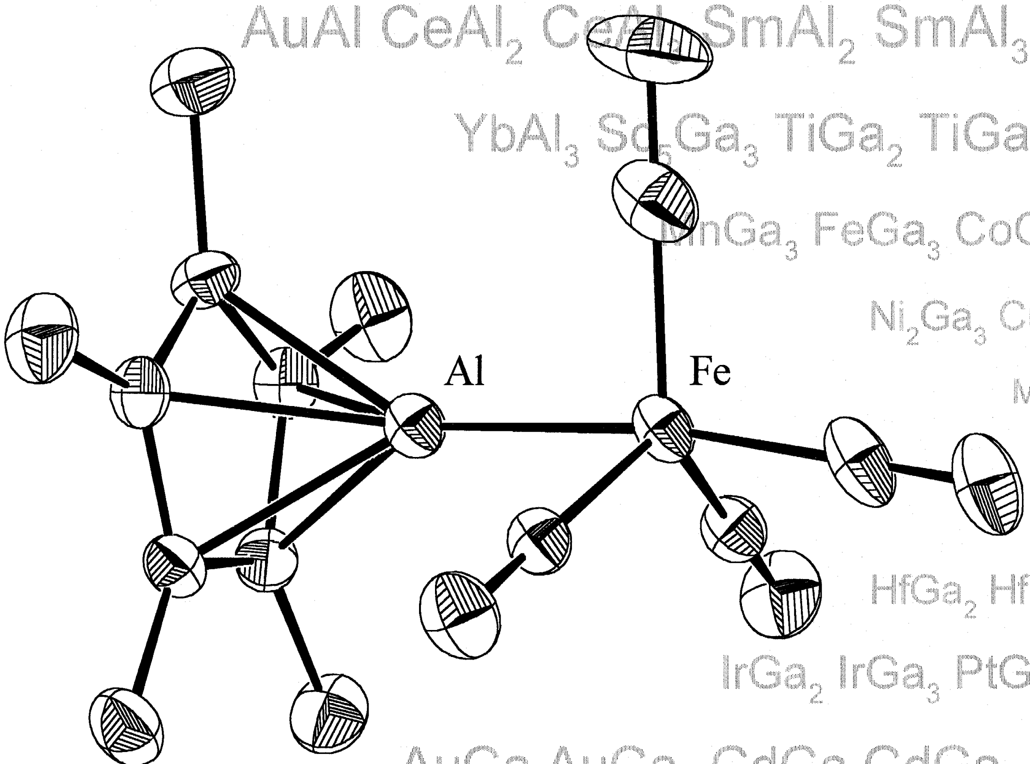
ANGEWANDTE
CHEMIE ©WILEY-VCH

$ScAl_2$
$TiAl$ $TiAl_3$
VAl $CrAl_4$ $MnAl$
$FeAl_2$ $FeAl_3$ $CoAl$ $NiAl$
$NiAl_3$ $CuAl_2$ YAl_2 $ZrAl$ $ZrAl_2$
$ZrAl_3$ Zr_2Al_3 $MoAl_2$ $MoAl_3$ $RuAl$ $RuAl_2$
$RhAl$ $PdAl$ Pd_2Al_3 $PdAl_3$ $LaAl_2$ $HfAl_2$ $HfAl_3$
$TaAl_3$ WAl_4 $ReAl_2$ $OsAl_2$ $IrAl$ Pt_2Al_3 $PtAl_2$ $PtAl_3$
$AuAl$ $CeAl_2$ $CeAl$ $SmAl_2$ $SmAl_3$ $ThAl_2$ $YbAl_2$
$YbAl_3$ Sc_5Ga_3 $TiGa_2$ $TiGa_3$ V_2Ga_5 $CrGa$
$MnGa_3$ $FeGa_3$ $CoGa$ $CoGa_3$ $NiGa$
Ni_2Ga_3 $CuGa_2$ YGa_2 $ZrGa$
Mo_3Ga $RuGa_3$ $RhGa_2$
$RhGa_3$ $PdGa$
$LaGa$ $LaGa_2$ $HfGa$
$HfGa_2$ $HfGa_3$ $TaGa_3$ OsG
$IrGa_2$ $IrGa_3$ $PtGa$ $PtGa_2$ Pt_2Ga_3
$AuGa$ $AuGa_2$ $GdGa$ $GdGa_2$ $HoGa_2$ $PrGa_2$
$SmGa_2$ $TbGa_2$ $ThGa_2$ $CeGa_2$ Sc_3In Ti_3In_4 $CrIn_3$
Mn_3In $CoIn$ $CoIn_2$ $NiIn$ Ni_2In_3 Cu_2In YIn_3 $ZrIn_3$
$RuIn_3$ $RhIn$ $RhIn_3$ $PdIn$ Pd_2In_3 $PdIn_3$ $LaIn_3$ Hf_3In_4
$IrIn_3$ $PtIn_2$ $AuIn$ $AuIn_2$ $CeIn_3$ $NdIn_3$ $TbIn_3$ Th_2In



Coordination Chemistry of Aluminum, Gallium, and Indium at Transition Metals

Roland A. Fischer* and Jurij Weiß

The surge in the interest in the coordination chemistry of aluminum, gallium, and indium at transition metals is attributed to impulses that have only recently become effective and which originate from two different motivations. One stems from the understanding that organometallic compounds are potential precursors for applications in the field of new materials, and the other from the resurgence of the chemistry of low-valent Group 13 metals (earth metals), which is currently being extended to the coordination chemistry at d-block metals. A special highlight is the compound $[Ni(InR)_4]$ ($R = C(SiMe_3)_3$), a first example for the existence of complexes that are homoleptic with respect to the earth metal as ligator. This compound and the complexes $[\{CpNi{-}AlCp^*\}_2]$, $[Cp^*Al{-}Fe(CO)_4]$, and $[(CO)_4Fe{-}GaAr^*]$ ($Ar^* = $ 2,6-bis(2,4,6-triisopropylphenyl)phenyl) illustrate the lively development and the current trends in this field. A series of reports on the quantum chemical description of the bonding have originated not least in connection with the debate on the postulated Fe–Ga triple bond in the complex $[(CO)_4Fe{-}GaAr^*]$. According to these theoretical papers the very polar M–E bonds of the different types of complexes fit well into the Lewis donor/acceptor concept for metal–ligand bonds. Multiple bonds in the traditional sense play only a minor role. Remarkably little is known about the reactivity of the M–E complexes if one disregards the chemistry relevant for metal-organic chemical vapor deposition (MOCVD).

Keywords: aluminum · chemical vapor deposition · density functional calculations · gallium · indium · metal–metal interactions

1. Introduction

Complexes with M – E bonds between d-block metals (M) and the earth metals aluminum, gallium, indium, and thallium (E) have a long tradition. Hieber, pioneer of systematic metal carbonyl chemistry, reported in 1942 the high-pressure carbonylation of a mixture of finely dispersed indium and cobalt to form $[In\{Co(CO)_4\}_3]$.[1] The existence of two-center, two-electron bonds, σ(In–Co), was later confirmed crystallographically by Robinson and Schussler.[2] Since then this chemistry has been stimulated time and again with new goals. Complexes of d-block metals and aluminum initially became important in the context of olefin polymerization by Ziegler–Natta catalysts. In 1960 Natta et al. reported a red, diamagnetic compound, which they obtained by treating $AlEt_3$ with $[Cp_2TiCl_2]$.[3] They originally considered the product to be a complex with a covalent Ti–Al bond comparable to the above-mentioned In–Co complex.[4] As we know today, typical M/Al complexes, though, involve bridging structures M-X-Al ($X = Cl, H, CO, CR_n$) and covalent M–Al bonds are absent.[5–7] The first complex with an σ(M–Al) bond, the Lewis acid/base adduct $[Cp(CO)_2Fe{-}AlPh_3]^-$[11] originates from the chemistry of metal bases, in which compounds of the type ER_3 (R = alkyl, aryl) serve as probes for Lewis base centers.[8–10]

Since the discovery of the Fischer-carbene and -carbyne complexes[12] the coordination chemistry and the bonding of carbene analogues or, more accurately, "isoelectronic" fragments of the higher homologues of carbon as well as neighboring main group elements have received unbroken attention. Two more recent examples are the Fe–Ge and Fe–Ga complexes $[\{Cp^*(CO)_2Fe{-}GeMe_2(dmap)^+\}]$ (dmap = 4-dimethylaminopyridine)[13] and $[(CO)_4Fe{-}GaAr^*]$ ($Ar^* = $ 2,6-bis(2,4,6-triisopropylphenyl)phenyl).[14] Ogino et al. discuss a Fe–Ge double bond, Robinson et al. refer to a Fe–Ga triple bond. The *cationic* Fe–Ge system prepapred by Ogino et al. is isoelectronic to the *neutral* gallium complex $[Cp(CO)_2Fe{-}GaR_2(py)]$ ($R = \eta^1\text{-}C_5H_4Me$),[15] the *neutral* Fe–Ga complex of Robinson et al. formally corresponds to a *cationic* Fischer-carbyne.[16–21] Since the mid-1980s the study of unusual multiple bond relations has shaped the chemistry of complexes from main group elements and d-block metals. This field was established by work by, among others, Huttner

---

[*] Prof. Dr. R. A. Fischer, Dr. J. Weiß
Lehrstuhl für Anorganische Chemie II der Universität
D-44780 Bochum (Germany)
Fax: (+49)234-7094-174
E-mail: rfischer@aci.ruhr-uni-bochum.de

et al. on inidene complexes[22] and by Herrmann et al. on complexes and metal cumulenes with substituent-free main group elements,[23] and has been covered in a series of review articles and monographies.[24–29] In comparison to the elements of Groups 14, 15, and 16 the respective chemistry of Group 13 (earth metals) has not attracted the same attention.[30] Important general summaries of synthetic and structural chemical conclusions have been compiled by M. J. Taylor (1975), A. T. T. Hsieh (1975), N. C. Norman et al. (1990), and P. P. Power et al. (1996).[31–34]

The recent surge in the interest in the coordination chemistry of aluminum, gallium, and indium at d-block metal fragments since the beginning of the 1990s stems from the finding that organometallic compounds are potential precursors for a whole host of applications in material science. Prototypical of this trend is the development of alternative precursors for the generation of III/V semiconductor layers (GaAs, InP) by chemical vapor deposition (CVD).[35–39] One basic idea that was taken up by many groups is the concept of single-source precursors. For compound semiconductors such as GaAs, precursors were developed which contain the atoms relevant for the material, Ga and As, covalently linked in one *single* molecule, and which indeed allow the deposition of the crystalline material in thin layers,[40–42] for example, GaAs or currently especially important: GaN. Accordingly single-source precursors were synthesized for other material systems like II/IV semiconductors, oxides, hard materials like carbides, borides, or nitrides, and analyzed in view of their suitability for MOCVD.[41–42] The concept of the single-source precursor also proved to be effective for intermetallic phases, as was shown among others by Kaesz et al., who described the deposition of the β-CoGa phase of the complex $[(CO)_4Co{-}GaCl_2(thf)]$ by a MOCVD method.[43, 44] The interest in this intermetallic phase in form of a thin layer comes from the fact that certain binary intermetallic phases of earth metals and d-block metals, for example Co/Ga, are suitable as interface-stable, epitaxial contact metals for (ideal) Schottky barriers and Ohmic contacts on III/V semiconductor surfaces (see the frontispiece of this article). The β-CoGa phase can be grown onto GaAs(100) epitaxially. The heteroepitaxial system forms an atomically abrupt interface, which is stable to diffusion of As up to 800 °C. We performed a series of experiments along these lines with the aim of preparing optimized precursors for the deposition of β-CoGa and related intermetallic phases on III/V semiconductor surfaces.[38, 41, 46–50] Thus, initially the coordination chemistry of aluminum, gallium, and indium at selected d-block metals had to be re-examined from the new perspective of using these complexes as precursors for MOCVD. Of special importance was the chemistry of organo-element fragments ER_a and their donor-stabilized derivatives $ER_a(L)_b$ ($a, b = 1, 2$; R = H, alkyl, aryl, Cp*, etc.). The required properties of MOCVD precursors are: volatility and long-term stability of the compounds under evaporation conditions, low heteroatom content in the ligand sphere around both metal centers (ideally mainly hydrocarbon ligands), and a bond as strong as possible between the atoms that constitute the layer. This had to be achieved for the combinations M/E.[51–64]

In parallel the chemistry of low-valent earth metal compounds also received significant attention. Examples are the cluster $[(Cp^*Al)_4]$,[65, 66] its alkyl analogues $[(ER')_4]$ and $[R''_2E{-}ER''_2]$ ($R' = C(SiMe_3)_3$, $R'' = CH(SiMe_3)_3$, E = Al, Ga, In)[67–73] and the anions $(R''_2Al{-}AlR''_2)^-$[74, 75] or $(Ar^*Ga{-}GaAr^*)^{2-}$.[76] Thus regardless of the aims mentioned

Roland A. Fischer, born in Rosenheim, Germany, in 1961 studied chemistry at the Technische Universität München (1981–1986). In 1989 he received his doctorate for work on alkyne complexes of rhenium under the guidance of W. A. Herrmann. After a postdoctoral fellowship at the University of California at Los Angeles with H. D. Kaesz (1989–1990), he returned to the Technische Universität München and completed his habilitation in 1995 on the coordination chemistry of aluminum, gallium, and indium at transition metals and on the use of these complexes as MOCVD sources for intermetallic phases. From 1996 to 1997 he was Professor for Inorganic Chemistry at the Ruprecht-Karls-University Heidelberg, and in 1998 he moved to the Ruhr-Universität Bochum. His scientific work has been honored among others with the Heinz-Meier-Leibnitz award from the Bundesministerium für Bildung und Forschung (Federal Ministry for Education and Science) (1993), a Karl-Winnacker scholarship (1995), and the award of the Alfried-Krupp-von-Bohlen-und-Halbach Foundation (1996). His research interests include the coordination chemistry of main group elements at transition metals, MOCVD of metals and semiconductors (especially gallium nitride) as well as the organometallic precursor chemistry for nanoscale materials (surfaces, colloids, ceramic compounds).


R. A. Fischer


J. Weiß

Jurij Weiß, born 1969 in Dachau, Germany, studied chemistry at the Technische Universität München (1989–1995). He completed his PhD thesis on the synthesis, structure and bonding of new aluminum and indium complexes, and the CVD functionalization of self-assembled organic monolayers at the Ruprecht-Karls-Universität Heidelberg in 1997. Since 1998 he is a member of the scientific staff at the Lehrstuhl II für Anorganische Chemie der Ruhr-Universität Bochum.

above the interests in this latter field were more and more directed towards the coordination chemistry of organoelement fragments to d-block metals. Especially fragments of the RE type played an important role, in which E exhibits the low formal oxidation state +1 and the substituents R are sterically demanding. Isolable RE compounds of this type were used as starting materials for complex syntheses. Noteworthy is the compound $[Ni(InR)_4]$ ($R = C(SiMe_3)_3$),[77] which represents a first example of the existence of complexes that are homoleptic with regard to an earth metal as ligator. This example and the complexes $[\{CpNiAlCp^*\}_2]$,[78] $[Cp^*Al{-}Fe(CO)_4]$,[79] and$[(CO)_4Fe{-}GaAr^*]$ (Ar^* = 2,6-bis(2,4,6-triisopropylphenyl)phenyl]$^{[14]}$ indicate the lively development and the current trends in this field.

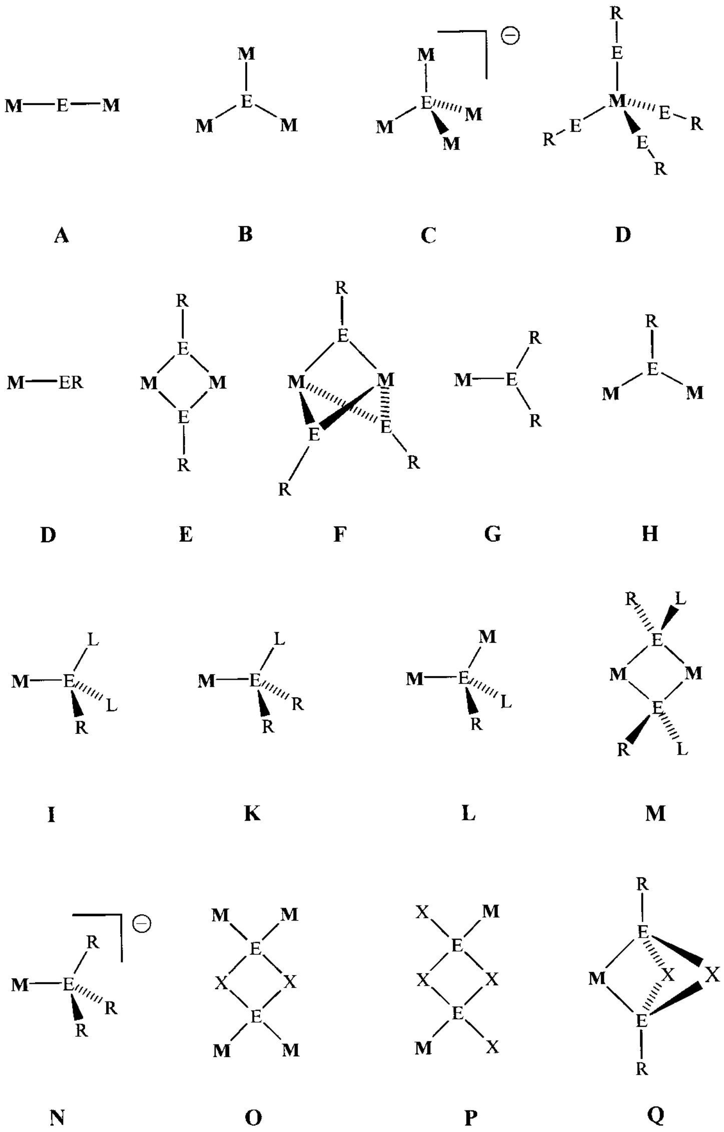


Figure 1. Structure types of M–E complexes (L = neutral 2e-σ donor ligand).

2. Constitutions and Structure Types

The main new development during the last few years has centered on the establishment of the chemistry of organo R_aE fragments (E = Al, Ga, and In; $a = 1$ and 2) in the coordination sphere of d-block metals. The steric shielding of the low-valent centers E as well as the intramolecular adduct stabilization proved to be successful guidelines. Both concepts have long-been known in different contexts but have only recently been increasingly used in the coordination chemistry of earth metals. The summary of representative results and the discussion of the ensuing perspectives is the main topic of this review.

For a better classification of the new results first of all a concise but comprehensive survey of the known constitutions and structures of M–E complexes (M = d-block metal, E = Al, Ga, In, or Tl) is given (Figure 1). Excluded are all those complexes which either do not contain a covalent or donor–acceptor bond between M–E or do have a heteroatom bridge between M and E in addition to the M–E bonds (here, heteroatoms are all those atoms except M and E). The types M_2E, M_3E, and M_4E (**A**–**C**) correspond to compounds containing substituent-free centers E, which are only di, tri-, or tetra-coordinated by d-block metal fragments M (homoleptic substitution with regard to E as center). Among these the monomeric, symmetrically substituted complexes of type **B**, being derivatives of the element trihalides EX_3, naturally form the biggest group. Their chemistry, especially for In and Tl, has been studied mainly by Norman et al. and is reviewed elsewhere.[33, 106–108] In comparison there is apparently only one representative with linear dicoordinate E, namely $[(CO)_5Cr{-}Tl{-}Cr(CO)_5]^-$ (Figure 1, type **A**).[109] For structure type **C** there are only few examples which have to be regarded as "ate" complexes or Lewis base adducts to the M_3E type **B**. Recently complexes have been found in which monoalkyl units RE (R = Cp*, $C(SiMe_3)_3$, Ar*) appear as formal CO analogues, and in terminal position (type **D**), or $\mu^{2,3}$-bridged (types **E** and **F**, Figure 1 and Scheme 5). Compounds displaying these structural elements are the subject of lively debate.[110] Noteworthy contributions in this area have been made by H. J. Haupt et al. In the sense of an isolobal relation between the alkyl group R and the 18e fragment $[(CO)_5M]^-$ (M = Mn, Re), the fragments RE and $[\{(CO)_5M\}E]$ correspond to each other. Metal carbonyl clusters in which the units $[\{M(CO)_5\}E]$ with E as ligator adopt CO-analogous, M–M bridging positions (type **E**), are also known from work by Haupt et al. (Figure 1).[111–114] As deduced from the alkyls ER_3, the donor-free complexes of types MER_2 (**G**) and M_2ER (**H**) with a tri-coordinate center E with sterically less demanding alkyl groups ($R = CH_3$, Et) for thermodynamic reasons often tend to decompose into the homoleptic products M_3E (**B**) and R_3E. Steric shielding (bulky alkyl groups and/or metal fragments M) stabilizes the structures **G** and **H** kinetically. A lot of complexes with tetra-coordinate centers E of the general formula $[M_aE(R,X)_b(L)_c]$ ($a+b+c=4$, types **I**–**N**) also do exist. In the case of simple groups R such as methyl or halide the complexes of type **D** are *unknown*, but these and the very rare representatives of type **G** and **H** have been isolated in the form of adducts (L = py, C_4H_8O, NR_3, tmeda, dmf, etc.): types **I**–**M** (Figure 1).

Complexes containing the d-block metal fragment as Lewis base complete the family: type **N** (R = alkyl or halide).

Halide-containing complexes with EX, EX_2, or ERX fragments in general form dimeric halide-bridged structures $[\{M_2EX\}_2]$ (type **O**) or $[\{MEX_2\}_2]$ (type **P**; (Figure 1). Starting from here with Lewis bases L (e.g. coordinating solvent molecule) the tetra-coordinate monomers of the types **K** and **L** are accessible. To our knowledge there is only one single example of form **Q**. It is a special case with intramolecular halide bridges. A consequence of the fact that most of the constitutions and structures are derived from the basic trihalides or trialkyl compounds EX_3 and ER_3, respectively, and their coordination chemistry is that the ratio of the metal atoms M and E in complexes typically is $M/E \geq 1$. Complexes that contain more than one earth metal per d-block metal are remarkably rare. In total only eight of these compounds have been described, which are listed in Table 1.

The type **D** complex $[Ni(InR)_4]$ ($R = C(SiMe_3)_3$, Figure 1) is quite interesting, as it can be viewed as an inverted type **C**, now homoleptic with regard to the substitution at the d-block metal. Moreover, it is notable from this overview that the examples from indium chemistry are dominant, followed by thallium and gallium, whereas the aluminum chemistry takes a special position. Even the corresponding chemistry of boron at metal centers, recently summarized in this journal, shows more examples.[115] The few crystallographically verified complexes with nonbridged M–Al structural elements are shown in Table 1. It is also remarkable that the majority of the described M–E compounds (including E = B) contain metal carbonyl fragments $\{L(CO)_nM\}$ (L = CO, PR_3, Cp). Complexes without CO ligands, for example those carrying only hydrocarbon-ligands or those stabilized by phosphane ligands, are extremely rare. Therefore the Ir–In complex $[(Me_3P)_3Ir(H)(Et)(InEt_2)]$, the Pt–Ga and Pt–In complexes $[L'_2Pt(R)(ER_2)]$ (E = Ga, In; Figure 2), which do correspond to type **G** [see also Eqs. (6) and (7)], and the Au–In cluster $[(dppe)_2Au_3In_3Cl_6(thf)_6]$, which belongs to type **K** (Figure 3) have to be emphasized.[105]

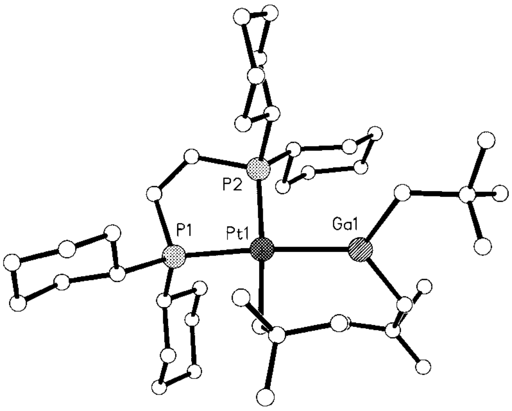


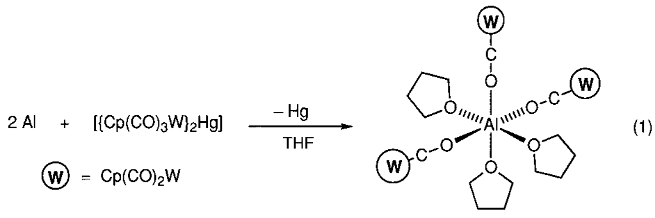
Figure 2. Molecular structure of [*cis*-$(Cy_2PCH_2CH_2Pcy_2)(Np)Pt–GaNp_2$] in the crystal. Np = neopentyl.[51]

Table 1. Selected examples for structurally characterized M/E complexes.

Compound	Structure	M/E	Ref.
aluminum complexes			
$[(CO)_5W–Al(R)(L_2)]$	**I**	1	[80]
($R = Cl$, Et, *t*Bu; L_2 = tmeda, tmpda)			
$[(CO)_4Fe–AlCp^*]$	**D**	1	[79]
$[(CO)_5CrAlCp^*]$	**D**	1	[172]
$[Cp(CO)_2Fe–Al(iBu)(R^N)]$	**K**	1	[60]
$[Cp(CO)_2Fe–AlPh_3]^-$	**N**	1	[11]
$[\{Cp(CO)_2Fe\}_2AlAr]$	**H**	2	[81]
$[Cp(CO)_2Fe–Al(tmp)_2]$	**G**	1	[82]
$[Co_2(CO)_6(\mu\text{-}AlCp^*)_2]$	**E**	1	[83]
gallium complexes			
$[(CO)_5Cr–GaCp^*]$	**D**	1	[84]
$[(CO)_5Cr–Ga(R)(tmeda)]$	**I**	1	[80, 85]
($R = Cl$, Me)			
$[\{(CO)_4Fe–Ga(C_2H_3)(thf)\}_2]$	**M**	1	[86]
$[(CO)_4Fe–GaCp^*]$	**D**	1	[84]
$[(CO)_4Fe–GaAr^*]$	**D**	1	[14]
$[(CO)_4Fe–GaCl(tmeda)]$	**I**	1	[87]
$[Fe_2(CO)_6(\mu\text{-}GaCp^*)_3]$	**F**	2/3	[84]
$[Fe_2(CO)_6\{\mu\text{-}GaSi(SiMe_3)_3\}_2(\mu\text{-}CO)]$	**F**	1	[88]
$[Fe_2(CO)_6\{\mu\text{-}GaSi(SiMe_3)_3\}_3]$	**F**	2/3	[88]
$[\{Cp(CO)_2Fe\}_4]Ga_4S_4$	**P**	1	[89]
$[(CO)_4Fe–Ga(Me)Fe(CO)_4]^{2-}$	**H**	2	[90]
$[Ru(CO)_3\{GaCl(thf)_2\}\{GaCl_2(thf)\}_2]$	**I/K**	1/3	[91]
$[Co_2(CO)_6(\mu\text{-}GaCp^*)_2]$	**E**	1	[84]
indium complexes			
$[(CO)_5CrInCp^*]$	**D**	1	[173]
$[(CO)_5Cr–In(Br)Cr(CO)_5]^{2-}$	**H**	2	[92]
$[\{(CO)_5Cr–InBr(thf)_\infty]$	**I**	1	[93]
$[(CO)_5W–In\{HB(3,5\text{-}Me_2pz)_3\}]$	**D**	1	[94]
$[\{Mn_2(CO)_8[\mu\text{-}InC(SiMe_3)_3]\}_2]$	**E**	1	[95]
$[Cp(CO)_2Mn–InAr^*]$	**D**	1	[96]
$[Cp(CO)_2Fe–In(R^N)_2]$	**K**	1	[59]
$[(CO)_4Fe–In\{HB(3,5\text{-}Me_2pz)_3\}]$	**D**	1	[94]
$[Fe_2(CO)_6\{\mu\text{-}InC(SiMe_3)_3\}_3]$	**F**	2/3	[97]
$[\{(Me_3Si)_3C–In(\mu\text{-}Cl)\}_2\{Fe(CO)_4\}]$	**Q**	1/2	[98]
$[Co_2(CO)_6\{\mu\text{-}InC(SiMe_3)_3\}_2]$	**E**	1	[99]
carbonyl-group-free d-block metal/earth metal complexes			
$[\{Cp_2Ti–AlEt_2\}_2]$	**G**	1	[4]
$[\{Cp^*(\eta^2\text{-}C_2H_4)Co–Al(C_2H_5)\}_2]$	**E**	1	[100]
$[Cp(PMe_3)_2Rh–AlMe(Cl)(\mu\text{-}Cl)AlMe_2(Cl)]$	**K**	1/2	[101]
$[Cp(PMe_3)_2Rh–AlMe_2(\mu\text{-}Cl)AlMe_2(Cl)]$	**K**	1/2	[101]
$[\{CpNiAlCp^*\}_2]$	**E**	1	[78]
$[Ni\{GaC(SiMe_3)_3\}_4]$	**K**	1/4	[73b]
[*cis*-$(Cy_2PCH_2CH_2PCy_2)(Np)PtGaNp_2$]	**G**	1	[51]
$[IrH(Et)(InEt_2)(PMe_3)_3]$	**G**	1	[102]
$[\{[Cp(PEt_3)Ni]_2InCl\}_2]$	**O**	2	[15b]
$[\{Cp(PEt_3)Ni\}_3In]$	**B**	3	[15b]
$[Cp(PPh_3)Ni–InBr_2(OPPh_3)]$	**K**	1	[103]
$[Cp^N(PMe_3)Ni–InI_2]$	**K**	1	[104]
$[Ni\{InC(SiMe_3)_3\}_4]$	**D**	1/4	[77]
[*cis*-$(Cy_2PCH_2CH_2PCy_2)(Np^{Si})Pt–GaNp_2^{Si}$	**G**	1	[54]
$[(dppe)_2Au_3In_3Cl_6(thf)_6]$	**K**	1	[105]

Ar = 2-(dimethylaminomethyl)phenyl; Ar* = 2,6-bis(2,4,6-triisopropylphenyl)-phenyl; Cp = η^5-C_5H_5; Cp* = η^5-C_5Me_5; Cp^N = [2-(dimethylamino)ethyl]cyclopentadienyl; Cy = cyclohexyl; dppe = 1,2-bis(diphenylphosphanyl)ethane; Np = neopentyl; Np^{Si} = trimethylsilylmethyl; pz = pyrazolyl; R^N = 3-(dimethylamino)propyl; tmeda = *N,N,N′,N′*-tetramethylethylendiamine; tmp = 2,2,6,6-tetramethylpiperidine; tmpda = *N,N,N′,N′*-tetramethylpropylendiamine.

A survey of CO-free complexes is given in Table 1. Aluminum centers that are not shielded by sterically demanding groups or by base-adduct formation in the case of metal carbonyl fragments tend to form isocarbonyl structures M-CO-Al. A classic example for this is the compound $[\{Cp(CO)_3W\}_3Al(thf)_3]$, which is obtained by transmetalation from Al and $[\{Cp(CO)_3W\}_2Hg]$ in THF, the structure of which does not correspond to type **B** (or a THF adduct) that is well known for Ga and In chemistry but contains the structural element W-CO-Al [Eq. (1)].[116] Suitable steric and coordinative shielding allows M–Al bond formation (Table 1). The



(1)

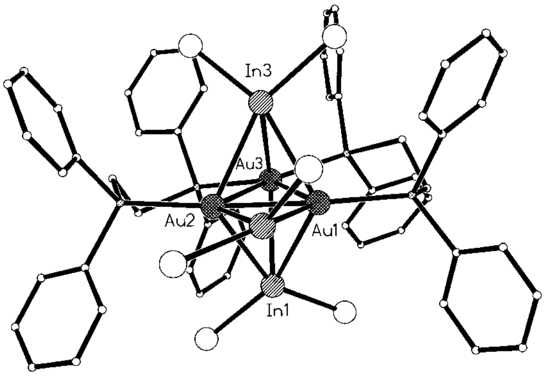


Figure 3. Molecular structure of $[(dppe)_2Au_3In_3Cl_6(thf)_6]$ in the crystal. The thf ligands are omitted for clarity.[105]

diamidoaluminum complex $[Cp(CO)_2Fe{-}Al(NR_2)_2]$ belongs to type **G**.[82] So far the only indication of an analogue dialkyl complex of aluminum is the correspondence of NMR-spectroscopic characteristics of $[(L)_2Pt(R)(AlR_2)]$ with the homologous gallium and indium complexes [Figure 2, see Eq. (7)], which are secured by single-crystal X-ray diffraction. Against this background the synthesis of the complexes $[(CO)_4FeAlCp^*]$ (see Scheme 4), $[\{CpNiAlCp^*\}_2]$ and $[\{(CO)_3CoAlCp^*\}_2]$ [Figure 4 and Eqs. (2) and (3)] marks important progress.

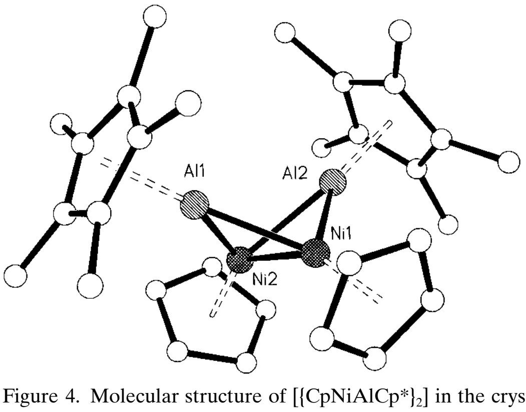
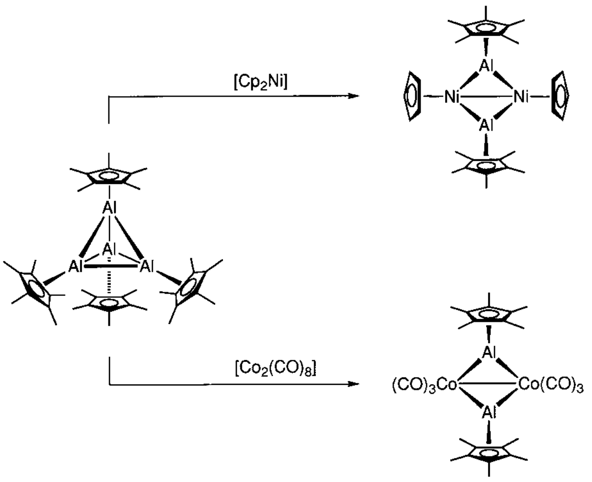


Figure 4. Molecular structure of $[\{CpNiAlCp^*\}_2]$ in the crystal.[78]

As will be discussed in the following section the dominance of metal carbonyl fragments in the coordination chemistry of earth metals at d-block metal fragments stems from synthetic limitations which have only been overcome recently mainly by the preparative availability of low-valent organo earth metal compounds RE.[72, 73]



(2)

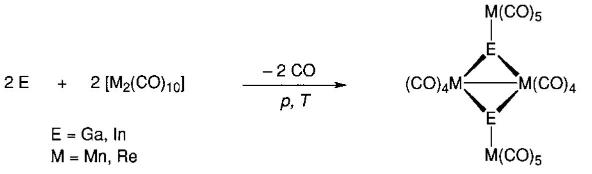
(3)

3. Synthesis

A whole series of methods has proved to be worthwhile for the synthesis of M–E complexes; for details we refer to former surveys.[31–34] The applicability and the preparative success strongly depends on the selected metal combination as well as on the type of d-block metal mainly stabilized with CO ligands.

3.1 Pressure Carbonylation

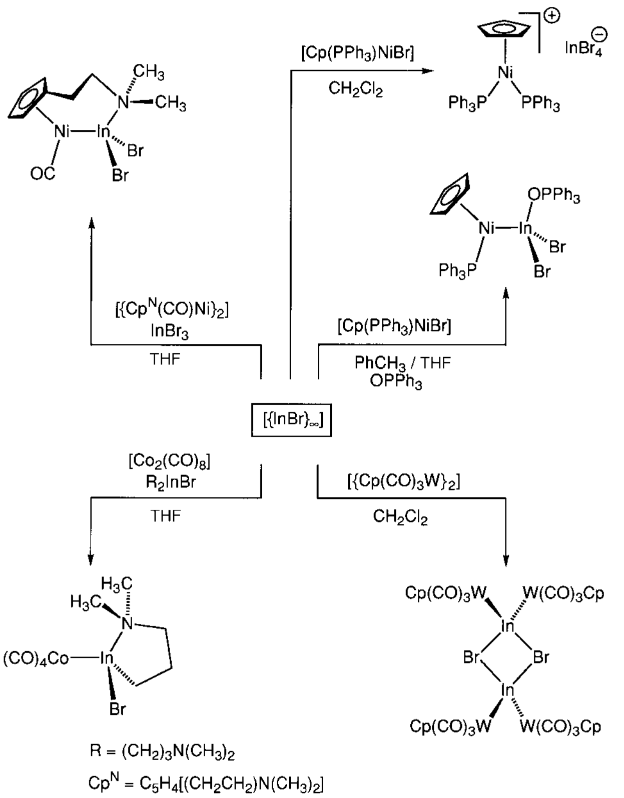
The heavy homologues Ga, In, and Tl react as elements with finely dispersed d-block metals, typically Co, Mn, Re, or their respective metal carbonyls under CO pressure (200 atm) at increased temperature (100–200°C) to give the corresponding carbonyl derivatives $[\{(CO)_nM\}_3E]$ or metal clusters such as $[\{M_2(CO)_8(\mu\text{-}EM(CO)_5\}_2]$ (M = Mn, Re; E = Ga, In)[111, 113] and $[Re_4(CO)_{12}\{\mu^3\text{-}InRe(CO)_5\}_4]$.[112, 114] The use of the halides EX_3, E_2X_4 (E = Ga, In) in respective reactions also leads to carbonyl clusters in which fragments of the type $[\{L(CO)_nM\}E]$ (isolobal to RE) appear in a bridging, CO-analogous position [Eq. (4)]. Aluminum complexes M-Al have not yet been obtained in this way.



(4)

3.2. Insertion Reactions

Insertion reactions of low-valent halides E_2X_4 and EX (E = Ga, In) in metal–metal bonds and metal–halide bonds also belong to the established repertoire. For metal carbonyl complexes this access is very reliable and has been well documented.[15, 32, 117–123] The insertion of InX into the M–M bonds of $[Cp(CO)_3M]_2$, leading to the dimer complexes $[\{InBr\{Cp(CO)_3M\}_2\}_2]$ (M = Cr, Mo, W) (Scheme 1)[124] is typical. The synthesis of the $RuGa_3$ complex $[(CO)_3Re$-



Scheme 1. Synthesis of M–In complexes by the insertion route.

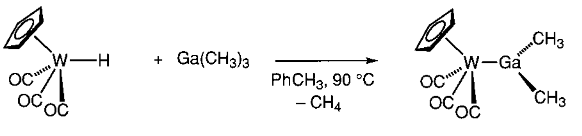
{GaCl(thf)$_2$}{GaCl$_2$(thf)}$_2$] from Ga_2Cl_4 and [$Ru_3(CO)_{12}$] is derived from the insertion concept as well.[91] Green et al. give an example for analogous reactions with "GaI".[15]

Nothing is known about insertions with low-valent AlX derivatives in M–M or M–X bonds. Insertions in "CO-free" d-block metal complexes are less well documented. Earlier work by Hsieh et al. contains references on reactions of [Ph_3PAuCl], [$(Et_3P)_2PtCl_2$], or *trans*-[Pt(Cl)(SiPh$_3$)(PMe$_2$Ph)$_2$] with InCl, in which the formation of complexes with a unit "M-InCl$_2$" were assumed on the basis of elemental analysis and IR-spectroscopic data.[122] Recent investigations of these reactions showed that this simple conception is not correct and that rather complex processes accompanied by redox processes take place. Thus in the system Ph_3PAuCl/InCl mainly the salt [$(Ph_3P)_2Au$][$InCl_4$] is formed and also in the case of the combination [(CO)$_5$Mn–AuPPh$_3$]/InBr, [(CO)$_5$Mn-InBr$_3$][(Ph$_3$P)$_2$Au] is obtained.[125] Only through addition of chelating phosphane ligands such as 1,2-bisdiphenylphosphinoethane (Diphos) was it possible to isolate various Au–In clusters from the reaction mixture of [(PPh$_3$)AuCl]/InCl (Figure 3).[105] There are no indications of a monomer or dimer species of the type [Ph$_3$PAu–InCl$_2$] (type **G** or **P**).

As with the chemistry of gold the product spectrum of the reaction of [Cp(Ph$_3$P)NiBr] with InBr strongly depends on the reaction conditions. The preferred redox product [Cp(Ph$_3$P)$_2$Ni][InBr$_4$] can only be avoided by using suitable reactant ligands such as O=PPh$_3$ or quinuclidine (NC_7H_{13}) as well as special reaction conditions (Scheme 1).[103] Because of the availability of low-valent organo-element compounds insertion proves to be very interesting for forming M–E bonds especially for CO-free systems. The reaction of [(Cp*Al)$_4$] with [Cp$_2$Ni] to form the butterfly cluster [{CpNiAlCp*}$_2$], which formally can be regarded as insertion of AlCp* into a Ni–C(Cp) bond [Eq. (2)] is currently the only example for this concept (Figure 4).[78]

3.3. Alkane Elimination

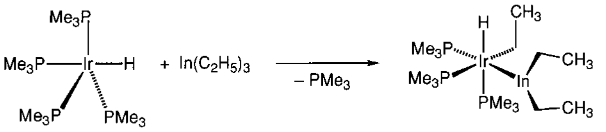
The first complex containing a GaR$_2$ unit (type **G**) was obtained by reacting [Cp(CO)$_3$WH] with Ga(CH$_3$)$_3$ with elimination of one equivalent of CH$_4$ [Eq. (5)]. Corresponding reactions are known for the chemistry of indium and thallium.[126, 127] This elimination of alkane, often formally classified as protolysis, presumably proceeds according to a radical mechanism.[127] In the past a few complexes were isolated and characterized according to this method. In principle this alkene elimination offers an elegant strategy for forming M–E bonds. A series of hydrides and polyhydrides with different substituent patterns, also CO-free systems, are known. Nevertheless selective reactions of this kind are rare and restricted to comparatively reactive M–H functions and apparently to simple sterically less hindered homoleptic organo compounds of the earth metals. In addition, raised reaction temperature and photoactivation are necessary in most cases. Both factors favor the redistribution of the substituents at the center E leading to release of ER$_3$. Thus complexes of the types **G** or **K** are only available with difficulty by this route.



(5)

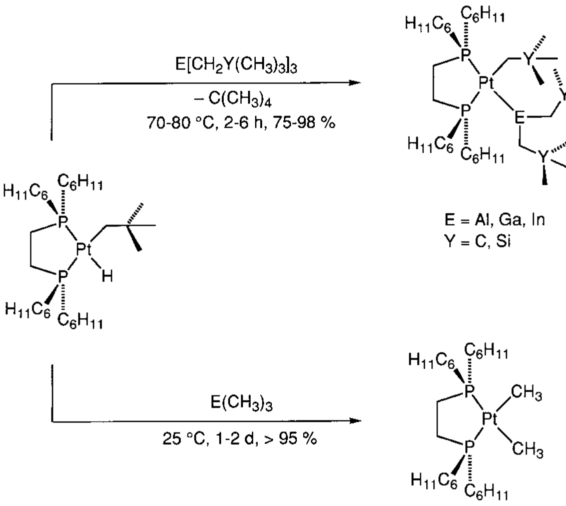
3.4. Bimolecular Addition Reactions of Alkyl Earth Metal Compounds at d-Block Metal Fragments

For this type of reaction only d-block metal complexes that do not carry any halide, alkoxide, or amide function or reactive M – H groups could be used. Otherwise unwanted alkylation or alkane elimination takes place (see above). In this context Thorn et al. have investigated the interaction of R$_3$E compounds (E = Al, Ga, In; R = Me, Et) with various CO-free and reactive d-block metal complexes of iridium, rhodium, and platinum.[102] Typically complex product mixtures were obtained from which pure substances could be isolated only in a few cases.[102] The characterization of the products was often achieved by in situ NMR spectroscopy of the reaction solution. Thus AlMe$_3$ reacts with [IrMe(PMe$_3$)] under excessive ligand exchange to give a mixture, which, on the basis of NMR spectroscopic data, probably consists of the complexes [Me$_3$AlPMe$_3$], [MeIr(PMe$_3$)$_x$AlMe$_3$], and [MeIr(AlMe$_2$)(PMe$_3$)$_3$]. Structurally characterized examples for M – Al chemistry which have been obtained similarly are listed in Table 1. InEt$_3$ exchanges with [Me$_2$Pt(cod)] to form [Et$_2$Pt(cod)] (cod = cyclooctadiene); [Me$_2$Pt(bpy)] (bpy = 2,2′-bipyridine) reacts reversibly with InMe$_3$, probably forming [$Me_2Pt(bpy)(InMe_2)$], and [(η^2-C_2H_4)$Pt(PPh_3)_2$] forms unstable [$(Me_2In)(Me)Pt(PPh_3)_2$] with $InMe_3$. Only the complex [*fac*-$(Me_3P)_3(H)(Et)Ir{-}InEt_2$], obtained in 20% yield according to Equation (6), could be characterized structurally.



(6)

A selective and quantitative synthesis of stable complexes of the type [$L_nM{-}ER_2$] (**G**) by formal oxidative addition of a E–C bond to a coordinated unsaturated d-block metal fragment is only known for the reaction of the alkylplatinum hydride [$(L)_2Pt(H)(CH_2tBu)$][128, 129] with R_3E (R = CH_2tBu, CH_2SiMe_3; E = Al, Ga, In; L = $(C_6H_{11})PCH_2CH_2P(C_6H_{11})$) as reaction partner and at the same time as solvent [Eq. (7)].[51, 54] Upon heating, the Pt complex slowly releases



(7)

(8)

neopentane in a controlled manner in a first-order reaction. The reactive fragment thus formed, [*cis*-$(L)_2Pt$], then is available for a series of subsequent reactions.[128, 129] It has to be emphasized that the course of the reaction is strongly influenced by small variations of the groups R. According to Equation (8) quantitative alkylation or alkyl exchange and the formation of [$(L)_2PtR_2$] is observed for R = CH_3, C_2H_5, isobutyl. The work of Schneider et al. on the interaction of alkylaluminum compounds with transition metal fragments should be noted in this context. Among complexes of this kind structurally characterized were those with the rare Co–Al bonds (see Table 1).[100]

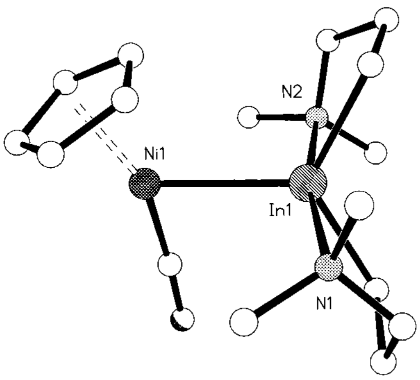
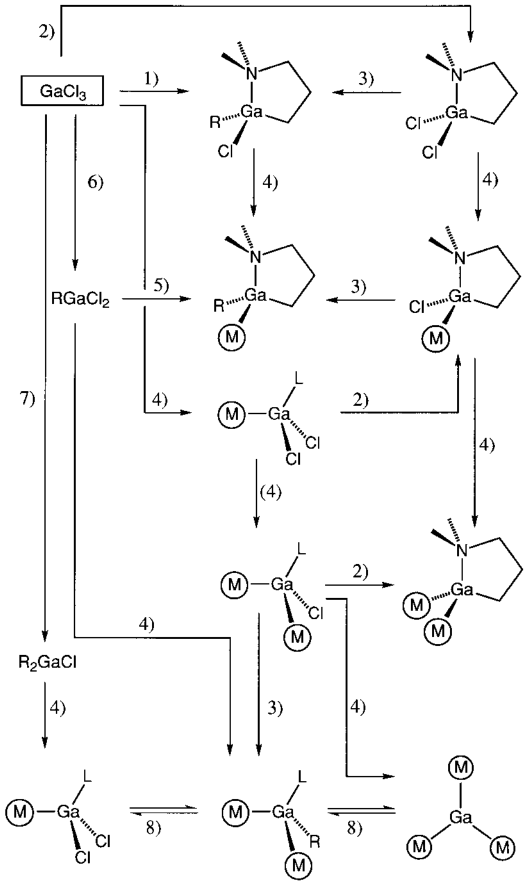


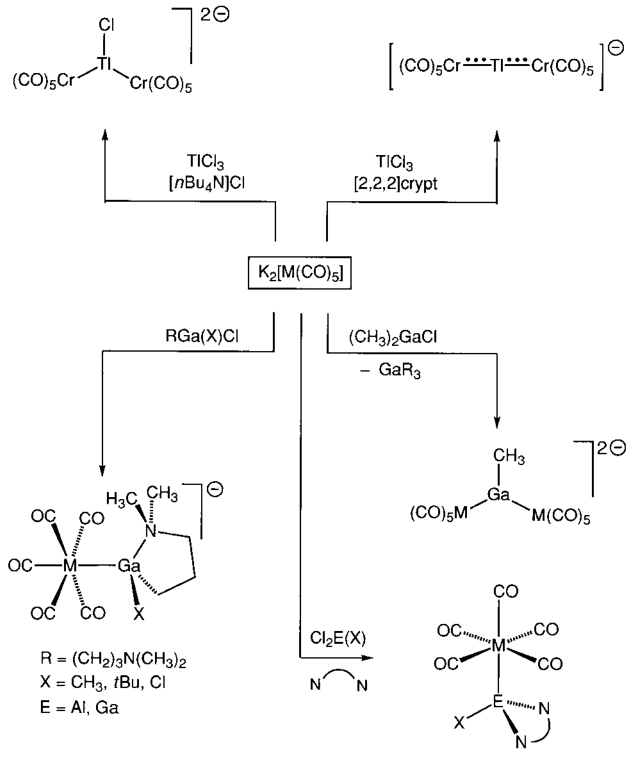
Figure 5. Molecular structure of [$Cp(CO)Ni{-}In(R^N)_2$] in the crystal [R^N = 3-(*N*,*N*-dimethylamino)propyl].[53]



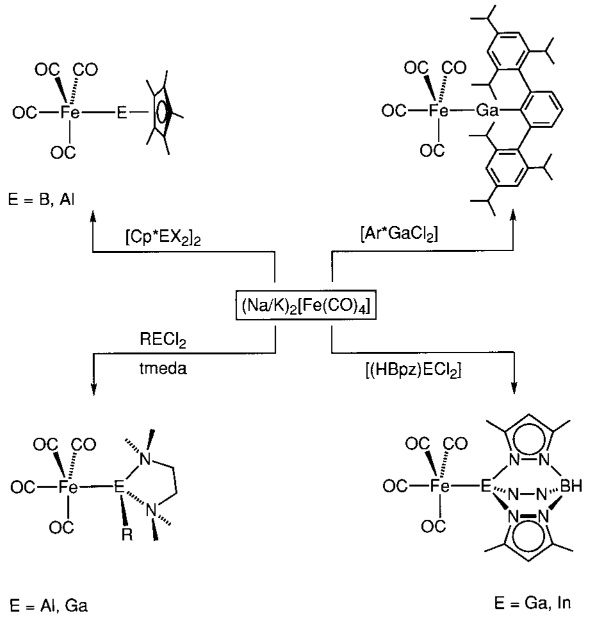
Scheme 2. Synthesis and modification of the transition metal-substituted gallanes of the general type [$L'(CO)_nM]_a[GaR_{3-a}(L)$] (M = Cr, Mo, W, Mn, Re, Fe, Ru, Co, Ni; L′ = Cp, Cp*, CO, PR_3; n = 1–4; a = 1, 2, 3; R = H, alkyl, aryl; L = O-, N-, P-Lewis donor). 1) 1. R_4Si; 2. Li[$(CH_2)_3NMe_2$], Et_2O; 2) Li[$(CH_2)_3NMe_2$], Et_2O, 25 °C; 3) R = alkyl, aryl: RLi, toluene; R = H: Li[BEt_3H], THF; R = BH_4: Li[BH_4], Et_2O; 4) [$L(CO)_nM$](Na/K); 5) R = H, alkyl: 1. Li[$(CH_2)_3NMe_2$], pentane; 2. [$L(CO)_nM$](Na/K); 6) Me_3SiH; 7) 1. 3 equiv RLi; 2. 0.5 equiv $GaCl_3$; 8) $T > 0$ °C, Do = THF, R = H, CH_3, C_2H_5.

3.5. Salt Elimination

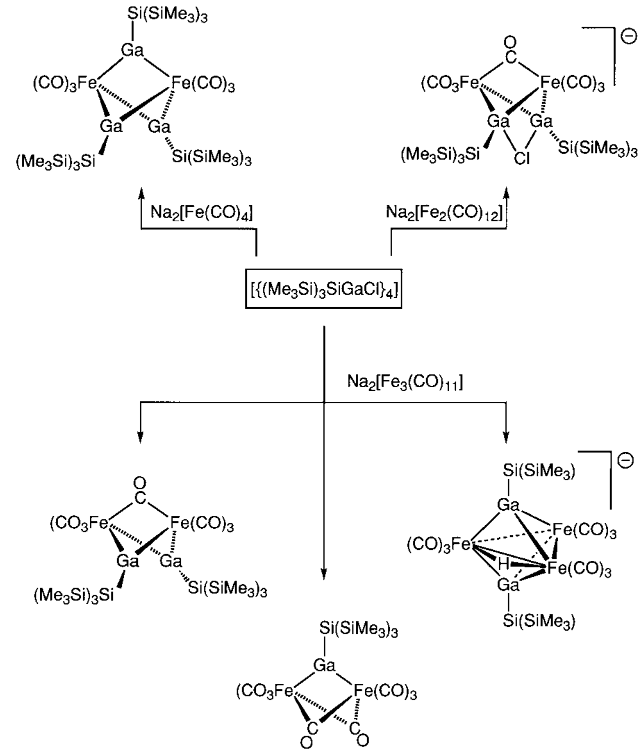
Salt metathesis of earth metal halides $X_{3-a}ER_a$ (a = 1, 2; R = H, alkyl, aryl, Cp*) with carbonylmetalates [$L(CO)_nM]^{m-}$ (L = CO, Cp, Cp*, PR_3; M = Cr, Mo, W, Mn, Re, Fe, Ru, Co, Ni) is the method of choice for the synthesis of the organyl derivatives of the types **I**–**N** (Figure 1, Figure 5; Schemes 2–5). Functionalization (e.g. alkylation) of halide derivatives (**O**, **P**) is possible, but the yields are not always good. Typical complications are the formation of "ate" complexes and the redistribution of substituents in the case of sterically unhindered, coordinatively unsaturated centers E. The nucleophil-



Scheme 3. Synthesis of M–E complexes of the types **A**, **H**, **I**, and **K** by salt metathesis with divalent carbonylmetalates (M = Cr, Mo, W).



Scheme 4. Synthesis of Fe–E complexes of the types **D** and **I** by salt metathesis.



Scheme 5. Synthesis of Fe–Ga clusters of the types **E** and **F** by salt metathesis.

icity of the carbonylmetalate compared to the solvent and the leaving group X as well as the Lewis acidity and the steric conditions at the center E are decisive for a successful synthesis. The weak nucleophiles $[(CO)_nM]^-$ (M = Co, Mn; $n = 4$, 5) do not react in polar, coordinating solvents (THF, CH_3CN, HMPT, etc.). In these solvents complexes of the type $[(CO)_nM{-}ER_2(L)]$ (type **K**) are subject to a heterolytic dissociation of the M–E bond according to the polarities M($\delta-$) and E($\delta+$). In the presence of dissolved halide ions as competing nucleophiles the organo-element halides reform. Syntheses with weak nucleophilic carbonylmetalates are ideally carried out in nonpolar, noncoordinating solvents, in which the insoluble carbonylmetalate is suspended. The alkali metal halide is also insoluble in this medium; however, the product complex is well soluble. The presence of equimolar amounts of a Lewis base for a coordinative saturation of the center E is often necessary, though. M–Al bonds can only be realized in this way with strong nucleophiles, otherwise isocarbonyl-bridged polynuclear complexes are formed [see Eq. (1)]. The latter is the case for reactions of $AlCl_3$ with $Na[Co(CO)_4]$ in toluene.[130] For $[Me_3P(CO)_3Co]^-$ as a stronger nucleophile in THF as medium, Co–Al-bonded complexes were obtained.[53]

Whereas for the majority of the syntheses monovalent carbonylmetalates were used, recently there has been a rising interest in the reactivity of divalent carbonylmetalates, for example $[(CO)_nM]^{2-}$ (M = Cr, Mo, W; Fe, Ru), toward earth metal halides (Figure 6). Thus according to Scheme 3 complexes of the metal cumulene type **A** or inidene type **H** have been obtained for E = Ga, In, and Tl.[90, 92, 109] Again, redox processes are possible and can be elegantly used. A nice series of Fe/Ga clusters, the structures of which all obey the Wade–Mingos rules, has been synthesized and characterized by G. Linti et al. (Scheme 5; Figure 7).[88]

The reaction of a suspension of $[(CO)_4Fe]K_2$ in THF with $ClGa(R)(R^N)$ ($R^N = CH_2CH_2CH_2NMe_2$) primarily leads to the soluble and isolable anion $[(CO)_4Fe{-}Ga(R)(R^N)]^-$. The digallium complex $[(CO)_4Fe\{Ga(R)(R^N)\}_2]$ (see Scheme 11) is only formed after an exchange of solvent (toluene for THF),

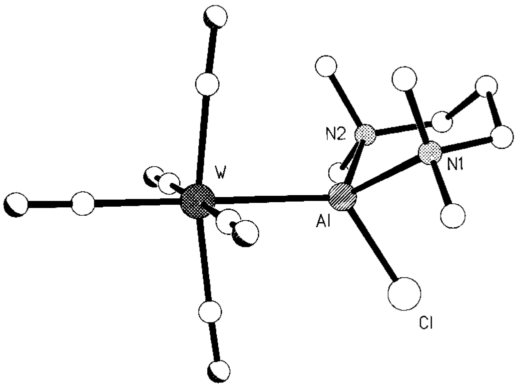


Figure 6. Molecular structure of [(CO)$_5$W–Al(Cl)(tmpda)] (tmpda = *N,N,N',N'*-tetra-methylpropylendiamine) in the crystal.[80]

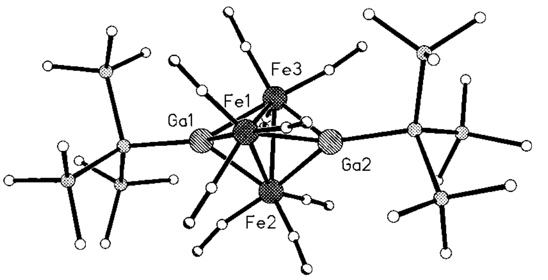
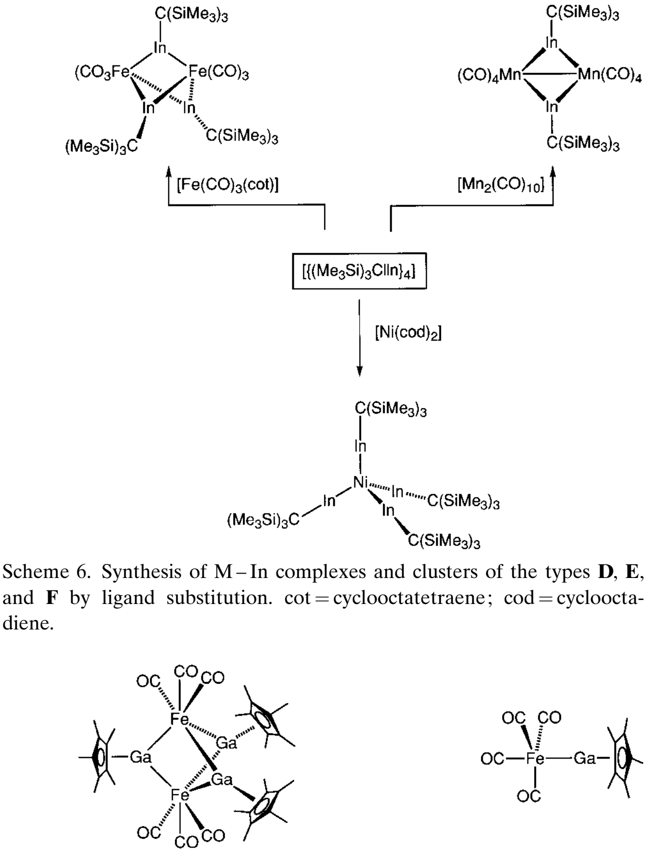


Figure 7. Molecular structure of the cluster ion [{(CO)$_3$Fe}$_3${GaSi(SiMe$_3$)$_3$}$_2$H]$^-$ in the crystal.[88]

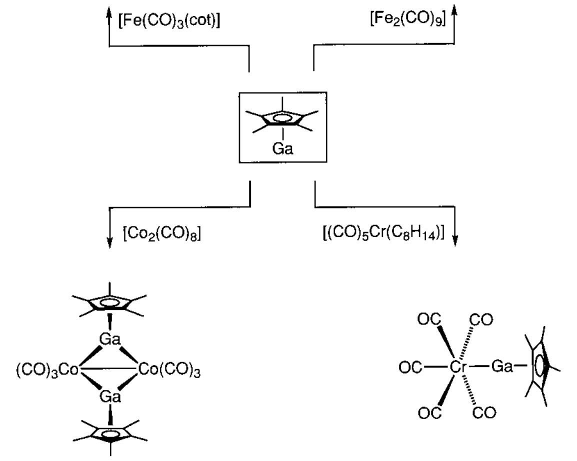
in accord with the lower nucleophilicity of the intermediate. The pentacarbonyl derivatives [(CO)$_5$M–Ga(R)(R^N)]$^-$, though, do not react further because of the higher steric demand and at the same time lower nucleophilicity (Scheme 3). The same is valid for [(NO)(CO)$_3$Mn–Ga(R)(R^N)]$^-$. The reaction of K$_2$[Fe(CO)$_4$] with Cl$_2$Ga(R^N) provides the dimeric complex [{[μ-Ga(R^N)][(CO)$_4$Fe]}$_2$]. Steric hinderance at the α-C atom in the case of Cl$_2$Ga{C(TMS)$_2$CH$_2$CH$_2$NMe$_2$} as gallium compound prevents dimerization and the reaction stops at the level of the monoanion.[63, 131, 132] The importance of sterically demanding groups R or intramolecular adduct stabilization is proved by the differing reaction behavior of ClGaR$_2$ (R = CH$_3$, C$_2$H$_5$) under otherwise identical reaction conditions. In these cases after elimination of GaR$_3$, the dianionic GaR-bridged complexes of the inidene type **H** (Scheme 3) are obtained. The complexes of types **D** and **I** can also be obtained by salt elimination starting from X$_2$ER. By adding strong Lewis bases (tmeda, NR$_3$) or by using special sterically very demanding groups R [R = Cp*, Ar*, {HB(3,5-Me$_2$pz)$_3$}] the formation of trinuclear complexes of type **H** is suppressed (Scheme 4). So far there are no results on the reactivity of tetravalent carbonylmetalates [(CO)$_n$M^{4-}].

3.6. Ligand Substitution

The availability of monovalent organo derivatives RE or clusters (RE)$_4$ (R = Cp*, C(SiMe$_3$)$_3$, Si(SiMe$_3$)$_3$) as starting materials for syntheses recently has allowed coordination of RE as a potent 2e-donor ligand to the d-block metal fragment by displacement of *weaker* bonded ligands (CO, alkenes). This route opens up truely new perspectives. The most striking example is the possibility to achieve complexes with "inverted" ratio E/M > 1. This is exemplified by the synthesis of the homoleptic NiIn$_4$ complex from [Ni(cod)$_2$] and [{[(SiMe$_3$)$_3$C]In}$_4$][77] or the [Fe$_2$(CO)$_9$] analogues [(CO$_3$Fe(μ-ER)$_3$Fe(CO)$_3$] (E = Ga, In; R = Cp*, C(SiMe$_3$)$_3$)[84, 97] [Scheme 6, Scheme 7; Eq. (3)]. Clusters such as [Ni$_4$(μ-Cp*Ga)$_4$(CO)$_6$] (Figure 8) with μ^2- and μ^3-bridging Cp*Ga units[84] or [(μ-Cp*Al)$_2$Co$_2$(CO)$_6$],[83] which were derived from [Ni(CO)$_4$] or [Co$_2$(CO)$_8$], respectively, by CO substitution impressively prove this method. Interesting results can be expected from this promising new field.[172, 173]



Scheme 6. Synthesis of M–In complexes and clusters of the types **D**, **E**, and **F** by ligand substitution. cot = cyclooctatetraene; cod = cyclooctadiene.



Scheme 7. Synthesis of M–Ga complexes and clusters of the types **D**, **E**, and **F** by ligand substitution.

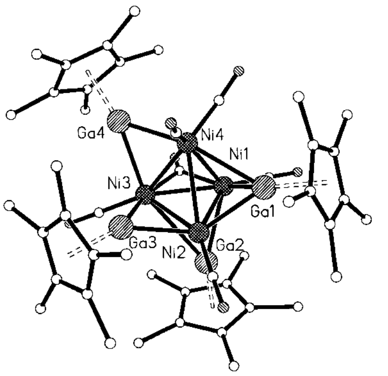
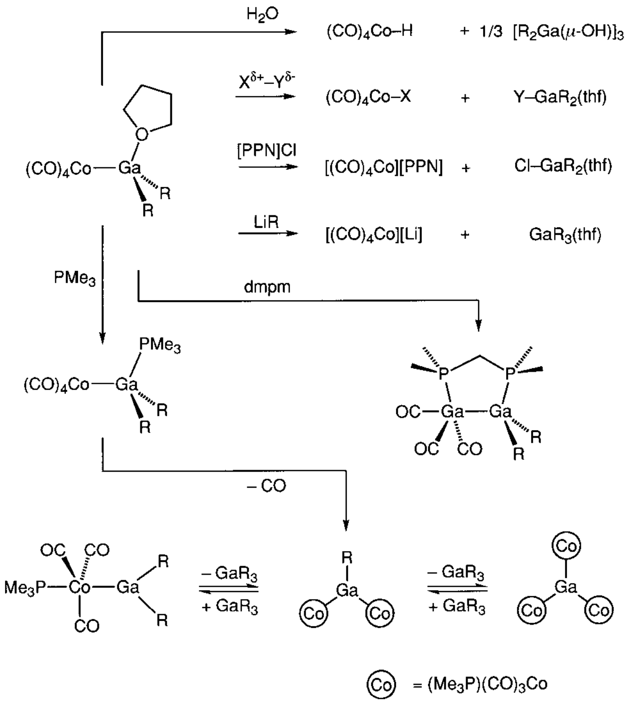


Figure 8. Molecular structure of $[Ni_4(\mu\text{-}GaCp^*)_4(CO)_6]$ in the crystal.[84]

4. Reactivity

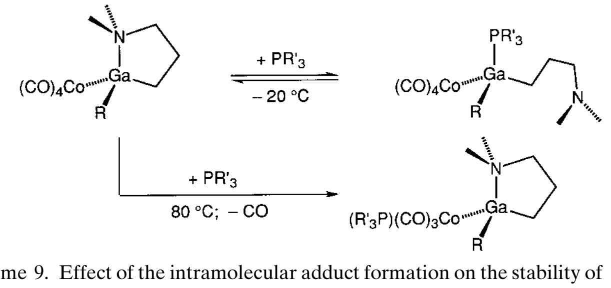
Remarkably few investigations have considered the chemical reactivity of M–E complexes, if one does not count the chemistry relevant for MOCVD applications (see Chapter 6). The typical Lewis acidity at the earth metal and the use of substituent exchange or transfer reactions for preparative purposes for halogeno complexes of the types **O** and **P** in combination with their homoleptic congeners **B** and **C** has already been discussed in previous surveys.[32, 33] Here, though, some conditions characteristic for the organo derivatives shall be stressed, for which the chemistry of the Co–Ga and Fe–Ga series are representative examples. The chemical properties of these M–Ga complexes (types **B**, **K**, and **L**) are characterized a) by the polar character of the M–Ga bond which can easily be split by electrophilic or nucleophilic reaction partners, b) by the competition of both metal centers for donor ligands, and c) by the selective conversion of Ga–X functions (X = halide).

According to Scheme 8 the reaction of Co–Ga complexes with one equivalent of water leads to the direct formation of $[(CO)_4CoH]$ and the trimeric (volatile) alkylgallium hydroxide. A selective hydrolysis to form transition metal substituted gallium oxide cage molecules (Fe–Ga) has recently been described.[174] Electrophilic reaction partners like trimethyl- and triphenylstannyl chloride (also mercury halides, bromine, iodine, etc.) instantly split the metal–metal bonds. This is also true for the complexes of types **D** and **I**. The instability of the Co–Ga bond of complexes of the general formula $[(L')(CO)_3CoGaR_2(L)]$ (type **K**) in solution is also apparent in their tendency to heterolytic dissociation depending on the substitution pattern at both metal centers as well as on the solvent. According to the IR solution spectra the complexes are undissociated in pentane, cyclohexane, or benzene. Only the four $\tilde{\nu}$(CO) absorptions that can be expected for C_S-symmetrical complexes $[LCo(CO)_4]$ (here, L stands for the earth metal fragment) appear. In THF the Co–Ga complexes start to dissociate, in acetonitrile, DMSO, and HMTP dissociation is completed. Dissociation is suppressed in the case of strong nucleophilic carbonylmetalates. Fast and quantitative nucleophilic cleavage of M–E bonds in $[(CO)_4Co{-}GaR_2(thf)]$ occurs if chloride ions are added to polar media (dichloromethane, THF, acetonitrile, DMSO) (Scheme 8). This also explains why salt elimination according to Scheme 2 in these solvents causes problems. Basic ligands such as THF coordinated to the Ga center can be displaced by phosphanes from −20 °C onwards. In solution the isolable adducts are unstable above 0 °C. For monodentate phosphanes, after thermal CO substitution the complexes are subject to substituent redistribution at the Ga center, and an equilibrium mixture is formed (Scheme 8). However, reactions with diphosphane chelate ligands to give Co–Ga-bridged systems proceed in a uniform manner. This again proves the instability of tricoordinate units $R_2Ga{-}M$.



Scheme 8. Selected examples for the reactivity of σ(Co–Ga) bonds. dmpm = bis(dimethylphosphanyl)methane.

In this context Scheme 9 shows how an effective suppression of the substituent redistribution can be achieved by intramolecular adduct stabilization if one wants to avoid the alternative, that is the introduction of sterically very demanding ligands of high-molar mass. This is of special importance with regard to the necessary volatility for MOCVD applications. A compromise has to be found between molar mass and stabilizing effects for adequately volatile as well as long-term stable M/E precursors. Sterically very demanding ligands or groups R thus are a problem. Intramolecular adduct formation is the preferred method. The reaction of intramolecularly adduct-stabilized Co–Ga model compounds of Scheme 2 with



Scheme 9. Effect of the intramolecular adduct formation on the stability of organogalliocobalt complexes compared to alkyl group substitution.

alkylphosphanes of the type PR_3 (R = CH_3, C_2H_5) in pentane at − 78 °C yields isolable phosphane adducts at low temperatures through opening of the chelate ring (Scheme 9). In a closed system (vacuum-sealed NMR tube; toluene solution) between − 80 °C and room temperature an equilibrium can be observed by ^{31}P NMR spectroscopy in which the Ga-coordinated phosphane exists with the open chelate, and free phosphane exists with the closed chelate ring. On heating to about + 80 °C, thermal decarbonylation takes place at the cobalt atom, while at the same time phosphane is coordinated *trans* to the gallium center. This process proved to be reversible. As the sample was cooled down to room temperature, the signal of Co-coordinated phosphane decreased ($\delta =$ 49.1 to 50) and the signals of Ga-coordinated and free phosphane increased in intensity (− 11.3 to − 12.8 and $\delta =$ − 17.2). Also in the related In compound $[\{(C_6H_5)_3P\}(CO)_3Co{-}InCl_2]$, the metal centers compete for the phosphane ligand; phosphane coordination at the In center is preferred for the Co–In complex.[139] In the open system (removal of the released CO by inert gas stream or by evacuation in vacuo) the *trans*-phosphane-substituted complexes were isolated in substance. For sterically more demanding phosphanes (PCy_3, PPh_3; Cy = cyclohexyl) the Ga–phosphane intermediates could not be identified spectroscopically. Alkyl exchange reactions took place in none of these cases. Selective derivatization of $GaCl_n$ functions ($n = 1$, 2) is possible in many cases (Scheme 2).

Reactions with carbonylmetalates lead to the corresponding M_nGa complexes ($n = 2$, 3). The introduction of alkyl groups or other nucleophilic groups is also possible for dissociation-stable M–Ga bonds, which is the case for strongly nucleophilic d-block metal fragments. One example of this is the selective insertion of hydrido and tetrahydridoboranate groups into Fe–Ga complexes to give $[Cp(CO)_2Fe{-}Ga(R^N)(Y)]$ (Y = H, BH_4) by means of superhydride, $Li[BEt_3H]$, or $Li[BH_4]$ in diethyl ether without splitting the Fe–Ga bond or attacking the Fe–CO ligands. The borane-derivative in Scheme 10 has to be regarded as the first example of a borane complex of gallium structurally characterized in the solid state. It was used as MOCVD precursor for FeGa films (Chapter 6).

Unlike the chemistry of d-block metal borylenes, which has been studied with regard to applications in organic synthesis up to the point where a d-block metal catalyzed borylation reaction has been developed,[115] the chemistry of the higher homologues of Group 13 has not really been investigated in any great detail.[174] Up to now the synthesis and the investigation of the structure and bonding conditions of the complexes have been in the foreground. A suggestion for future investigations is as follows: The M – E complexes can be regarded as potential carriers of negatively polarized d-block metal fragments $L_nM^{(\delta-)}$. This is above all important in the case of d-block metal fragments which, in contrast to carbonylmetalates, are not easily available as a nucleophilic synthetic building block. Thus the insertion or the bimolecular addition for the synthesis of M–E complexes, for example starting from $M^{(\delta+)}$-$Y^{(\delta-)}$ functions (Y = H, halide, alkyl), can also be regarded as a reversion of the polarity of the d-block metal fragments (i.e. reduction). A lot can be expected in this direction.

5. Bonding Conditions

The neutral d-block metal complexes of the terminal coordinated donor-free fragments EX, EX_2, RE, and R_2E (types **D** and **G**) are isoelectronic to cationic carbyne or carbene complexes or the corresponding complexes of the higher homologues of Group 14. This fact and the observation that M – E bond lengths vary systematically over a wide range, depending on the substituents at both metal centers and on the coordination number at the center E, might be responsible for the recently increased discussion on the degree of backbonding of the type $M(d_\pi) - E(p_\pi)$. Power et al. have considered this problem for M–E complexes with tricoordinate centers E mainly on the basis of structural data and arrive at the conclusion that π multiple bonds are hardly of any importance.[34] The concept proposed by Robinson et al.[14] of a Fe–Ga triple bond in the complex $[(CO)_4Fe{-}GaAr^*]$ based on a very short Fe–Ga distance was criticized.[140] In the light of a fast developing chemistry of low-coordinate centers E, some remarks on the M–E bonding conditions and the substituent effects seem to be warranted. Quantum chemical DFT calculations have meanwhile been carried out by several groups on the model complexes $[(CO)_4Fe{-}AlCp]$,[79, 83] $[(CO)_5CrAlCp]$,[172] $[(CO)_4Fe{-}Ga(\eta^1\text{-}C_6H_5)]$,[136, 140] $[(CO)_5M{-}EX]$, $[(CO)_5M{-}EXL_2]$ (E = B, Al, Ga, In, Tl; X = H, Cl; L = NH_3)[80] and $[L'(CO)_3Co\text{-}GaX_2L]$ (X = H, Cl; L′ = PH_3).[141] All model complexes were compared to closely related examples, the molecular structures of which were known. This is also true for the Fe/Ga clusters mentioned in Section 3.5 (Scheme 5).[88] Thus the characteristic environments for terminally coordinated earth metal fragments of types **D**, **I**, and **K** have been recorded, namely linearly dicoordinate as well as the tetracoordinate adduct-stabilized variations. Thus the discussion of the structures and bonding conditions shall be limited to these examples. For complexes of the types **B**, **G**, and **P** see the references.[34]

5.1. M–E Bond Lengths and Calculated Dissociation Energies

The most comprehensive data material is available for the series of the earth metal complexes at $(CO)_5M$ fragments (M = Cr, Mo, W).[80] Let us first turn to the donor-stabilized species (type **I**). The optimized C_S-symmetrical structures of the model complexes agree very well with the X-ray crystallographic data. The tendency to a certain shortening of the bond in the series X = alkyl, H, halide (model examples: $[(CO)_5W{-}Al(H)(NH_3)_2]$ 260.5 pm and $[(CO)_5W{-}Al(Cl)(NH_3)_2]$ 257.5 pm) corresponds to the experimental conditions: $[(CO)_5Cr{-}Ga(Et)(tmeda)]$ 251.71(4) pm and $[(CO)_5Cr{-}Ga(Cl)(tmeda)]$ 245.55(11) pm. This variation in bond lengths becomes more significant if also the structurally characterized complexes **K** or the solvent-free systems **D** are included in the comparison. In the series $[(L')(CO)_3Co{-}GaX_2(L)]$ the extreme values vary in a range of 25 pm: $[Me_3P(CO)_3Co{-}GaCl_2(NMe_3)]$ 234.2(1) pm and $[(CO)_4Co{-}Ga(CH_2tBu)_2(thf)]$ 257.83(4) pm (Table 2, Figure 9).

Table 2. Structurally characterized cobalt–gallium complexes: σ(Co–Ga) bond lengths and IR data.

Compound	d(Co–Ga) [pm]	$\tilde{\nu}$(CO) [cm^{-1}]	Ref.
$[(PMe_3)(CO)_3Co{-}GaCl_2(NMe_3)]$	234.2(1)	1992 (m), 1953 (vs), 1940 (vs)[a]	[133]
$[(PPh_3)(CO)_3Co{-}Ga\{(CH_2)_3NEt_2\}(Cl)]$	237.78(4)	2010 (w), 1946 (vs), 1925 (vs)[a]	[64]
$[Co_2(CO)_6(\mu\text{-}GaCp^*)_2]$	237.84(5)–239.59(5)	2023 (s), 1989 (s), 1953 (vs), 1948 (vs, sh)[b]	[84]
$[\{(CO)_4Co\}_2Ga(2,4,6\text{-}t\text{Bu}_3C_6H_2)]$	248.1(2)	2092 (s), 2076 (s), 2017 (m), 2002 (s), 1993 (s), 1982 (s), 1964 (m)[b]	[134]
$[(PPh_3)(CO)_3Co{-}Ga\{(CH_2)_3NEt_2\}(CH_3)]$	249.5(1)	1929 (vs), 1941 (vs)[c]	[64]
$[\{(CO)_4Co\}_2Ga\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}]$	253.6(19), 260.2(16)	2080 (s), 2059 (s), 2013 (m), 1986 (s), 1973 (s), 1878 (m)[b]	[135]
$[\{(CO)_4Co\}_2Ga\{(CH_2)_3NEt_2\}]$	254.02(9), 254.60(9)	2083 (s), 2066 (s), 2019 (s), 2009 (s), 1997 (vs), 1975 (vs), 1962 (s)[c]	[57]
$[(CO)_4Co - GaNp_2(thf)]$	257.83(4)	2066 (s), 1997 (s), 1968 (vs), 1955 (vs)[d]	[56]
$[(CO)_4Co{-}GaEt_2(NC_7H_{13})]$	258.67(10)	2065 (s), 2010 (m), 1980 (sh), 1957 (vs)[a]	[133]

[a] Toluene. [b] KBr pellet. [c] *n*-Pentane. [d] *n*-Hexane.

Table 3. Structurally characterized iron–gallium complexes: σ(Fe–Ga) bond lengths and IR data.

Compound	d(Fe–Ga) [pm]	$\tilde{\nu}$(CO) [cm^{-1}]	Ref.
$[(CO)_4Fe{-}GaAr^*]$	222.48(7)	2032 (s), 1959 (s), 1941 (vs), 1929 (vs)[a]	[14]
$[(CO)_4Fe{-}GaPh]$[#]	225.6	2038, 1985, 1959	[136]
$[(CO)_4Fe{-}GaCp^*]$	227.31(4)	2037 (s), 1966 (s), 1942 (vs)[b]	[84]
$[(CO)_4Fe{-}GaCp]$[#]	232.7	2040, 1983, 1959	[136]
$[\{(CO)_3Fe\}_3\{GaSi(SiMe_3)_3\}_2\{GaFe(CO)_4\}]^-$	228.9(1)–254.7(1)	–	[88]
$[\{Cp(CO)_2Fe{-}GaS\}_4]$	233.7(1)	2001 (s), 1993 (vs), 1976 (vs), 1923 (vs), 1896 (vs)	[89]
$[(CO)_4Fe{-}GaCl(tmeda)]$	233.78(15)	2011 (vs), 1928 (vs), 1881 (vs)[c]	[87]
$[\{Cp(CO)_2Fe{-}GaSe\}_4]$	234.7(1)	2001 (s), 1991 (vs), 1975 (vs), 1922 (vs), 1895 (sh)	[89]
$[Fe_2(CO)_6(\mu\text{-}GaCp^*)_3]$	235.4(4)-245.4(3)	1951 (vs, sh), 1923 (vs)[d]	[84]
$[\{Cp(CO)_2Fe{-}GaTe\}_4]$	235.7(2)	2001 (s), 1998 (vs), 1984 (vs), 1927 (s)	[89]
$[Cp(CO)_2Fe{-}GaCl_2(NMe_3)]$	236.18(3)	1989 (vs), 1934 (vs)[e]	[64]
$[Cp(CO)_2Fe{-}Ga(R^N)(BH_4)]$	237.5(1)	1975 (vs), 1920 (vs)[e]	[58]
$[\{\mu\text{-}GaSi(SiMe_3)_3\}_2(\mu\text{-}CO)Fe_2(CO)_6]$	238.15(8)–239.38(6)	2026 (s), 1999 (s), 1971 (s), 1962 (s), 1948 (s), 1920 (s), 1784 (s)[c]	[88]
$[\{Fe_2(CO)_6[\mu\text{-}GaSi(SiMe_3)_3]\}_3]$	238.18(7)	1964 (s), 1921 (s)[d]	[88]
$[\{Cp(CO)_2Fe\}_2Ga(t\text{Bu})]$	240.6(1), 241.6(1)	1978 (vw, sh), 1967 (vs), 1927 (vs), 1915 (vw)	[137]
$[(CO)_4Fe{-}Ga(Me)Fe(CO)_4]^{2-}$	241.58(6)	1952 (vs), 1874 (vs, sh), 1851 (vs), 1827 (vs, sh)[f]	[90]
$[Cp(CO)_2Fe{-}Ga(t\text{Bu})_2]$	241.7(1)	1980 (vs), 1928 (vs)	[137]
$[\{(CO)_3Fe\}_3\{GaSi(SiMe_3)_3\}_2H]^-$	242.3(2)-251.0(2)	2009 (w), 1971 (s), 1956 (m), 1943 (s), 1920 (m), 1914 (s), 1903 (m), 1888 (m), 1873 (m)[d]	[88]
$[Cp(CO)_2FeGa(\eta^1\text{-}C_5H_4Me)_2(NC_5H_5)]$	242.72(9)	–	[15]
$[\{Cp(CO)_2Fe\}_3Ga]$	243.6(1)-245.6(1)	1987 (m), 1965 (s), 1929 (s)[f]	[138]
$[Cp(CO)_2Fe{-}Ga(t\text{Bu})_2\{Cp(CO)_2Fe\}_2]$	244.1(1)	1982 (ssh), 1963 (vs), 1930 (vs), 1915 (ssh), 1788 (s), 1758 (s)	[137]
$[Fe_2(CO)_6\{\mu\text{-}GaSi(SiMe_3)_3\}_2(\mu\text{-}CO)]\cdot Na(thf)(OEt_2)_2Cl$	244.1(2)–245.5(2)	2013 (s), 2005 (s), 1995 (s), 1984 (s), 1977 (sh), 1939 (s), 1818 (w)[d]	[88]
$[Cp(CO)_2Fe{-}Ga(R^N)(Et)]$	245.65(4)	1968 (s), 1960 (vs), 1911 (s), 1904 (vs)[g]	[58]
$[(CO)_4FeGa_3\{Si(SiMe_3)_3\}_3(OH)_4]$	248.36(12)–248.98(12)	–	[88]
$[\{(CO)_4Fe{-}Ga(\eta^1\text{-}C_2H_3)(thf)\}_2]$	251.0(1)	–	[86]

[#] Data for bond lengths and IR frequencies determined on the basis of DFT calculations. [a] Nujol pulverization. [b] *n*-Hexane. [c] CH_2Cl_2. [d] KBr pellet. [e] Toluene. [f] THF. [g] *n*-Pentane. Abbreviations see Table 1.

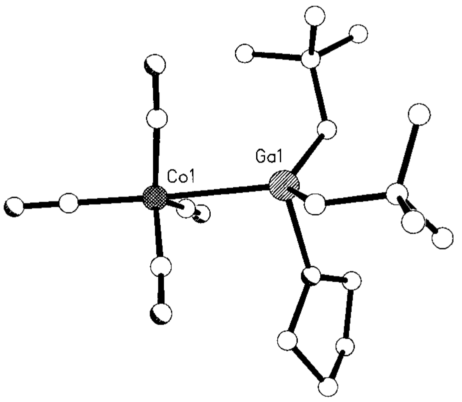


Figure 9. Molecular structure of $[(CO)_4Co{-}GaNp_2(thf)]$ in the crystal. Np = neopentyl.[56]

The same is true for the series $[Cp(CO)_2Fe{-}GaX_2(NR_3)]$, the Fe–Ga distances of which vary between 236.18(3) pm for X = Cl and 245.65(4) pm for X = alkyl (Table 3). An unusually short Fe–Ga bond length of 222.48(7) pm is found for $[(CO)_4Fe{-}GaAr^*]$ with a linearly dicoordinate Ga atom (Table 3). The complex $[Cp(CO)_2Fe{-}Al(iBu)(R^N)]$ with a tetracoordinate Al center has a Fe–Al distance of 245.6(1) pm. A parallel to this for the $(CO)_5M$ series can be found in the comparison of $[(CO)_5Cr{-}GaCp^*]$ (240.46(7) pm) with $[(CO)_5Cr{-}Ga(Et)(tmeda)]$ (251.71(4) pm).

The relative ordering of the calculated bond dissociation energies (MP2/II level) of the model complexes $[(CO)_5W{-}L]$ (L = earth metal fragment) in $\{(CO)_5W\}$ and L are very interesting (Table 4). For W–Al bonds the energies of around 90–100 kcal mol^{-1} are found for the tetracoordinate deriva-

Table 4. Results of the NBO analysis at the MP2/II-level.[80] Partial charges q; hybridization of the lone-pair donor orbital at the atom E[a] (s contribution); calculated dissociation energies D_e of the W–E bond.[a]

Molecule	q(W)	q(W(CO)$_5$)	q(E)[a]	s Contribution [%]	D_e [kcal mol^{-1}]
$[(CO)_5WAlH(NH_3)_2]$	−0.67	−0.93	1.09	23.0	100.9
$[(CO)_5WAlCl(NH_3)_2]$	−0.72	−0.90	1.24	23.9	93.1
$[(CO)_5WAlH]$	−0.93	−0.64	1.07	62.5	70.0
$[(CO)_5WAlCl]$	−0.94	−0.58	1.13	64.1	58.4
$[AlH(NH_3)_2]$	–	–	0.32	77.5	33.1[b]
$[AlCl(NH_3)_2]$	–	–	0.54	84.0	30.5[b]
AlH	–	–	0.60	91.5	–
AlCl	–	–	0.68	93.8	–
$[(CO)_5WGaCl(NH_3)_2]$	−0.73	−0.72	1.07	18.3	70.9
$[(CO)_5WBCl(NH_3)_2]$	−0.53	−0.63	0.19	35.2	119.6
$[(CO)_5WInCl(NH_3)_2]$	−0.71	−0.77	1.18	19.8	70.5
$[(CO)_5WTlCl(NH_3)_2]$	−0.70	−0.61	1.08	36.2	47.8

[a] E = B, Al, Ga, In, Tl. [b] Dissociation energies for two NH_3 ligands.

tives. As expected the tendency to dissociate decreases from Al to Tl. The high bonding energy of the hypothetical W–B complexes is remarkable. Quite recently the first d-block metal complexes with terminal borylene units, $[(CO)_4Fe{-}BCp^*]$ and $[(CO)_5W{-}BN(SiMe_3)_2]$ as homologues to the above-mentioned Al and Ga complexes, have been described.[142] The dissociation energy of $[W(CO)_6]$ into $\{W(CO)_5\}$ and CO (calculated at the same level) is 54.9 kcal mol^{-1}, whereas the experimental value is 46.0 ± 2 kcal.[143] Thus the W–B bonds are very strong compared to the W–CO bonds, which explains the substitution of CO for the fragments RE. The calculated dissociation energy of about 53 kcal mol^{-1} for $[(CO)_4Fe{-}AlCp]$ corresponds to the general tendency towards weaker metal–metal bonds for the 3d series than for the 4d and 5d series. That the donor-stabilized fragments EXL_2 show significantly higher dissociation energies than the donor-free variants EX is most remarkable (Table 4). This is in a way opposed to the drastically shortened bond lengths described above for the donor-free, dicoordinate complexes of the type MEX and MER, if the shorter bonds are taken as an indication for stronger bonds and correspondingly significant π interactions are inferred which should be possible for MEX but not for $MEXL_2$.[14, 88] The term "multiple bond" in the classical sense often implies a higher bond strength and shorter bonds; however, this view is quite problematic.[34, 144] The opinion underlying the interpretation of the Fe–Ga bond in $[(CO)_4Fe{-}GaAr^*]$ that significantly short bonds are diagnostic for an increased bonding order, for π-multiple bonds thus "strong" bonds, has repeatedly been critically discussed in literature, especially when metal–metal bonds and heavy elements are concerned.[144] The longer W–Al bond of the donor-stabilized model complexes is explained within the framework of fragment formalism from the increased coordination number at Al and the thus different hybridization of the 2e-σ donor orbital on the Al side relevant for the W–Al bond. The lone pair of electrons of a (hypothetical) fragment AlH has 91.5 % s character, while the corresponding donor orbital of a fragment $AlH(NH_3)_2$ has an s proportion of 77.5 %. Also the weaker substituent effects follow this line: 85 % s character for $AlCl(NH_3)_2$ and a correspondingly shorter bond than in $AlH(NH_3)_2$, but lower dissociation energy (Table 4). The closest relatives of the complexes of CpE and EX_2L fragments discussed here are pyrazolylborato derivatives such as $[(CO)_nM{-}E\{HB(3,5Me_2pz)_3H\}]$.[94, 145]

5.2. Bonding Polarity

The shortening of the bond lengths Al–Cl and Al–N in the complexes compared to those of the "free" ligand fragments is also informative (Table 4), which is connected to the electron donation $Al \Rightarrow W$. The calculated partial increase of the positive nature of the Al center is clearly greater than in the hypothetically "free" ligands (Table 4). The effect of the donor ligands on the calculated charge distribution is also informative. While the conditions at the earth metal center change only slightly on going from EX to EXL_2 (from +1.08 to 1.24, Table 4), the amine ligands transfer the charge density to the $\{(CO)_5W\}$ fragment (from −0.58 to −0.93, Table 4). The Cp* and the pyrazolylborato ligands also fit into these considerations, as they, being strong η^5- and η^3-bonded π and σ donors, respectively, have a similar effect on the charge distribution between the metal centers as the presence of amine ligands in EXL_2 fragments. Being a soft donor, the Cp* ligand is rather flexible and the distance E–Cp* is a sensitive measure of the positive polarization of the centre E in the M–E complexes.[83, 84, 172] Already the very different electronegativities of the metal atoms M and E suggest strong polar M–E bonds, and the more so if the group electronegativity of the carbonyl metal fragments, which are similar to O and F atoms, is taken into account.[146] Thus the description of the fragments Cp*E in the carbonyl metal complexes in the sense of a formally lower oxidation state of +I for E has also been criticized.

Thus, the model complex $[(CO)_4Fe{-}AlCp]$ was compared with a series of relevant molecules, including the hypothetical particle $[CpAl{=}O]$ and the structurally valid cation $[Cp^*_2Al]^+$, and the charge distributions (Mullikan population analysis) were calculated. The comparison showed that the increase of the positive nature of the Al center of $[CpAl{=}O]$ and $[Cp^*_2Al]^+$ is quite similar (+0.42 and +0.36, respectively), whereas a stronger increase of the positive nature of the Al atom of +0.7 was calculated for $[(CO)_4Fe{-}AlCp]$. This trend is also apparent from the Al–C distances, which for $[Cp^*_2Al]^+$

are 213.7(8) – 218.4(8) pm and for [$(CO)_4Fe{-}AlCp^*$] are 214.0(5) – 215.3(5) pm. The Al–C distances in [$Cp^*Al]_4$ are 229.2(13) – 237.8(11) pm and thus significantly longer. The calculated positive partial charge at the Al center in the model fragment {CpAl} is correspondingly low: +0.16. Thus for [$(CO)_4Fe{-}AlCp^*$] a polar description as contact ion pair [$(CO)_4Fe^{2-}$][$AlCp^{*2+}$] was preferred over a covalent view in the sense of complex stabilization of the Cp*Al fragment. Consequently, the carbenoid character of the {Cp*Al} unit does not exist in the complex, it is rather an Al^{III} center.[83]

Within the SEN formalism (shared electron number), which is used as means to get a standard number for the covalent bond strength, the SEN for the complex [$(CO)_4Fe{-}AlCp$] is 1.48 and for the Co–Al bonds in the Co/Al cluster ([Eq. (3)]) the SEN is 1.12. For the series of Fe/Ga clusters (Table 3, Scheme 5) the SENs for the various Fe–Ga bonds are between 1.14 and 1.89, the latter result applying to the hypothetical model complex [$(CO)_4Fe{-}GaH$].[88] For comparison: C–C bonds have a SEN of around 1.4, C=C of around 2.2, and the NaF molecule of around 0.3. Thus, we favor the description of M–E bonds as strong polar but covalent donor – acceptor bonds over the extreme formulation as contact ion pairs. The fragments RE (R = Cp*, {HB(3,5-$Me_2pz)_3$}; E = Al, Ga, In) and EXL_2 (X = H, halide, alkyl; E = Al, Ga) should be seen as potent 2e-donor ligands, similar to the ligands of the amine or phosphane type. The pyrazolylborato derivatives and the Cp and Cp* complexes smoothly fit into this picture. This relationship is also evident from the electron spectra (absorption and luminescence) of representatives of this family of compounds such as [$(CO)_5W{-}Al(X)(tmpda)$] (X = Cl, *i*Bu; tmpda = *N*,*N*,*N*′,*N*′-tetramethylpropylenediamine), which in their characteristics, also in terms of the substituent effects at the “ligand” EXL_2, totally correspond to the well-known pyridine complexes [$(CO)_5W(py)$].[147] This connection could also be of interest for the photochemistry of M–E complexes. In the lowest electronically excited state an efficient dissociation of the W–N bond of [$(CO)_5W(py)$] takes place.[148] In accordance with the calculated dissociation energies and correcting an earlier note[80] it must be emphasized that the W–Al bonds do not dissociate thermally. A displacement by other ligands (CO, isocyanides, phosphanes) and a splitting of the fragments EXL_2 can probably only be achieved by using photochemistry.

5.3. π-Backbonding

Is it justified to discuss significant π-bond components in complexes like [$(CO)_4Fe{-}GaAr^*$] starting out from the structural and spectroscopic facts and based on different quantum chemical methods? On the basis of semiempirical EHMO calculations on M–In complexes of the type M_3E (type **B**) the extent of possible M–In π-backbonding was rated to be very small and the favorable relative orientation of the M fragments in the solid for such bonds was attributed to the minimization of steric interactions.[106] The lack of a rotation barrier around the Fe–Ga bond in [$Cp(CO)_2Fe{-}Ga(tBu)_2$] and the $\tilde{\nu}$(CO) absorptions which are very clearly shifted by around 32 cm^{-1} to lower wave numbers compared to the boryl analogue [$Cp(CO)_2Fe{-}B(C_6H_5)_2$] were also taken as an indication for insignificant Fe–Ga π interactions.[137] Backbonding into energetically matching σ*(E–X) bonds (X = Cl, NR_2, CR_3) corresponding to the interpretation of acceptor properties of PR_3 ligands in phosphane complexes (σ*-P-X)[149] were also taken into account but later discarded because of the results of Fenske – Hall calculations.[94] The typical apical position of the E fragment in complexes of the [$(CO)_4M$] type has also been taken as an indication against classic π-bonds.[34]

Recent DFT calculations on [$(CO)_4Fe{-}Ga(\eta^5\text{-}Cp)$] (**M1**) and [$(CO)_4Fe{-}Ga(\eta^1\text{-}Ph)$] (**M2**) as models for the Robinson compound with a linearly dicoordinated Ga center now show that within the charge decomposition analysis (CDA) formalism[136] apparently increased π-backbonding components Ga ← Fe can be calculated for **M2** in comparison to **M1**. For **M2** a donor/acceptor relation of 1.51 was determined, for **M1**, however, the value of 2.94 was obtained. Values around 0.35 e were found for the population of the 4p(π) orbital in **M2**. Interestingly, a calculation of the CO-stretching vibration frequencies at the BP86/I level for **M1** and **M2** revealed that they hardly differ from each other. The experimental values for the complexes [$(CO)_4Fe{-}GaR$] (R = Cp* and Ar*) are quite similar to each other but clearly shifted to higher wave numbers compared to [$(CO)_4Fe{-}GaCl(tmeda)$] and [$(CO)_4Fe{-}Ga\{HB(3,5\text{-}Me_2pz)_3\}$] (Table 3). The position of the $\tilde{\nu}$(CO) frequencies, however, depends on purely electrostatic polarization effects as well as on the extent of the assumed, covalent π-backbonding M ⇒ CO. Thus especially in the case of polar bonds M – E the importance of π backbonds M ⇒ E can hardly be inferred from the $\tilde{\nu}$(CO) frequencies![150]

On balance this reasoning stresses that none of the discussed observable quantities, namely bond lengths, rotation barriers, and the position of the $\tilde{\nu}$(CO) frequencies require the concept of a Fe–Ga multiple bond and considerable Fe ⇒ Ga backbonding for [$(CO)_4Fe{-}GaAr^*$] and related compounds. Depending on the level of the quantum chemical calculations and the chosen description model (especially the method and concepts used for calculating the charge distributions) more or less detailed pictures of the bonding conditions are obtained, the common and dominating factor of which is the bond polarity. This can be determined according to the series $E(R)L_2 > E(X)L_2 > ER$ and Al > Ga, In depending on the coordination number of E and the substituents R, X, and L bonded to E. Especially the coordinatively saturated fragments $EX(L)_2$ here widely correspond to the amine or phosphane ligands (py, NR_3, PR_3) but because of the more electropositive character of the center E allow clearly increased negative charge densities at the d-block metal. The preference of Cr – Ga versus Cr – P coordination in η^5-phospholylgallium complexes of the $(CO)_5$ fragment nicely shows this situation.[175] The M–E bonds in the discussed complexes thus should best be viewed as strong polar Lewis acid/base adducts. There is certainly an analogy of the RE ligands to the CO ligand in a structural or coordination chemical view. The answer to the question of whether a distinctive π-acceptor capacity of the fragments RE does or does not exist or whether it is limited to Ar*Ga or $(SiMe_3)SiGa$ or $(SiMe_3)_3ClIn$, very much depends on the standard of the theoretical way of looking at things, however, there still is no experimental evidence.

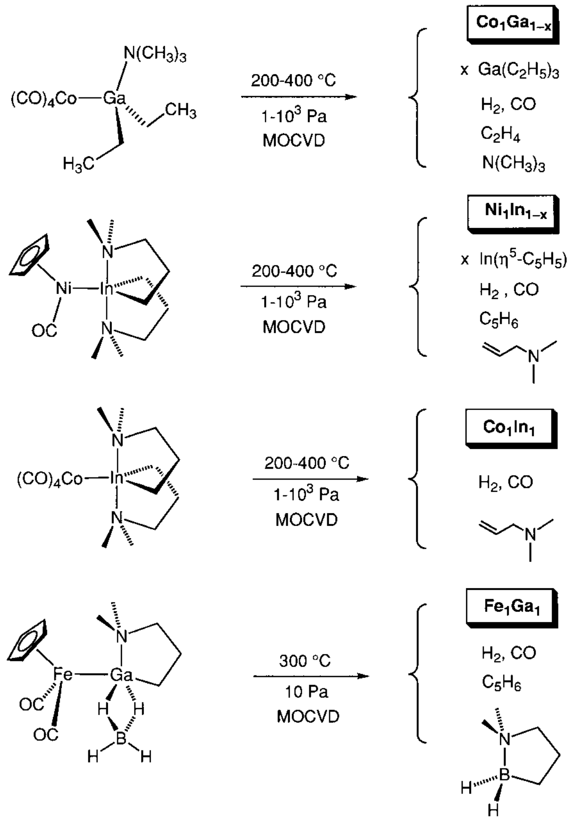
6. Precursor for MOCVD of Intermetallic Phases

The general interest in organometallic precursors for new materials and especially for MOCVD as an alternative to physical coating methods was, as mentioned in the introduction, an important impulse for the renaissance of the coordination chemistry of M–E complexes. While the precursor chemistry for MOCVD for pure elemental metals (e.g. Cu, Al, Pt, Pd, Au) and a whole host of metal oxides, carbides, and nitrides as well as for semiconductors of the III/V and II/VI types continues to be intensively investigated, there are hardly any surveys on precursors for the deposition of intermetallic phases.[36, 151–153]

As was set out in the introduction, certain intermetallic phases from combinations of Al, Ga, and In with d-block metals are especially suitable as epitaxial metallizations being inert against unwanted interface reactions and useful for Schottky barriers for III/V semiconductor techniques; thus MOCVD processes are of interest for these materials.[154–157] Thin films from CoGa or similar phases have been discussed for the fabrication of hetero bipolar transistors (HEMT), resonant tunnel diodes or transistors (DBRT, RTBTs), and quantum dot hetero structures. Examples for these "thermodynamically stable metal contacts" are Ni/Al (GaAs),[158–160] Mn/Al (AlAs),[161] Pt/Ga (GaAs),[162] Co/Ga (GaAs)[163] and Rh/Ga (GaAs)[164] systems prepared by molecular-beam orientation crystallization according to UHV techniques (MBE, molecular beam epitaxy). The system Co/Ga on GaAs is prototypical for this: The ternary Co-Ga-As phase diagram contains two intermetallic phases $CoGa_3$ and $Co_{1-\delta}Ga_\delta$ $(0.36 > \delta > 0.64)$ which are coexistent with GaAs. Because the arsenide phases Co_xAs_y, equally thermodynamically stable towards GaAs, are semiconductors, they are less interesting as metallizations than the metallic cobalt gallides. The β-CoGa phase (CsCl-type) exhibits a defect structure, the lattice constant of which is very close to half of the characteristic lattice constant of GaAs (ZnS-type). Stoichiometric β-$Co_{1-\delta}Ga_\delta$ $(\delta = 0.50)$ with a lattice misfit of about 2% is stable up to about 600°C, perfectly epitaxial β-$Co_{1-\delta}Ga_\delta$ with $\delta = 0.62$ is stable up to about 800°C against GaAs. The Schottky barrier height of 0.76 eV remains unchanged even after tempering at 500 to 600°C.

Starting from two independent precursors $[CpCo(CO)_2]$ and $GaEt_3$ Kaesz et al. proved the organometallic chemical vapor-phase epitaxy (OMVPE) of β-CoGa on GaAs(100).[168] Control of the composition of such multinary CVD films in technical applications is effected from a precise adjustment of the mole fractions of the different precursors for the film constituting components in the gas phase. The molecular source components, however, show individual homogenous and heterogenous fragmentation chemistry and kinetics, physi- and chemisorption as well as different surface mobilities of the molecular fragments. A difficult optimization problem can result from that for a binary or multinary CVD process.

One approach to widely reduce control engineering and to make such binary metal films easily available by process engineering is the inclusion of all kinds of film-constituting atoms into one single precursor molecule. This is called a single-source precursor. Process control in this case is shifted to the constitutional and structural optimization of the precursor. The property profile comprises: properly selected metal combination, acceptable vapor pressure (>1 Pa at 25°C), low proportion of heteroatoms in the ligand sphere, weakly bonded ligands, mild pyrolysis (T > 400°C), and sufficient long-term stability under evaporation conditions. The alkyl derivatives of the types **L** and **M** (Figure 1) agree with this profile. An example for this group of substances is the vapor pressure of the CoIn system (Scheme 10), which at 20°C is approximately 0.0250(5) mbar and which allows film growth rates around 1 μm h^{-1} (10 Å s^{-1}).[171] In comparison to this halide-containing complexes of the types **K**, **O**, or **P** are less volatile and, furthermore, as a source of impurities of the films the halide group is unwelcome. The analysis of the deposited films and exhaust gases revealed that the metal composition of the precursors in the deposited films is not necessarily reproduced. The loss of earth metal was a frequent effect which under given conditions is controlled by the ligands at both metal centers (Scheme 10).



Scheme 10. Ligand control of the film composition for the MOCVD of M/E films using precursors of the type **K**.

In principle, also films rich in earth metals $M_1E_{1+\delta}$ are obtained from precursors with E/M > 1. According to mass spectrometric investigations the liberation of the donor ligand

L at the center E together with the liberation of CO are the favored first steps of molecular degradation. The composition of the film is determined by the competition between (alkyl) ligand fragmentation and ligand reorganization combined with the cleavage of the M–E bonds. This was investigated with a series of CoGa precursors.[169] Cobalt-rich films are obtained at a substrate temperature of 200 °C from $[(CO)_4Co–GaEt_2(NMe_3)]$ and a corresponding proportion of $GaEt_3$ gets into the waste gas; at higher substrate temperatures of around 350 °C stoichiometric films $Co_{0.50}Ga_{0.50}$ are formed (Figure 10). The fragmentation of the Ga–C bond then takes place fast enough. Similarly, the deposition of CoGa from a 1:1 mixture of $Ga(C_2H_5)_3$ and $[Cp(CO)_2Co]$ at 250–300 °C and 1010 mbar (flow reactor) provides cobalt-rich, metastable α-$Co_1Ga_{1-\xi}$ films ($\xi \geq 0.41$). Only a tenfold excess of the gallium precursor compensates the inefficient pyrolysis of these films and – in a mass transport limited regime – leads to β-CoGa films. The degradation of the single-component sources to the film is, however, kinetically controlled, as Co and Ga fragments are transported to the surface in the same proportion independent of pressure and temperature.

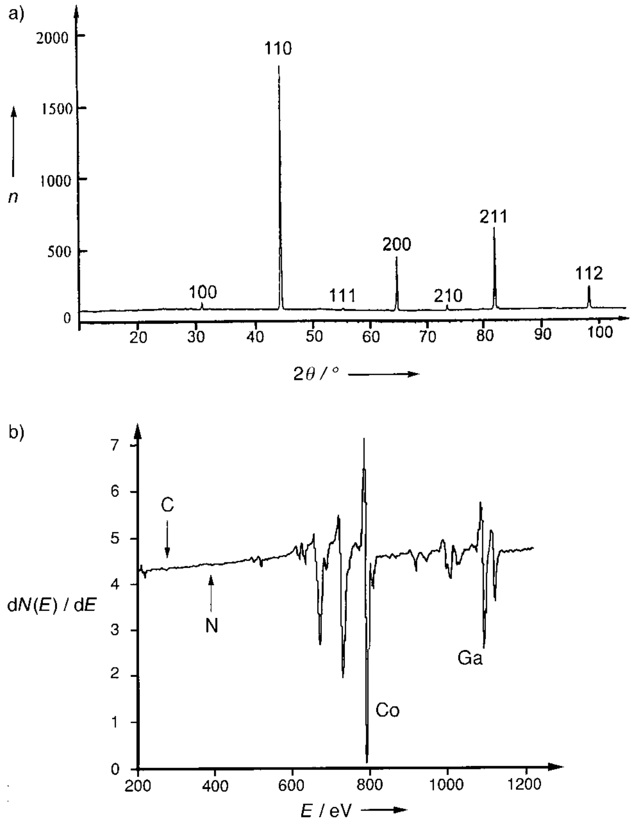


Figure 10. a) X-ray diffractogram of a CoGa film obtained from the precursor $[(CO)_4Co–GaEt_2(NMe_3)]$ at a substrate temperature of 350 °C and a pressure of 10^{-2} Torr by MOCVD; n = count rate. b) Auger electron spectrum (AES) of the film after short-time purification of the surface by sputtering with Ar ions.

The complexes are mostly less stable than the homoleptic alkylgallium compounds. Thus it is possible to define the composition of the film by temperature control and structure optimization of the precursor. If the formation of thermally stable metal-containing degradation products during film growth is insignificant the limiting value $M/E_{(precursor)} = M/E_{(film)}$ will already be reached at low temperatures. The deposition of mixed-metal CrGa films from the precursor $[(CO)_5Cr–Ga(Et)(tmeda)]$ already leading to CrGa films at low temperatures of 250 °C onwards without the loss of Ga[85] corresponds to this concept. Formation of $GaEt_3$ was not observed. In this context the fragmentation behavior of the complexes after ionization in the mass spectrometer is of interest. Complexes of the type **K** show a complicated fragmentation pattern in which breakage of the M–E bond often dominates.[170] In contrast, complexes of the type **I** decompose more clearly, and fragments with intact M–E bond are frequent. For $[(CO)_5Cr–ECp^*]$ the ion $[CrECp^*]^+$ is found as base peak (E = Al, Ga).[84, 172]

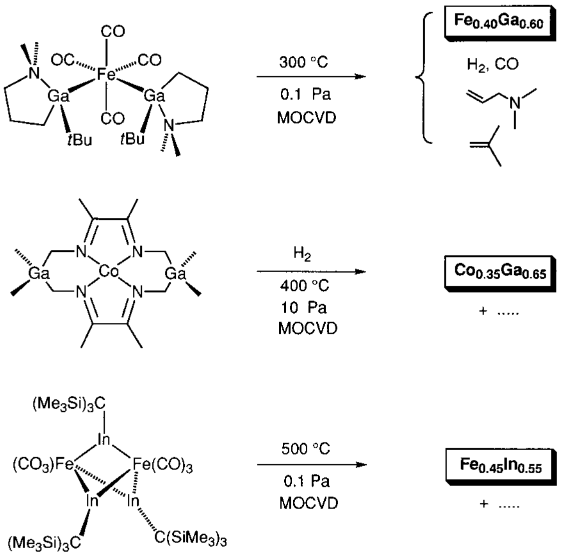
The fragmentation behavior of a potential MOCVD precursor under the conditions prevailing in a mass spectrometer cannot automatically be compared to the conditions of a thermal MOCVD experiment. In the cases we examined, however, a correlation was observed. Precursors whose mass spectra are rich in mixed-metal fragments provide films, the metal concentration of which corresponds to the structure of the precursor.

Not only the substituents at the earth metal control the degradation process, but also the ligands at the d-block metal are important (Scheme 10). While $[(CO)_4Co–In(R^N)_2]$ ($R^N = CH_2CH_2CH_2NMe_2$) only provides Co_1In_1 films, the closely related NiIn source $[Cp(CO)Ni–In(R^N)_2]$ yields films with Ni/In = 3.0 to 1.0 depending on the substrate temperature. This an example of an unexpected Cp transfer to the In atom, leading to stable [CpIn], which desorbs and gets into the exhaust gas.[61] Also transportation of the d-block metal is possible, as shown by the release of ferrocenes in the MOCVD of Fe/In films from $[Cp(CO)_2Fe–In(R^N)_2]$. Such a ligand control of the film composition is an important aspect of the MOCVD chemistry. This is especially true if during pyrolysis part of the ligand sphere takes part in rearrangements or redistributions and is bonded without fragmentation in the form of stable and volatile by-products.

An example for the use of such a reaction process is the selective formation of Fe/Ga films from the tetrahydridoboranate-substituted system $[Cp(CO)_2Fe–Ga(R^N)(BH_4)]$ (Scheme 10).[62] This result is the more remarkable if one considers that the formation of iron boride would thermodynamically be preferred here. The majority of the obtained M/E films was remarkably low in impurities. Typical values are 1–4 atom % C and ≥1 atom % O (N, P not detectable; XPS and AES analyses). The best conductivities are close to literature values, for example, for CoGa around 120 $\mu\Omega\,cm^{-1}$. It turned out that the residual content of carbon is due to the hydrocarbon groups and not to the CO ligands. Oxygen contaminations are determined by the leakage rate of the reactor and the sample manipulation or the purity of the precursors which are partly very sensitive to hydrolysis. The films are composed according to the binary phase diagram of the metal combination in question (thermodynamic control). All CoGa films obtained from the CoGa precursors of type **K** proved to be, for example, single-phase, polycrystalline β-CoGa with a dominant [110] reflection or with strong preferred orientation in 100 direction on GaAs substrates.[169]

In the Co/In system only $CoIn_2$ and $CoIn_3$ are stable. Co_1In_1 films deposited from $[(CO)_4Co{-}In(R^N)_2]$ display reflections which have to be assigned to these phases.[171] The phase diagrams of other interesting alloys such as Mn/Al, Mn/Ga, Co/Al, Fe/Ga, Ni/Ga, and Ni/In are more complex, the homogeneity area is more narrow. Thus it is very difficult to get single-phase films. This was successfully demonstrated for NiIn films deposited from $[Cp(CO)Ni{-}In(R^N)_2]$ at 350 °C. The fully indexed X-ray diffractogram only contains reflections of the hexagonal ε-NiIn phase.[61]

The suitability of the M/E complexes as single-source precursors for MOCVD thus has been comprehensively documented. However, technical relevance in the field of microelectronics has not yet become apparent. For that it would be necessary to produce a currently important material in a uniquely simple way compared to other processes. This would mean in the case discussed here to epitaxially deposit the Ga-rich phase β-$Co_{1-\delta}Ga_\delta$ with $\delta = 0.62$ from a volatile precursor in pure form at $T < 400\,^\circ C$ on GaAs (100). The single-source precursor for this process needs the composition $CoGa_2$. The Co–Ga complex shown in Scheme 11 fulfils this criterion and has indeed been used as a MOCVD precursor for Ga-rich CoGa films.[43] But the vapor pressure of the compound is too low and the obtained film purity remained unsatisfactory due to the structure bridged by heteroatoms. The outlined coordination chemistry of {Cp*Ga} fragments at d-bolck metals could be a step further if it were possible to derive compounds such as $[CpCo(GaCp^*)_2]$ or $[(NO)(CO)Co(GaCp^*)_2]$. These hypothetical complexes should to exist and should be characterized by strong enough Co–Ga bonds; however, the stability of the fragment {Cp*Ga} could be a problem. In chemical beam epitaxy (CBE) experiments it survives substrate temperatures up to 600 °C without problems.[84] A loss of earth metal during deposition seems to be predeterminded. It remains to be seen if an elegant solution will be found for these contrary effects, that is stability and volatility of the precursors on the one hand and the kinetic conditions of the decomposition chemistry under MOCVD requirements on the other.



Scheme 11. Single-source precursor for MOCVD of M/E films rich in earth metals.

7. Summary and Outlook

This review summarizes a selecton of results and current trends of the past decade in the field of the coordination chemistry of the earth metals Al, Ga, and In at d-block metals. Important progress has been made with the expansion of the coordination chemistry of (intramolecular) donor-stabilized fragments ER_2L and ERL_2 to the coordinatively unsaturated, "donor-free" analogues RE ($R = Cp^*$, Ar* and $C(SiMe_3)_3$). The synthetic potential of low-valent earth metal compounds in coordination chemistry is impressively documented and holds promise for some more surprises in the future. Thus for the first time mixed M–E clusters and complexes with a relation $E/M > 1$ are available. The latter compounds also offer new prespectives as novel MOCVD precursors for intermetallic phases and alloys, which could be interesting for III/V semiconductors in form of epitaxial films as special metal contacts. The discussion on the existence of a Fe–Ga triple bond in the complex $[(CO)_4Fe{-}GaAr^*]$ has led to a series of reports on the quantum chemical description of the bonding conditions in M–E complexes at the DFT level. The M–E bonds in the different types of complexes agree well with the usual donor/acceptor concept. The dominating factor is the bonding polarity (i.e. ionic contributions). Multiple bonds in the traditional sense only play a minor role. These findings are only strictly valid if one considers carbonylmetalates to be the bonding partners. The variation of the ligands as well as the coordination at the center, E, is now quite well understood.[136] However, experimental and theoretical studies regarding ligands surrounding the transition metal center M are lacking, and the synthesis of M–E complexes without strong π-acceptors (e.g. CO, Cp) is therefore encouraged. These complexes may provide interesting insight into how a reduction of the ionic contribution in the M–E bond influences the stability and reactivity of the compounds. Remarkably little is still known about the reactivity of the M–E complexes. The question remains open as to what extent the many new compounds can be used as building blocks for further synthesis.

We are indebted to the Fonds der Chemischen Industrie, the Deutsche Forschungsgemeinschaft, and the Alfried-Krupp-von-Bohlen-und-Halbach Foundation for their long-term generous support. R. A. F. would like to thank his co-workers H. Fölsing, H. Hoffmann, A. Miehr, T. Priermeier, W. Rogge, M. Schulte, O. Segnitz, D. Weiß, and J. Weiß for their perseverance and creativity without which many of the results set down in this article would not have been produced. He would also like to thank G. Frenking (Marburg) for the fruitful cooperation over the past years. Special thanks go to all colleagues who have contributed to this work by means of data material, critical comments, and good advice.

Received: September 18, 1998 [A301IE]
German version: *Angew. Chem.* **1999**, *111*, 3002–3022

[1] W. Hieber, U. Teller, *Z. Anorg. Allg. Chem.* **1942**, *249*, 43–57.

[2] W. R. Robinson, D. P. Schussler, *Inorg. Chem.* **1973**, *12*, 848–854.

[3] G. Natta, G. Mazzanti, *Tetrahedron* **1960**, *8*, 86–100.

[4] P. Corradini, A. Sirigu, *Inorg. Chem.* **1967**, *6*, 601–605.

[5] F. N. Tebbe, L. J. Guggenberger, *J. Chem. Soc. Chem. Commun.* **1973**, 227–228.

[6] G. Erker, R. Zwettler, C. Krüger, R. Noe, S. Werner, *J. Am. Chem. Soc.* **1990**, *112*, 9620–9621.

[7] G. Erker, M. Albrecht, C. Krüger, S. Werner, P. Binger, F. Langhauser, *Organometallics* **1992**, *11*, 3517–3525.

[8] H. Brunner, P. C. Wailes, H. D. Kaesz, *Inorg. Nucl. Chem. Lett.* **1965**, *1*, 125–129.

[9] R. Kumar, H. Rahbarnoohi, M. J. Heeg, D. G. Dick, J. P. Oliver, *Inorg. Chem.* **1994**, *33*, 1103–1108.

[10] A. Alich, N. J. Nelson, D. Strope, D. F. Shriver, *Inorg. Chem.* **1972**, *11*, 2976–2983.

[11] J. M. Burlitch, M. E. Leonowicz, R. B. Petersen, R. E. Hughes, *Inorg. Chem.* **1979**, *18*, 1097–1105.

[12] E. O. Fischer, *Angew. Chem.* **1974**, *86*, 651–663.

[13] H. Tobita, K. Ishiyama, Y. Kawano, S. Inomata, H. Ogino, *Organometallics* **1998**, *17*, 789–794.

[14] J. Su, X.-W. Li, R. C. Crittendon, C. F. Campana, G. H. Robinson, *Organometallics* **1997**, *16*, 4511–4513.

[15] a) M. L. H. Green, P. Mountford, G. J. Smout, S. R. Speel, *Polyhedron* **1990**, *9*, 2763–2765; b) J. J. Schneider, U. Denninger, J. Hagen, C. Krüger, D. Bläser, R. Boese, *Chem. Ber.* **1997**, *130*, 1433–1440.

[16] E. O. Fischer, D. Wittmann, D. Himmelreich, U. Schubert, K. Ackermann, *Chem. Ber.* **1982**, *115*, 3141–3151.

[17] H. Fischer, A. Motsch, U. Schubert, D. Neugebauer, *Angew. Chem.* **1981**, *93*, 483–487; *Angew. Chem. Int. Ed. Engl.* **1981**, *20*, 463–465.

[18] U. Schubert, E. O. Fischer, D. Wittmann, *Angew. Chem.* **1980**, *92*, 662–663; *Angew. Chem. Int. Ed. Engl.* **1980**, *19*, 643–644.

[19] M. R. Terry, C. Kelley, N. Lugan, G. L. Geoffroy, B. S. Haggerty, A. L. Rheingold, *Organometallics* **1993**, *12*, 3607–3617.

[20] M. Bottrill, M. Green, A. G. Orpen, D. R. Saunders, I. D. Williams, *J. Chem. Soc. Dalton Trans.* **1989**, 511–518.

[21] M. Green, A. G. Orpen, I. D. Williams, *J. Chem. Soc. Chem. Commun.* **1982**, 493–495.

[22] G. Huttner, *Acc. Chem. Res.* **1986**, *19*, 406–413.

[23] W. A. Herrmann, *Angew. Chem.* **1986**, *98*, 57–77; *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 56–76.

[24] T. P. Fehlner, *Comments Inorg. Chem.* **1988**, *7*, 307–332.

[25] O. J. Scherer, *Angew. Chem.* **1985**, *97*, 905–924; *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 924–943.

[26] O. J. Scherer, *Comments Inorg. Chem.* **1987**, *6*, 1–22.

[27] M. D. Vaira, P. Stoppioni, M. Peruzzini, *Polyhedron* **1987**, *6*, 351–382.

[28] K. H. Whitmire, *J. Coord. Chem.* **1988**, *17*, 95–204.

[29] W. A. Nugent, *Metal-Ligand Multiple Bonds*, Wiley, New York, **1988**.

[30] S. K. Boocock, S. G. Shore, *Comprehensive Organometallic Chemistry*, Pergamon, Oxford, **1982**.

[31] M. J. Taylor, *Metal to Metal Bonding*, Academic Press, London, **1975**.

[32] A. T. T. Hsieh, *Inorg. Chim. Acta* **1975**, *14*, 87–104.

[33] N. A. Compton, R. J. Errington, N. C. Norman, *Adv. Organomet. Chem.* **1990**, *31*, 91–182.

[34] P. J. Brothers, P. P. Power, *Adv. Organomet. Chem.* **1996**, *39*, 1–69.

[35] G. B. Stringfellow, *Organometallic Vapor-Phase Epitaxy, Theory and Practice*, Academic Press, San Diego, **1989**.

[36] M. L. Hitchman, K. F. Jensen, *Chemical Vapor Deposition*, Academic Press, London, **1993**.

[37] C. J. Carmalt, S. R. Whaley, P. S. Lall, A. H. Cowley, R. A. Jones, B. G. McBurnett, J. G. Ekerdt, *J. Chem. Soc. Dalton Trans.* **1998**, 553–557.

[38] A. H. Cowley, R. A. Jones, *Angew. Chem.* **1989**, *101*, 1235–1243; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 1208–1216.

[39] a) M. Bochmann, *Chem. Vap. Deposition* **1996**, *2*, 85–96; b) D. G. Colombo, D. C. Gilmer, V. G. Young, S. A. Campbell, W. L. Gladfelter, *Chem. Vap. Deposition* **1998**, *4*, 220–222.

[40] A. H. Cowley, B. L. Benac, J. G. Ekerdt, R. A. Jones, K. B. Kidd, J. Y. Lee, J. E. Miller, *J. Am. Chem. Soc.* **1988**, *110*, 6248–6249.

[41] J. E. Miller, J. G. Ekerdt, *Chem. Mater.* **1992**, *4*, 7–9.

[42] a) V. Lakhotia, D. A. Neumayer, A. H. Cowley, R. A. Jones, J. G. Ekerdt, *Chem. Mater.* **1995**, *7*, 546–552; b) H. S. Park, S. D. Waezsada, A. H. Cowley, H. W. Roesky, *Chem. Mater.* **1998**, *10*, 2251–2257.

[43] F. Maury, L. Brandt, H. D. Kaesz, *J. Organomet. Chem.* **1993**, *449*, 159–165.

[44] Y.-J. Chen, H. D. Kaesz, Y. K. Kim, H.-J. Müller, R. S. Williams, Z. Xue, *Appl. Phys. Lett.* **1989**, *55*, 2760–2762.

[45] R. S. Williams, *Appl. Surf. Sci.* **1992**, *60/61*, 613–618.

[46] H. M. Manasevit, W. I. Simpson, *J. Electrochem. Soc.* **1969**, *116*, 1725–1732.

[47] H. M. Manasevit, *Appl. Phys. Lett.* **1968**, *12*, 156–159.

[48] H. M. Manasevit, *J. Cryst. Growth* **1972**, *13/14*, 306–314.

[49] E. Yablonovith, *Science* **1989**, *246*, 347–351.

[50] D. Bradley, *New Sci.* **1988**, *14*, 38–41.

[51] R. A. Fischer, H. D. Kaesz, S. I. Khan, H.-J. Müller, *Inorg. Chem.* **1990**, *29*, 1601–1602.

[52] R. A. Fischer, W. Scherer, M. Kleine, *Angew. Chem.* **1993**, *105*, 778–780; *Angew. Chem. Int. Ed. Engl.* **1993**, *105*, 774–776.

[53] R. A. Fischer, J. Behm, T. Priermeier, W. Scherer, *Angew. Chem.* **1993**, *105*, 776–778; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 772–774.

[54] R. A. Fischer, J. Behm, *J. Organomet. Chem.* **1991**, *413*, C10–C14.

[55] R. A. Fischer, J. Behm, E. Herdtweck, C. Kronseder, *J. Organomet. Chem.* **1992**, *437*, C29–C34.

[56] R. A. Fischer, J. Behm, *Chem. Ber.* **1992**, *125*, 37–42.

[57] R. A. Fischer, J. Behm, T. Priermeier, *J. Organomet. Chem.* **1992**, *429*, 275–286.

[58] R. A. Fischer, T. Priermeier, W. Scherer, *J. Organomet. Chem.* **1993**, *459*, 65–71.

[59] R. A. Fischer, E. Herdtweck, T. Priermeier, *Inorg. Chem.* **1994**, *33*, 934–943.

[60] R. A. Fischer, T. Priermeier, *Organometallics* **1994**, *13*, 4306–4314.

[61] R. A. Fischer, M. Kleine, O. Lehmann, M. Stuke, *Chem. Mater.* **1995**, *7*, 1863–1872.

[62] R. A. Fischer, A. Miehr, M. M. Schulte, *Adv. Mater.* **1995**, *7*, 58–61.

[63] R. A. Fischer, M. M. Schulte, T. Priermeier, *J. Organomet. Chem.* **1995**, *493*, 139–142.

[64] R. A. Fischer, A. Miehr, T. Priermeier, *Chem. Ber.* **1995**, *128*, 831–843.

[65] C. Dohmeier, C. Robl, M. Tacke, H. Schnöckel, *Angew. Chem.* **1991**, *103*, 594–595; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 564–565.

[66] S. Schulz, H. W. Roesky, H. J. Koch, G. M. Sheldrick, D. Stalke, A. Kuhn, *Angew. Chem.* **1993**, *105*, 1828–1830; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1729–1732.

[67] C. Schnitter, H. W. Roesky, C. Röpken, R. Herbst-Irmer, H.-G. Schmidt, M. Noltemeyer, *Angew. Chem.* **1998**, *110*, 2059–2062; *Angew. Chem. Int. Ed.* **1998**, *37*, 1952–1955.

[68] W. Uhl, A. Jantschak, *J. Organomet. Chem.* **1998**, *555*, 263–269.

[69] W. Uhl, W. Hiller, M. Layh, W. Schwarz, *Angew. Chem.* **1992**, *104*, 1378–1380; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1364–1366.

[70] W. Uhl, R. Graupner, M. Layh, U. Schütz, *J. Organomet. Chem.* **1995**, *493*, C1–C5.

[71] W. Uhl, S. U. Keimling, K. W. Klinkhammer, W. Schwarz, *Angew. Chem.* **1997**, *109*, 64–66; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 64–66.

[72] C. Dohmeier, D. Loos, H. Schnöckel, *Angew. Chem.* **1996**, *108*, 141–161; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 129–149.

[73] a) W. Uhl, *Angew. Chem.* **1993**, *105*, 1449–1461; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1386–1397; b) W. Uhl, *Rev. Inorg. Chem.* **1998**, *18*, 239–282.

[74] R. J. Wehmschulte, K. Ruhlandt-Senge, M. M. Olmstead, H. Hope, B. E. Sturgeon, P. P. Power, *Inorg. Chem.* **1993**, *32*, 2983–2984.

[75] W. Uhl, A. Vester, W. Kaim, J. Poppe, *J. Organomet. Chem.* **1993**, *454*, 9–13.

[76] J. Su, X.-W. Li, C. Crittendon, G. H. Robinson, *J. Am. Chem. Soc.* **1997**, *119*, 5471–5472.

[77] W. Uhl, M. Pohlmann, R. Wartchow, *Angew. Chem.* **1998**, *110*, 1007–1009; *Angew. Chem. Int. Ed.* **1998**, *37*, 961–963.

[78] C. Dohmeier, H. Krautscheid, H. Schnöckel, *Angew. Chem.* **1994**, *106*, 2570–2571; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 2482–2483.

[79] J. Weiß, D. Stetzkamp, B. Nuber, R. A. Fischer, C. Boehme, G. Frenking, *Angew. Chem.* **1997**, *109*, 95–97; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 70–72.

[80] R. A. Fischer, M. M. Schulte, J. Weiß, L. Zsolnai, A. Jacobi, G. Huttner, G. Frenking, C. Boehme, S. F. Vyboishchikov, *J. Am. Chem. Soc.* **1998**, *120*, 1237 – 1248.
[81] H. Braunschweig, J. Müller, B. Ganter, *Inorg. Chem.* **1996**, *35*, 7443 – 7444.
[82] B. N. Anand, I. Krossing, H. Nöth, *Inorg. Chem.* **1997**, *36*, 1979 – 1981.
[83] C. Üffing, A. Ecker, R. Köppe, H. Schnöckel, *Organometallics* **1998**, *17*, 2373 – 2375.
[84] P. Jutzi, B. Neumann, G. Reumann, H.-G. Stammler, *Organometallics* **1998**, *17*, 1305 – 1314.
[85] M. M. Schulte, E. Herdtweck, G. Raudaschl-Sieber, R. A. Fischer, *Angew. Chem.* **1996**, *108*, 489 – 491; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 424 – 426.
[86] J. C. Vanderhooft, R. D. Ernst, F. W. Cagle, R. J. Neustadt, T. H. Cymbaluk, *Inorg. Chem.* **1982**, *21*, 1876 – 1880.
[87] M. M. Schulte, Dissertation, Technische Universität München, **1996**.
[88] G. Linti, W. Köstler, *Chem. Eur. J.* **1998**, *4*, 942 – 949.
[89] U. App, K. Merzweiler, *Z. Anorg. Allg. Chem.* **1997**, *623*, 478 – 482.
[90] R. A. Fischer, M. M. Schulte, E. Herdtweck, M. R. Mattner, *Inorg. Chem.* **1997**, *36*, 2010 – 2017.
[91] G. N. Harakas, B. R. Whittlesey, *Inorg. Chem.* **1997**, *36*, 2704 – 2707.
[92] O. J. Curnow, B. Schiemenz, G. Huttner, L. Zsolnai, *J. Organomet. Chem.* **1993**, *459*, 17 – 20.
[93] H. Behrens, M. Moll, E. Sixtus, G. Thiele, *Z. Naturforsch. B* **1977**, *32*, 1109 – 1113.
[94] D. L. Reger, S. S. Mason, A. L. Rheingold, B. S. Haggerty, F. P. Arnold, *Organometallics* **1994**, *13*, 5049 – 5053.
[95] W. Uhl, S. U. Keimling, W. Hiller, M. Neumayer, *Chem. Ber.* **1995**, *128*, 1137 – 1139.
[96] S. T. Haubrich, P. P. Power, *J. Am. Chem. Soc.* **1998**, *120*, 2202 – 2203.
[97] W. Uhl, M. Pohlmann, *Organometallics* **1997**, *16*, 2478 – 2480.
[98] J. L. Atwood, S. G. Bott, P. B. Hitchcock, C. Eaborn, R. S. Shariffudin, J. D. Smith, A. C. Sullivan, *J. Chem. Soc. Dalton Trans.* **1987**, 747 – 755.
[99] W. Uhl, S. U. Keimling, W. Hiller, M. Neumayer, *Chem. Ber.* **1996**, *129*, 397 – 400.
[100] J. J. Schneider, C. Krüger, M. Nolte, I. Abraham, T. S. Ertel, H. Bertagnolli, *Angew. Chem.* **1994**, *106*, 2537 – 2540; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 2435 – 2438.
[101] J. M. Mayer, J. C. Calabrese, *Organometallics* **1984**, *3*, 1292 – 1298.
[102] D. L. Thorn, R. L. Harlow, *J. Am. Chem. Soc.* **1989**, *111*, 2575 – 2580.
[103] J. Weiß, T. Priermeier, R. A. Fischer, *Inorg. Chem.* **1996**, *35*, 71 – 75.
[104] R. A. Fischer, S. Nlate, H. Hoffmann, E. Herdtweck, J. Blümel, *Organometallics* **1996**, *15*, 5746 – 5752.
[105] a) F. P. Gabbaï, A. Schier, J. Riede, H. Schmidbaur, *Inorg. Chem.* **1995**, *34*, 3855 – 3856; b) F. P. Gabbaï, S.-C. Chung, A. Schier, S. Krüger, N. Rösch, H. Schmidbaur, *Inorg. Chem.* **1997**, *36*, 5699 – 5705.
[106] M. L. Clarkson, W. Clegg, D. C. R. Hockless, N. C. Norman, T. B. Marder, *J. Chem. Soc. Dalton Trans.* **1991**, 2229 – 2239.
[107] W. Schatz, H.-P. Neumann, B. Nuber, B. Kanellakopulos, M. L. Ziegler, *Chem. Ber.* **1991**, *124*, 453 – 463.
[108] J. C. Calabrese, L. M. Clarkson, T. B. Marder, N. C. Norman, N. J. Taylor, *J. Chem. Soc. Dalton Trans.* **1992**, 3525 – 3529.
[109] B. Schiemenz, G. Huttner, *Angew. Chem.* **1993**, *105*, 1840 – 1841; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1772 – 1773.
[110] R. Dagani, *Chem. Eng. News* **1998**, *76*, 31 – 35.
[111] H. Preut, H.-J. Haupt, *Chem. Ber.* **1974**, *107*, 2860 – 2869.
[112] H. Preut, H.-J. Haupt, *Acta Crystallogr. Sect. B* **1979**, *35*, 1205 – 1207.
[113] H.-J. Haupt, F. Neumann, *J. Organomet. Chem.* **1974**, *74*, 185 – 195.
[114] U. Flörke, P. Balsaa, H.-J. Haupt, *Acta Crystallogr. Sect. C* **1986**, *42*, 275 – 277.
[115] a) H. Braunschweig, *Angew. Chem.* **1998**, *110*, 1882 – 1898; *Angew. Chem. Int. Ed.* **1998**, *37*, 1786 – 1801; b) G. J. Irvine, M. J. G. Lesley, T. B. Marder, N. C. Norman, C. R. Rice, E. G. Robins, W. R. Roper, G. R. Whittell, L. J. Wright, *Chem. Rev.* **1998**, *98*, 2685 – 2722.
[116] R. B. Petersen, J. J. Stezowski, C. Wan, J. Burlith, R. E. Hughes, *J. Am. Chem. Soc.* **1971**, *93*, 3532 – 3533.
[117] A. T. T. Hsieh, M. J. Mays, *J. Organomet. Chem.* **1972**, *37*, 9 – 14.
[118] D. J. Patmore, W. A. G. Graham, *J. Chem. Soc. Chem. Commun.* **1965**, 591.
[119] D. J. Patmore, W. A. G. Graham, *Inorg. Chem.* **1966**, *5*, 1586 – 1590.
[120] J. Chatt, C. Eaborn, P. N. Kapoor, *J. Organomet. Chem.* **1970**, *23*, 109 – 115.
[121] J. Hoyano, D. J. Patmore, W. A. G. Graham, *Inorg. Nucl. Chem. Lett.* **1968**, *4*, 201 – 203.
[122] A. T. T. Hsieh, M. J. Mays, *Inorg. Nucl. Chem. Lett.* **1971**, *7*, 223 – 225.
[123] A. T. T. Hsieh, M. J. Mays, *J. Chem. Soc. Chem. Commun.* **1971**, 1234 – 1235.
[124] L. M. Clarkson, W. Clegg, D. C. R. Hockless, N. C. Norman, L. J. Farrugia, S. G. Bott, J. L. Atwood, *J. Chem. Soc. Dalton Trans.* **1991**, 2241 – 2252.
[125] J. Weiß, Dissertation, Ruprecht-Karls-Universität Heidelberg, **1997**.
[126] a) B. Walther, C. Rockstroh, *J. Organomet. Chem.* **1972**, *44*, C4 – C6; b) J. N. StDenis, W. Butler, M. D. Glick, J. P. Oliver, *J. Organomet. Chem.* **1977**, *129*, 1 – 16.
[127] D. L. Thorn, *J. Organomet. Chem.* **1991**, *405*, 161 – 171.
[128] M. Hackett, J. A. Ibers, G. M. Whitesides, *J. Am. Chem. Soc.* **1988**, *110*, 1436 – 1448.
[129] M. Hackett, G. M. Whitesides, *J. Am. Chem. Soc.* **1988**, *110*, 1449 – 1462.
[130] a) K. E. Schwarzhans, H. Steiger, *Angew. Chem.* **1972**, *84*, 587 – 588; *Angew. Chem. Int. Ed. Engl.* **1972**, *11*, 535 – 536; b) J. J. Schneider, U. Denninger, C. Krüger, *Z. Naturforsch. B* **1994**, *49*, 1549 – 1553.
[131] M. M. Schulte, R. A. Fischer, *J. Chem. Soc. Chem. Commun.* **1994**, 2609 – 2610.
[132] R. A. Fischer, A. Miehr, M. M. Schulte, E. Herdtweck, *J. Chem. Soc. Chem. Commun.* **1995**, 337 – 338.
[133] A. Miehr, Dissertation, Technische Universität München, **1996**.
[134] A. H. Cowley, A. Decken, C. A. Olazabal, N. C. Norman, *Inorg. Chem.* **1994**, *33*, 3435 – 3437.
[135] C. A. Olazabal, F. P. Gabbai, A. H. Cowley, C. J. Carrano, L. M. Mokry, M. R. Bond, *Organometallics* **1994**, *13*, 421 – 423.
[136] a) C. Boehme, Dissertation, Universität Marburg, **1998**; b) C. Boehme, G. Frenking, *Chem. Eur. J.* **1999**, *5*, 2814 – 2190.
[137] X. He, R. A. Bartlett, P. P. Power, *Organometallics* **1994**, *13*, 548 – 552.
[138] R. M. Campbell, L. M. Clarkson, W. Clegg, D. C. R. Hockless, N. L. Pickett, N. C. Norman, *Chem. Ber.* **1992**, *125*, 55 – 59.
[139] L. M. Clarkson, K. McCrudden, N. C. Norman, *Polyhedron* **1990**, *9*, 2533 – 2547.
[140] F. A. Cotton, X. Feng, *Organometallics* **1998**, *17*, 128 – 130.
[141] G. Frenking, personal communication, **1997**, **1998**.
[142] a) A. H. Cowley, V. Lomeli, A. Voigt, *J. Am. Chem. Soc.* **1998**, *120*, 6401 – 6402; b) H. Braunschweig, C. Kollann, U. Englert, *Angew. Chem.* **1998**, *110*, 3355 – 3356; *Angew. Chem. Int. Ed.* **1998**, *37*, 3177 – 3178.
[143] K. E. Lewis, D. M. Golden, G. P. Smith, *J. Am. Chem. Soc.* **1984**, *106*, 3905 – 3913.
[144] K. W. Klinkammer, *Angew. Chem.* **1997**, *109*, 2414 – 2416; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2320 – 2322.
[145] D. L. Reger, D. G. Garza, A. L. Rheingold, G. P. A. Yap, *Organometallics* **1998**, *17*, 3624 – 3626.
[146] K. D. Sen, M. C. Böhm, P. C. Schmidt, *Structure and Bonding*, Springer, Berlin, **1987**.
[147] J. Weiß, R. A. Fischer, Y. Pelletier, C. Reber, *Inorg. Chem.* **1998**, *37*, 3316 – 3320.
[148] C. H. Langford, C. Moralejo, E. Lindsay, D. K. Sharma, *Coord. Chem. Rev.* **1991**, *111*, 337 – 343.
[149] A. G. Orpen, N. G. Connelly, *Organometallics* **1990**, *9*, 1206 – 1210.
[150] a) S. Dapprich, G. Frenking, *J. Phys. Chem.* **1995**, *99*, 9352 – 9362; b) A. J. Lupinetti, S. Fau, G. Frenking, S. H. Strauss, *J. Phys. Chem. A* **1997**, *101*, 9551 – 9559.
[151] T. T. Kodas, M. J. Hampden-Smith, *The Chemistry of Metal CVD*, VCH, Weinheim, **1994**.
[152] W. S. Rees, *CVD of Nonmetals*, VCH, Weinheim, **1996**.
[153] A. C. Jones, P. O'Brien, *CVD of Compound Semiconductors*, VCH, Weinheim, **1996**.
[154] H. D. Kaesz, R. S. Williams, R. F. Hicks, J. I. Zink, Y.-J. Chen, H.-J. Müller, Z. Xue, D. Xu, D. K. Shuh, Y. K. Kim, *New J. Chem.* **1990**, *14*, 527 – 534.
[155] F. Y. Shiau, Y. A. Chang, L. J. Chen, *J. Electron. Mater.* **1988**, *17*, 433 – 441.
[156] J. S. Solomon, S. R. Smith, *J. Vac. Sci. Technol.* **1987**, *A5*, 1809 – 1815.

[157] K. M. You, W. Walukiewicz, L. M. Jaklevic, H. H. Heller, *Appl. Phys. Lett.* **1987**, *51*, 189–191.

[158] J. P. Harbison, T. Sands, N. Tabatabaie, W. K. Chan, L. T. Florez, G. Karamidas, *Appl. Phys. Lett.* **1988**, *53*, 1717–1719.

[159] N. Tabatabaie, T. Sands, J. P. Harbison, L. H. Gilchrist, V. G. Karamidas, *Appl. Phys. Lett.* **1988**, *53*, 2528–2530.

[160] T. Sands, J. P. Harbison, W. K. Chan, A. Schwarz, C. C. Chang, J. Palmstrom, V. G. Karamidas, *Appl. Phys. Lett.* **1988**, *52*, 1216–1218.

[161] J. P. Harbison, T. Sands, R. Ramesh, L. T. Florez, B. J. Wilkens, V. G. Karamidas, *J. Cryst. Growth* **1991**, *111*, 978–983.

[162] Y. K. Kim, D. A. Baugh, D. K. Shuh, R. S. Williams, L. P. Sadwick, K. L. Wang, *J. Mater. Res.* **1990**, *5*, 2139–2151.

[163] D. A. Baugh, A. A. Talin, R. S. Williams, T.-C. Kuo, K. L. Wang, *J. Vac. Sci. Technol.* **1991**, *B9*, 2154–2157.

[164] A. Guivarc'h, M. Secoue, B. Guenais, *Appl. Phys. Lett.* **1988**, *52*, 948–950.

[165] F.-Y. Shiau, Y. Zuo, J.-C. Lin, X.-Y. Zheng, Y. A. Chang, *Z. Metallkd.* **1989**, *80*, 544–548.

[166] F.-Y. Shiau, S.-L. Chen, M. Loomans, Y. A. Chang, *Mater. Res. Soc. Symp. Proc.* **1992**, *230*, 40–45.

[167] F.-Y. Shiau, Y. A. Chang, *Mater. Res. Soc. Symp. Proc.* **1992**, *230*, 47–52.

[168] F. Maury, A. A. Talin, H. D. Kaesz, R. S. Williams, *Chem. Mater.* **1993**, *5*, 84–89.

[169] R. A. Fischer, A. Miehr, *Chem. Mater.* **1996**, *8*, 497–508.

[170] C. Kronseder, T. Schindler, C. Berg, R. A. Fischer, G. Niednerschatteburg, V. E. Bondybey, *J. Organomet. Chem.* **1994**, *475*, 247–256.

[171] R. A. Fischer, J. Weiß, W. Rogge, *Polyhedron* **1998**, *17*, 1203–1210.

[172] Q. Yu, A. Purat, A. Douchev, H. Schnöckel, *J. Organomet. Chem.* **1999**, *584*, 94–97.

[173] P. Jutzi, B. Neumann, G. Revmann, L. O. Schebaum, H.-G. Stammler, *Organometallics* **1999**, *18*, 2550–2552.

[174] A. S. Borovik, S. G. Bott, A. R. Barron, *Organometallics* **1999**, *18*, 2668–2676.

[175] A. Schnepf, G. Stößer, D. Carmichael, F. Mathey, M. G. Schnöckel, *Angew. Chem.* **1999**, *111*, 1757–1759; *Angew. Chem. Int. Ed.* **1999**, *38*, 1646–1649.