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The preparation of finely divided metal powders and transition metal complexes using "organically solvated" magnesium *

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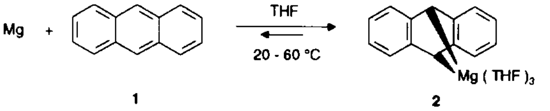
Abstract

Treatment of commercial magnesium powder in THF with a small amount of anthracene generates a highly active form of magnesium (Mg*). The Mg* is an excellent *in situ* reducing agent for transition metal salts, giving highly reactive metal powders of Groups 8–12. In the presence of electron donor ligands, this reduction provides a useful one-step route to organotransition metal complexes. The application of 35 kHz ultrasound during the reaction improves the dispersity of the metal powders and enhances the yields of the complexes.

1. Introduction

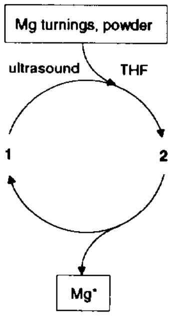
Finely divided metal powders [1,2] and transition metal complex compounds [3–5] form the basis of a plethora of stoichiometric and catalytic transformations in organic chemistry. Both types of reagents are accessible by the metal evaporation technique [6], electrolysis [7], and various chemical reduction methods [8,9]. Because of its low toxicity and general availability, magnesium metal appears to be most suitable as a reducing agent. However, its reactivity strongly depends on the size and the purity of its active surface [10,11].

In the light of the observation that anthracene reversibly forms an electron transfer complex with magnesium and that the equilibrium (eqn. (1)) acts as an effective phase transfer system for elemental magnesium [12] we have developed a general method for the reduction of metal salts by "organically solvated" magnesium.



(1)

The reaction cycle (eqn. (2)) depicts the catalytic function of the anthracene in the activation of magnesium powder or turnings. Small amounts of **1** react with an excess of the bulk metal to give the soluble adduct **2**. Highly reactive Mg* is formed in the equilibrium and the anthracene is regenerated. An important advantage for the synthetic use of the system (2) is that the catalytic cycle supplies Mg* continuously in high yield. Ultrasound treatment in a conventional cleaning bath [13] was found to improve the efficiency of the phase transfer reaction considerably.



(2)

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* Dedicated to Professor Gian Paolo Chiusoli on the occasion of his 70th birthday.

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For the catalytic formation of Mg* from bulk magnesium **2** may be prepared *in situ* in the presence of an excess of magnesium. Alternatively pre-prepared **2** may be added as the activator. Mg* in THF is a powerful reducing agent for transition metal salts in the presence or absence of electron donors.

2. Results and discussion

These findings allowed for the first time the use of bulk magnesium for the reductive synthesis of either highly dispersed transition metals [14] or transition metal complexes of various types [15,16].

2.1. Finely divided metal powders [14]

The reduction of nickel halides by magnesium in THF or ethanol for preparing hydrogenation catalysts of the Raney nickel type has been described [17]. The obvious disadvantage of this procedure is that the reduction is effected at a reasonable rate only at elevated temperatures, *i.e.* in refluxing THF or ethanol, giving relatively coarse nickel particles. However, the lower the reaction temperature, the finer are the metal particles.

Commercial magnesium powder (50–300 mesh), activated with catalytic amounts of **1** to form Mg* in THF, reduces suspended salts of metals M of Groups 8–12 at room temperature to give slurries of metal powders (M*) along with the corresponding salts of magnesium. The strong activating influence of anthracene on the course of the metal halide reduction was exemplified by the reduction of $FeCl_2 \cdot 2THF$ to Fe* at room temperature. As shown in Fig. 1, both the rate and the extent of the reduction increase with increasing anthracene concentration.

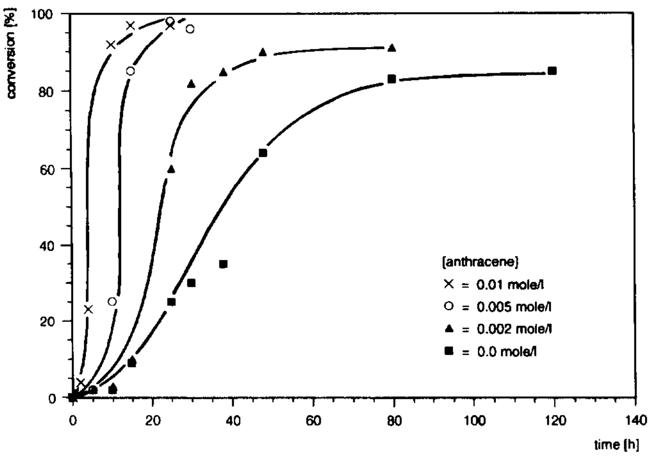


Fig. 1. Influence of anthracene on the rate of reduction of $FeCl_2 \cdot 2THF$ to metallic iron (Fe*) by magnesium powder in THF at room temperature. (1:1 molar ratio; 0.1 mol of $FeCl_2 \cdot 2THF/1THF$). See Experimental section.

For purification of M*, the magnesium salt formed as a by-product must be removed by careful washing with THF, ethanol or water. This procedure may be troublesome and can be avoided by using metal chlorides or acetylacetonates suspended in THF as the starting materials. Since $MgCl_2$ or $Mg(acac)_2$ dissolve *in situ* in the supernatant THF, the metal powders M* can be isolated after the reduction step (3) by simple filtration (Table 1).

$$MX_n + \frac{n}{2}Mg^* \xrightarrow[20^\circ C]{THF} M^* + \frac{n}{2}MgX_2 \qquad (3)$$

M = Fe, Co, Ni, Pd, Pt, Cu, Zn
X = Cl, Br, acac

The specific surface areas of M* were found to be comparable to those obtained by alkali-metal reductions [9], or metal vapor techniques [18]. The dispersion of M* can be increased by carrying out the reduction (3) in a 35 kHz ultrasound cleaning bath. The Ni* resulting from a sonicated batch showed a surface area of 54.7 $m^2\ g^{-1}$, Pd* of 103.4 $m^2\ g^{-1}$, Cu* of 10.5 $m^2\ g^{-1}$, as determined by the BET method. The metal powders M* listed in Table 1 are highly reactive to-

TABLE 1. Preparation of finely divided metal powders (M*) [a]

No.	MX_n	g/mmol	Mg [b] (g/mmol)	Anthracene (g/mmol)	THF (ml)	Reaction time (h)	M* (g)	Composition in %					Specific surface area ($m^2\ g^{-1}$)
								M	Mg	C	H	X	
1 [a]	$NiCl_2$	2.60/20	0.49/20	0.36/2	200	28	1.46	78.9	2.7	12.5	1.3	1.1	7.2
2	$CoCl_2$	5.19/40	0.98/40	0.18/1	200	10	2.62	86.6	3.7	7.0	0.8	3.5	57.3
3	$FeCl_2 \cdot 2\,THF$	8.52/40	0.98/40	0.18/1	200	26	2.90	73.9	3.7	7.7	1.1	0.4	96.2
4	$PdCl_2$	8.85/50	1.2/50	0.55/3	400	6	5.33	90.6	6.8	–	–	1.7	57.6
5	CuCl	9.9/100	1.2/50	1.1/6	400	8	5.90	97.7	0.3	–	–	1.6	6.0
6	$ZnCl_2$	13.6/100	2.4/100	1.1/6	500	5	6.15	97.1	0.7	–	–	2.1	8.1
7	CuBr	14.4/100	1.2/50	0.55/3	300	5	6.10	94.6	0.4	1.3	0.4	4.2	6.6
8	$Fe(acac)_3$ [c]	11.8/33.3	1.2/50	0.55/3	300	0.5	1.0	74.7	10.9	9.4	1.2	-	96.2

[a] For a typical procedure see Experimental section. [b] Mg powder 50 mesh. [c] Fe acetylacetonate.

wards oxidative addition reagents, which may be used for the synthesis of organometallic compounds. For example, Ni* was transformed from the slurry into a bis(aryl)nickel complex at room temperature (eqn. (4)).

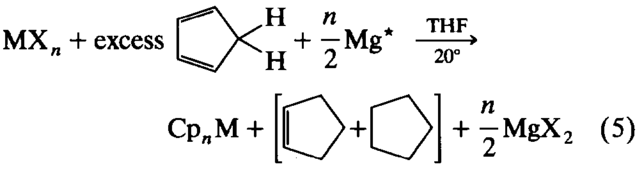
$$2Ni^* + 2C_6F_5J + 2P(C_6H_5)_3 \xrightarrow{41\%} [P(C_6H_5)_3]_2Ni[C_6F_5]_2 + NiJ_2 \quad (4)$$

The fine metal powders M* can be used in heterogeneous catalysis; e.g. for hydrogenation. An application of recent interest is the provision of an easy route to air-stable Ni-doped magnesium powders having an improved ability to take up hydrogen for the purpose of hydrogen and heat storage by reversible Mg/MgH_2 systems [19,20]. Using magnesium anthracene phase-transfer catalysis, the doping step can be brought about quite smoothly; a large excess of Mg, activated with small amounts of anthracene in THF according to (2), is treated with $NiCl_2$ or $Ni(acac)_2$ at room temperature to bring about homogeneous doping of the magnesium surface with highly dispersed Ni particles. The advantages of this procedure lie in the superior kinetics and in the high reversible hydrogen storage capacity (7%) of the resulting Ni-doped Mg in the subsequent hydrogenation/dehydrogenation cycles [14] (see Experimental section).

2.2. *Organo transition metal complexes [15,16]*

There have been isolated reports on the use of elemental magnesium for the reductive synthesis of organo transition metal complexes [21,22], but no generally applicable method for the preparation of transition metal complexes by this method has so far been developed. Starting from the observation that the reaction cycle (2) provides an efficient *in situ* source of highly reactive Mg*, we have worked out a simple preparative route to various types of transition metal complexes of practical importance, such as metallocenes, olefine–metal(0) compounds, η^3-allyl-metal complexes, and phosphine complexes.

For example, Fe, Co, and V salts react smoothly with Mg* in the presence of cyclopentadiene to yield the corresponding η^5-cyclopentadienyl metal complexes (eqn. (5)). The active hydrogen from the CpH is transferred during the reduction step to an excess of cyclopentadiene present in the reaction mixture. Carrying out reaction (5) in an ultrasonic bath (35 kHz) increases the rate considerably and enhances the yields.



M = Fe, Co, V

X = Cl, acac

Table 2 indicates the reaction conditions and shows some typical results.

η^5-cyclopentadienyl cobalt olefine half-sandwich compounds, which cannot be obtained in a single step by previously known methods, are readily accessible by use of anthracene-activated Mg*. For example, $Co(acac)_3$ in the presence of 1,5-cyclooctadiene (COD) and cyclopentadiene reacts vigorously with sonicated Mg* to give, Co(η^4-COD)(η^5-cyclopentadienyl) in one step and in very good yield. An excess of COD takes up the active hydrogen from the cyclopentadiene to give cyclooctene (eqn. (6)).

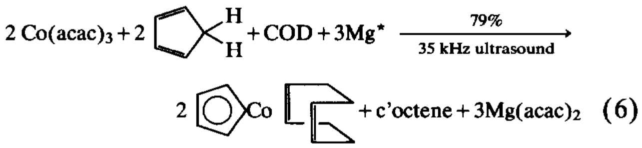


TABLE 2. Synthesis of metallocenes [a]

No.	Complex	Metal salt [mmol/addition time (min)]	Reducing agent/ activator [b], (mmol/mmol)	Cyclopentadienyl compound (mmol)	THF [ml/temperature (°C)]	Yield (%)
1	Cp_2Fe	$FeCl_3$ 100/60	Mg/anthracene 150/3.4	CpH 300	300/65	69
2 [a]	Cp_2Co	$Co(acac)_3$ 100/20	Mg/anthracene 600/6.2	CpH 300	300/60	63.7
3	Ind_2Co	$Co(acac)_3$ 100/40	Mg/anthracene 600/6.2	indene 300	350/60	35.5
4	Cp_3V	VCl_3 100/10	Mg/anthracene 300/6.2	CpH 400	300/65	18.8

[a] For a typical procedure see Experimental section. [b] Ultrasonic bath (35 kHz, continuous HF output 240 W). acac acetylacetonate; Cp, η^5-cyclopentadienyl; CpH, cyclopentadiene; Ind, η^5-indenyl.

Cp–Co half-sandwich compounds are of importance as catalysts for the production of pyridine derivatives from alkynes and nitriles [23–25], and so we have extended reaction (6) to provide a versatile method for making this class of cobalt complexes. The results are summarized in Table 3. As can be seen from a comparison of experiments 12 and 13, the omission of anthracene, *i.e.* the activation catalyst, results in considerably lower yield of the complex or in incomplete reduction. For full experimental details and structural characterizations of the individual compounds, see ref. 24.

Biscycloocta(1,5)diene compounds of Ni, Pt, and Pd have found wide application in organometallic chemistry and in organic synthesis [8,26]. There has been a report of the preparation of $Ni(COD)_2$ from nickel halide and COD by reduction with, *inter alia*, magnesium [27]. However, the product was described as unstable and addition of stabilizers was required. When sonicated Mg* is used, the reductive synthesis of bis(COD)–metal(0) complexes proceeds effectively, and the pure products can be isolated in good yields (eqn. (7)).

$$MX_2 + 2\,COD + Mg^{*} \xrightarrow[35\ \text{kHz ultrasound}]{THF} M(COD)_2 + MgX_2 \qquad (7)$$

M = Ni, Pd, Pt
X = Halide

TABLE 3. Synthesis of CpCo half-sandwich type complexes

No.	Complex	Cobalt salt [mmol/ addition time (min)]	Reducing agent/ activator [a] (mmol/mmol)	Cyclopentadienyl compound (mmol)	Olefine (mmol)	THF [ml/ temperature (°C)]	Yield	Ref. 24
1	Cp Co COD	$Co(acac)_3$ 100/20	Mg/anthracene 300/6.2	CpH 111	COD 250	300/66	79.1	pp. 94, 150
2	Cp Co COD	$Co(OEt)_2$ 100/40	Mg/anthracene 400/7.5	CpH 250	COD 250	400/65	45.1	
3	MeCp Co COD	$Co(acac)_3$ 100/35	Mg/anthracene 300/6.2	MeCpH 110	COD 250	300/67	71.1	p. 150
4	t-butCp Co COD	$Co(acac)_3$ 50/15	Mg/anthracene 150/3.1	t-butCpH 57	COD 125	150/65	41.7	p. 151
5	$SiMe_3Cp$ Co COD	$Co(acac)_3$ 100/20	Mg/anthracene 300/6.2	$SiMe_3CpH$ 110	COD 250	300/65	70.0	p. 154
6	PhenylCp Co COD	$Co(acac)_3$ 100/16	Mg/anthracene 300/6.2	PhenylCpH 90	COD 250	300/69	*ca.* 40	p. 153
7	Ind Co COD	$Co(acac)_3$ 100/40	Mg/anthracene 300/6.2	Indene 250	COD 250	300/65	85.1	pp. 94, 154
8	Ind Co COD	$Co(ac)_2$ 100/35	Mg/anthracene 200/6.2	Indene 250	COD 250	300/65	80.5	
9	Ind Co COD	$CoCl_2$ 100/20	Mg/anthracene 108/6.2	Indene 250	COD 250	300/65	73.8	p. 154
10	Ind Co COD	$Co(acac)_3$ 100/30	Mg/anthracene 300/6.2	Indene 250	COD 250	Diglyme 300/70–88	70.2	
11	Ind Co COD	$Co(acac)_3$ 100/35	Mg/anthracene 300/6.2	Indene 110	COD 110	300/65	51.0	
12 [b]	Ind Co COD	$CoCl_2$ 100/30	Mg act. with J_2 100	Indene 250	COD 250	300/65	19.2	
13 [b]	Ind Co COD	$CoCl_2$ 100/30	Mg act. with MeJ 104	Indene 245	COD 257	300/30	6.0	
14	Ind Co NBD	$Co(acac)_3$ 100/40	Mg/anthracene 300/6.2	Indene 250	NBD 250	300/69	30.5	p. 157
15	Me Ind Co COD	$Co(acac)_3$ 100/20	Mg/anthracene 300/6.2	Me-indene 107	COD 253	300/65	48.3	p. 155
16	$SiMe_3$Ind Co COD	$Co(acac)_3$ 100/20	Mg/anthracene 300/6.2	$SiMe_3$-indene 115	COD 250	300/69	50.6	p. 156
17	η^6-Phenylborinato Co COD	$Co(acac)_3$ 1.99/10	Mg/anthracene 6/0.13	1-Phenyl-1,4 dihydrobora-benzene 2.27	COD 5.09	6/65	42.2	p. 157

[a] Ultrasonic bath (35 kHz, continuous HF output 240 W). [b] Without anthracene for comparison. ac, acetate; acac, acetylacetonate; OEt, ethylate; Cp, η^5-cyclopentadienyl; CpH, cyclopentadiene; Ind, η^5-indenyl; Me, methyl; t-but, tert-butyl; COD, cycloocta-(1,5)-dien; NBD, norbornadiene.

TABLE 4. Synthesis of olefine–metal(0) compounds [a]

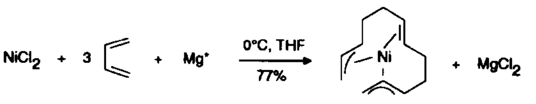
No.	Complex	Metal salt [mmol/addition time (min)]	Reducing agent/ activator [b] (mmol/mmol)	Olefine (mmol)	THF [ml/temperature (°C)]	Yield (%)
1 [a]	$Ni(COD)_2$	$NiCl_2$ 100/–	Mg/anthracene 300/6.2	COD 500	300/0	60
2 [a]	$Pt(COD)_2$	$PtCl_2$ 20/20	Mg/anthracene 20/0.4	COD 150	50/65	45
3	$Pd(COD)_2$	$CODPdCl_2$ 25/30	Mg/anthracene 25/0.5	COD 300	60/–40	15
4	$Mo(butadiene)_3$	$MoCl_5$ 35.8/30	Mg/anthracene 135.8/0.84	Butadiene 23 ml	500/–30	40

[a] For a typical procedure, see Experimental section. [b] Ultrasonic bath (35 kHz, continuous HF output 240 W). COD, cycloocta-(1,5)-diene.

Wilke and Gausing [22] used magnesium metal for the reductive synthesis of tris(butadiene)-molybdenum; but the reaction time was 48 h. With sonicated Mg* the reaction (8) can be completed within 40 min, and the olefine complex isolated in 40% yield.

$$MoCl_5 + \text{butadiene(excess)} + 2.5\ Mg^* \xrightarrow[\text{35 kHz ultrasound}]{\text{THF, 40\%}} Mo(C_4H_6)_3 + 2.5\ MgCl_2 \quad (8)$$

The results obtained in the reductive synthesis of olefine–metal(0) compounds using Mg* are summarized in Table 4. The thermally unstable η^3-allyl metal olefine complexes **3** and **4** are also readily accessible by using Mg* at low temperatures. The organonickel compound **3**, an important intermediate in nickel-catalyzed olefine transformations [28], was first obtained and characterized by Wilke and co-workers [29] by reduction of $Ni(acac)_2$ with organoaluminium in the presence of an excess of butadiene. Use of Mg* as the reducing agent at 0°C in THF gives **3** in very good yield (eqn. (9)).



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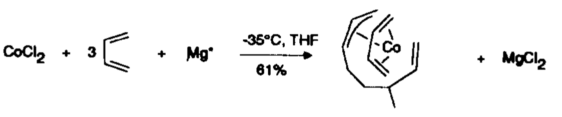
η^3-5-Methylheptadienyl cobalt butadiene **4** was obtained as long ago as 1965 by Natta *et al.* [30] from the reaction of $CoCl_2$ with butadiene and $NaBH_4$ at –30°C. Complex **4** was among the first organocobalt(I) catalysts for the synthesis of pyridines from nitriles and alkynes [23–25]. The low temperature reduction (eqn. (10)) with Mg* provides an easy route to this thermally labile complex.



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A summary of the experimental data for the synthesis of **3** and **4** is given in Table 5.

Phosphine complexes of zero valent transition metals are easily accessible by use of Mg* as the reducing agent. Ethylenebis(tri-*o*-tolylphosphite)nickel(0) (**5**) [31,32], a useful catalyst for many diene reactions [33], has been prepared by reduction of $Ni(acac)_2$ with triethylaluminium in the presence of the ligand. However, this procedure is greatly facilitated by use of the non-pyrophoric Mg* (eqn. (11)).

$$Ni(acac)_2 + C_2H_4 + 2P(o\text{-}OC_6H_4CH_3)_3 + Mg^* \xrightarrow[65\%]{\text{THF, 0°C}} Ni(C_2H_4)[P(o\text{-}OC_6H_4CH_3)_3]_2 + Mg(acac)_2 \quad (11)$$

(**5**)

The synthesis of tris(tri-*o*-tolylphosphite)nickel(0) [34] and the very versatile catalyst $Pd[(P(C_6H_5)_3]_4$ [35] are further examples for the broad applicability of the

TABLE 5. Synthesis of η^3-allyl-metal-olefine compounds [a]

No.	Complex	Metal salt [mmol/addition time (min)]	Reducing agent/ activator [b] (mmol/mmol)	Butadiene (mmol)	THF [ml/temperature (°C)]	Yield (%)
1 [a]	**3**	$NiCl_2$ 100/30	Mg/anthracene 100/2	300	150/0	77
2 [a]	**4**	$CoCl_2$ 100/60	Mg/anthracene 100/6.2	3700	200/–40	61

[a] For a typical procedure, see Experimental section. [b] Ultrasonic bath (35 kHz, continuous HF output 240 W).

TABLE 6. Synthesis of transition metal posphane compounds [a]

No.	Complex	Metal salt [mmol/addition time (min)]	Reducing agent/ activator [b] (mmol/mmol)	Ligand (mmol)	THF [ml/temperature (°C)]	Yield (%)
1	**5**	$Ni(acac)_2$ 100/180	Mg/anthracene 100/6.2	Ethylene gas $P(o\text{-}OC_6H_4CH_3)_3$ 200	300/0–15	65
2	$Ni[P(o\text{-}OC_6H_4CH_3)_3]_3$	$Ni(acac)_2$ 60/20	Mg/anthracene 60/3.7	$P(o\text{-}OC_6H_4CH_3)_3$ 200	180/23	75
3 [a]	$Pd[P(C_6H_5)_3]_4$	$Pd(acac)_2$ 20/20	Mg/anthracene 20/0.45	$P(C_6H_5)_3$ 20	40/65	89.5

[a] For a typical procedure, see Experimental section. [b] Ultrasonic bath (35 kHz, continuous HF output 240 W).

anthracene-activated magnesium in preparative coordination chemistry (eqn. (12))

$$M(acac)_2 + nL + Mg^* \longrightarrow ML_n + Mg(acac)_2 \quad (12)$$

$M = Ni, Pd$

$L = P(C_6H_5)_3, P(o\text{-}OC_6H_4CH_3)_3$

$n = 3$, Ni; 4, Pd

The experimental details are given in Table 6.

Treatment of $Pd(acac)_2$ with Mg powder in the absence of anthracene for 3 h resulted in incomplete reduction of the starting material. After work-up, only small amounts of an impure product were obtained. By use of Mg^* at 65°C, however, the Pd^{2+} is converted into the zerovalent metal–phosphine complex in high yield in 30 min.

3. Experimental details

The experiments were carried out under argon; pre-dried THF was distilled over diethylmagnesium; all metal salts were used in the anhydrous form and anthracene was recrystallized from toluene. Anhydrous $FeCl_2$ (Ventron) was extracted in a Soxhlet apparatus with THF. Magnesium was used in the form of turnings or powder of 50 or 270 mesh (Ventron). Ultrasound: 35 kHz cleaning bath, continuous HF output 240 W.

3.1. Preparation of metal powders (Table 1)

3.1.1. Ni (No. 1)*

To a suspension of 0.49 g (20 mmol) of magnesium powder (50 mesh) in 200 ml of THF were added 0.36 g (2 mmol) of anthracene and 2 drops of ethyl bromide; the mixture was stirred at room temperature until the orange magnesium anthracene precipitated out (2–5 h). Then 2.60 g (mmol) of anhydrous $NiCl_2$ were added, the mixture was stirred at room temperature for 28 h, and the black precipitate filtered off, washed three to five times with THF, and dried *in vacuo* (10^{-3} mbar), to give 1.56 g of a black pyrophoric powder with the composition: Ni, 78.9; Mg, 2.7; C, 12.5; H, 1.3; Cl, 1.1%. The specific surface area of the powder (BET method) was 7.2 $m^2\ g^{-1}$.

3.1.2. M (Table 1, Nos. 2–8)*

Experiments 2–8 were carried out in the same way as for No. 1. Relevant data are given in Table 1.

3.2. Determination of the extent of conversion during the reduction of $FeCl_2 \cdot 2THF$ to Fe^* by Mg powder in THF (Fig. 1)

In each of the four experiments, 243 mg (10 mmol) of Mg powder (particle size 50 mesh) were suspended in 100 ml of THF, the relevant amount of anthracene (0.2, 0.5 and 1.0 mmol) and 1–2 drops of ethyl bromide added, and the mixture stirred for 5 h at room temperature to allow completion of the formation of magnesium anthracene. Subsequently, in each of the experiments 2.70 g (10 mmol) of $FeCl_2 \cdot 2THF$ were added and the suspension was stirred at room temperature. At regular intervals, after interruption of the stirring and allowing the suspension to settle down, a 10-ml sample was taken from the supernatant solution and added to water. The mixture was boiled to remove THF and the solution filtered. The Mg^{2+} content of the water solutions was determined by EDTA titration.

3.3. Preparation of bis(triphenylphosphine)bis(pentafluorophenyl)nickel(II) from a Ni slurry (eqn. (4))*

To a nickel slurry (8.5 mmol) in THF, prepared from nickel chloride (10 mmol), was added iodopentafluorobenzene (2.49 g, 10 mmol) and the mixture stirred for 24 h at room temperature and then for 16 h at 65°C and triphenylphosphine (2.7 g, 10 mmol) then added to the reddish brown mixture. The mixture was stirred at room temperature for 24 h, the solvent was removed under reduced pressure, and the residue dissolved in toluene (25 ml). The mixture was filtered and the filtrate was concentrated to about 10 ml. Methanol (25 ml) was added and the yellow crystalline product separated out immediately and was filtered off. Recrystallization from toluene/methanol gave yellow crystals of bis(triphenylphosphine) bis(pentafluorophenyl)nickel-(II) [36]: 1.61 g (41.3%); m.p. 201–203°C. Elemental analysis: C, 62.72; H, 3.37; P, 6.81; F, 20.58; Ni, 6.28%.

3.4. *Preparation of nickel-doped Mg [37]*

To a suspension of 50.0 g (2.06 mmol) of magnesium powder (270 mesh) in 130 ml of THF were added 0.23 g (1.3 mmol) of anthracene and 2 drops of ethyl bromide. The mixture was stirred at room temperature until the orange magnesium anthracene had separated (about 5 h) and 1.70 g (13.1 mmol) of anhydrous $NiCl_2$ were then added. The mixture was stirred for 20 h and the magnesium powder filtered off, washed with THF and dried under high vacuum, to give 48.0 g of the air-stable magnesium powder doped with nickel, having the composition: Mg, 97.4; Ni, 1.0; C, 0.6; H, 0.7; Cl, 0.2%. A 15.1 g sample of this powder was subjected to a series of 28 hydrogenation-dehydrogenation cycles in a completely automatic electronically controlled apparatus, the hydrogenation pressure and temperature being varied. In the first cycle, hydrogenation was performed at 336°C (oven temperature)/16 bar/5 h, in the following two cycles at 345°C/6 bar/2 h and in the remaining cycles at 270°C/2–6 bar/2–4 h. The dehydrogenation in all cycles was carried out at 350–370°C/2 h under normal pressure. During these cycles the H_2-capacity and the kinetic characteristics of the storage material remained constant. The reversible hydrogen content of the sample was between 6.5 and 7.1 wt.%.

3.5. *Preparation of transition metal complexes*

3.5.1. *Metallocenes (Table 2)*

Cobaltocene (No. 1). A mixture of 1.1 g (6.2 mmol) of anthracene, 300 ml of THF, and 0.1 ml of methyl iodide was added to 14.4 g (600 mmol) of magnesium powder in an inert gas atmosphere, and the mixture was stirred at 20°C. A yellow green solution was formed and orange-colored magnesium anthracene separated after about 2 h. The reaction mixture was sonicated for about 3 h in an ultrasonic bath and then heated with stirring to 60°C. After the addition of 19.8 g (300 mmol) of monomeric cyclopentadiene, the heat source was removed and 35.6 g (100 mmol) of solid cobalt(III)acetyl acetonate were added during 20 min. The mixture became dark brown, with vigorous evolution of heat and refluxing (66°C). The mixture was allowed to cool to 20°C, residual magnesium was removed by filtration through a G-3-glass frit, and the clear dark-brown filtrate evaporated to dryness (max. bath temperature 30°C) under reduced pressure (10^{-3} Torr). The residue was taken up in 500 ml of pentane and any undissolved material filtered off through a G-3 glass frit. The residue on the frit cake was washed several times with a total of 500 ml of pentane until the filtrate was essentially colorless. The clear red-brown filtrate was concentrated to *ca.* 200 ml and the complex allowed to crystallize out at −80°C. The supernatant mother liquor was removed under pressure and washed 2–3 times with *ca.* 50 ml of pentane cooled to −80°C. Drying *in vacuo* (0.1 Torr) gave 12.4 g (63.7 mmol, 63.7% yield) of pure cobaltocene as black-violet crystals, melting (in an inert gas atmosphere) at 172.5°C.

3.5.2. *Cp–Co half-sandwich-type compounds (Table 3)*

For full experimental details, see ref. 24, pp. 147–160.

3.5.3. *Olefine–metal(0) compounds (Table 4)*

$Ni(COD)_2$ (No. 1). The atmosphere above a mixture of 7.2 g (300 mmol) of magnesium powder and 1.1 g (6.2 mmol) of anthracene (Mg/Ant = 48.1) was pumped out and replaced by one of argon. The mixture was suspended in 300 ml of THF (dried over $LiAlH_4$) and 0.1 ml of ethyl bromide was added. After a few minutes, the solution became yellow-green and orange-colored magnesium anthracene soon began to precipitate. The reaction was normally over within 3 h. The mixture was cooled to 0°C and 61 ml (54 g, 500 mmol) of cycloocta-(1,5)-diene and *ca.* 15 ml of liquid butadiene were siphoned in with stirring, and 12.96 g (100 mmol) of solid anhydrous nickel chloride then added. The suspension soon became dark in colour and was set aside overnight with cooling with ice. (Very little heat evolution was observed.) The solution, which had become deep violet, was freed from residual magnesium by filtration through a D-4-frit and the magnesium was washed with 50 ml of THF (recovered Mg *ca.* 3.5 g), then kept for 3 h at −80°C. The resulting fine yellow crystals were filtered off at −80°C through a D-4-jacket frit and rinsed twice with a little THF and pentane, freed from the deep violet solution, the pale yellow colour of the $Ni(COD)_2$ now being visible. The product was dried for 30 min at 23°C under an oil pump vacuum and subsequently transferred to a suitable vessel. (This intermediate isolation is not absolutely essential). Yield: 21.0 g.

For purification and for complete separation from $NiCl_2$, the $Ni(COD)_2$ was transferred to a medium-sized D-4-frit, and treated with *ca.* 200 ml of toluene warmed to 40°C. The solution obtained was stirred then rapidly introduced under pressure into a receiver cooled to 0°C. The toluene washing was repeated until the crystals were substantially dissolved. The filtrate was kept for 2 h at −80°C and the resulting crystals filtered off through a D-4-frit at −80°C, washed twice with a little pentane, dried and transferred. Yield: 16.5 g of fine lemon-yellow flakes of $Ni(COD)_2$ = 60% of the theoretical (based on $NiCl_2$). Elemental analysis: Found: C, 69.89; H, 9.06; Ni, 21.12%. Calc.: C, 69.86; H, 8.79; Ni, 21.34%.

$Pt(COD)_2$ (No. 2). After 0.49 g (20 mmol) of Mg had been activated with 71 mg (0.4 mmol) of anthracene in 50 ml of THF, the orange reaction mixture was heated to 65°C, and 16.2 g (150 mmol) of 1,5-cyclooctadiene were added subsequently. Then 5.32 g (20 mmol) of solid platinum(II) chloride was introduced during 20 min, the mixture becoming red-brown with a vigorous heat evolution (warming up to 79°C). After being allowed to cool to 23°C, the mixture was evaporated to dryness under reduced pressure (10^{-3} Torr) and the residue extracted six times with 100-ml portions of toluene. The brown solution was filtered through an Al_2O_3 column (5 cm deactivated with 7% of H_2O) and the filtrate was concentrated *in vacuo* to *ca.* 30 ml. The mother liquor was removed under pressure from the light coloured precipitate, which was then washed with cold toluene, to give bis-cycloocta-(1,5)-diene platinum (3.7 g, 9 mmol, 45%). Mass spectrum: *m/e* 410 (M^+); 302.

3.5.4. η^3-Allyl metal complexes (Table 5)

η^3,η^2,η^3-dodeca-2,6,10-triene-1,10-diyl nickel (No. 1). Anthracene (0.36 g, 2 mmol) and 0.1 ml of ethylbromide were added to 2.43 g (0.10 mol) of magnesium powder (50 mesh) in 150 ml of THF and the mixture stirred at room temperature until the orange-coloured magnesium anthracene had separated (*ca.* 2 h), and 26 ml (0.3 mol) of liquid butadiene were then added with stirring at 0°C. Subsequently, 13.0 g (0.10 mol) of anhydrous $NiCl_2$ was added with stirring during 30 min. The mixture was stirred for 20 h at 0°C then cooled to −78°C, and $MgCl_2$, residual magnesium and $NiCl_2$ were filtered off at that temperature, and the solid on the filter was washed with cold THF. The deep red filtrate contained 82.5% of the nickel used in soluble form. A 10-ml sample of the filtrate (275 ml in all) took up 328 ml of H_2 on hydrogenation (25°C/1 bar), metallic nickel separating out quantitatively. The removal of THF and subsequent distillation under a high vacuum left 0.62 g of saturated hydrocarbons having the following composition (in % by weight, according to analysis by gas chromatography): n-dodecane 76.8, cyclododecane 10.3, n-octane 3.1 and n-hexadecane 0.5% (remainder unknown compounds). The quantity of n-dodecane corresponded to a yield of η^3,η^2,η^3-dodeca-2,6,10-triene-1,10-diyl nickel of 77% (based on the $NiCl_2$ used). The molar ratio of Ni to n-dodecane was 1.00:0.93 (theoretical 1:1).

The procedure was repeated using the same quantities of materials, but without anthracene. In this case, only 37% of the nickel used was present in solution after filtration at low temperatures.

η^3-(5-Methylheptadienyl)η^4-(butadiene)cobalt (No. 2). After 2.4 g (100 mmol) of magnesium powder had been activated with 1.1 g (6.2 mmol) of anthracene in 200 ml of THF, the orange mixture was cooled to −40°C. After the addition of 200 g (3700 mmol) of liquid 1,3-butadiene, 13.0 g (100 mmol) of solid Co^{II} chloride were introduced over a period of 60 min, during which the colour of the mixture changed from grey-green to grey-brown, with a slight increase in temperature (max. −34°C). After overnight stirring at −40°C, the mixture was cooled to −80°C and filtered at −80°C to remove any insoluble or precipitated materials at −80°C. The clear brown filtrate was evaporated under reduced pressure (10^{-3} Torr) at −80°C to −30°C, the residue taken up in 150–200 ml of ethanol, and the complex crystallized at −90°C to −100°C. The supernatant mother liquor was removed under pressure and the crystals washed twice with 20 ml of pentane cooled to −100°C. Drying under reduced pressure (10^{-3} Torr) at −30°C gave 13.5 g (60.9 mmol, 60.8% yield) of η^3-(5-methyl-heptadienyl)η^4-(butadiene)cobalt. Mass spectrum: *m/e* 222 (M^+).

3.5.5. Phosphine complexes (Table 6)

$Pd[P(C_6H_5)_3]_4$ (No. 3). After activation of 0.49 g (20 mmol) of Mg with 0.1 mg (0.45 mmol) of anthracene in 40 ml of THF, the orange mixture was heated to 65°C and treated with 21.0 g (80 mmol) of triphenylphosphine. Then 6.1 g (20 mmol) of solid $Pd(acac)_2$ were added during 20 min. The complex precipitated out from the dark orange reaction mixture with evolution of heat (up to 69°C). After cooling of the solution to 23°C, the crystals were filtered off on a G-3-frit and washed with 30 ml of pentane. Drying *in vacuo* (10^{-1} Torr) gave 20.6 g (17.9 mmol, 89.5% yield) of yellow crystals melting at 116°C.

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