system [$Ti(MgCl)_2(THF)_x]_q$ (**1**),[8] we were able to show



1

that titanium is indeed bonded to magnesium. **1** displays the shortest Ti–Mg interatomic distance yet observed, 2.72 Å, which is close to the sum of the Pauling single bond metallic radii, 2.69 Å, and thus corresponds to a covalent Ti–Mg bond. On the basis of the complete structural environment about Ti as determined through the EXAFS study and the known crystal structure of the Mo dimer, [$Cp_2Mo(H)MgBr(OEt_2)MgBr(C_6H_{11})]_2$,[3a] a similar dimeric structural model for **1** can be proposed.

In comparison to the first inorganic Grignard complexes[1–3] isolated 15–20 years ago, notwithstanding THF solvent molecules, these novel metal–magnesium systems are characterized by the absence of any stabilizing ligands such as Cp or phosphines. This is particularly advantageous in applying these systems as inorganic Grignard *reagents* in synthetic inorganic chemistry. Furthermore, the metal is found in a lowvalent state or in other words is negatively charged and thus represents a strong, chemically reactive nucleophile. In this paper we describe the preparation and characterization of a series of novel group 8–10 metal Grignard analogues and, more importantly, to demonstrate how these systems can be utilized as inorganic Grignard reagents for *wet-chemical synthesis*[9] of highly active, nanocrystalline materials including metals, intermetallics and alloys.[6a] [THF-soluble metal–magnesium systems can also be prepared by reacting transition-metal halides with an excess of catalytically prepared magnesium hydride (MgH_2*)[10] or especially a solubilized form of magnesium hydride (MgH_2').[11] In these cases the transition metal–magnesium–halide systems probably reveal hydrogen as an additional ligand.[6a] Their preparation and application in the synthesis of finely divided metals and intermetallics will be the subject of a forthcoming publication.]

Results and Discussion

1. Preparation and Characterization of Inorganic Grignard Reagents of Group 8–10 Transition Metals.

*1.1. [$(NiMgCl)_2 \cdot MgCl_2$] (**2**) and [$(FeMgCl)_2 \cdot MgCl_2$] (**5**).* The existence of a nickel Grignard analogue was initially noted during experiments aimed at the preparation of Ni-doped Mg powders to be later employed as hydrogen and heat stores.[12] During these experiments, THF suspensions of Mg powder were treated with small amounts of anhydrous $NiCl_2$ with activators such as anthracene. It was observed that simultaneous to the deposition of metallic nickel on the surface of Mg particles and the formation of THF-soluble $MgCl_2$ (eq 1, A = anthracene) variable amounts of nickel

$$NiCl_2 + Mg\ (\text{excess}) \xrightarrow[A]{THF} \text{“Ni-doped Mg”} + \text{Ni-containing sol} + MgCl_2 \quad (1)$$

remain dissolved in THF in the form of black-colored solutions. Hydrolysis of these black solutions consistently delivered roughly 1.5 mol of H_2/mol of nickel dissolved in the solution (see Table 1). Since colloidal, dispersed Ni^0 would give upon hydrolysis 1 mol of H_2/mol Ni, the observed results indicate that nickel is not present in solution as a colloidal metal. Furthermore the amount of hydrogen released during hydrolysis points to a formal oxidation state of −1 for nickel. Quantitative analyses of the solutions also showed that they contain significantly more magnesium than expected, i.e., more than the 1 mol of $MgCl_2$/mol of $NiCl_2$ reactant in eq 1 and that the Cl to Mg ratio in solution is less than 2, i.e., next to $MgCl_2$ magnesium is found in solution. These results together with those of the hydrolysis experiments indicates the existence of a new nickel–magnesium system with a general composition $Ni_2Mg \cdot nMgCl_2$. Analogous reactions using NiI_2, in which the THF-insoluble MgI_2 would be generated, did not lead to the formation of the nickel Grignard analogue. This indicates that the n number of $MgCl_2$ of the formula $Ni_2Mg \cdot nMgCl_2$ is an essential component of the Grignard system.

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(7) Soluble lowvalent bimetallic species generated from transition metal halides and Mg in THF have been previously investigated in particular by Sobota et al.: Sobota, P.; Jezowska-Trzebiatowska, B. *Coord. Chem. Rev.* **1978**, *26*, 71. Sobota, P.; Pluzinski, T.; Jezowska-Trzebiatowska, B.; Rummel, S. *J. Organomet. Chem.* **1980**, *185*, 69.

(8) Aleandri, L. E.; Bogdanović, B.; Gaidies, A.; Jones, D. J.; Liao, S.; Michalowicz, A.; Rozière, J.; Schott, A. *J. Organomet. Chem.* **1993**, *459*, 87.

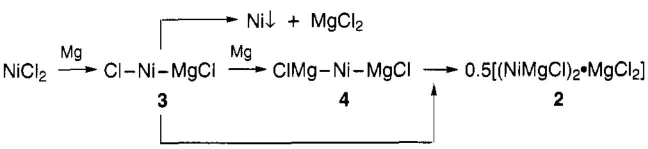
(9) Kornowski, A.; Giersig, M.; Vogel, R.; Chemseddine, A.; Weller, H. *Adv. Mater.* **1993**, *5*, 634.

(10) Bogdanović, B.; Bons, P.; Konstantinović, S.; Schwickardi, M.; Westeppe, U. *Chem. Ber.* **1993**, *126*, 1371 and references therein.

(11) Bogdanović, B.; Bons, P.; Schwickardi, M.; Seevogel, K. *Chem. Ber.* **1991**, *124*, 1041.

(12) Bogdanović, B.; Hartwig, T.; Spliethoff, B. *Int. J. Hydrogen Energy* **1993**, *18*, 575.

Scheme 1



The value of *n* was established through careful quantitative analyses of the reaction products of a series of experiments aimed at improving the yield of the new nickel Grignard analogue. As seen in Table 1, after correcting for the presence of $MgCl_2$ generated during the reduction of $NiCl_2$ to Ni metal and the activator in the form of magnesium anthracene, $MgCl_2$, etc., the value of *n* in $Ni_2Mg{\cdot}nMgCl_2$ ranges from 1.8 to 2.8 with an average value of 2.2; thus *n* is taken to be 2 and the final empirical formula of Grignard system is given as $[(NiMgCl)_2{\cdot}MgCl_2]$ (**2**).

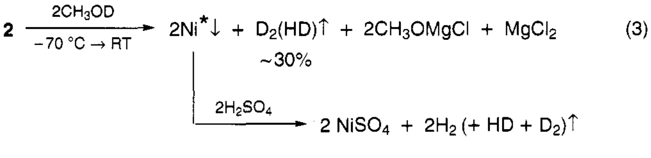
The initial modest yields (~20%) of **2** obtained in reactions employing anthracene as an activator could be increased to nearly 50% by replacing the activator with $MgBr_2$, generated in situ from CH_2BrCH_2Br and Mg (experiment 3). A substantially higher yield of **2** (67%, experiment 4) could be achieved by applying active magnesium (Mg*, generated by decomposition of magnesium anthracene[13]) instead of commercially available Mg powder. The best yield of **2**, 80–90%, was obtained by reducing $NiCl_2$ with Mg in the presence of a high concentration of $MgCl_2$ ($MgCl_2$:$NiCl_2$ = 2:1) in conjunction with ultrasonic treatment.

2 may represent an one to one association between a "mono-" (**3**) and a "di-Grignard" of $NiCl_2$ (**4**) as shown in Scheme 1. According to this scheme, the formation of **2** would then be in competition with the deposition of metallic nickel and dependent on the rate that the unstable intermediate **3** reacts with magnesium to give **4**. Thus the application of stoichiometrically excess amounts of magnesium or highly reactive forms of magnesium as well as activators for metallic magnesium (anthracene, ultrasonic treatment[14]) would drive this decisive step toward the formation of **4** (and thus **2**), as experimentally proven, and repress the disintegration of **3** into Ni and $MgCl_2$. Furthermore, this also explains the observation that by performing the reduction in the presence of $MgCl_2$ high yields of **2** are realized.

As mentioned above, upon hydrolysis with H_2SO_4, **2** delivers 1.5 mol of H_2/mol of Ni according to

$$\mathbf{2} \xrightarrow{3H_2SO_4} 2NiSO_4 + MgSO_4 + 2MgCl_2 + 3H_2\uparrow \quad (2)$$

Accordingly upon alcoholysis with CH_3OH (or CH_3OD), the evolution of 0.5 mol of H_2 (D_2)/mol of Ni would be expected (see eq 3). However, when an aliquot of **2** (experiment 1.4) is treated with CH_3OD (at −70 °C to room temperature, RT) only 0.15 mol of a D_2/HD gas mixture per mol of Ni is observed along with the precipitation of finely divided, ferromagnetic nickel (Ni*). The appearance of HD indicates that a rapid H/D exchange with the solvent takes place in the presence of Ni*. The observed low yield of (D_2 and HD) upon deutero alcoholysis, i.e., 30% of the expected amount, is surprising especially in comparison with the almost quantitative amount of H_2 liberated upon *hydrolysis* of **2** (~1.5 mol of H_2/mol of Ni, eq 2). This suggest that during alcoholysis that some unexpected and unidentified side reactions could be taking place or a proportion of the hydrogen (or here D_2) remains physioadsorbed on Ni*. To test whether the Ni deposit from the deutero alcoholyis contains D_2, the Ni* suspension was treated with aqueous H_2SO_4. Referring to the specific experiment described above, when the missing 0.35 mol of D_2/mol Ni is adsorbed on Ni* protolysis should deliver 1.35 mol of a H_2/D_2 gas mixture per mol Ni having a H_2 to D_2 ratio of 1:0.35. Upon the reaction with H_2SO_4, a gas mixture (1.1 mol/mol of Ni) consisting of H_2, HD and D_2 in a ratio of 1:0.08:0.03 was liberated. The low concentration of D_2 and HD in the gaseous products of the Ni* hydrolysis shows that only a small fraction of D_2 produced during deutero alcoholysis of **2** remains bound to Ni*:


$$\mathbf{2} \xrightarrow[-70\ ^\circ C \to RT]{2CH_3OD} 2Ni^*\downarrow + D_2(HD)\uparrow + 2CH_3OMgCl + MgCl_2 \quad (3)$$
$$\sim 30\%$$
$$Ni^* \xrightarrow{2H_2SO_4} 2\ NiSO_4 + 2H_2\,(+\ HD + D_2)\uparrow$$

Anhydrous $FeCl_2$ can be reacted with excess Mg powder (a $FeCl_2$:Mg molar ratio of 1:10) in THF with ultrasonic treatment, to give, besides a precipitate of finely divided metallic iron, a dark-brown THF solution containing roughly 13% of Fe initially used. The yield of the soluble Fe–Mg–Cl system can be increased to 26% by performing the same reaction in the presence of quinuclidine. Similar to the Ni–Mg–Cl system, such solutions deliver upon hydrolysis with H_2SO_4, 1.5 mol of H_2/mol of *dissolved* Fe. Thus in analogy to the Ni Grignard compound, it is assumed that the reaction between $FeCl_2$ and Mg in THF also yields a Grignard analogue with iron, $[(FeMgCl)_2{\cdot}MgCl_2]$ (**5**), and the hydrolysis reaction can be represented by eq 4. Since the yields of **5** are relatively low, we have not explored the application of this system as an inorganic Grignard *reagent*.

$$\underset{\mathbf{5}}{[(FeMgCl)_2{\cdot}MgCl_2]} \xrightarrow{3H_2SO_4} 2FeSO_4 + MgSO_4 + 2MgCl_2 + 3H_2\uparrow \quad (4)$$

*1.2. [Pd(MgCl)$_2$] (**6**) and [Pt(MgCl)$_2$] (**7**).* The low-temperature reaction between $PdCl_2$ and Et_2Mg in the molar ratio 1:2 in THF proceeds with the liberation of a nearly one-to-one gas mixture of C_2H_6 and C_2H_4 and the formation of a dark-brown solution as well as a small amount of bimetallic precipitate (corresponding to about 10% of the Pd used). After the cessation of gas evolution, the concentration of Et_2Mg in solution is found to be nearly zero; Pd, Mg, and Cl remain in soution with an approximate molar ratio of 1:2:2. The course of the reaction can thus be represented by eq 5, giving a palladium Grignard reagent with general composition $[Pd(MgCl)_2]$ (**6**). Most likely **6** represents an oligomeric structure, i.e., $[Pd(MgCl)_2]_x$; however, for simplicity the Pd Grignard along with the other metal Grignard systems described in this paper are designated by their most fundamental stoichiometry. To verify the composition of the bimetallic system, reactions with

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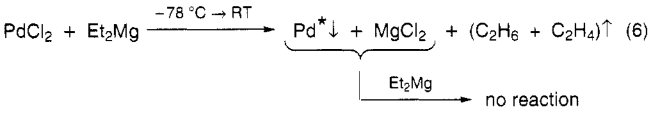
[13] Bartmann, E.; Bogdanović, B.; Janke, N.; Liao, S.; Schlichte, K.; Spliethoff, B.; Treber, J.; Westeppe, U.; Wilczok, U. *Chem. Ber.* **1990**, *123*, 1517.

[14] Bogdanović, B. *Acc. Chem. Res.* **1988**, *21*, 261.

varying $PdCl_2$ to Et_2Mg reactant molar ratios were carried out. An experiment utilizing a 1:1 molar ratio leads to a suspension of finely divided, metallic Pd (Pd*) (eq 6). Subsequent treatment of the reaction suspension with an additional mol of Et_2Mg does not give **6**. Interestingly, the reaction starting with a $PdCl_2$ to Et_2Mg molar ratio of 1:1.5 can be viewed as a combination of the "1:2" and "1:1" reactions. Almost exactly one-half of the $PdCl_2$ reacts with diethylmagnesium to give Pd* and the other half to generate a solution containing **6** (eq 7).

$$PdCl_2 + 2Et_2Mg \xrightarrow{-78\,°C \to RT} \underset{\mathbf{6}}{[Pd(MgCl)_2]} + 2(C_2H_6 + C_2H_4)\uparrow(+[Mg,Pd]\downarrow) \quad (5)$$

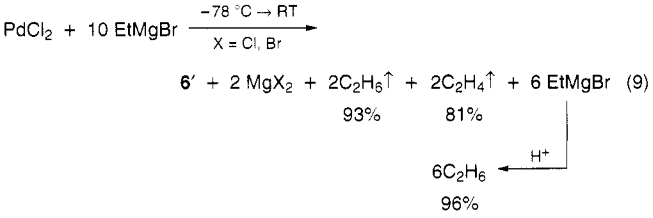


$$PdCl_2 + Et_2Mg \xrightarrow{-78\,°C \to RT} \underbrace{Pd^*\downarrow + MgCl_2}_{\xrightarrow{Et_2Mg}\ \text{no reaction}} + (C_2H_6 + C_2H_4)\uparrow \quad (6)$$

$$PdCl_2 + 1.5Et_2Mg \xrightarrow{-78\,°C \to RT} 0.5\mathbf{6} + 1.5(C_2H_6 + C_2H_4)\uparrow + 0.5Pd^*\downarrow + 0.5MgCl_2 \quad (7)$$

A mixed-halogen Pd–Mg system (**6′**), can be prepared by reacting $PdCl_2$ with EtMgBr in the molar ratio 1:4 (eq 8). However, when the reaction is performed in a 1:10 molar ratio, still only 4 mol of C_2H_6/C_2H_4 per mol of $PdCl_2$ are liberated. In other words, even with an excess of EtMgBr, only 4 mol of EtMgBr react per mol of $PdCl_2$, giving Pd–Mg–X (X = Cl, Br) compound having a 1:2:2 stoichiometry. The presence of 6 equiv of unreacted EtMgBr in the reaction product mixture was verified by hydrolysis (eq 9).

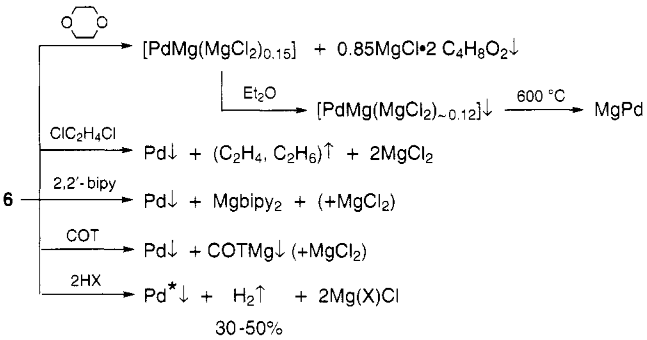
$$PdCl_2 + 4EtMgBr \xrightarrow{-78\,°C \to RT} \underset{\mathbf{6'}}{[Pd(MgX)_2]} + 2MgX_2 + 2(C_2H_6 + C_2H_4)\uparrow \quad (8)$$
$$X = Cl, Br$$



$$PdCl_2 + 10\,EtMgBr \xrightarrow[X\,=\,Cl,\,Br]{-78\,°C \to RT} \mathbf{6'} + 2\,MgX_2 + \underset{93\%}{2C_2H_6\uparrow} + \underset{81\%}{2C_2H_4\uparrow} + 6\,EtMgBr \quad (9)$$
$$6\,EtMgBr \xrightarrow{H^+} \underset{96\%}{6C_2H_6}$$

6 can be transformed into the intermetallic phase MgPd. By addition of 1,4-dioxane to a solution of **6** (Scheme 2), $MgCl_2$ precipitates out of the solution as the THF-insoluble $MgCl_2{\cdot}2C_4H_8O_2$ adduct, leaving a Pd–Mg system with composition $[PdMg(MgCl_2)_{0.15}]$. Through the addition of ether, a solid of the corresponding composition can be isolated. After annealing this material at 600 °C, it exhibits in its X-ray powder diagram diffuse reflections corresponding to alloy MgPd.[15] Since $MgCl_2$ can be extracted from the soluble Pd–Mg system without detrimental effects, **6** may exist in a "Schlenk-type" equilibrium in THF, i.e., an equilibrium composed of **6** on one side and $MgCl_2$-poorer Pd species, such as $[PdMg(MgCl_2)_{0.15}]$, with free $MgCl_2$ on the other side. **6** may exist as heterometallic Pd–Mg particles stabilized in THF through interactions with $MgCl_2$ and THF. The composition of **6** isolated as a dried (i.e., the solvent evaporated off), redissolvable solid corresponds to $Pd(MgCl)_2{\sim}3THF$; IR spectroscopy of the solid indicates that the residual THF is complexed.

Scheme 2



To further characterize **6**, a series of reactions were performed as summarized in Scheme 2. In THF **6** reacts with 1,2-dichloroethane, 2,2′-bipyridyl(bipy) and cyclooctatetraene (COT) to give as the inorganic products Pd metal precipitate and $MgCl_2$, or $Mg(bipy)_2$ or MgCOT (Scheme 2). This is remarkable in light of the fact that anhydrous $MgCl_2$, $Mg(bipy)_2$, and MgCOT are typically prepared by reacting *metallic* magnesium with 1,2-dichloroethane,[16] bipy,[17] or COT,[18] respectively. Thus, here **6** behaves as a source of "dissolved zerovalent magnesium".

Alcoholysis or hydrolysis results in the quantitative precipitation of a finely divided, X-ray amorphous palladium (Pd content 98%) accompanied by the formation of 0.3–0.5 mol of H_2/mol of Pd and the corresponding Mg^{2+} salts. Thus the protolysis of **6** can be used as a method to produce highly active palladium (Pd*) under extremely mild conditions in organic solvents. For example, one can envision the utility of such a technique in the preparation of heterogeneous catalyst systems based on palladium. The same is valid for the protolysis of other transition metal Grignard reagents described here. The evolution of hydrogen during alcoholysis is most likely the result of heterolytic cleavage of Pd–Mg bonds, assumed to be present in **6**, and the subsequent decomposition of a palladium hydride intermediate (eq 10). Surprisingly only 30–50% of the expected amount hydrogen gas is released upon hydrolysis (1 mol of H_2/mol of Pd is expected). This could be explained by the well-known propensity of metallic palladium to absorb molecular hydrogen. The low yield of hydrogen during protolysis of the Pd–Mg–Cl system could also be the consequence of the production of Mg-cleaved THF during the initial synthesis of **6**. It is well-known that magnesium can cleave THF to give a cyclic magnesium–

$$\underset{\mathbf{6}}{[ClMg{-}Pd{-}MgCl]} \xrightarrow[-2ROMgCl]{-2ROH} [PdH_2] \rightarrow PdH_{2-y}\downarrow + y/2H_2\uparrow \quad (10)$$

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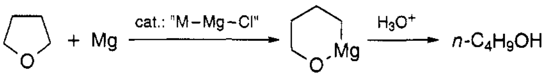
(15) Nayeb-Hashemi, A. A.; Clark, J. B. *Bull. Alloy Phase Diagrams* **1985**, *6*, 164.

(16) Reference 10, p 1375.

(17) Herzog, S.; Taube, R. *Z. Chem.* **1962**, *2*, 208, 225. Constable, E. C. *Adv. Inorg. Chem.* **1989**, *34*, 1.

(18) Lehmkuhl, H.; Kintopf, S.; Mehler, K. *J. Organomet. Chem.* **1972**, *46*, C1.

organo compound[19] as shown in eq 11 and this reaction



(11)

is catalyzed by metal–magnesium species.[8,20] Upon protolysis, the magnesiaoxacyclohexane yields n-butanol instead of hydrogen gas. Thus the protolysis of a mixture containing the transition metal Grignard analogue together with the magnesiaoxacycloheaxane would give less hydrogen gas as expected based on the concentration of the transition metal in solution. The extent of THF cleavage during the preparation of the inorganic Grignard reagents can be monitored by analyzing the protolysis product mixture for n-butanol (this of course was performed routinuely). For example, only 0.04 mol of n-butanol/mol of Pd was found in the protolysis products of **6**. Thus the extent of THF cleavage remained low, which is most likely due to the fact that **6** is prepared at RT or lower. THF cleavage becomes, as we will seen below in the case of the Pt Grignard system, more important at higher reaction temperatures, i.e., reflux.

Although the reactions between $PtCl_2$ with Et_2Mg in THF are similar to those between $PdCl_2$ and Et_2Mg, there are however some remarkable distinctions between the two systems. For example when $PtCl_2$ is allowed to react with Et_2Mg in the molar ratio of 1:2 under the same conditions as $PdCl_2$, the reaction does not go to completion at RT even after a very long reaction time (see experiment 3.1). The evolution of gas ceases after 85 h of stirring, although only 62% of the amount gas expected according to eq 12 has been generated. By heating the reaction mixture to reflux for 2 h, gas evolution resumes (an additional 15% of the expected amount of the $C_2H_6-C_2H_4$ mixture is isolated). The amount of hydrogen obtained upon hydrolysis of a sample of the final product solution, 0.3 mol of H_2/mol of Pt, is much lower than the expected 1 mol of H_2/mol of Pt. Alcoholysis of the same solution yields 0.21 mol of n-C_4H_9OH/mol of Pt, indicating that the THF cleavage reaction according to eq 11 took place to a considerable extent. Evaporating the solvent off the product solution gives a solid of the composition $PtMg_{2.1}Cl_{1.9}\cdot 2.1THF$, i.e., $[Pt(MgCl)_2]$ (**7**). The structural environment about Pt in **7** as well as in the intermediate product at RT (in THF solutions and as the dried solids) were investigated through EXAFS.[21] [The presence of a Mg coordination shell (Pt–Mg = 2.78 Å) as well as a Pt shell (Pt–Pt = 2.69 Å) in **7** was confirmed by the EXAFS analyses. The results suggest that the bimetallic cluster **7** may consist of a Pt core with Mg (or better $MgCl_y(THF)_x$ groups) on the outside.[21] The coordination sphere about Pt in **7** is therefore very different from that found for Ti in $[Ti(MgCl)_2(THF)_x]_q$ (**1**) which did not reveal any Ti neighbors.[8] (Note added upon revision.)]

Thus-modified synthesis routes toward the Pt Grignard system **7** were employed involving variation of the RT and of the reflux temperature reaction time:

$$PtCl_2 + 2Et_2Mg \xrightarrow[RT \to bp]{-78\text{ °C} \to RT} \underset{\mathbf{7}}{[Pt(MgCl)_2]} + 2(C_2H_6 + C_2H_4)\uparrow$$

$$\xrightarrow{2HCl} Pt^{*}\downarrow + \underset{30\text{-}50\%}{H_2\uparrow} + 2MgCl_2 \qquad (12)$$

After reaction at RT for 24 h, 50% conversion is reached, based on the amount of gas mixture released with respect to eq 12. Hydrolysis of an aliquot of the reaction mixture at this stage yields finely divided metallic platinum precipitate, 2 mol of C_2H_6/mol Pt (from the unreacted Et_2Mg), and no hydrogen gas. After reaction *at the reflux temperature* for 17 h, nearly quantitative conversion is observed (93% of the theoretical amount of the $C_2H_6-C_2H_4$ mixture and $0.48H_2$/Pt upon hydrolysis were evolved). The optimal result with respect to the preparation of **7** was achieved with RT reaction time of 24 h and reflux temperature reaction time of 4 h, whereby the extent of the THF cleavage reaction could be reduced to 0.07 mol of n-C_4H_9OH/mol Pt (experiment 3.2).

In contrast to the Pd–Mg–Cl system whereby Pd Grignard analogue **6** cannot be prepared via a two-step reaction as described by eq 6, the synthesis of the corresponding Pt Grignard reagent is possible. $PtCl_2$ reacts with *1* equiv of Et_2Mg in THF to give a suspension of finely divided platinum metal (Pt*) in a $MgCl_2$–THF solution and the evolution of a $C_2H_6-C_2H_4$ gas mixture (2 mol of $(C_2H_6$-$C_2H_4)$/mol of Pt; eq 13). Upon the addition of a second equivalent of Et_2Mg to the Pt*–$MgCl_2$–THF suspension, *the dissolution of Pt** occurs together with the evolution of the $C_2H_6-C_2H_4$ gas mixture conforming to the formation of **7** (eq 13).

$$PtCl_2 + Et_2Mg \xrightarrow{-78\text{ °C} \to RT} \underbrace{Pt^{*}\downarrow + MgCl_2} + (C_2H_6 + C_2H_4)\uparrow \qquad (13)$$

$$\xrightarrow{Et_2Mg} \mathbf{7} + (C_2H_6 + C_2H_4)\uparrow$$

The formation of the Pd and Pt Grignard reagents from MCl_2 (M = Pd, Pt) and Et_2Mg probably occurs over an organo–M–Mg intermediate, whereby ethyl groups are transferred from Mg to the transition metal. The organobimetallic intermediate would then subsequently decompose via β-hydrogen and reductive elimination to give the transition-metal Grignard, C_2H_4, and C_2H_6. Such a mechanism has been verified by the identification, through ^1H and ^{13}C NMR, of alkyl–Pd–Mg intermediates in a related reaction between bis(η^3-allyl)-palladium and Et_2Mg yielding a solid-state, X-ray amorphous material, $MgPdC_xH_y$.[22]

1.3. Inorganic Grignard Reagents of Ru, Rh, and Ir. The preparation of Grignard reagents of Ru, Rh, and Ir through the reaction of the appropriate chloride $M'Cl_3$ (M′ = Ru, Rh, Ir) with stoichiometrically excess amounts[5] of Et_2Mg or Mg*[13] in THF have also been investigated. The preliminary results are summarized in Table 4. In the Ru– and Ir–Mg–Cl systems, it appears that two

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[19] Freijee, F.; Schat, G.; Mierop, R.; Blomberg, C.; Bickelhaupt, F. *Heterocycles* **1977**, *7*, 237.

[20] Bartmann, E. *J. Organomet. Chem.* **1985**, *284*, 149.

[21] Aleandri, L. E.; Bogdanović, B.; Dürr, C.; Wilczok, U.; Jones, D. J.; Rozière, J. *Proc. XAFS VIII*, Berlin, 28th August to 2nd September 1994, *Physica B*, in press.

[22] (a) Jones, D. J.; Rozière, J.; Aleandri, L. E.; Bogdanović, B.; Huckett, S. C. *Chem. Mater.* **1992**, *4*, 620. (b) Bogdanović, B.; Huckett, S. C.; Wilczok, U.; Rufinska, A. *Angew. Chem.* **1988**, *100*, 1569; *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1513.

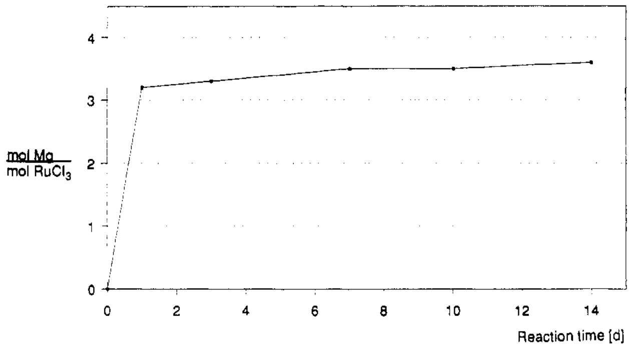

Figure 1. Reaction of $RuCl_3$ with "active magnesium" (molar ratio 1:5.7) in THF at room temperature.

different metal Grignard reagents, $[Ru(MgCl)_2{\cdot}0.5MgCl_2]$ (**8a**) or $[IrMgCl{\cdot}MgCl_2]$ (**10a**) and $[M'(MgCl)_3]$ (M′ = Ru (**8b**) or Ir (**10b**)), can be prepared through the application of Et_2Mg and Mg*, respectively.

The reaction between $RuCl_3$ and Et_2Mg in the molar ratio of 1:2.6 in THF at RT and subsequently under reflux results in the nearly quantitative elimination of the ethyl groups from Et_2Mg in the form of a C_2H_6-C_2H_4 (5:1) mixture (5 mol/mol of Ru) and the generation of a completely THF-soluble reaction product. A proportion of the product solution was evaporated to isolate a solid sample for elemental analysis, the solid revealed a composition corresponding to $Ru(MgCl)_2{\cdot}0.5\ Mg_{1.2}Cl_2{\cdot}1.9$ THF **8a** (experiment 4.1). Hydrolysis of an aliquot of the product solution (containing **8a**) led to the precipitation of ruthenium metal without any concomitant evolution of hydrogen (cf. hydrolysis of **8b**). The extent of the THF cleavage reaction in the course of the preparation of **8a** proved to be low (after protolysis only 0.05 mol of n-C_4H_9OH/mol of Ru were detected). By performing the experiment in d_8-THF it could be shown that the unexpected high proportion of C_2H_6 with respect to C_2H_4 (~5:1) observed in the synthesis **8a** results from hydrogen (or D) transfer from the solvent.

Also experiments performed in d_8-THF were used to establish the reaction stoichiometry. For example, an experiment employing a $RuCl_3$:Et_2Mg molar ratio of 1:2.5 in d_8-THF did not reveal any signals corresponding to the ethyl groups of Et_2Mg in the ^1H NMR spectrum of the final product solution (i.e., after gas evolution stopped). In contrast if the reaction was conducted under the same conditions but now with molar ratio of 1:2.9, a total of 5.3 mol of C_2H_6−C_2H_4 mixture/mol of $RuCl_3$ were liberated during the reaction and upon hydrolysis of an aliquot of the reaction solution 0.44 mol of C_2H_6/mol of Ru were detected, an evidence for the presence of still unreacted Et−Mg groups. These results suggest that under reaction conditions applied, $RuCl_3$ reacts with Et_2Mg in the 1:2.5 molar ratio as given in eq 14.

In contrast $RuCl_3$ appears to react with Mg* in a molar ratio 1 to 3. In experiments initiating with ratio of ~1:3 or higher (experiments 4.2 and 4.3), a spontaneous exothermic reaction ensues with the dissolution of ~3 mol of Mg*/mol of Ru. When an excess of Mg* (1:5.7; experiment 4.3) is utilized, the Mg/Ru ratio in the solution slowly increases above a ratio of 3:1 only after long reaction times (14 days) at RT (Figure 1) which is due to the formation of magnesia-oxa-cyclohexane from the cleavage of THF (eq 11). These results can be explained by assuming the generation of a Grignard reagent of Ru having a composition $[Ru(MgCl)_3]$ **8b** (eq 15). Hydrolysis of reaction solutions containing **8b** produce 0.9−1.2 mol of H_2/mol of Ru with concomittant precipitation of Ru metal.

$$RuCl_3 + 2.5Et_2Mg \rightarrow \underset{\textbf{8a}}{[Ru(MgCl)_2{\cdot}0.5MgCl_2]} + 5(C_2H_6,\ C_2H_4)\uparrow \quad (14)$$

$$RuCl_3 + 3Mg^* \rightarrow \underset{\textbf{8b}}{[Ru(MgCl)_3]} \xrightarrow{3HCl} \underset{60-80\%}{Ru^*\downarrow + 1.5H_2\uparrow} + 3MgCl_2 \quad (15)$$

The reaction between $RhCl_3$ and Et_2Mg in the molar ratio of 1:2 at RT proceeds with the complete elimination of the ethyl groups as a C_2H_6−C_2H_4 gas mixture (4 mol/mol of Rh) and the formation of a dark-colored THF solution (experiment 4.4). When the reaction is conducted with a $RhCl_3$:Et_2Mg molar ratio 1:3, still only 4 mol of a C_2H_6−C_2H_4 gas mixture per mol Rh are liberated. And upon hydrolysis of reaction solution 2 mol of C_2H_6/mol of $RhCl_3$ are generated, corresponding to the 1 equiv of unreacted Et_2Mg. Also through ^1H NMR spectroscopy it was confirmed that $RhCl_3$ reacts with Et_2Mg in a molar ratio 1:2, thus yielding a Rh Grignard reagent $[RhMgCl{\cdot}MgCl_2]$ (**9**, eq 16). The reaction of $RhCl_3$ with Mg* (molar ratio of 1:3) proceeds with the formation of a solid precipitate (~60% of Rh weighed in) and THF product solution containing Rh, Mg, and Cl.

$$RhCl_3 + 2Et_2Mg \rightarrow \underset{\textbf{9}}{[RhMgCl{\cdot}MgCl_2]} + 4(C_2H_6,\ C_2H_4)\uparrow \quad (16)$$

The reaction of $IrCl_3$ with Et_2Mg in the molar ratio of 1:3 (experiment 4.5) proceeds with the evolution of ~4 mol of a C_2H_6−C_2H_4 gas mixture/mol of Ir. Hence a proportion of the Et_2Mg used remains unreacted (approximately 1 equiv of Et_2Mg/equiv of $IrCl_3$); 2 mol of C_2H_6/mol of Ir are released during the hydrolysis of the reaction mixture (eq 17). Thus the formation of the corresponding Grignard reagent $[IrMgCl{\cdot}MgCl_2]$ (**10a**) is assumed. Reactions of $IrCl_3$ with Mg* (molar ratios of 1:3 or higher), on the other hand, proceed, like the analogous reactions with $RuCl_3$, with the dissolution of ~3 mol of Mg*/mol of $IrCl_3$ (experiment 4.6). Again when the experiment is performed with excess amounts of Mg* (e.g., 1:5 molar ratio of $IrCl_3$:Mg*), the Mg concentration in the THF solution slowly increases above a level corresponding to 3 mol of Mg/mol of Ir as a result of the THF cleavage reaction. Hydrolysis of THF solutions prepared from $IrCl_3$ with 3 or 5 equiv of Mg* result in the evolution of 0.8−1.3 mol of H_2/mol of Ir and the precipitation of metallic Ir. The composition of this second Grignard reagent of Ir, **10b**, is therefore given as $[Ir(MgCl)_3]$ (eq 18).

$$IrCl_3 + 3Et_2Mg \rightarrow \underset{\textbf{10a}}{[IrMgCl{\cdot}MgCl_2]} + 4(C_2H_6,\ C_2H_4)\uparrow + Et_2Mg \xrightarrow{H_3O^-} \underset{95\%}{2C_2H_6} \quad (17)$$

$$IrCl_3 + 3Mg^* \rightarrow \underset{\textbf{10b}}{[Ir(MgCl)_3]} \xrightarrow{3HCl} Ir^*\downarrow + \underset{50-85\%}{1.5H_2\uparrow} + 3MgCl_2 \quad (18)$$

2. Reactive Alloys, Intermetallics, and Metals Synthesized via Inorganic Grignard Reagents. The preparation of highly reactive, nanocrystalline, alloys, intermetallics, and metals through solution chemistry is possible in a controlled manner through the application of the novel THF-soluble inorganic Grignard reagents described here.[6a] The transition-metal Grignards, with the generalized formula $[M^1(MgCl)_m]$, react with metal chlorides M^2Cl_n in the molar ratio of n:m generating alloys and intermetallics of the composition $M^1_nM^2_m$ as shown in eq 19. In a similar fashion the reaction of $[M^1(MgCl)_m]$ with its corresponding chloride M^1Cl_n can be employed as a method for the preparation of finely divided metal precipitate M^1 (eq 20). However, as detailed below in section 2.1, the reaction of an inorganic Grignard reagent with a metal halide can also be more complex than that represented by eqs 19 and 20. During the process of alloy or metal precipitation, the coprecipitation of $MgCl_2$ (solubility in THF: ~0.5 mol/L at RT) and the inclusion of THF solvent molecules in the resulting solid (to a minor extent) are unavoidable. In several cases it has been demonstrated to be possible to diminish effectively the $MgCl_2$ and the C and H content of the solids by washing them with air-free water and hydrogenation respectively.

$$n[M^1(MgCl)_m] + mM^2Cl_n \xrightarrow[m,\,n\,=\,1,\,2,\,3]{THF} M^1_nM^2_m\downarrow + mnMgCl_2 \quad (19)$$

$$n[M^1(MgCl)_m] + mM^1Cl_n \xrightarrow{THF} (m+n)M^1\downarrow + mnMgCl_2 \quad (20)$$

*2.1. Titanium Alloys and Intermetallics Obtained from the Titanium Grignard Reagent **1** and Metal Chlorides.*[23] THF solutions of the titanium Grignard reagent **1**[8] react at RT with a range of metal chlorides M^2Cl_2 (M^2 = Fe, Cr, Sn, Mn, Co or Ni) in a 1:1 molar ratio to give black, air-sensitive, X-ray amorphous precipitates having the general composition $Ti_{1-n}M^2$, $0 \le n \le \sim 0.9$, as well as minor quantities of $MgCl_2$ and THF. The amount of M^2 found in the resulting solid is almost always nearly quantitative whereas the Ti content fluctuates. The Ti:M^2 atomic ratio in the solid products varies from 1:1 (Ti−Sn solid) to less than 0.1:1 (Ti−Ni solid). The "missing" titanium is still located in the solution in the THF-soluble complex $[TiMgCl_2(THF)_y]$ (**1a**)[8] (eq 21, Table 5).

$$\underset{\mathbf{1}}{[Ti(MgCl)_2(THF)_x]} + M^2Cl_2 \rightarrow \underset{0 \le n \le \sim 0.9}{Ti_{1-n}M^2\downarrow} + \underset{\mathbf{1a}}{n[TiMgCl_2(THF)_y]} + (2-n)MgCl_2 \quad (21)$$

For the Ti−Fe product, $Ti_{0.7}FeMg_{0.04}Cl_{0.14}(THF)_{0.11}$, from experiment 5.1 (eq 21; M^2 = Fe), it is possible to use ^{57}Fe Mössbauer (MB) spectroscopy to determine whether the X-ray amorphous solid is a bimetallic alloy or simply a mixture of fine Ti and Fe particles. The MB spectrum of the solid measured at 4.2 K is represented in Figure 2. The characteristic singlet of the intermetallic phase TiFe (δ = −0.046 mm/s) can be recognized in the center of the spectrum. By comparing the MB spectrum with those measured for the TiFe and $TiFe_2$ alloys and with other reference spectra,[24] the remaining features of the spectrum (a doublet at δ = −0.145 mm/s with ΔE_Q = 0.39 mm/s and a sextet at δ = −0.170 mm/s with 2ϵ = 0.0990 mm/s and B_{HF} = 9.71 T) can be definitively assigned to the $TiFe_2$ Laves phase. [We denote the central line shift (isomer shift) as δ. The measured central line shift at temperature T is given by $\delta(T) = \delta_{ch} + \delta_{SOD}(T)$. The chemical isomer shift δ_{ch} is proportional to the total s-electron density at the nucleus: $\delta_{ch} = \alpha\langle|\Psi(0)|^2\rangle$ with $\alpha < 0$ for ^{57}Fe. Thus δ reflects chemical properties and changes. The second-order Doppler shift $\delta_{SOD}(T)$ depends on the lattice vibration and is not important here. We denote the electric quadrupole line splitting of the doublet as ΔE_Q, proportional to the largest absolute value in the electric field gradient (EFG) tensor, $|V_{ZZ}$. The EFG tensor reflects local symmetry properties (for example, for cubic symmetry is zero). We denote the hyperfine magnetic field as B_{hf}, in magnetically ordered systems a measure of the local magnetic moment. In nonhomogeneous, B_{hf} is distributed. The electric quadrupole effect in the presence of dominating hyperfine magnetic field B_{hf} leads to a line shift 2ϵ, where ϵ depends on V_{ZZ} (and sign of V_{ZZ}, and the angle between the direction associated with V_{ZZ}, and B_{hf}.] According to the area of the two curves, the ratio of the two phases TiFe and $TiFe_2$ in the sample amounts to approximately 2:1 (63%:37%). No evidence for elemental iron was found in the MB spectrum of the bimetallic Ti−Fe product.

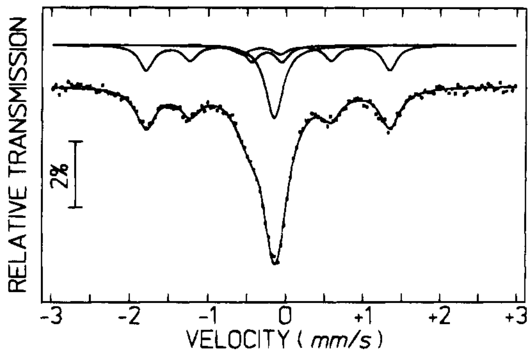

Figure 2. Mössbauer spectrum for the solid composed of TiFe and $TiFe_2$, measured at 4.2 K.

On the molecular level, the formation of the TiFe intermetallic phase in solution may proceed through the succesive elimination of 2 equiv of $MgCl_2$ from **1** and $FeCl_2$ with a concomitant formation of Ti−Fe bonds (eq 22). The Fe-richer alloy is produced through a one-to-one reaction between **1** and $FeCl_2$ whereby besides the

$$\underset{\mathbf{1}}{[ClMgTiMgCl]} + ClFeCl \longrightarrow [ClMgTi{-}FeCl] + MgCl_2 \longrightarrow \cdots \longrightarrow TiFe\downarrow + 2MgCl_2 \quad (22)$$

$$\mathbf{1} + FeCl_2 \longrightarrow 0.5TiFe_2\downarrow + 0.5\underset{\mathbf{1a}}{[TiMgCl_2(THF)_y]} + 1.5MgCl_2 \quad (23)$$

$$21 + 2FeCl_2 \longrightarrow \underbrace{(TiFe + 0.5TiFe_2)}_{\text{"}Ti_{0.75}Fe\text{"}}\downarrow + 0.51\mathbf{a} + 3.5MgCl_2 \quad (24)$$

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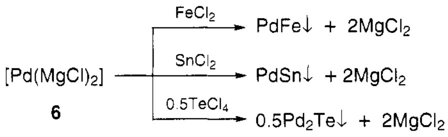
(23) (a) Aleandri, L. E.; Bogdanović, B.; Dürr, C.; Gaidies, A.; Jones, D. J.; Lagarden, M.; Liao, S.; Rozière, J.; Schott, A.; Wilczok, U. *24. GDCh-Hauptversammlung*, Hamburg, 5.-11.9, 1993; p 173. (b) Gaidies, A. Dissertation, Bochum University, 1992.

(24) Gibb, T. C. *Principles of Mössbauer Spectroscopy*; Chapman and Hall: London, 1976.

Scheme 3



intermetallic $TiFe_2$ and $MgCl_2$, the Mg-poor Ti Grignard **1a** is formed (see eq 23). (It has been experimentally demonstrated that **1a** can be generated through a comparable redox reaction between **1** and $TiCl_3$[8]). The results of the MB study indicate that both reaction pathways take place to give TiFe and $TiFe_2$. Thus the reaction between **1** and $FeCl_2$ can be described as the sum of eqs 22 and 23 to give eq 24. When neither of the reaction pathways (eq 22 or 23) is favored over the other, i.e., each proceeds with equal probability, the product ratio of TiFe to $TiFe_2$ should be near 2:1, as shown in eq 24 and experimentally found via MB spectroscopy. Analogous reactions can also be envisaged for the formation of other $Ti_{1-n}M^2$ solids.

*2.2. Bimetallic Ni, Pd, and Pt Alloys Prepared via the Reaction between **2**, **6**, **7**, and Metal Chlorides.* The reduction of either $FeCl_2$ or $CuCl_2$ with the Ni Grignard reagent **2** (1:1 molar ratio at RT in THF) yields bimetallic precipitates showing the following compositions, $\sim Ni_2Fe(MgCl_2)_{0.5}(THF)_{0.3}$ and $\sim Ni_2Cu_{1.3}(MgCl_2)_{0.3}(THF)_{0.1}$ (eq 19, Table 6). In both cases, the raw product is X-ray amorphous. After heating the Ni–Cu solid to 200 °C under vacuum, the X-ray powder diagram exhibits broad reflections which could result from either NiCu, Ni or Cu metal. Following annealing at 600 °C under Ar, the X-ray powder diagram showed sharp reflections which could be assigned to a Ni–Cu alloy. The same effect upon annealing was observed for the Ni–Fe product.

The reaction of the Pd Grignard analogue **6** with $PdCl_2$ gives finely divided palladium according to eq 20. A proportion of the newly formed Pd remains in solution as a colloidal metal. Bimetallic Pd–M^2 products can be prepared by reacting **6** with $FeCl_2$, $SnCl_2$, and $TeCl_4$ in THF at RT. The resulting X-ray amorphous solid products contain both metals in the molar ratio depicted in Scheme 3 as well as minor quantities of Mg, Cl, C, and H (Table 7). It proved possible to reduce the C and H content by hydrogenation under pressure (for example see experiment 7.1). Unlike the bimetallic Ni systems, subsequent annealing at 600 °C did not lead to polycrystalline materials which would give X-ray powder diffraction patterns. Thus to investigate these systems, DSC as well as MB spectroscopy were employed. The MB spectrum (measured at 4.2 K; Figure 3) of the Pd–Fe solid product taken directly from the reaction solution exhibits a sextet with an average $\delta = 0.395$ mm/s. The experimental average B_{HF} value (comprising an isomeric shift of 0.294 mm/s) amounts to 32.3 T, whereas the literature B_{HF} value for the bcc Fe at 4.2 K is 33.7 T.[24] In addition, there is a very large distribution of hyperfine fields (standard deviation of about 9 T) which shows that we are dealing with an Fe alloy, not elemental Fe mixed with Pd metal. The DSC diagram of the Pd_2Te solid, raw product, is characterized by the absence of a thermal effect in the region of the melting point of Te (449.6 °C) and the presence of endothermal signals at 465, 477 (shoulder), and 594 °C. These signals can be tentatively assigned to a phase transformation and the subequent incongruent melting of the intermetallic phase Pd_2Te at 460 and 590 °C,[25] respectively (cf. also ref 26).

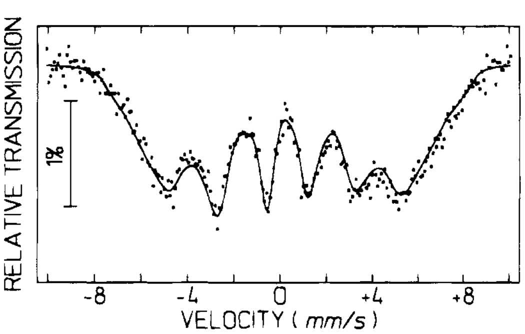


Figure 3. Mössbauer spectrum for the amorphous solid PdFe, measured at 4.2 K.

Reactions of the Pt Grignard reagent **7** with $FeCl_2$, $CuCl_2$ or $SnCl_2$ in a 1:1 molar ratio and with $RhCl_3$ or $BiCl_3$ in a 3:2 molar ratio in THF give bimetallic X-ray amorphous precipitates in the corresponding ratios, see eqs 25 and 26 and Table 8.

$$\underset{\mathbf{7}}{[Pt(MgCl)_2]} + M^2Cl_2 \xrightarrow[M^2 = Fe, Cu, Sn]{} PtM^2\downarrow + 2MgCl_2 \qquad (25)$$

$$3\mathbf{7} + 2M^2Cl_3 \xrightarrow[M^2 = Rh, Bi]{} Pt_3M^2_2\downarrow + 6MgCl_2 \qquad (26)$$

The bimetallic products prepared according to eq 25 can be easily crystallized via thermal treatment at 600 or 700 °C under argon. The X-ray powder patterns of the FePt precipitate and a sample thermally treated are shown in Figure 4. After annealing a crystalline FePt intermetallic is isolated which according to its powder pattern has a tetragonal unit cell and an ordered HgMn structure type. To verify alloy formation during the reaction in solution, the raw product and the annealled material were investigated by MB spectroscopy. Their MB spectra are given in Figure 5 in comparison to that for elemental bcc-Fe. The B_{HF} value observed for the crystalline FePt compound is 30.5 T, and for the FePt raw product the average B_{HF} value is 34.7 T. These results indicate that in both samples iron is present in metallic state but not in the form of elemental bcc-Fe. The sharp lines observed for the crystalline sample reflect the strong long-range ordering of iron in the binary intermetallic. In contrast the broad lines in the spectrum of the nonannealled raw precipitate indicate that the bimetallic alloy product is either amorphous or nanocrystalline with a highly disordered iron substructure. TEM reveals the presence of nanocrystalline particles in the range 2–3.5 nm and EDX analyses confirmed that both Fe and Pt are present in every particle measured.

The X-ray powder diagram of thermally treated PtSn reveals no other diffraction lines except those of PtSn.[27] The X-ray diffraction pattern of PtCu (see experimental

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(25) Massalski, T. B., Ed. *Binary Alloy Phase Diagrams*; American Society for Metals: Ohio, 1986; Vol. 2, p 1876.

(26) (a) Chattopadhyay, G.; Bhatt, Y. J.; Khera, S. K. *J. Less-Common Met.* **1986**, *123*, 251. (b) Ipser, H.; Schuster, W. *Ibid.* **1986**, *125*, 183.

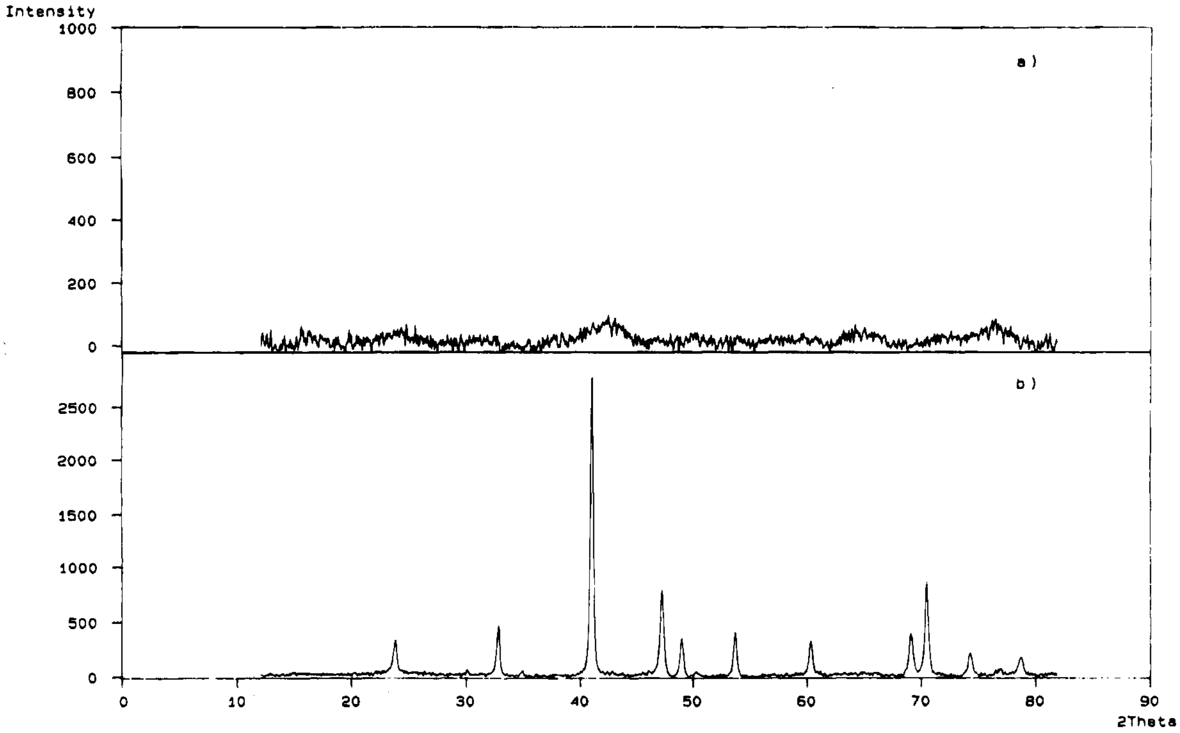

Figure 4. XRD spectrum for amorphous (a) and crystalline PtFe (b).

part) could not yet be assigned to a PtCu alloy.[28] The DSC diagram of Pt_3Bi_2, raw product, shows no thermal effect in the region of the melting point of Bi (271.4 °C).

*2.3. Bimetallic Ru, Rh, and Ir Alloys Prepared from **8a**, **8b**, **9**, and **10b** and $PtCl_2$ or $SnCl_2$.* The Ru Grignard reagents **8a** and **8b** react at RT with $PtCl_2$ in either 1:1 or 2:3 molar ratio in THF to yield black precipitates. The X-ray amorphous solids, after washing with air-free water and acetone, reveal the compositions $RuPt(MgCl_2)_{0.07}C_{4.4}H_{5.4}$ and $Ru_2Pt_{2.8}(MgCl_2)_{0.06}C_{2.6}H_{3.0}$, respectively (Eqs. 27, 28; Table 9). According to high-resolution TEM photographs (Figure 6a,c), both (pyrophoric!) solids are nanocrystalline and consist of globular particles of 2.5–4.5 nm in diameter. After annealing, the resulting microcrystalline alloys were identified via X-ray powder diffraction as cubic Ru–Pt solid solutions,[29] free of metallic Pt or Ru. The TEM photographs of the X-ray crystalline alloys (represented in Figures 6b,d) reveal the presence of a homogeneous structure.

$$\underset{\textbf{8a}}{[Ru(MgCl)_2{\bullet}0.5\,MgC_2]} + PtCl_2 \xrightarrow{THF} RuPt{\bullet}0.5\,MgCl_2{\bullet}1.4THF\downarrow + 2.0MgCl_2 \qquad (27)$$

$$\xrightarrow{H_2O} RuPt\downarrow + 0.5MgCl_2$$

$$\underset{\textbf{8b}}{2[Ru(MgCl)_3]} + 3PtCl_2 \xrightarrow{THF} Ru_2Pt_{2.7}{\bullet}0.5\,MgCl_2{\bullet}0.5THF\downarrow + 5.5MgCl_2 \qquad (28)$$

$$\xrightarrow{H_2O} Ru_2Pt_{2.8}\downarrow + 0.5MgCl_2$$

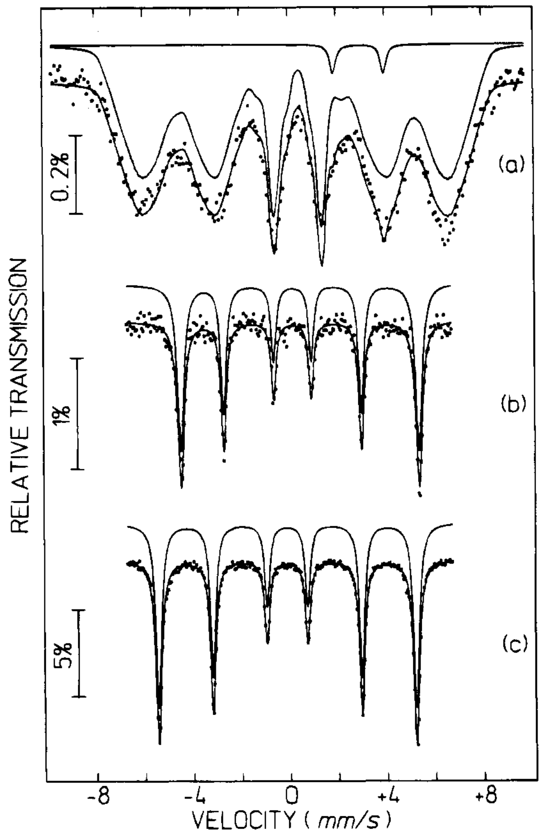

Figure 5. Mössbauer spectra for amorphous (a) and crystalline PtFe (b) (at 4.2 K) in comparison to that for elemental bcc-Fe (c, RT).

The X-ray amorphous solids $Rh_2Sn_{0.8}(MgCl_2)_{0.5}(THF)_{1.5}$ and $Rh_2Pt(MgCl_2)_{0.3}(THF)_{1.5}$ (Table 9) were prepared through the reaction between the Rh Grignard reagent

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(27) (a) Landolt-Börnstein, Neue Serie, Gruppe III, Bd. 6, Springer-Verlag: Berlin, 1971; p 843. (b) Srinivasan, R.; De Angelis, R. J.; Davis, B. H. *J. Catal.* **1987**, *106*, 449. (c) Li, Y.-X.; Klabunde, K. J. *Langmuir* **1987**, *3*, 558. (c) Cabri, L. J.; Harris, D. C. *Mineral. Mag.* **1972**, *38*, 794.

(28) (a) Reference 27a, p 513. (b) Linde, J. O. *Ann. Phys.* **1937**, *30*, 151.

(29) Reference 25, p 1906. (b) Giroir-Fendler, A.; Richard, D.; Gallezot, P. *Faraday Discuss.* **1991**, *92*, 69. (c) Del Angel, G.; Bertin, V.; Bosch, P.; Gomez, R.; Gonzalez, R. D. *New J. Chem.* **1991**, *15*, 643.

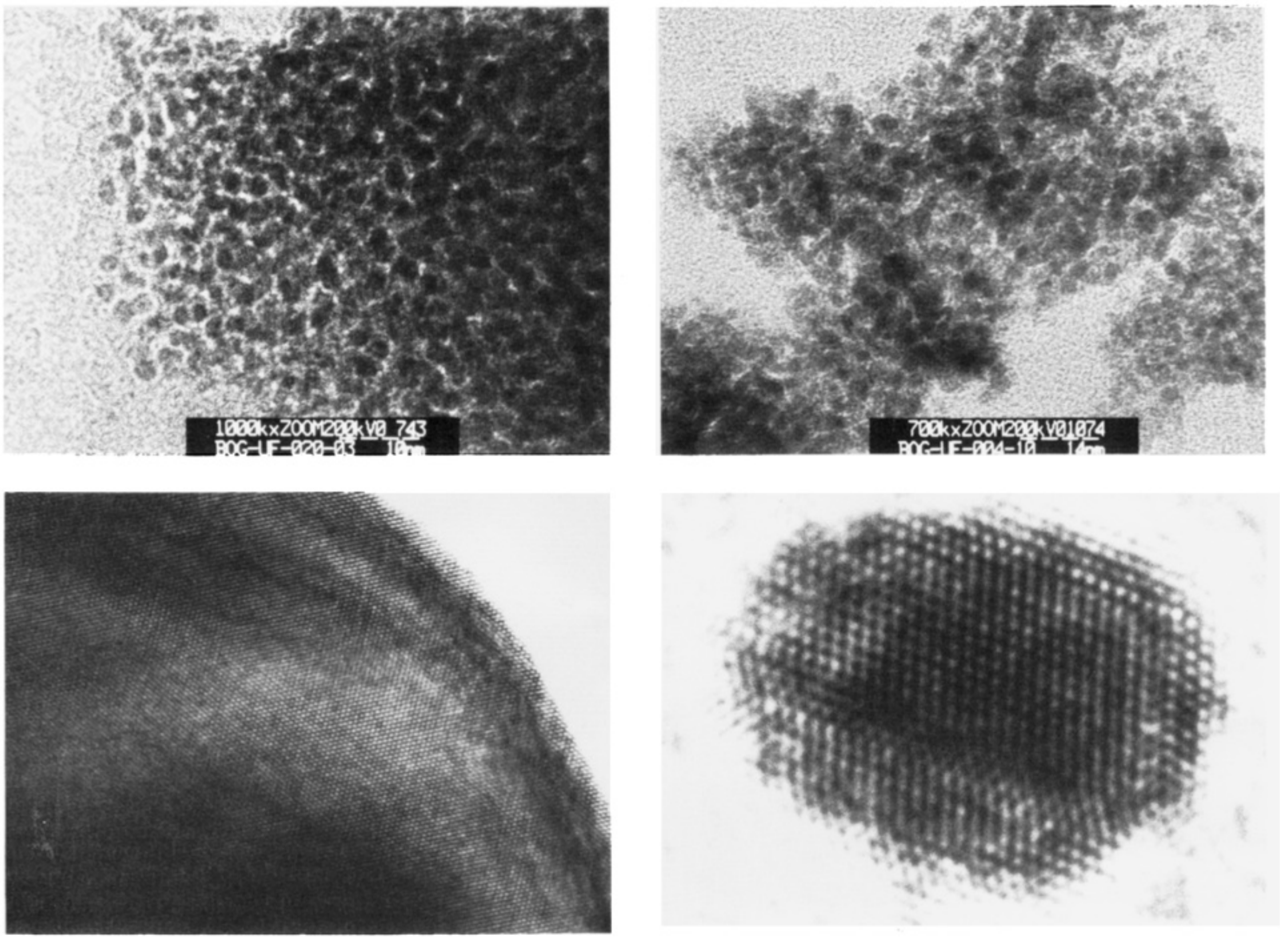
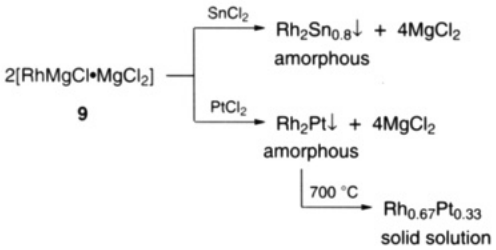


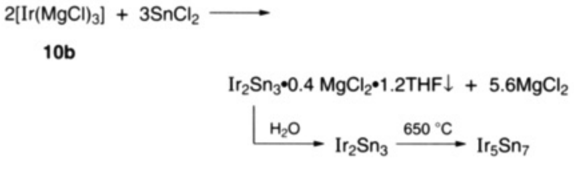
Figure 6. High-resolution TEM images of nano- (a, top left) and microcrystalline RuPt (b, bottom left) and of nano- (c, top right) and microcrystalline $Ru_2Pt_{2.8}$ (d, bottom right).

Scheme 4



9 and $SnCl_2$ and $PtCl_2$ (Scheme 4), respectively. By annealing the amorphous Rh−Pt solid at 700 °C a crystalline material could be obtained which based on its X-ray powder pattern contains the cubic alloy $Rh_{0.67}Pt_{0.33}$.[30] Pt−Rh alloys of the composition $Rh_{0.57}Pt_{0.43}$ and $Pt_{0.68}Rh_{0.32}$ are known in native form as minerals platinian−rhodium and rhodian−platinum, respectively.[30] Noteworthy is the observation that two Rh−Pt alloys with differing stoichiometry $Rh_{0.4}Pt_{0.6}$ and $Rh_{0.67}Pt_{0.33}$ could be prepared through the application of two different inorganic Grignard reagents, **7** and **9**.

The reaction of the Ir Grignard reagent **10b** with $SnCl_2$ in a 2:3 molar ratio in THF (eq 29) proceeds with



$$\underset{\mathbf{10b}}{2[Ir(MgCl)_3]} + 3SnCl_2 \longrightarrow Ir_2Sn_3{\bullet}0.4\,MgCl_2{\bullet}1.2THF\downarrow + 5.6MgCl_2 \xrightarrow{H_2O} Ir_2Sn_3 \xrightarrow{650\ ^\circ C} Ir_5Sn_7$$

the precipitation of an X-ray amorphous solid $Ir_2Sn_3(MgCl_2)_{0.4}(THF)_{1.2}$ (Table 9). After washing with air-free water and acetone, the Mg content of the resulting X-ray amorphous, *pyrophoric* Ir_2Sn_3 dropped to 0.02%. The TEM photograph of Ir_2Sn_3 (Figure 7a) reveals *amorphous* particles of <2−2.5 nm diameter. Through annealing, the amorphous Ir_2Sn_3 could be transformed into crystalline Ir_5Sn_7 which was identified via X-ray powder analysis (Figure 8).[31] The TEM photograph of the thus prepared Ir_5Sn_7 (Figure 7b) reveals nanocrystalline particles (~4 nm).

Conclusion and Outlook

The previously known methods for the wet-chemical syntheses[9] of nanoparticular intermetallics and alloys involve mainly simultaneous reduction of two (or more) metal salts using various reducing agents in suitable solvents[32] or the metal vapor method.[33]

According to the present method, nanoparticular bimetallic systems can be prepared in a controlled, two-

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(30) (a) Reference 25, p 1905. (b) Cabri, L. J.; Laflamme, J. H. G. *Can. Mineral.* **1974**, *12*, 399.

(31) *Pearson's Handbook of Crystallographic Data for Intermetallic Phases*, **1991**, *4*, 4130. (b) JCPDS File 32−462. (c) Mayer, H. W.; Ellner, M.; Schubert, K. J. *Less-Common Met.* **1978**, *61*, P1.

(32) (a) Van Wonterghem, J.; Mørup, S.; Koch, C. J. W.; Charles, S. W.; Wells, S. *Nature* **1986**, *322*, 622. (b) Bönnemann, H.; Brijoux, W.; Brinkmann, R.; Fretzen, R.; Joussen. Th.; Köppler, R.; Korall, B.; Neiteler, P.; Richter, J. *J. Mol. Catal.* **1994**, *86*, 129, and references therein. (c) Fürstner, A. *Angew. Chem.* **1993**, *105*, 171; *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 164. Guczi, L.; Sarkany, A. *Catalysis*, The Royal Society of Chemistry: London, **1994**; Vol. 11 p 318.

(33) Klabunde, K. J.; Li, Y.-X.; Tan, B.-J., *Chem. Mater.* **1991**, *3*, 30. Klabunde, K. J.; Zhang, D.; Glavee, G. N.; Sorensen, C. M. *Chem. Mater.* **1994**, *6*, 784.

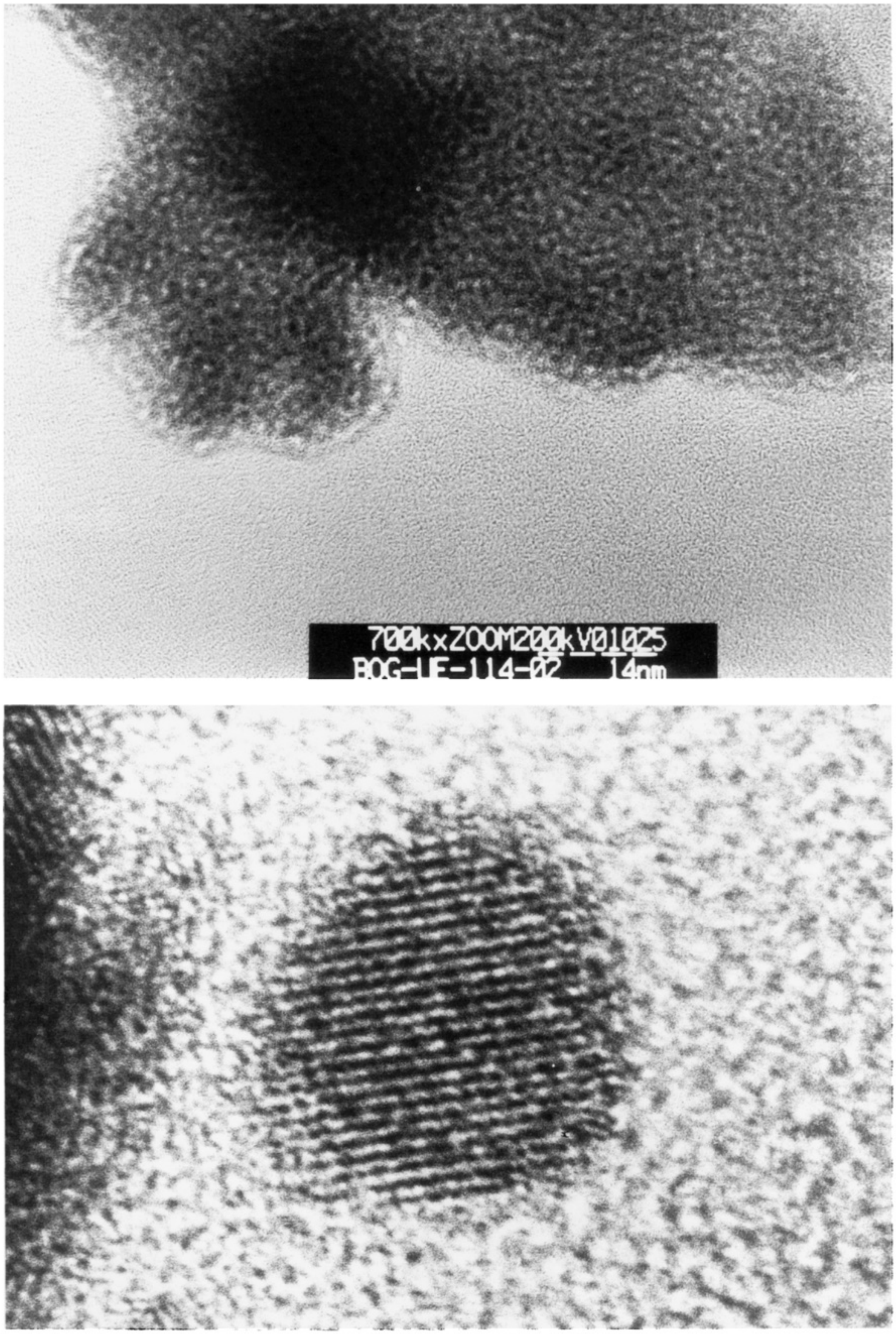

Figure 7. High-resolution TEM images for amorphous Ir_2Sn_3 and crystalline Ir_5Sn_7 (b).

step process. In the first step (section 1), the respective transition metal chloride is converted into a definite inorganic Grignard reagent. In the second step (eq 19), the THF solution of the latter is reacted with the M^2-Cl_n component, resulting in the precipitation of an X-ray amorphous, nanocrystalline (TEM!) alloy or intermetallic. This low-temperature, kinetically controlled process is particularly suitable for the synthesis of

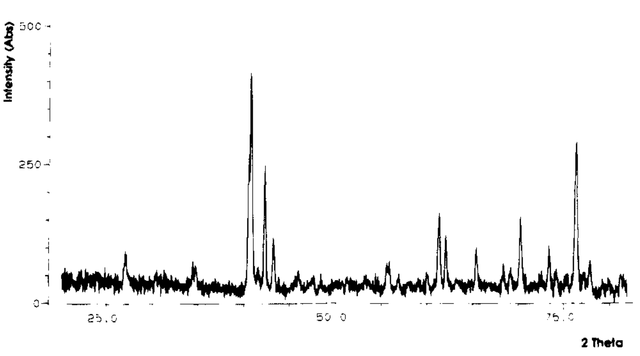

Figure 8. XRD spectrum for crystalline Ir_5Sn_7.

metastable systems. By varying the applied inorganic Grignard reagent, the M^2Cl_n component and the synthesis conditions, bimetallic systems with differing metal ratios ($Rh_{0.4}Pt_{0.6}$ and $Rh_{0.67}Pt_{0.33}$ or RuPt and $Ru_2Pt_{\sim 3}$) and thus with different physicochemical properties can be purposely prepared. Physical characterization of these bimetallic systems through Mössbauer spectra and DSC analyses has shown up to now that the alloy products obtained directly from solution do not contain monometallic proportions. Removal of residual magnesium salts and solvent from the solid, raw products can be achieved by washing with air-free water and hydrogenation, respectively. Thermal annealing of the purified solid products leads in most cases to crystalline alloys or intermetallics which could subsequently be identified through X-ray powder diffraction.

For the preparation of *homo*metallic nanoparticles, inorganic Grignard reagents offer following possibilities: (i) protolysis or hydrolysis of their THF solutions (eqs 3, 10, 12, 15, 18); if conducted in the presence of suitable inorganic supports, these reactions can be used for the preparation of heterogeneous catalysts. (ii) reaction of solution of a metal Grignard reagent with a halide of the same metal (eq 20) (or reduction of metal halides with Et_2Mg, magnesium anthracene[21] or Mg*, e.g., eq 13).

Besides their application toward the peparation of highly dispersed mono- or bimetallic particles, inorganic Grignard reagents are highly promising for the synthesis of other inorganic materials. Of particular interest is the question whether metal–element structures can be built up from inorganic Grignard reagents and various electrophiles other than metal halides.

Experimental Section

Instruments. Mössbauer spectroscopy: Wissel mechanical drive with home-built multichannel and Reuter-Stokes proportional counter. ^{57}Co Mössbauer isotope in Rh foil from DuPont. Computer analysis using Normos-90 program package (R.A. Brand). X-ray diffraction patterns: STOE, STAD/2/PL powder diffractometer, Cu $K\alpha_1$ radiation; the samples were filled into glass capillaries. HREM images: field emission TEM, Hitachi HF 2000, 200 keV. DSC: DuPont 9900. MS: CH7, Finnigan MAT.

Analyses. Elemental analyses and AAS measurements: Dornis and Kolbe, Mülheim an der Ruhr.

Materials. $RuCl_3$, $PdCl_2$: Heraeus Co. $RhCl_3$, $IrCl_3$, $PtCl_2$: Degussa. Mg powder (270 mesh, PK-31): Eckart-Werke, Fürth, Germany. Et_2Mg was prepared from an EtMgBr solution in Et_2O through addition of 1,4-dioxane,[34] removal of the solvent in vacuum and drying the resulting solid product. The content of Et_2Mg in the solid product was determined by hydrolysis and MS analysis of the evolved EtH. THF was boiled for several hours over magnesium anthracene[35] and subsequently distilled under argon. All reactions with air-sensitive materials were performed under a dry argon atmosphere. Vacuum = 0.1–0.2 mbar; high vacuum = 10^{-3} mbar.

***2** from $NiCl_2$ and anthracene-activated Mg powder (Table 1, experiment 1):* To a suspension of 20.17 g (0.83 mol) of Mg powder in 1.0 l of THF, 1.23 g (6.9 mmol) of anthracene and 0.1 mL (1.3 mmol) of EtBr were added. The mixture was then stirred at RT for 24 h. (The formation of magnesium anthracene·3THF,[34] an orange precipitate, is usually complete after 2–3 h of stirring.) Anhydrous $NiCl_2$ (10.38 g, 80.0 mmol) (the residual H_2O found in the commercial available $NiCl_2$ was removed by according to ref 36) was then added to the reaction suspension which was stirred further for 22 h at RT. The resulting black suspension was filtered (D4 glas frit) and the solid residue washed with THF. Five mL aliquots of the filtrate product (total volume 1020 mL) were hydrolyzed with 5 N H_2SO_4 and the resulting aqueous solutions were titrimetrically analyzed for Mg^{2+}, Ni^{2+}, and Cl^-/Br^-; 97.7 mmol of Mg^{2+}, 16.4 mmol of Ni^{2+} (20.5%), and 156.1 mmol (96%) of Cl^-/Br^- were found. A 20.0 mL aliquot of the filtrate after centrifugation (10 000 rpm, 1 h) delivered during hydrolysis with 5 N H_2SO_4 (ice-cooling) 13.1 mL of gas consisting of 92% H_2 (MS analysis) corresponding to 1.54 mol of H_2/mol of Ni. A 5.0 mL sample of the filtrate was protolyzed by CH_3OH and analyzed by gas chromatography using $n\text{-}C_8H_{18}$ and $n\text{-}C_{16}H_{34}$ as internal standards: 2.2 mmol of 9,10-dihydroanthracene, 1.0 mmol of anthracene, and 5.2 mmol of $n\text{-}C_4H_9OH$ (5.3% with respect to Mg) were detected. Solutions of **2** can be kept under argon at RT without decomposition.

***2** from $NiCl_2$ and CH_2BrCH_2Br-activated Mg powder (Table 1, experiment 2):* To a suspension of 20.0 g (0.82 mol) of Mg powder in 100 mL of THF, 0.2 mL (2.3 mmol) of CH_2BrCH_2Br were added; the mixture was stirred at RT for 3.5 h. Subsequently 3.57 g (15.2 mmol) of $NiCl_2$·1.5 THF[37] was added and the suspension was stirred for an additional 46 h. Workup and analyses in this and in following experiments concerning the preparation of **2** and **5** were conducted analogously as for experiment 1.1; results are given in Table 1 and discussed in section 1.1.

***2** from $NiCl_2$ and active magnesium (Mg*) (Table 1, experiment 3):* 1.59 g of anhydrous $NiCl_2$ (dried over $SOCl_2$; 96% $NiCl_2$; 11.8 mmol) was transfered to a stirred, cooled (0 °C) suspension of 0.90 g (95.2% Mg, 3.52 mmol) of Mg* (prepared through the decomposition of magnesium anthracene in warm toluene[13]) in 70 mL of THF. The mixture was slowly warmed to RT and stirred for 12 h.

***2** from $NiCl_2$ and Mg powder in the presence of $MgCl_2$ (Table 1, experiment 4):* 40.0 mL of a 0.50 M solution of $MgCl_2$ in THF[16] (20.0 mmol) were diluted with 20.0 mL of THF; after the addition of 2.44 g (0.1 mol) of Mg powder; the suspension was subjected to ultrasound treatment for 2 h and then stirred for 16 h at RT. $NiCl_2$·1.5 THF[37] (2.20 g, 10.4 mmol) was transferred to the Mg suspension and the mixture was again treated with ultrasound for 15 min (maximum temperature rise +50 °C) and then stirred for 5 h at RT . A stepwise deuterolysis/hydrolysis of **2**: An aliquot of the solution of **2** was treated with an excess amount of CH_3OD at −70 °C; upon warming the mixture to RT, precipitation of Ni* and evolution of 0.15 mol of a D_2/HD mixture mol Ni took place. Subsequent hydrolysis of the Ni* suspension with 2 N H_2SO_4 gave 1.1 mol of a H_2/HD/D_2 mixture/mol Ni; composition (MS); 72.9% H_2, 5.6% HD, 2.4% D_2.

***5** from $FeCl_2$ and Mg powder:* A suspension of 4.86 g (0.20 mol) of Mg powder in 130 mL of THF was activated through

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[34] *Houben-Weyl, Methoden der Organischen Chemie,* 1973; Vol XIII/2a, p 197.

[35] Bogdanović, B.; Liao, S.; Schlichte, K.; Westeppe, U. In *Organometallic Syntheses*; King, R. B., Eisch, J. J., Eds., Elsevier: Amsterdam, 1988; Vol. 4, p 410.

[36] Köster, R.; Fenzl, W. *Liebigs Ann. Chem.* **1974**, 69.

[37] Lehmkuhl, H.; Mehler, K.; Hauschild, G. *Chem. Ber.* **1983**, *116*, 438.

Table 2. Preparation of $[Pd(MgCl)_2]$ (6) from $PdCl_2$ and Et_2Mg or EtMgBr

expt	$PdCl_2$, g (mmol)	Mg reagent (mmol)	Pd:Mg ratio	THF [mL]	reaction temp [°C]/ reaction time [h]	mol of evolved gas/ mol $PdCl_2$	% Pd in solid	% Pd in solution
1	2.48 (14.0)	Et_2Mg (28.5)	1:2.04	110	−78/12 −78 → RT/3 RT/12	2.02 C_2H_6 1.77 C_2H_4	10	88
2	1.15 (6.5)	Et_2Mg (6.5)	1:1	50	−78/12	1.5 C_2H_6 0.6 C_2H_4	91.4	0.0
3	2.01 (11.4)	Et_2Mg (11.3)	1:1	45	−78/12	*a*	*a*	*a*
		Et_2Mg (12.3)	1:1.08	25	RT/24 + 60/7	*a*	95.6	1.2
4	2.34 (13.2)	Et_2Mg (19.4)	1:1.47	100	same as in expt 2.1	1.62 C_2H_6 1.47 C_2H_4	48.6	50.6
5	2.12 (12.0)	EtMgBr (47.8)	1:4	140	same as in expt 2.1	1.9 C_2H_6 1.7 C_2H_4	13.3	*a*
6	1.77 (10.0)	EtMgBr (99.5)	1:10	200	same as in expt 2.1	1.86 C_2H_6 1.62 C_2H_4	0.0	100

[a] Not determined.

the addition of 3 drops of EtBr and ultrasonic treatment for ~2 h. Thereafter 2.53 g (19.9 mmol) of anhydrous $FeCl_2$ were added, the mixture again treated with ultrasound for 1 h and then stirred for 18 h at RT.

***5** from $FeCl_2$ and Mg powder in the presence of quinuclidine*: The experiment was conducted in the same way as the one described above but in the presence of 26.4 mmol of quinuclidine.

6** from $PdCl_2$ and Et_2Mg (molar ratio of 1:2; Table 2, experiment 1)*: 2.48 g (14.0 mmol) of the anhydrous $PdCl_2$ was added in small portions to a stirred suspension of 2.34 g (28.5 mmol) of $MgEt_2$ in 110 mL of THF maintained at −78 °C (the color turns black!). After stirring the suspension for 12 h at −78 °C, the reaction vessel was connected to an automatic gas buret[38] and the reaction suspension was allowed, under continuous stirring, to warm to RT over 3 h. The suspension was then stirred at RT for another 12 h. The gas collected in the gas buret during the reaction together with the dissolved C_2-hydrocarbons products isolated from the product solution were analyzed by MS; 2.02 mol of C_2H_6/mol of Pd and 1.77 mol of C_2H_4/mol of Pd were found. The volume of C_2-hydrocarbons dissolved in the reaction mixture was determined in the following way: the volatile components of the reaction mixture were condensed under vacuum (0.2 mbar) in two cold traps (-78 and −196 °C) connected in series. Under these conditions the C_2-hydrocarbons to be analyzed are frozen out only in the −196 °C cold trap; the −196 °C cold trap is then connected to gas buret and warmed to RT. The residue isolated after removing the solvent and the volatile products was resuspended in 100 mL of fresh THF. The suspension was stirred at RT for a short time and then filtered. The precipitate washed several times with 100 mL of THF and twice with 10 mL of pentane and then dried under high vacuum. A black powder (0.25 g) was obtained having the composition Pd 61.35, Mg 12.11, Cl 4.20, C 6.71, and H 1.09%. The deep-brown colored THF filtrate (total volume 204 mL) was hydrolyzed with dilute HCl, oxidized with H_2O_2, and analyzed for Mg^{2+} and Cl^- via complexometric titration (28.8 and 28.6 mmol, respectively) and for Pd^{2+} by atomic absorption (12.3 mmol and a final Pd:Mg:Cl ratio of 1.00:2.34:2.33). The preparation of **6** according to this route has been repeated several times with slight changes in reaction conditions to give identical results. *Protolysis of **6: A 80.0 mL sample of a THF solution described above (containing 4.83 mmol of Pd, 11.3 mmol of Mg, and 11.2 mmol of Cl) was hydrolyzed at −78 °C with 1.30 mL (22.3 mmol) of EtOH added dropwise and under stirring. The temperature of the reaction mixture was slowly elevated from −78 °C to RT over 20 h. At about −50 °C the formation of a black precipitate was observed. The amount of gas collected during protolysis amounted to 70 mL[38] consisting of 79% H_2 (0.48 mol of H_2/mol of Pd) and 21% C_2H_6 as determined by MS. The black precipitate was filtered, washed with THF and dried under high vacuum. Elemental analysis of the black solid (0.424 g): Pd 97.78 (81%), Mg 1.51, Cl 0.48, C 0.85, H 0.10%. The THF filtrate contained 11.2 mmol of Mg and 11.2 mmol of Cl but was free of Pd. An aliquot of the solution of **6** was evaporated in vacuum, and the residue treated with toluene and dilute HCl. The aqueous layer was extracted with toluene, and the combined extracts were dried with $NaHCO_3$/$MgSO_4$ and analyzed for n-C_4H_9OH by GLC using n-C_8H_{18} as an internal standard; found 0.04 mol of n-C_4H_9OH/mol of Pd.

Pd from $PdCl_2$ and Et_2Mg (molar ratio of 1:1; Table 2, experiment 2)*: The experiment was conducted and analyzed in the same way as the 2.1 reaction. Insoluble product: 0.68 g (EA: Pd 92.94, Mg 0.48, Cl 2.68, C 3.20, H 0.31%). The filtrate was colorless and contained 6.0 mmol of Mg and 11.0 mmol of Cl. The X-ray powder pattern of the insoluble precipitate revealed broad and very weak diffraction peaks. However, after annealing the solid (600 °C, 72 h), four distinct diffraction lines corresponding to Pd metal were observed in the X-ray powder pattern.

*Attempt to prepare **6** by reacting $PdCl_2$ successively with 2 equiv of Et_2Mg* (Table 2, experiment 3): The first reaction step between $PdCl_2$ with Et_2Mg in the molar ratio of 1:1 was performed in the same way as the 2.2 experiment. After reacting at RT for 18 h, the second equivalent of Et_2Mg (dissolved in 25 mL of THF) was added. The reaction was then stirred at RT for 24 h and then at 60 °C for 7 h. Only negligible amounts of Pd (1.2% of the total amount of Pd) were found "dissolved" in the THF solution.

***6** from $PdCl_2$ and Et_2Mg (molar ratio 1:1.5; Table 2, experiment 4)*: The experiment was conducted and analyzed as in the 2.1 reaction. The insoluble reaction residue amounted to 0.85 g (EA: Pd 80.10, Mg 9.33, Cl 4.67, C 5.11, H 0.81%). The THF solution of **6** totaled 99.5 mL and revealed a Pd:Mg:Cl ratio of 1:2.53:3.84 (6.68 mmol of Pd, 16.9 mmol of Mg, 25.7 mmol of Cl). The THF solution (70.0 mL) **6** was protolyzed through the addition of 0.52 mL of EtOH. Gas evolution: 18.0 mL. MS analysis: 82.4% H_2 (0.13 mol of H_2/mol of Pd), 17.6% C_2H_6. The solid obtained after filtration (0.435 g) was found to be 94.54% Pd; remainder: Mg 2.02, Cl 1.34, C 1.63, H 0.31%.

***6** from $PdCl_2$ and EtMgBr (molar ratio 1:4; Table 2, experiment 5)*: The experiment was performed and worked up in the same way as for experiment 2.1. Insoluble residue: 0.21 g (EA: Pd 80.42, Mg 10.25, Cl 3.17, C 4.85, H 1.12%).

***6** from $PdCl_2$ and EtMgBr (molar ratio of 1:10; Table 2, experiment 6)*: Procedure and analysis are the same as for experiment 2.1. Insoluble residue: 0.0 g. The THF solution of **6** revealed 99.3 mmol of Mg and 117.3 mmol of Cl/Br. The protolysis of the THF solution gave 57.2 mmol of C_2H_6 (MS analysis).

*MgPd from **6***: 1,4-Dioxane (26.3 mL, 0.31 mol) was added dropwise over the course of several hours to 78 mL of a stirred solution of **6** (prepared according to experiment 2.1) containing 8.98 mmol of Pd, 24.6 mmol of Mg, and 26.5 mmol of Cl, and the mixture stirred overnight. The suspension was filtered, the solid washed with 1,4-dioxane and dried under high vacuum. The $MgCl_2 \cdot 2C_4H_8O_2$ (2.99 g) thus obtained was a white powder which contained 11.5 mmol of Mg and 22.4 mmol of Cl. The filtrate was also analyzed and 4.2 mmol of Cl was detected. Thereafter, the filtrate was concentrated under

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(38) Bogdanović, B.; Spliethoff, B. *Chem.-Ing.-Tech.* **1983**, *55*, 156.

Table 3. Preparation of $[Pt(MgCl)_2]$ (7) from $PtCl_2$ and Et_2Mg (Molar Ratio 1:2)

expt	$PtCl_2$, g (mmol)	Et_2Mg [mmol]	THF [mL]	reaction temp [°C]/ reaction time [h]	mol of evolved gas/mol of $PtCl_2$ during reaction	solid [g]	mol of gas/mol $PtCl_2$ during hydrolysis
1	2.77 (10.4)	21.1	100	−70/19 −70→RT/12.5 RT/85	1.3 C_2H_6 1.2 C_2H_4	0.0	1.1 C_2H_6
				RF[a]/2	0.25 C_2H_6 0.35 C_2H_4		0.29 H_2 0.2 C_2H_6[b]
2	4.07 (15.3)	30.8	100	−70/13 −70 → RT/9 RT/24	1.43 C_2H_6 2.39 C_2H_4	0.0	0.43 H_2[c] 0.0 C_2H_6
				RF[a]/4			

[a] Reflux temperature (68 °C). [b] 0.21 mol of n-C_4H_9OH/mol of $PtCl_2$. [c] 0.07 mol of n-C_4H_9OH/mol of $PtCl_2$.

vacuum to 80 mL, diluted with 300 mL of ether, and then stirred overnight. The resulting black precipitate was filtered, washed with ether and dried under high vacuum. EA of the black solid after being heated from RT to 400 °C with 1 °C/min, (0.97 g): Pd 72.36, Mg 19.38, C 1.74, H 0.20, Cl 6.14% $[PdMg(MgCl_2)_{\sim0.12}]$. After annealing (600 °C, 24 h) the solid exhibits in X-ray powder diagram a number of diffuse reflections corresponding to MgPd.[15]

*Reaction of **6** with 1,2-dichloroethane*: A solution of 1.0 mL (12.7 mmol) of 1,2-dichloroethane in 5 mL of THF was added dropwise via a gastight syringe (through a septum) to 100 mL of a stirred THF solution of **6** (prepared according to experiment 2.1) containing 3.72 mmol of Pd, 8.40 mmol of Mg and 8.24 mmol of Cl. The gas evolution was monitored via an automatic gas burette.[38] After stirring for several hours at RT and the cessation of gas evolution, the reaction mixture was worked up as described for experiment 2.1. Amount of gas liberated (MS): 2.2 mmol of C_2H_4 and 1.8 mmol of C_2H_6 ($\Sigma C_2 = 4.0$ mmol; 1.08 mol of C_2/mol of Pd). EA of the insoluble product (0.38 g): Pd 86.88 (84% of the Pd amount was used for the experiment) Mg 2.92, Cl 3.58, C 5.66, H 0.72%. The THF solution contained 8.9 mmol of Mg and 16.7 mmol of Cl.

*$Mg(bipy)_2$ from **6** and bipy*: A solution of 1.93 g (12.4 mmol) of bipy in 27 mL of THF was added dropwise to 75 mL of a stirred solution of **6** (prepared according to experiment 2.1) containing 2.63 mmol of Pd, 6.19 mmol of Mg and 6.68 mmol of Cl, whereby the color of the solution turned deep red. After stirring for 36 h, the suspension was filtered. The solid was washed with THF and dried under vacuum. EA of the brown solid (1.56 g): Pd 15.29 (85% of Pd used for the experiment), Mg 7.12, Cl 15.22, C 39.39, H 4.78%. Pentane (300 mL) was added to the red-colored filtrate, and the mixture stirred for 24 h. The precipitate was isolated by filtering. EA of the reddish brown solid (1.05 g): Mg 4.36 (30% of Mg used for the experiment) N 13.94, C 64.15 H 4.91%. The solid was identified as $Mg(bipy)_2$ via IR spectroscopy.[17]

*MgCOT from **6** and COT*: COT (0.79 g, 7.0 mmol) was added to 75 mL of a stirred solution of **6** as the one used for the reaction with bipy (see above). Already after a few minutes, the formation of a black precipitate could be observed. Following 24 h of stirring, the precipitate was isolated by filtration. EA of the black, pyrophoric solid (0.63 g): Pd 44.70, Mg 10.36, Cl 5.60, C 29.98, H 5.60%. The IR spectrum of the solid (Nujol): 1348w, 1295vw, 1064w, 1020s (THF), 915w, 870s (THF), 789m, 741m, 691s, 671s cm^{-1}. The absorption bands at 789, 741, 691, and 671 cm^{-1} can be assigned to MgCOT.[18]

***7** from $PtCl_2$ and Et_2Mg (Table 3, experiment 1)*: To a stirred solution of 1.75 g of Et_2Mg (90.6% purity, according to the amount of C_2H_6 produced during protolysis; 21.1 mmol) in 100 mL of THF were added at −70 °C in the period of 10 min in small portions 2.77 g (10.4 mmol) of $PtCl_2$. The temperature of the reaction mixture and the gas evolution during the reaction were registered by means of a thermocouple and an automatic gas buret[38] connected to the reaction flask. Under permanent stirring, the reaction mixture was first kept during 19 h at −70 °C and then allowed over the course of 12.5 h gradually to warm to RT. From ∼−50 °C onward, the solution turned brown. The stirring at RT was continued until, after ∼85 h, the gas evolution stopped. At this stage of the reaction, the total amount of gas evolved (cf. experiment 2.1), was determined to be 1.3 C_2H_6/Pt and 1.2 C_2H_4/Pt (Table 3.1). The black residue which remained after removal of the solvent in vacuum was dissolved in 93.5 mL of THF. The solution (15.0 mL) were concentrated in vacuum to ∼5 mL; addition, under ice-water cooling, of 5 mL of dilute HCl (concentrated HCl + H_2O in 1:1 ratio) to the solution resulted in the evolution of 51 ml (20 °C) of a gas composed of 87.4% C_2H_6 (1.1 C_2H_6/Pt), 3.8% C_4H_{10} and 3.0 H_2 (MS). (As a result of this and the following hydrolysis or alcoholysis experiments, *a black fluffy precipitate of metallic Pt and a clear, colorless solution is produced.* In one such experiment, after washing the precipitate with water, the Pt content of the solid was determined to be 99.16%, remainder being Mg, Cl, C, and H). The remaining solution was heated to reflux during 2 h (until no more gas evolved) and the amount of gas developed during the heating was determined to be 0.35 C_2H_4/Pt and 0.25 C_2H_6/Pt. The dark-brown solution of **7** thus obtained (tolal volume: 65 mL) was free of solid material. Repeated hydrolysis of an aliquot of the solution (10 mL) gave the result: 0.29 H_2/Pt and 0.20 C_2H_6/Pt (MS). A 5 mL aliquot of the solution gave upon *alcoholysis* with 5 mL of EtOH and 1 drop of dilute HCl at 0 °C the black Pt precipitate and a clear solution. The volatile components of the suspension were distilled off in vacuum and the distillate was analyzed by GLC using n-C_8H_{18} as an internal standard; found: 10.3 mg of n-C_4H_9OH (0.21 of n-C_4H_9OH/Pt). A part of the solution of **7** was evaporated to dryness under vacuum, leaving a solid whose elemental composition (Pt 42.10, Mg 11.02, Cl 14.50, C 21.41, H 3.59, O (remainder) 7.38%) corresponds to $PtMg_{2.1}Cl_{1.9}\cdot 2.1THF$. Both the THF solution and the thus obtained solid were investigated by the EXAFS method.[21]

***7** from $PtCl_2$ and Et_2Mg (Table 3, experiment 2)*: Reaction conditions for and results of the experiment are given in Table 3. Analyses were carried out as described for experiment 3.1.

***8a** from $RuCl_3$ and Et_2Mg (Table 4, experiment 1)*: A solution of 1.87 g of Et_2Mg (90.4% purity, cf. experiment 3.1, 20.6 mmol) in 35 mL of THF was placed in a reaction flask equipped with a sidearm charged with $RuCl_3$. The reaction apparatus was then connected to an automatic gas buret.[38] Solid anhydrous $RuCl_3$ (1.65 g, 7.95 mmol) was added at RT in small portions to the stirred Et_2Mg solution with the immediate evolution of gas. After stirring for 4 h at RT and the formation of 440 mL of gas, the liberation of gas stopped. Upon heating to reflux for 6.5 h, an additional 260 mL of gas was generated. After isolating the gas dissolved in the product solution, the volume of the gaseous products corresponded to 953 mL, and according to MS analysis, the gas was composed to 80.1% of C_2H_6 (4.1 C_2H_6/Ru) and to 16.3% of C_2H_4 (0.8 C_2H_4/Ru). The residue obtained after evaporating the solvent (cf. experiment 2.1) was redissolved in fresh THF, stirred for a short time, and filtered. Upon filtration of the solution of **8a**, no solid was isolated. A solution of **8a** (10.0 mL, total volume 56 mL) was evaporated to dryness under vacuum and the residue heated to 200 °C under high vacuum, affording 460.8 mg of a black, X-ray amorphous solid. EA: Ru 24.92, Mg 15.66, Cl 25.66, C 23.14, H 3.10%; $RuMg_{2.61}Cl_{2.94}C_{7.81}H_{12.47}$ corresponding to $\sim Ru(MgCl)_2\cdot 0.5Mg_{1.2}Cl_2\cdot 1.9THF$. Upon hydrolysis of a second 10.0 mL aliquot of **8a** with 2−3 mL of concentrated HCl, only 6.7 mL of gas composed of C_2H_6 and THF were evolved. The resulting dark-brown solution was evaporated to dryness under vacuum. NH_4Cl and toluene were added to the distillate, the resulting two layers separated and the organic layer dried with anhydrous Na_2SO_4/$NaHCO_3$. The organic layer was analyzed by GLC and coupled GLC/MS (n-

Table 4. Preparation of Inorganic Grignard Reagent Solutions [$M'(MgCl)_m$] from $M'Cl_3$, M′ = Ru, Rh, Ir, and Et_2Mg or Mg*[a]

expt	$M'Cl_3$[g] (mmol)	Mg reagent (mmol)	M′:Mg ratio	THF [mL]	reaction temp/ reaction time [h]	mol of gas/ mol $M'Cl_3$	solid [g]	mol of gas/mol M′ (hydrolysis)	[$M'(MgCl)_m$] solution
1	$RuCl_3$ [1.65] (7.95)	Et_2Mg (20.6)	1:2.6	35	RT/20 RF[b]/6.5	4.1 C_2H_6 0.8 C_2H_4	0.0	0.0	**8a**
2	$RuCl_3$ [2.22] (10.7)	Mg* (33.9)	1:3.2	40	RT/24 RF[b]/5	0.0	0.1	1.24 H_2	**8b**
3	$RuCl_3$ [1.41] (6.78)	Mg* (38.6)	1:5.7	40	RT/14d[c]	0.0		0.91 H_2	**8b**
4	$RhCl_3$ [1.89] (9.06)	Et_2Mg (18.4)	1:2.0	50	RT/60	2.8 C_2H_6 1.5 C_2H_4 0.2 C_2H_2	0.0	0.0	**9**
5	$IrCl_3$ [2.99] (9.90)	Et_2Mg (31.0)	1:3.1	60	RT/7d[c]	2.3 C_2H_6 1.2 C_2H_4 0.2 C_2H_2	0.0	1.90 C_2H_6	**10a**
6	$IrCl_3$ [1.95] (6.55)	Mg* (19.6)	1:3.0	20	RT/17	0.0	0.06	0.80 H_2	**10b**

[a] Active magnesium. [b] Reflux temperature. [c] d = days.

C_8H_{18} was used as an internal standard), 5.1 mg of n-C_4H_9OH (0.05 mol of n-C_4H_9OH/mol of Ru) and 26.5 mg of chlorobutanol (a cleavage product of THF under the influence of HCl[39]) were detected.

***8b** from $RuCl_3$ and Mg^* (Table 4, experiment 2)*: Solid $RuCl_3$ (2.22 g, 10.7 mmol) was added in small portions over 25 min to a stirred suspension of 0.88 g of Mg* (from dehydrogenation of MgH_2^*,[13] 93.2% purity, 33.9 mmol) in 40 mL of THF, whereupon a slight temperature increase up to 26 °C was recorded. After ~1 h of stirring, a strong exothermic reaction with a temperature jump up to 70 °C took place! The mixture was stirred overnight at RT and then heated to reflux for 5 h. The suspension was cooled to RT, filtered and the solid on the frit washed with THF. After drying under vacuum, 104 mg of a black X-ray amorphous solid were isolated consisting of 9.76% C, 2.24% H, 14.49% Mg, and 8.45% Cl. The remainder (65.06%) corresponds to Ru (6.3% of the amount of Ru utilized for the experiment). After annealing (600 °C, 24 h), the solid exhibited in the X-ray powder diagram diffraction lines of Ru and MgO. The volume of the solution of **8b** amounted to 82.5 mL. During the hydrolysis of a 10.0 mL aliquot of **8b** with 2 mL of dilute HCl (conc. HCl : H_2O = 1:1), 45.4 mL of a gas composed of 79.6% H_2 (MS analysis; remainder CH_4, C_4H_{10}) were evolved representing 1.24 mol of H_2/mol of Ru in solution.

***8b** from $RuCl_3$ and Mg^* (Table 4, experiment 3)*: The experiment was carried out in the same manner as for experiment 4.2, however, the reactant molar ratio of $RuCl_3$ to Mg* corresponded to 1:5.7. A strong exothermic reaction (cf. experiment 4.2) was observed after a reaction time of ~40 min. The suspension was stirred over a period of 14 days at RT, whereby periodically 2.0 mL samples were taken from the solution, hydrolyzed with EtOH and dilute HNO_3 and analyzed for Mg^{2+} and Cl^- content. The increase in Mg concentration in solution with respect to the reaction time and in relation to the amount of $RuCl_3$ used for the experiment is represented in Figure 1. The concentration of Cl in the THF solution after a reaction time of 24 h was found to correpond to 3.0 mol of Cl/mol of $RuCl_3$. After stirring for 14 days, the reaction suspension was filtered in order to remove the excess Mg*. A 15.0 mL sample of the product solution (total volume 40 mL) was concentrated to half of its volume and then treated with EtOH and dilute HCl (cf. experiment 3.1) giving 79 mL of a gas composed of 70.4% of H_2 (MS analysis; 0.91 H_2/Ru; remainder: CH_4, C_3H_8, C_4H_{10}). The solution resulting from hydrolysis was evaporated to dryness under vacuum and the distillate analyzed for n-C_4H_9OH by GLC (see experiment 4.1), 0.35 mol of n-C_4H_9OH/mol of $RuCl_3$ were found.

***9** from $RhCl_3$ and Et_2Mg (Table 4, experiment 4)*: The experiment was performed and the resulting products were analyzed in the same manner as for experiment 4.1. The composition of gaseous products varied according to the reaction time: a sample analyzed after a reaction time of 2 h showed a C_2H_6:C_2H_4:C_2H_2 molar ratio of 1:1:0.1, whereas at the end of the experiment (60 h reaction time) the gas consisted of C_2H_6 and C_2H_2 in a 1:0.08 molar ratio. Upon filtering the reaction mixture it was found that *the reaction products were completely dissolved in THF* (i.e., no solid was isolated). The volume of the product solution containing **9** amounted to 70.5 mL. In a parallel experiment, an aliquote part of the solution containing **9** was hydrolyzed by addition of toluene and dilute HCl, whereby no gas evolution was observed. In the toluene solution (cf. experiment 4.1) were determined by GLC 0.13 mol of n-C_4H_9OH/mol of $RhCl_3$. Another aliquote part of the THF solution containing **9** gave as a result of hydrolysis with H_2O and dilute HCl, a black precipitate containing 84.6% Rh (80% of total Rh used for the experiment).

***10a** from $IrCl_3$ and Et_2Mg (Table 4, experiment 5)*: The experiment was performed and the resulting products were analyzed in the same way as for experiment 4.1, except that a solution of Et_2Mg in 20 mL of THF was added dropwise over 2 h into a stirred suspension of $IrCl_3$ in 40 mL of THF. After reacting for 22 h, 2.25 mol of C_2H_6, 0.84 mol of C_2H_4, and 0.17 mol of C_2H_2 per mol of $IrCl_3$ were generated as determined by MS. After stirring further for 7 days only an addtional 0.07 mol of C_2H_6 and 0.36 mol of C_2H_4 per mol of $IrCl_3$ were evolved (MS analysis). Upon filtering the reaction mixture no solid was isolated, i.e., *the reaction products were completely dissolved in THF*. Hydrolysis of a 15.0 mL sample of the **10a** solution (total volume 50.0 mL) with 4 mL of dilute HCl (cf. experiment 4.2) led to the formation of 150 mL of a gas containing 90.8% C_2H_6 which confirms the presence of 1.9 mol of EtMg groups per mol Ir in solution.

***10b** from $IrCl_3$ and Mg^* (Table 4, experiment 6)*: The experiment was conducted in the same manner as for experiment 4.2. A strongly exothermic reaction (temperature jump to 70 °C; cf. experiment 4.2) was noted after ~1 h of stirring. Thereafter the suspension was stirred for an additional 16 h at RT, filtered and the solid washed with THF. After drying under high vacuum, a black solid was isolated (62.4 mg) which exhibits in its X-ray powder diagram sharp reflexions corresponding to metallic Ir. A solution (41.0 mL) containing **10b** was obtained.

*FeTi/Fe_2Ti from **1** and $FeCl_2$ (Table 5, experiment 1)*: A THF solution of **1** was prepared according to the procedure reported in ref 8. The solution contained 42.7 mmol of Ti, 108.0 mmol of Mg, and 136.6 mmol of Cl (Ti:Mg:Cl = 1:2.5:3.2) in 374 mL of THF and gave 2.5 mol of H_2/mol of Ti upon hydrolysis (of an aliquot). Anhydrous (5.42 g, 42.8 mmol) $FeCl_2$ was added in small portions over 1 h to the stirred solution of **1** (the reaction of **1** with $FeCl_2$ is exothermic!). After the $FeCl_2$ addition was complete, the reaction mixture was stirred at RT for 24 h. The black product suspension was filtered and the isolated solid washed with THF until the washing liquid was colorless and then with pentane. After drying under high vacuum at RT, 5.11 g of a black pyrophoric X-ray amorphous solid was obtained (composition is given in Table 5). The Mössbauer spectrum of the solid is represented in Figure 2, section 2.1. Hydrolysis of the THF filtrate plus washings yielded an aqueous solution containing 106.7 mmol of Mg^{2+}, 215.0 mmol of Cl^- (titrimetric analysis), and 12.1 mmol of Ti^{4+} (photometric analysis); concentration of Fe^{2+} was below the limit of detection.

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[39] Reppe, W. *Liebigs Ann. Chem.* **1955**, *596*, 89.

Table 5. Ti Alloys Prepared by Reacting $[Ti(MgCl)_2(THF)_x]$ (1) with Metal Chlorides M^2Cl_2 in the Molar Ratio 1:1 in THF at RT[a,23b]

expt	solution of Ti/Mg/Cl [mmol]	**1**[b] THF [mL]	M^2Cl_2 (mmol)	solid [g]	elem composition [%][c]						% Ti in the solid[d]	method for investigation of the solid
					Ti	M^2	Mg	Cl	C	H		
					empirical formula							
1	42.7/108/137	347	$FeCl_2$	5.11	28.8	46.8	0.85	3.4	4.8	1.0	72	MB[e]
			(42.8)		$Ti_{0.7}FeMg_{0.04}Cl_{0.14}C_{0.4}H_{1.2}$							
2	26.7/65/83	200	$CrCl_2$	3.87	27.4	37.1	5.6	14.8	6.5	0.15	83	X-ray[f,g]
			(26.0)		$Ti_{0.8}CrMg_{0.3}Cl_{0.5}C_{0.7}H_{0.2}$							
3	27.6/69/85	200	$SnCl_2$	7.25	18.2	49.7	3.7	10.9	11.8	1.7	100	X-ray[f,g]
			(27.9)		$TiSn_{1.1}Mg_{0.4}Cl_{0.8}C_{2.6}H_{4.5}$							
4	12.8/32/40	90	$MnCl_2$	0.59	8.5	73.1	1.7	6.2	3.7	0.9	8	X-ray[f,h]
			(12.4)		$Ti_{0.1}MnMg_{0.05}Cl_{0.13}C_{0.2}H_{0.7}$							
5	34.2/87/103	210	$CoCl_2$	2.91	10.2	70.2	nd	nd	11.3	1.9	18	X-ray[f,h]
			(34.5)		$Ti_{0.2}CoC_{0.6}H_{1.6}$							
6	37.5/95/113	230	$NiCl_2$	2.17	6.0	75.4	nd	nd	8.6	1.6	7	X-ray[f,i]
			(37.6)		$Ti_{0.1}NiC_{0.6}H_{1.3}$							

[a] Reaction time 24 h. [b] In the presence of 0.5 mol $MgCl_2$/mol Ti[8]. [c] Elemental analysis. [d] With respect to the total amount of Ti used in the experiment. [e] Mössbauer spectroscopy. [f] X-ray powder spectroscopy. [g] Amorphous. [h] The sample remained X-ray amorphous after annealing at 400 °C for 24 h. [i] After annealing at 400 6C the sample shows diffraction lines of elemental Ni.

Table 6. Ni Alloys Prepared from THF Solutions of $[(NiMgCl)_2{\cdot}MgCl_2]$ (2) and Metal Chlorides M^2Cl_2 at RT

expt	solution of **2** Ni/Mg/Cl [mmol]	THF [mL]	M^2Cl_2 (mmol)	Ni:M^2 ratio	solid [g]	elem composition [%][a]						% Ni in the solid[b]	X-ray[c]
						Ni	M^2	Mg	Cl	C	H		
						empirical formula							
1	6.4/15/20.4	67	$FeCl_2$ (3.1)	1:0.5	0.73	43.6	23.8	4.2	nd	9.9	1.6	84	Ni_2Fe[d]
						$Ni_2Fe_{1.2}Mg_{0.5}C_{2.2}H_{4.3}$							
2	8.8/25/38.4	140	$CuCl_2$ (3.8)	1:0.43	0.75	52.7	36.0	3.0	6.6	1.6	0.1	76	Ni_2Cu[d]
						$Ni_2Cu_{1.26}Mg_{0.3}Cl_{0.4}C_{0.3}H_{0.2}$							

[a] Elemental analysis. [b] With respect to the total amount of Ni used in the experiment. [c] X-ray powder spectroscopy. [d] After annealing at 600 °C for 24 h.

Experiments 5.2–6 were performed, and the resulting products were analyzed in the same manner as experiment 5.1.

*Ni_2Fe from **2** and $FeCl_2$ (Table 6, experiment 1)*: Anhydrous $FeCl_2$ (0.39 g, 3.1 mmol) (Alfa Ventron) was added at 0 °C to a stirred THF solution of **2** from experiment 1.2 (67 mL containing 6.4 mmol of Ni, 15.0 mmol of Mg, and 20.4 mmol of Cl). The reaction suspension was slowly warmed to RT (~2 h) and stirred for 20 h. The black suspension was filtered, the solid washed with THF and dried under high vacuum at RT. The resulting black, pyrophoric, X-ray amorphous powder (0.73 g; EA, see Table 6) was annealed for 24 h at 600 °C to give a crystalline Ni_2Fe alloy as determined through X-ray powder diffraction.

d spacing [Å]	2.062	1.786	1.263
relative intensity [%]	100	46.4	27.3
hkl	[111]	[200]	[220]

Hydrolysis of the THF filtrate together with the washings yielded an aqueous solution containing 0.6 mmol of Ni^{2+}, 12.6 mmol of Mg^{2+}, 23.7 mmol of Cl^-, and 0.1 mmol of Fe^{2-}.

Experiment 6.2 was carried out and worked up in the same manner as experiment 6.1, except that $CuCl_2$ was added at *RT* to the THF solutions of **2**.

*PdFe from **6** and $FeCl_2$ (Table 7, experiment 1)*: 100.0 mL of a THF solution of **6** (prepared following experiment 2.1) containing 4.28 mmol of Pd, 9.22 mmol of Mg, and 9.42 mmol of Cl were added to a stirred suspension of 0.52 g (4.11 mmol) of anhydrous $FeCl_2$ in 10 mL of THF. After stirring 2 days at RT, the black precipitate was isolated and analyzed in the same way as described for the preparation of FeTi/Fe_2Ti. EA of the X-ray amorphous PdFe product (0.77 g) in given in Table 7. The ^{57}Fe Mössbauer spectrum of the raw product is represented in Figure 3. The C and H content of the amorphous material could be reduced (from 7.2 and 1.3 to 0.66 and 0.76%, respectively) through hydrogenation (14 bar H_2, 200 °C, 24 h). Analysis of the THF filtrate (after hydrolysis): 0.77 mmol of Pd^{2+}, 9.31 mmol of Mg^{2+}, 16.16 mmol of Cl^- and 0.46 mmol of Fe^{2+}.

Experiments 7.2 and 7.3 were carried out in the same manner as for experiment 7.1.

Pd from **6** and $PdCl_2$ (Table 7, experiment 4)*: 0.29 g (1.7 mmol) of $PdCl_2$, were added to a THF solution of **6** (56 mL, 1.32 mmol of Pd prepared as in experiment 2.1). The suspension was stirred for several days at RT and centrifuged. The isolated solid was washed with THF and dried under high vacuum to give 0.16 g of Pd*. The composition of the solid is given in Table 7.

*PtFe from **7** and $FeCl_2$ (Table 8, experiment 1)*: A THF solution of **7** (31.0 mL) (prepared according to experiment 3.2 except that the solution of **7** was not heated to reflux) containing 4.37 mmol of Pt, 8.8 mmol of Mg and 9.7 mmol of Cl were added over a period of 25 min to a stirred suspension of 0.95 g (4.39 mmol) of $FeCl_2{\cdot}1.3$ THF[37] in 20 mL of THF (the reaction is slightly exothermic!). After stirring 2 days at RT, the reaction mixture was heated to reflux for 4 h. The *hot* suspension was filtered, the isolated solid was washed with THF and pentane. After drying under high vacuum at RT, 0.82 g of a black X-ray amorphous solid (PtFe) was obtained; the composition is listed in Table 8. The ^{57}Fe Mössbauer spectrum of the amorphous and crystalline PtFe is represented in Figure 5. After annealing for 72 h at 600 °C a crystalline PtFe alloy (the solid shows an overall composition $PtFe_{1.1}Mg_{0.7}Cl_{0.6}C_{0.6}H_{1.3}$) was obtained as verified through X-ray diffraction

Table 7. Pd Alloys and Active Pd Prepared from THF Solutions of $[Pd(MgCl)_2]$ (6) and Metal Chlorides M^2Cl_n at RT

expt	solution of **6** Pd/Mg/Cl [mmol]	THF [mL]	M^2Cl_n (mmol)	Pd:M^2 ratio	solid [g]	elem composition [%][a]						% Pd in the solid[b]	method for investigation of the solid
						Pd	M^2	Mg	Cl	C	H		
						empirical formula							
1	4.3/9.2/9.4	100	$FeCl_2$ (4.1)	1:1	0.77[c]	48.1	25.7	2.9	7.0	7.2[d]	1.3	81	MB,[e] X-ray[f]
						$PdFeMg_{0.3}Cl_{0.4}C_{0.1}H_{1.7}$							
2	4.5/	80	$SnCl_2$ (4.5)	1:1	1.02[g]	43.5	42.8	2.0	4.6	5.9	1.0	93	X-ray[f]
						$PdSn_{0.9}Mg_{0.2}Cl_{0.3}C_{1.2}H_{2.4}$							
3	4.3/9.2/9.4	100	$TeCl_4$ (2.1)	1:0.5	0.78[c]	56.4	33.7	1.2	1.9	1.2	0.5	96	X-ray,[f] DSC[h]
						$Pd_2TeMg_{0.2}Cl_{0.2}C_{0.4}H_{1.7}$							
4	1.32/	56	$PdCl_2$ (1.7)	1:1.3	0.16	89							

[a] Elemental analysis. [b] With respect to the total amount of Pd used in the experiment. [c] Reaction time 48 h. [d] After hydrogenation (14 bar, 200 °C, 24 h) the C and H contents decreased to 0.66 and 0.76%, respectively. [e] Mossbauer spectroscopy. [f] X-ray powder spectroscopy. [g] Reaction time 72 h. [h] Differential scanning calorimetry.

Table 8. Pt Alloys Prepared from THF Solutions of $[Pt(MgCl)_2]$ (7) and Metal Chlorides M^2Cl_n at RT

expt	solution of **7** Pt/Mg/Cl [mmol]	THF [mL]	M^2Cl_n (mmol)	Pt;M^2 ratio	solid [g]	elem composition [%][a]						% Pt in the solid[b]	method for investigation of the solid
						Pt	M^2	Mg	Cl	C	H		
						empirical formula							
1	4.37/8.8/9.7	31	$FeCl_2$−1.3THF (4.39)	1:1	0.82[c]	48.6	18.3	3.4	12.7	11.2	2.2	47	MB,[d] X-ray[e]
						$PtFe_{1.3}Mg_{0.6}Cl_{1.4}C_{3.7}H_{8.4}$							
2	4.84/10.2/10.6	100	$CuCl_2$ (4.93)	1:1.02	1.90[f]	44.2	15.3	2.3	12.3	10.5	1.7	89	X-ray[e]
						$PtCu_{1.1}Mg_{0.4}Cl_{1.5}C_{0.2}H_{2.6}$							
3	6.87/13.4/13.7	30	$RhCl_3$ (4.54)	1:0.66	1.84[g]	70.0	21.9[h]			7.3	9.8	96	X-ray[e]
						$Pt_3Rh_{1.8}C_{5.1}H_{6.7}$							
4	5.83/13.0/11.7	50	$SnCl_2$ (5.88)	1:1	1.69[i]	55.2	33.9	1.3	3.3	3.8	0.8	82	X-ray[e]
						$PtSnMg_{0.2}Cl_{0.33}C_{1.1}H_{2.8}$							
5	4.38/9.3/9.0	100	BiCl3 (2.86)	1:0.65	1.59[i]	53.6	32.8	0.4	2.6	1.8	0.3	100	X-ray,[e] DSC[j]
						$Pt_3Bi_{1.8}Mg_{0.2}Cl_{0.8}C_{1.6}H_{3.4}$							

[a] Elemental analysis. [b] With respect to the total amount of Pt used for the experiment. [c] Reaction time 48 h at RT, thereafter 4 h at reflux temperature. [d] Mössbauer spectroscopy. [e] X-ray powder spectroscopy. [f] Reaction time 72 h. [g] Reaction time 96 h. [h] Percent of Rh calculated from the difference to 100%; Mg and Cl content of the solid was negligible. [i] Reaction time 48 h. [j] Differential scanning calorimetry.

(see Figure 4). Analysis of the THF filtrate plus washings (after hydrolysis): 2.23 mmol of Pt^{2+}, 7.7 mmol of Mg^{2+}, 12.3 mmol of Cl^-, and 1.0 mmol of Fe^{2+}.

*PtCu from **7** and $CuCl_2$ (Table 8, experiment 2)*: The experiment was carried out and the resulting products were analyzed in the same manner as experiment 7.1. A black, X-ray amorphous solid (1.90 g ~CuPt; overall composition given in Table 8) was obtained. The C and H content of the product could be reduced (from 10.5 and 1.7 to 0.61 and 0.60% respectively) through hydrogenation. After annealing (600 °C, 24 h) a sample of the raw product, the sample exhibited in its X-ray powder diffraction diagram the following diffraction lines:

d spacing [Å]	4.349	2.299	2.197	1.902	1.350	1.338
relative intensity	14.7	15.3	100.0	49.4	40.8	21.3

*Pt_3Rh_2 from **7** and $RhCl_3$ (Table 8, experiment 3)*: The experiment was conducted, and the resulting X-ray amorphous product (Pt_3Rh_2) was isolated and analyzed in the same manner as for experiment 5.1.

*PtSn from **7** and $SnCl_2$ (Table 8, experiment 4)*: A solution of 1.12 g (5.88 mmol) of $SnCl_2$ in 25 mL of THF was added dropwise to a stirred solution (50 mL) of **7** (prepared according to experiment 3.2); the formation of a black precipitate followed immediately. An additional 30 mL of THF were added and the suspension was stirred for 48 h at RT. A bimetallic PtSn product 1.69 g was isolated as a black X-ray amorphous powder after filtering the reaction suspension, washing with THF, and drying under high vacuum. A crystalline product could be obtained by annealing (700 °C, 24 h), which contains only PtSn as determined through X-ray powder diffraction.

*Pt_3Bi_2 from **7** and $BiCl_3$ (Table 8, experiment 5)*: The experiment was performed and the resulting products were analyzed in the same manner as experiment 7.1. A bimetallic material (Pt_3Bi_2) 1.59 g was isolated as a black, X-ray amorphous powder. The DSC analysis of Pt_3Bi_2 exhibited two sharp endothermic peaks at 357 and 460.6 °C as well as two broad endothermic peaks between 520 and 540 °C. In the range of the melting point of Bi (271.4 °C) no peak was observed, indicating that elemental Bi is not present in the bimetallic product.

*RuPt from **8a** and $PtCl_2$ (Table 9, experiment 1)*: 1.19 g (4.47 mmol) of $PtCl_2$ were added in small portions to a stirred solution of **8a** (37 mL) from experiment 4.1. The suspension was stirred for 48 h at RT. The bimetallic RuPt precipitate (1.59 g) of the composition given in Table 9 was isolated as a black X-ray amorphous solid after filtering, washing with THF and drying under high vacuum. The solid (1.07 g) was suspended in 5 mL of THF, transferred to a D-4 glas frit and washed five times with air-free water and then with acetone and dried in vacuum. Elemental analysis of the resulting *pyrophoric* solid (0.85 g): Ru 28.58, Pt 52.48, Mg 0.47, Cl 1.5, C 14.26, H. 1.46% ($RuPt(MgCl_2)_{0.07}C_{4.4}H_{5.4}$); TEM record is reproduced in Figure 6a. The solid was annealled at 500 °C for 60 h and thereupon at 650 °C for 24 h; an X-ray powder diagram shows reflections of the RuPt solid solution[29] which are shifted with respect to those of Pt; TEM: (Figure 6b).

*Ru_2Pt_3 from **8b** and $PtCl_2$ (Table 9, experiment 2)*: The experiment was conducted and the resulting X-ray amorphous Ru_2Pt_3 product (2.21 g) of the composition given in Table 9

Table 9. Ru, Rh, and Ir Alloys Prepared from Inorganic Grignard Reagents [$M'(MgCl)_m$], M′ = Ru, Rh, Ir, and $PtCl_2$ or $SnCl_2$ in THF

expt	$M'(MgCl)_m$ [mmol M′]	THF [mL]	M^2Cl_2 (mmol)	M′:M^2 ratio	reaction temp/ reaction time [h]	solid [g]	elem composition [%]						% yield of the alloy[a]	method for investigation of the alloy
							M′	M^2	Mg	Cl	C	H		
							empirical formula							
1	**8a**	37	$PtCl_2$	1:1	RT/48	1.59	23.4	46.1	2.9	8.9	15.9	2.2[b]	82	X-ray,[c] TEM[d]
	4.47		(4.47)				$RuPt(MgCl_2)_{0.5}(THF)_{1.4}$							
2	**8b**	40	$PtCl_2$	1:1.54	RT/24	2.21	24.3	63.2	1.4	4.4	5.8	0.8[e]	100	X-ray,[c] TEM[d]
	4.85		(7.49)				$Ru_2Pt_{2.7}(MgCl_2)_{0.5}(THF)_{1.0}$							
3	**9**	50	$SnCl_2$	1:0.5	RF/6	0.60	44.0	21.2	2.7	7.8	15.4	2.0	50	X-ray[c]
	5.10		(2.56)		RT/72		$Rh_2Sn_{0.8}(MgCl_2)_{0.5}C_{6.0}H_{9.1}$							
4	**9**	30	PtCl2	1:0.47	RT/158	0.78	40.9	38.4	1.6	3.5	14.0	1.6	80	X-ray[c]
	3.80		(1.82)				$Rh_2Pt(MgCl_2)_{0.3}C_{5.9}H_{8.2}$							
5	**10b**	20	$SnCl_2$	1:1.52	RT/24	1.35	44.4[f]	41.2	1.2	5.3	6.8	1.1	98	X-ray,[c] TEM[d]
	3.20		(4.82)				$Ir_2Sn_3(MgCl_2)_{0.4}(THF)_{1.2}$[e]							

[a] With respect to M′. [b] After being washed with air-free water and acetone (see text), the elemental composition of the alloy corresponded to $RuPt(MgCl)_{0.07}C_{4.4}H_{5.4}$. [c] X-ray powder spectroscopy. [d] Transmission electron microscopy. [e] Elemental composition after removal of $MgCl_2$ by washing with air-free water is given in the text. [f] Percent of Ir calculated from the difference of the sum of the elements to 100%.

was isolated in the same manner as experiment 9.1. The THF solution of **8b** (40 mL) utilized was obtained from experiment 4.2. The solid (1.01 g) was suspended in 10 mL of air-free water, filtered, washed with acetone, and dried under high vacuum. Elemental analysis of the resulting *pyrophoric* solid (0.90 g): Ru 24.47, Pt 65.55, Mg 0.16, Cl 0.69 C 3.75, H 0.37% ($Ru_2Pt_{2.8}(MgCl_2)_{0.06}C_{2.6}H_{3.0}$; TEM record: Figure 6c). The solid was annealed at 650 °C for 24 h; an X-ray powder diagram reveals broad reflections of the RuPt solid solution.[29] TEM: Figure 6d.

*Rh_2Sn from **9** and $SnCl_2$ (Table 9, experiment 3)*: A solution of 0.49 g (2.56 mmol) of $SnCl_2$ in 12 mL of THF was added dropwise to a stirred solution of **9** (50 ml) from experiment 4.4, resulting in the formation of a black precipitate. The suspension was heated to reflux for 6 h and thereafter stirred for 72 h at RT. A bimetallic Rh_2Sn product (0.60 g) was isolated as a black X-ray amorphous solid through filtering, washing with THF and drying under high vacuum.

*Rh_2Pt from **9** and $PtCl_2$ (Table 9, experiment 4)*: The experiment was conducted and the resulting X-ray amorphous Rh_2Pt product (0.78 g) was isolated and analyzed in the same manner as experiment 9.1. The solution of **9** utilized for the preparative reaction was obtained from experiment 4.4. After annealing (700 °C, 24 h) the raw product, a crystalline solid corresponding to a $Rh_{0.67}Pt_{0.33}$ solid solution was obtained as identified by X-ray powder diffraction. The cubic lattice constant determined for $Rh_{0.67}Pt_{0.33}$ is 3.86 Å which falls between the known values for Rh and Pt metal, 3.803 and 3.924 Å, respectively.[30]

*Ir_2Sn_3 from **10b** and $SnCl_2$ (Table 9, experiment 5)*: The experiment was conducted, and the resulting X-ray amorphous Ir_2Sn_3 product (1.35 g) was isolated and analyzed in the same way as experiment 9.1. A solution of **10b** (20 mL) utilized in the preparation was obtained from experiment 4.6. The solid (0.67 g) was washed with air-free water and acetone in the same way as described for experiment 9.1. Elemental composition of the resulting *pyrophoric* solid (0.53 g): Mg 0.02, Cl 0.69, C 2.89, H 0.73%, remainder Ir, Sn; the TEM record is reproduced in Figure 7a. The solid was annealled to 500 °C for 48 h and thereafter at 650 °C for 24 h; X-ray powder diagram: Figure 8; TEM: Figure 7b.

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