

Four-Coordinate Group-14 Elements in the Formal Oxidation State of Zero – Syntheses, Structures, and Dynamics of $[(\text{CO})_5\text{Cr}]_2\text{Sn}(\text{L}_2)$ and Related Species[☆]

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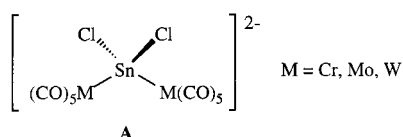
The sodium salts $\text{Na}_2\{[(\text{CO})_5\text{M}]_2\text{EX}_2\}$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$; $\text{E} = \text{Ge}, \text{Sn}, \text{Pb}$; $\text{X} = \text{Cl}, \text{I}, \text{OOCCH}_3$) react with 2,2'-bipyridine (bipy) to form neutral compounds $\{[(\text{CO})_5\text{M}]_2\text{E}(\text{bipy})\}$ ($\text{E} = \text{Sn}$: **1a–1c**; $\text{E} = \text{Ge}$: **3a**; $\text{E} = \text{Pb}$: **4**). 1,10-Phenanthroline (phen) analogues of compounds **1a–1c** and **3a** $\{[(\text{CO})_5\text{M}]_2\text{E}(\text{phen})\}$ ($\text{E} = \text{Sn}$: **1d–1f**, $\text{E} = \text{Ge}$: **3b**) are as well accessible. The 2,2'-bipyridine ligand in **1** may be formally replaced by two pyridine (py) ligands resulting in $\{[(\text{CO})_5\text{M}]_2\text{Sn}(\text{py})_2\}$ (**1g**: $\text{M} = \text{Cr}$, **1h**: $\text{M} = \text{W}$). The bis-bidentate ligand 2,2'-bipyrimidine (bpmd) is found to coordinate just one $\{[(\text{CO})_5\text{M}]_2\text{Sn}\}$ entity in $\{[(\text{CO})_5\text{M}]_2\text{Sn}(\text{bpmd})\}$ (**2b**: $\text{M} = \text{Cr}$, **2c**: $\text{M} = \text{W}$). The biimidazolato (biim) ligand binds two $\{[(\text{CO})_5\text{Cr}]_2\text{Sn}\}$ moieties in $\{[(\text{CO})_5\text{Cr}]_2\text{Sn}(\text{biim})\text{Sn}\{[\text{Cr}(\text{CO})_5]_2\}^{2-}\}$, **2a**. It is shown by ^1H -NMR that the pyrimidine entities in these

compounds (**2b**, **2c**) are able to rotate by a full 180° turn-around with respect to one another. This process must involve complete de-coordination of at least one of the two nitrogen donors in again at least one of the chelate cycles, the activation energy for this process being around 60 kJ/mol. By ^{119}Sn -NMR spectroscopy of almost all of the tin compounds described it is shown that equilibria between $\{[(\text{CO})_5\text{M}]_2\text{Sn}(\text{L}_2)\}$ and $\{[(\text{CO})_5\text{M}]_2\text{Sn}(\text{L})\} + \text{L}$ exist in all cases. From the temperature dependence of the δ values it is concluded that the activation barriers for this association/dissociation process is below 10 kJ/mol. The structures of all new compounds are documented by X-ray analyses and all compounds are characterized by the usual analytical and spectroscopical techniques.

Introduction

The chemistry of low-valent main-group compounds may considerably be expanded by using organometallic protective groups to electronically and sterically inhibit the decomposition of such species. Thus while neither Bi_2 nor Sn_6^{2-} are known as such at ambient temperature their organometallic derivatives $\{[(\text{CO})_5\text{W}]_3\text{Bi}_2\}^{[1]}$ and $\{[(\text{CO})_5\text{Cr}]_6\text{Sn}_6\}^{2- [2]}$ are well characterized species. In order to exploit the unconventional chemistry of compounds containing low-valent tin aggregates embedded in an organometallic matrix, starting materials which contain reactive tin–halide bonds and have the tin centers already coordinated to organometallic building blocks should be useful. With this idea in mind syntheses of various salts containing anions of type **A** (Figure 1) had been developed^{[3][4]}.

Figure 1. Anions of type **A**



It had been found that the salts formed with $[\text{Ph}_4\text{P}]^+$ counter ions are quite unreactive and correspondingly indefinitely stable at room temperature under an inert atmosphere^[4]. When, however, these salts are metathesized with

$\text{Na}[\text{BPh}_4]$ the highly reactive sodium salts $[\text{Na}(\text{solvent})_x]_2\{[(\text{CO})_5\text{M}]_2\text{SnCl}_2\}$ are formed^[4]. The difference in reactivity of these two types of salts is illustrated by the observation that the phosphonium salts do not react with sodium 8-oxoquinolate, $\text{Na}[\text{C}_9\text{H}_6\text{NO}]$, while the sodium salt $[\text{Na}(\text{solvent})_x]_2\{[(\text{CO})_5\text{Cr}]_2\text{SnCl}_2\}$ instantaneously does^[4]. The resulting anion $\{[(\text{CO})_5\text{Cr}]_2\text{Sn}(\text{oxinato})\}^-$ contains a tetrahedrally coordinated tin center (formal oxidation state: Sn^0) with two coordination positions occupied by the anionic chelate ligand^[4].

We report here that an analogous procedure allows for the replacement of the two halide substituents in **A** by neutral nitrogen-based chelate ligands leading to neutral adducts of types **1** and **2** which as well contain tin in the formal oxidation state of zero. Analogous reactivity is observed for the homologues of type **A** anions containing germanium or lead instead of tin. 2,2'-Bipyridine or 1,10-phenanthroline adducts of Ge^0 , **3**, and Pb^0 , **4**, stabilized by coordination to two $[(\text{CO})_5\text{Cr}]$ groups are thus obtained.

Results and Discussion

a) Compounds **1** Containing 2,2'-Bipyridine or 1,10-Phenanthroline as Chelating Ligands

THF solutions of the sodium salts of the anions of type **A**, $\{[(\text{CO})_5\text{M}]_2\text{SnCl}_2\}^{2-}$, are prepared from $[\text{Ph}_4\text{P}]_2\{[(\text{CO})_5\text{M}]_2\text{SnCl}_2\}$ by salt metathesis with $\text{Na}[\text{BPh}_4]$

as described^[4]. Upon addition of 2,2'-bipyridine (bipy) or 1,10-phenanthroline (phen) the initially yellow solutions turn deep red immediately and take on a turbid appearance caused by the precipitation of NaCl.

Table 1. Complexes of type 1

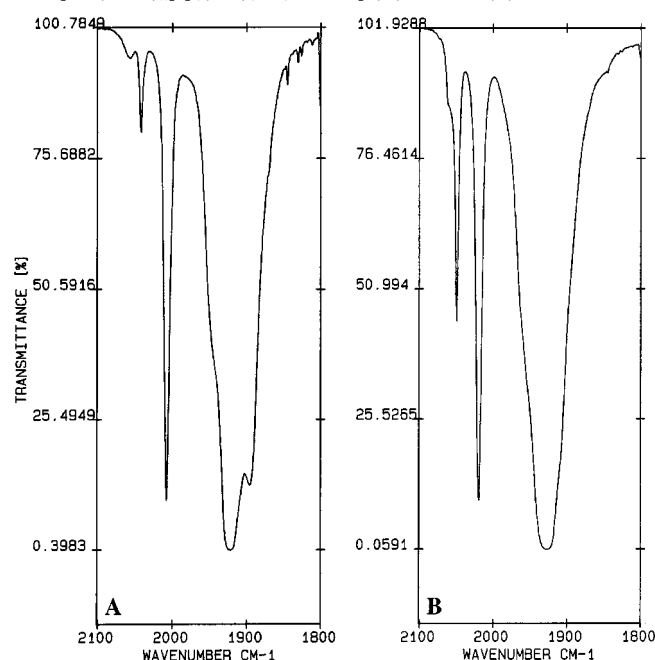
no.	M	N N
$\left[\begin{array}{c} \text{Cl} \quad \text{Cl} \\ \diagdown \quad \diagup \\ \text{Sn} \\ \diagup \quad \diagdown \\ (\text{CO})_5\text{M} \quad \text{M}(\text{CO})_5 \end{array} \right]^{2-}$ A $+ \text{N} \text{---} \text{N} \quad - 2 \text{NaCl}$ $\downarrow$ $\begin{array}{c} \text{N} \quad \text{N} \\ \diagdown \quad \diagup \\ \text{Sn} \\ \diagup \quad \diagdown \\ (\text{CO})_5\text{M} \quad \text{M}(\text{CO})_5 \end{array}$ 1	1a 1b 1c 1d 1e 1f 1g 1h	bipy bipy bipy phen phen phen 2 · py 2 · py

Chromatographic workup, separating compounds **1** from the decomposition products $[\text{M}(\text{CO})_6]$, $[\text{M}(\text{CO})_4(\text{bipy})]$, and $[\text{M}(\text{CO})_4(\text{phen})]$, respectively, leads to **1a–1f** in yields of around 50%. The compounds are obtained as microcrystalline deep red materials of analytical purity. Crystals suitable for X-ray analyses are obtained by vapour diffusion from THF/diethyl ether/petroleum ether (boiling range 40–60 °C). **1a–1f** are analogues of the known species $[\{\text{Cp}'(\text{CO})_2\text{Mn}\}_2\text{Sn}(\text{bipy})]^{[5]}$ and $[\{\text{Cp}'(\text{CO})_2\text{Mn}\}_2\text{Sn}(\text{phen})]^{[6]}$.

The IR- ν_{CO} spectra of **1a–1f** show the three-band pattern (Table 4, Figure 2) characteristic of $[\text{LM}(\text{CO})_5]$ species^[7]; in a few cases an additional shoulder around 1960 cm^{-1} is observed (Table 4) indicating either a local symmetry lower than C_{4v} or coupling between the two $[(\text{CO})_5\text{M}]$ chromophores. The IR- ν_{CO} absorptions of the neutral compounds **1** are shifted to somewhat higher energies relative to the absorptions of the dianionic starting materials (e.g. $[\text{Na}(\text{THF})_x]_2[\{(\text{CO})_5\text{Cr}\}_2\text{SnCl}_2]$: ν_{CO} (THF) = 2040 w, 2007 s, 1920 vs, 1895 sh cm^{-1} , Figure 2) as would be expected when reducing the charge in an $[\text{LM}(\text{CO})_5]$ compound^[8].

The ^1H -NMR spectra show the expected shifts of the proton resonances of the ligands (Table 2). The observed low-field shifts are somewhat higher than those found for the $[\text{Cp}'(\text{CO})_2\text{Mn}]$ analogues of compounds **1**^{[5][6]}. This indicates that the coordination of the chelate ligands is somewhat stronger for **1a–1f** as compared to their $[\text{Cp}'(\text{CO})_2\text{Mn}]$ analogues^{[5][6]}.

This is in fact what would be expected taking into account the relative π -donor capabilities of $[\text{Cp}'(\text{CO})_2\text{Mn}]$ and $[(\text{CO})_5\text{M}]$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$): with $[\text{Cp}'(\text{CO})_2\text{Mn}]$ being the stronger π -donor^[9] the cumulene-type compounds $[\text{Cp}^{\text{R}}(\text{CO})_2\text{Mn}=\text{Sn}=\text{Mn}(\text{CO})_2\text{Cp}^{\text{R}}]$ ($\text{Cp}^{\text{R}} = \text{Cp}, \text{Cp}', \text{Cp}^*$)^[10] are available as such. Their 2,2'-bipyridine and 1,10-phenanthroline derivatives corresponding to **1a–1f** are directly obtained from the cumulenes by adding the chelate

Figure 2. Carbonyl region of the IR-absorption spectra of $[\text{Na}(\text{THF})_x]_2[\{(\text{CO})_5\text{Cr}\}_2\text{SnCl}_2]$ (A) and **1a** (B) in THFTable 2. ^1H -NMR-spectroscopic data ($[\text{D}_6]$ acetone, 25 °C) for the uncoordinated ligands and compounds **1–4**

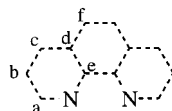
	H _a	H _b	H _c	H _d	H _f
bipyridine	8.67 ^[a]	7.38 ^[b]	7.89 ^[c]	8.51 ^[d]	—
1a	9.18 ^[a]	8.17 ^[b]	8.60 ^[c]	9.12 ^[d]	—
1b	9.25 ^[a]	8.11 ^[b]	8.55 ^[c]	9.10 ^[d]	—
1c	9.23 ^[a]	8.14 ^[b]	8.57 ^[c]	9.08 ^[d]	—
3a	9.13 ^[a]	8.28 ^[b]	8.67 ^[c]	9.23 ^[d]	—
4	9.13 ^[a]	7.90 ^[b]	8.37 ^[c]	8.76 ^[d]	—
phenanthroline	9.13 ^[e]	7.72	8.42 ^[f]	—	7.91 ^[g]
1d	9.61 ^[e]	8.48	9.19 ^[f]	—	8.53 ^[g]
1e	9.68 ^[e]	8.42	9.13 ^[f]	—	8.51 ^[g]
1f	9.64 ^[e]	8.44	9.13 ^[f]	—	8.50 ^[g]
3b	9.57 ^[e]	8.59	9.26 ^[f]	—	8.62 ^[g]
pyridine	8.62 ^[h]	7.32 ^[i]	7.72 ^[k]	—	—
1g	8.89 ^[i]	8.00 ^[j]	8.36 ^[i]	—	—
1h	8.94 ^[h]	7.96 ^[j]	8.34 ^[k]	—	—
bipyrimidine	9.00 ^[l]	7.60 ^[m]	—	—	—
2b ^[n]	9.71 ^[l]	8.44 ^[m]	9.68 ^[l]	—	—
2c ^[n]	9.74 ^[l]	8.39 ^[m]	9.64 ^[l]	—	—

^[a] $^3J(\text{H}, \text{H}) = 4.8\text{--}5.5$ Hz. — ^[b] $^3J(\text{H}, \text{H}) = 8.0\text{--}8.4$ Hz. — ^[c] $^3J(\text{H}, \text{H}) = 7.7\text{--}8.0$ Hz. — ^[d] $^3J(\text{H}, \text{H}) = 4.7\text{--}5.8$ Hz. — ^[e] $^3J(\text{H}, \text{H}) = 4.0\text{--}5.1$ Hz. — ^[f] $^3J(\text{H}, \text{H}) = 8.0$ Hz. — ^[g] $^3J(\text{H}, \text{H}) = 4.0\text{--}5.5/8.0$ Hz. — ^[h] $^3J(\text{H}, \text{H}) = 6.4$ Hz. — ^[i] broad signal, no coupling observable. — ^[j] $^3J(\text{H}, \text{H}) = 6.4/7.6$ Hz. — ^[k] $^3J(\text{H}, \text{H}) = 7.6$ Hz. — ^[l] $^3J(\text{H}, \text{H}) = 4.8\text{--}5.0$ Hz. — ^[m] $^3J(\text{H}, \text{H}) = 4.8\text{--}5.0$ Hz. — ^[n] Measured at -50 °C.

bases^{[5][6]} and the compounds may thus be considered as Lewis base stabilized organometallic cumulenes. The interaction with the Lewis base chelate ligands remains weak in

this case reflecting the extensive Mn-d π –Sn-p π back-donation which effectively stabilizes even the base-free cumulenes. The weaker back-donation from the [(CO) $_5$ M] fragments makes the cumulene compounds [(CO) $_5$ M=Sn=M(CO) $_5$] so unstable that they have not yet been isolated as such^[11]. Compounds **1a–1f** may be considered as base-stabilized forms of such species. Due to the inherent lack of sufficient back-donation from the metals the tin center in the hypothetical cumulenes [(CO) $_5$ M=Sn=M(CO) $_5$] is highly electron-deficient and will act as an effective Lewis acidic center towards the chelate bases. The shifts of the ^1H -NMR resonances of the ligands upon coordination are indicative of this interaction.

Table 3. ^{13}C -NMR-spectroscopic data ([D $_6$]acetone, 25°C) for the uncoordinated ligands and compounds **1–4**



	CO _{ax}	CO _{eq}	C _a ^[a]	C _b ^[b]	C _c ^[c]	C _d ^[d]	C _e	C _f
bipyridine	—	—	149.9	124.6	137.5	121.3	156.7	—
1a	227.4	221.1	148.2	127.9	143.0	125.8	152.6	—
1b	—	210.6	148.0	127.4	142.3	125.8	—	—
1c	204.5	201.3	147.8	127.8	142.6	125.7	153.6	—
3a	227.1	220.4	145.8	127.6	142.8	125.6	146.0	—
4	221.3	219.3	148.8	126.6	141.0	125.1	152.3	—
phenanthroline	—	—	150.6	123.9	136.7	129.5	147.1	127.4
1d	227.0	220.9	149.4	126.3	141.8	132.2	140.4	129.1
1e	216.3	210.6	149.2	125.8	141.0	132.3	140.5	129.1
1f	206.0	201.4	148.9	126.2	141.3	132.2	140.4	129.1
3b	226.9	220.2	146.8	126.2	141.1	131.9	137.6	129.1
pyridine	—	—	150.6	124.4	136.5	—	—	—
1g	226.7	220.9	149.0	127.2	142.2	—	—	—
1h	204.7	201.5	149.7	127.6	142.0	—	—	—
bipyrimidine	—	—	158.2	122.0	—	—	164.4	—
2b ^[e]	226.5	220.8	156.4	125.0	163.9	—	—	—
2c ^[f]	203.6	200.9	155.5	124.3	162.8	—	155.7	—

^[a] C_a: $^1J(^1\text{H}, ^{13}\text{C}; \text{bipy}) = 178 \text{ Hz}$; $^1J(^1\text{H}, ^{13}\text{C}; \mathbf{1a}) = 184 \text{ Hz}$; $^1J(^1\text{H}, ^{13}\text{C}; \mathbf{3a}) = 161 \text{ Hz}$. — ^[b] C_b: $^1J(^1\text{H}, ^{13}\text{C}; \text{bipy}) = 165 \text{ Hz}$; $^1J(^1\text{H}, ^{13}\text{C}; \mathbf{1a}) = 171 \text{ Hz}$; $^1J(^1\text{H}, ^{13}\text{C}; \mathbf{3a}) = 165 \text{ Hz}$. — ^[c] C_c: $^1J(^1\text{H}, ^{13}\text{C}; \text{bipy}) = 162 \text{ Hz}$; $^1J(^1\text{H}, ^{13}\text{C}; \mathbf{1a}) = 171 \text{ Hz}$; $^1J(^1\text{H}, ^{13}\text{C}; \mathbf{3a}) = 166 \text{ Hz}$. — ^[d] C_d: $^1J(^1\text{H}, ^{13}\text{C}; \text{bipy}) = 163 \text{ Hz}$; $^1J(^1\text{H}, ^{13}\text{C}; \mathbf{1a}) = 165 \text{ Hz}$; $^1J(^1\text{H}, ^{13}\text{C}; \mathbf{3a}) = 170 \text{ Hz}$. — ^[e] Measured at 0°C. — ^[f] Measured at –60°C.

This interaction is mirrored by the ^{13}C -NMR resonances (Table 3). With reference to the ^{13}C -NMR data of the free ligands the ^{13}C signals of the coordinated ligands consistently show the high-field (C_a, C_e) and low-field (C_b, C_c, C_d, and C_f) shifts which are known to be characteristic of the coordination of these chelate bases^[12]. A theoretical explanation of this characteristic pattern of high- and low-field shifts has been put forward^[13]. The individual resonances for the carbonyl carbon atoms C_{ax} and C_{eq} of the [(CO) $_5$ M] entities are generally well resolved (Table 3); only in the case of **1b** the quality of the spectroscopic data did not reveal the resonance of the axial carbonyl group.

Table 4. IR- ν_{CO} and $^{119}\text{Sn}\{^1\text{H}\}$ -NMR-spectroscopic data for compounds **1–4**

	$\tilde{\nu}_{\text{CO}}/\text{cm}^{-1}$ ^[a]			$^{119}\text{Sn}\{^1\text{H}\}$ (δ/ppm) ^[b]
1a	2045 (m)	2016 (s)	1922 (vs)	1336
1b	2056 (m)	2034 (s)	1932 (vs)	1354
1c	2057 (m)	2035 (s)	1960 (sh)	1021 ^[c]
1d	2045 (m)	2016 (s)	1922 (vs)	1327
1e	2056 (m)	2034 (s)	1932 (vs)	1349
1f	2057 (m)	2035 (s)	1959 (sh)	996 ^[d]
1g	2046 (m)	2016 (s)	1924 (vs)	1515
1h	2058 (m)	2036 (s)	1928 (vs)	1200 ^[e]
2a	2052 (w)	2011 (m)	1938 (sh)	1897 (sh) 1149
2b	2048 (m)	2018 (s)	1928 (vs)	1372
2c	2059 (m)	2038 (s)	1963 (sh)	1026 ^[f]
3a	2047 (m)	2021 (s)	1956 (sh)	1923 (vs) —
3b	2047 (m)	2021 (s)	1956 (sh)	1923 (vs) 1906 (sh) —
4	2050 (m)	2017 (s)	1931 (vs)	—

^[a] In THF. — ^[b] In [D $_6$]acetone, 25°C. — ^[c] $^1J(^{183}\text{W}, ^{119}\text{Sn}) = 578 \text{ Hz}$; intensity ratio of peaks 15:100:15. — ^[d] $^1J(^{183}\text{W}, ^{119}\text{Sn}) = 520 \text{ Hz}$; intensity ratio of peaks 14:100:15. — ^[e] $^1J(^{183}\text{W}, ^{119}\text{Sn}) = 575 \text{ Hz}$; intensity ratio of peaks 16:100:14. — ^[f] $^1J(^{183}\text{W}, ^{119}\text{Sn}) = 540 \text{ Hz}$; intensity ratio of peaks 19:100:20. — ^{[c]–[f]} The intensity of the satellites is close to the value of 29% as expected from coupling of a tin nucleus with two equivalent tungsten nuclei.

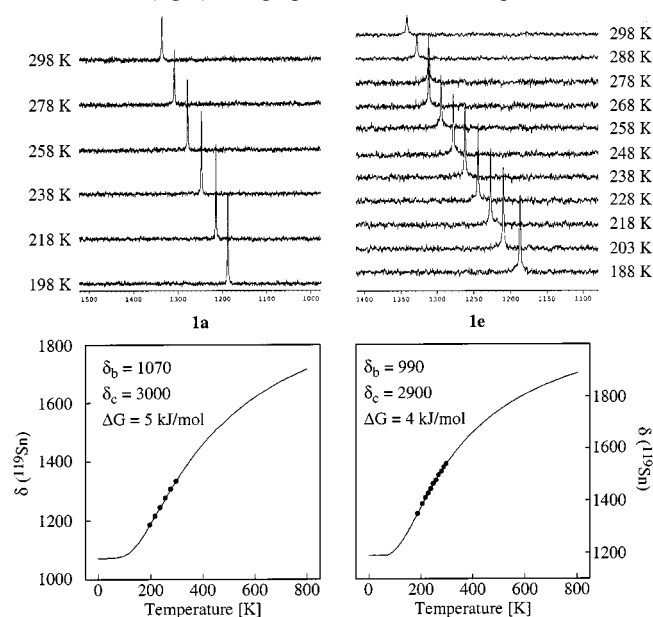
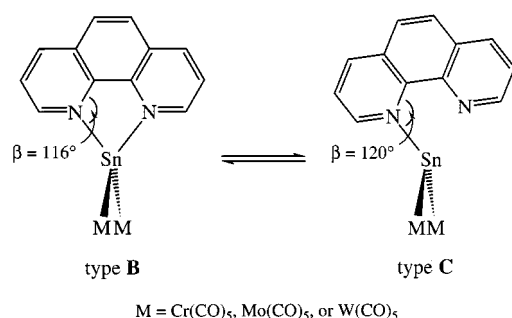
The NMR data which are most characteristic for the particular bonding situation in compounds **1** are the ^{119}Sn -NMR resonances (Table 4). The absorptions occur at relatively low field in the broad range of shifts^[14] hitherto observed for tin compounds of $\delta = -2171$ (Cp $_2$ Sn^[15]) to $\delta = +3301$ ([{Cp*(CO) $_2$ Mn} $_3$ Sn]^[16]).

The resonances observed for the tungsten compounds **1c** and **1f** consistently occur at higher fields similar to those of their chromium and molybdenum analogues^[4].

The ^{119}Sn -NMR shifts of all compounds **1** are strongly temperature-dependent throughout. In the observable range of temperatures the shifts increase with a slope of around 1.5 ppm/K with increasing temperature. This increase is monotonic though not strictly linear (cf. Figure 3).

This behavior may be rationalized by the assumption of two different species which are close in energy to each other, but which have widely different ^{119}Sn -NMR shifts. One of these species should contain four-coordinate tin (type **B**, Figure 4) in accord with the solid-state structure (vide infra). The other one is assumed to be a species where one of the two nitrogen atoms of the chelate ligand is de-coordinated (type **C**, Figure 4). This type of arrangement would lead to a bonding situation close to the one characteristic of indenyl-type compounds $\text{L}_n\text{---X(R)}\text{---ML}_n$ ^[17].

The 3-center-4- π system characterizing the bonding situation in indenyl compounds has a dramatic effect on the NMR shift of the central atom X. It has been found that with phosphorus in this position ^{31}P -NMR shifts range from $\delta = 900$ to $\delta = 1400$, well out of the range of shifts documented for all other phosphorus compounds^[18]. This strong low-field shift is in addition well correlated with the inverse of the energy ΔE ($1/\Delta E$) of the π - π^* transition in these compounds^[18]. Taken together these observations lend strong weight to an interpretation which relates the

Figure 3. Temperature-dependent ^{119}Sn -NMR spectrum of **1a** (left) and **1e** (right) and graphs obtained from Equation 1Figure 4. Equilibrium between four- and three-coordinated tin species **1d–1f**

observed low-field shifts to the low HOMO-LUMO gap characterizing the 3-center- $\text{M} \equiv \text{X} \equiv \text{M}-4\pi$ systems. The same type of arguments has been used to rationalize the extreme ^{119}Sn -NMR low-field shift of around $\delta = 3300$ for a compound containing a $\text{M} \equiv \text{X} \equiv \text{M}-\pi$ system as well^[16]. A species of the type **C** as shown in Figure 4 would thus be expected to have its resonance around $\delta = 3000$.

A guess for the shift which should be expected for a compound with four-coordinate tin (type **B**) may be based on the observation that $[\text{Ph}_4\text{P}]_2[\{(\text{CO})_5\text{Cr}\}_2\text{SnCl}_2]$ shows one single temperature-independent signal at $\delta = 924$ with its tungsten analogue $[\text{Ph}_4\text{P}]_2[\{(\text{CO})_5\text{W}\}_2\text{SnCl}_2]$ resonating at $\delta = 605$ again independent of temperature. The resonances of the chelate compounds of type **B** (Figure 4) would hence be expected somewhere around $\delta = 500$ to $\delta = 1000$.

An equilibrium as depicted in Figure 4 does not appear to be ruled out by MO considerations: EHT calculations^[19] give an energy difference of only around 10 kJ/mol between the two isomers (type **B** and **C**, Figure 4) with the chelate compound (type **B**) being the more stable.

The experimental observations are well in accord with the above assumptions. If a dynamic equilibrium as given in Figure 4 is assumed the ^{119}Sn -NMR shift of the equilibrium mixture of the two isomers is given by $\delta_{\text{obs.}} = x_B\delta_B + x_C\delta_C$ with the molar fractions x_B and x_C and the shifts of the pure isomers δ_B and δ_C , respectively. The observed temperature dependence of $\delta_{\text{obs.}}$ is then a consequence of the temperature dependence of the equilibrium constant pertaining to this isomerisation process and is given by Equation 1.

$$\delta_{\text{obs.}} = \frac{\delta_B + \delta_C \cdot e^{-\frac{\Delta G}{RT}}}{1 + e^{-\frac{\Delta G}{RT}}} \quad (1)$$

Fitting the parameters of δ_B , δ_C , and ΔG of the corresponding Equation 1 to the observed values results in a favorable agreement with the assumptions made above: the values for δ_B are estimated by this procedure in a range of $\delta = 990$ to $\delta = 1070$ for all four-coordinate compounds of type **B** (Figure 4). The values estimated for δ_C are in a range of $\delta = 2900$ to $\delta = 3000$. The values of ΔG range between 4 and 5 kJ/mol. All these values and ranges of values are completely independent of any guess made for the quantitative items δ_B , δ_C , and ΔG above. They are extracted from the observed material alone by the single assumption of a dynamic equilibrium as given in Figure 4 with no quantitative restrictions put on this equilibrium other than the experimental data. Graphs typical for the quality of fit obtained are shown for **1a** and **1e** in Figure 3. It is evident that quite some extrapolation is involved when the values δ_B and especially δ_C are to be determined by the fitting procedure. Nevertheless the ranges of δ_B and δ_C compare favorably with the expectations and the observed temperature dependence of $\delta_{\text{obs.}}$ is neatly reproduced.

The interpretation of the temperature dependence of the ^{119}Sn -NMR shifts in terms of an intramolecular equilibrium is further corroborated by the observation that addition of the free ligands (bipy, phen) to the solutions does not change the appearance of the ^{119}Sn -NMR spectra.

The equilibrium between species with η^2 -coordinated ligands (type **B**) and η^1 -coordinated ones (type **C**) as delineated should mirror itself into an appropriate behavior of the proton resonances of the ligands.

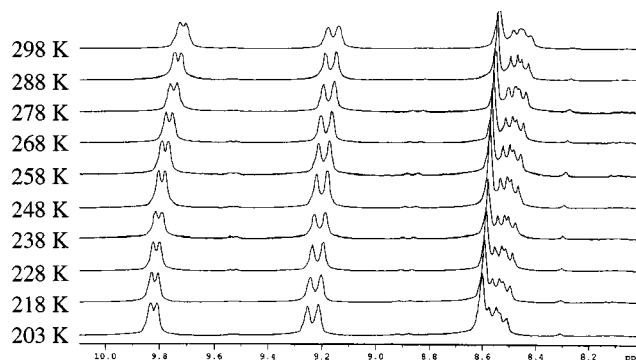
Figure 5. Temperature-dependent ^1H -NMR spectrum of **1e**

Figure 5 showing the temperature dependence of the ^1H -NMR spectrum of **1e** as an example demonstrates that with raising temperature all of the signals are continuously shifted to higher fields. Qualitatively this is well in accord with what would be expected on the basis of the partial de-coordination of the ligand characterizing the equilibrium depicted in Figure 4: with the ligands being less tightly bound in the mean with increasing temperature their signals should move towards the ones of the free ligands (Table 2).

Applying Equation 1 to the ^1H -NMR data of **1e** (Figure 5) with one set of limiting resonances fixed on the values of the free ligand [$\delta_{\text{C}} = 9.13$ (H_{a}), 8.42 (H_{c}), 7.91 (H_{f}), 7.72 (H_{b})] the other set of limiting resonances is derived as [$\delta_{\text{B}} = 9.96$ (H_{a}), 9.57 (H_{c}), 8.87 (H_{f}), 8.70 (H_{b})]. The value of ΔG characterizing the equilibrium is obtained as 2 kJ/mol and is – with respect to experimental accuracy (Figure 5) and the narrow range of temperatures studied – in satisfying agreement with the value of $\Delta G = 4$ kJ/mol as extracted from ^{119}Sn -NMR measurements (vide supra). It is worth noting that the worst quality of fit is obtained for the data pertaining to the protons H_{a} of the α -CH groups. The sensitivity of the resonances of these protons to minor changes in the coordination environment is amply been demonstrated in the literature^[20]. Overall the successful modeling of the temperature dependence of the NMR spectra of compounds **1** and the qualitative agreement of the estimates made by these models for the reaction enthalpy, independent of whether ^{119}Sn - or ^1H -NMR data are analyzed, are in favor of the belief that the underlying basic assumption of an equilibrium (Figure 4) is correct.

The equilibrium (Figure 4) suggests that species with just one donor ligand should be stable as such without the necessity of a second donor ligand. Under these premises it appeared worthwhile to probe whether, excluding the chelate effect, one pyridine (py) molecule as a Lewis base would suffice to stabilize the underlying cumulene-type compounds to such an extent that inidene like adducts $[(\text{CO})_5\text{M} \equiv \text{Sn}(\text{py}) \equiv \text{M}(\text{CO})_5]$ could be isolated or whether a second pyridine molecule would coordinate, leading to $[(\text{CO})_5\text{M} \equiv \text{Sn}(\text{py})_2 \equiv \text{M}(\text{CO})_5]$, compounds, formally isoelectronic to the dianions $[\{(\text{CO})_5\text{M}\}_2\text{SnHal}_2]^{2-}$ ^{[3][4]}.

b) Compounds **1** Containing Two Pyridine Donors

When THF solutions of the sodium salts $[\text{Na}(\text{THF})_x]_2[\{(\text{CO})_5\text{M}\}_2\text{SnCl}_2]$ (type **A**) are treated with a fourfold equimolar excess of pyridine, adduct formation is indicated by a change in the IR- ν_{CO} pattern. Isolation of the pyridine adducts **1g** and **1h**, albeit in yields below 20%, is possible by column chromatography. Compounds **1g** and **1h** are obtained as yellow microcrystalline solids. **1g** and **1h** are definitely less stable than the chelate adducts **1a–1f**: under conditions where **1a–1f** are indefinitely stable in THF solutions **1g** and **1h** gradually disintegrate to produce insoluble greenish materials.

The IR- ν_{CO} absorptions (Table 4) of **1g** and **1h** are within a few wavenumbers found at the same positions as those of the corresponding 2,2'-bipyridine adducts **1a** and **1c**.

The ^1H -NMR spectra of **1g** and **1h** in $[\text{D}_6]\text{acetone}$ (Table 2) with the corresponding low-field shifts relative to free pyridine clearly reveal the coordination of the pyridine ligands. The proton signals shift to lower fields as the temperature is lowered with the same type of observation having already been described for **1a–1f**.

The ^{13}C -NMR data (Table 3) equally well demonstrate the coordination of the heterocycles in **1g** and **1h**. Again the individual resonances of the carbonyl carbon atoms are observable and distinguishable (Table 3).

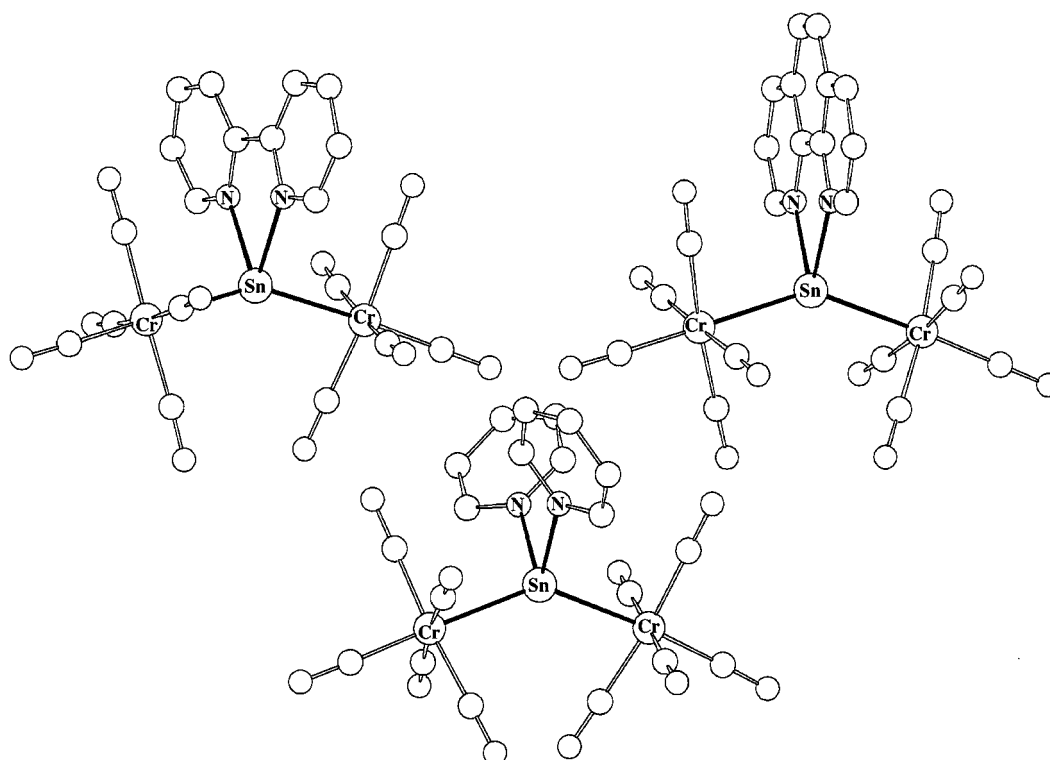
The ^{119}Sn -NMR data are indicative of dynamic equilibria in these cases as well. When CD_2Cl_2 is used as the solvent for **1h** sharp tungsten-modulated signals are observed over the whole range of temperatures (298–168 K). With decreasing temperature a monotonically increasing high-field shift of the signal is observed: at 298 K the resonance occurs at $\delta = 1271$ at 168 K is found at $\delta = 1164$. If it is assumed that the underlying chemical process is again a coordination/de-coordination equilibrium similar to the one shown in Figure 4 and if it is further assumed that the pyridine, when de-coordinated remains close to the tin in the solvent cage an analysis as performed for the chelate compounds (vide supra) results in $\delta_{\text{B}} = 1100$, $\delta_{\text{C}} = 2200$, and $\Delta G = 5$ kJ/mol, respectively, with the species of type **B** being the more stable. The quality of fit is similar to the one shown in Figure 3 for the chelate compounds **1a** and **1e**. This refers to the data from solutions of **1h** in CD_2Cl_2 .

Solutions of **1h** in $[\text{D}_6]\text{acetone}$ show the same type of temperature dependence of the ^{119}Sn -NMR signal with the additional complication that the signal starts to broaden at 240 K and is completely vanishing in the background at 230 K reappearing as a sharp signal at 210 K. It is assumed that some exchange with the $[\text{D}_6]\text{acetone}$ solvent is responsible for this phenomenon. With the chelate compounds **1a** and **1e** this type of observation is not made; steric reasons are a rationale for this difference in behavior. Anyhow, the dynamic situation with **1h** is more complicated than the one described for **1a** and **1e** since addition of the free ligand pyridine is found to cause a high-field shift in the ^{119}Sn -NMR spectrum while starting with pure **1h** increasing dilution will shift the signal to the low-field side. These experiments indicate that coordination/de-coordination equilibria of the same type as depicted in Figure 4 must be at the basis of the observed phenomena.

c) Molecular Structures of Compounds **1a–1h**

The molecular structures of all the compounds of **1a–1h** have been determined by X-ray analyses (Tables 5, 10, and 11). The similar all-over geometry of the individual molecules within each class (**1a–1c**, **1d–1f**, **1g** and **1h**) warrants the discussion of the structures with reference to Figure 6, showing only the $[(\text{CO})_5\text{Cr}]$ derivatives^[21].

This similarity is also illustrated by the fact that the crystal structures of **1a–1c** are isotypic (Table 10) as are those of **1d–1f** which include one THF solvate per molecule **1** (Tables 10 and 11) and those of **1g** and **1h** (Table 11). The environment of the tin centers in **1a–1h** is distorted tetrahedral (Table 5).

Figure 6. Molecular structures of compounds **1a**, **1c**, and **1g**Table 5. Selected bond lengths [pm], angles [°] and torsion angles [°] of compounds **1a–1h**^[a]

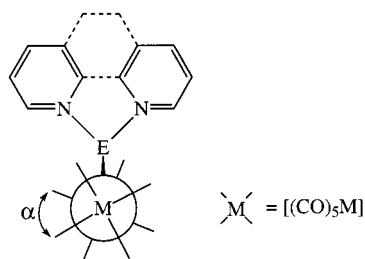
$[(\text{CO})_5\text{M}]_2\text{Sn}(\text{N}^-\text{N})$	1a M = Cr	1b M = Mo	1c M = W	1d M = Cr	1e M = Mo	1f M = W	1g M = Cr	1h M = W
M–Sn	262.2 (1) 261.9 (1)	276.1 (1) 275.6 (1)	276.0 (1) 275.8 (1)	262.3 (1) 263.0 (1)	274.4 (1) 274.5 (1)	275.3 (1) 275.8 (1)	260.3 (1) 261.8 (1)	277.9 (2) 278.9 (2)
M–C _{CO(ax)} ^[b]	186.5 (5)	200.1 (7)	201 (1)	188.3 (6)	200.5 (5)	200 (1)	186.4 (3)	203 (2)
M–C _{CO(eq)} ^[b]	189.6 (5)	203.3 (7)	203 (1)	190.2 (6)	203.4 (5)	204 (1)	188.9 (4)	206 (2)
Sn–N	229.6 (3) 227.5 (3)	228.2 (5) 227.2 (5)	228 (1) 227 (1)	230.3 (4) 230.5 (4)	227.9 (3) 228.0 (3)	227.1 (9) 229.1 (9)	231.2 (3) 232.9 (3)	231 (1) 236 (1)
M–Sn–M	148.66(3)	149.37(2)	149.07(4)	143.92(3)	146.09(2)	145.71(4)	139.24(2)	139.87(4)
N–Sn–N	71.5 (1)	71.2 (1)	71.3 (3)	72.3 (1)	72.4 (1)	72.4 (3)	86.9 (1)	86.1 (3)
M–Sn–N	103.98(8) 100.62(8)	104.0 (1) 100.2 (1)	103.8 (3) 99.9 (2)	103.6 (1) 104.6 (1)	103.27(9) 104.41(9)	104.7 (2) 103.4 (2)	102.96(7) 108.01(7)	103.2 (3) 107.8 (3)
Sn–N–C _{ipso} ^[b]	101.60(8) 104.48(8)	101.3 (1) 104.2 (1)	101.5 (3) 104.4 (2)	105.8 (1) 103.9 (1)	104.49(9) 102.27(9)	102.6 (2) 104.3 (2)	106.00(7) 101.56(7)	105.6 (2) 101.4 (2)
Sn–M–C _{CO(ax)} ^[b]	117.9 (3)	118.7 (5)	118.7 (8)	116.3 (3)	116.3 (3)	116.4 (7)	-	-
Sn–M–C _{CO(eq)} ^[b]	177.7 (1)	177.6 (2)	177.5 (4)	177.8 (2)	178.2 (2)	177.9 (4)	175.6 (1)	175.1 (4)
C _{CO(eq)} –M–C _{CO(ax)} ^[b]	88.0 (1)	87.7 (2)	87.7 (4)	87.7 (2)	87.3 (2)	87.3 (4)	87.9 (1)	88.2 (4)
C _{CO(eq)} –M–C _{CO(eq)} ^[b]	92.0 (1)	92.3 (2)	92.3 (6)	92.3 (2)	91.4 (2)	92.7 (6)	92.0 (2)	91.9 (5)
	89.9 (1)	89.9 (2)	89.9 (6)	89.9 (2)	89.9 (2)	89.7 (5)	89.9 (1)	89.9 (5)
	174.5 (1)	173.9 (2)	173.6 (6)	175.2 (2)	174.5 (2)	174.4 (5)	175.2 (1)	175.3 (5)
N–C–C–N	12 (1)	10.5 (8)	11 (1)	2.1 (8)	0.4 (5)	1.5 (9)	-	-
torsion angle α ^[c]	25	24	24	40	40	40	44	44

^[a] Estimated standard deviations in units of the least significant figures given in each case are quoted in parentheses. – ^[b] Average values; the standard deviations refer to the largest individual esd in each set. – ^[c] α refers to the torsion angle $\text{C}_{\text{CO}(\text{eq})}\text{--M--M--C}_{\text{CO}(\text{eq})}$ as defined in Figure 7.

The tin–metal distances in compounds **1a–1h** are very similar (Table 5) within each class (Sn–Cr, Sn–Mo, Sn–W) for the three types of compounds (**1a–1c**, **1d–1f**, **1g**, and **1h**). Within each individual compound the two tin–

metal distances are close of being even numerically equal. The geometric data characterizing the $\text{Sn}-\{\text{M}(\text{CO})_5\}$ entities in each compound are again very similar (Table 5). While the distances are appropriately modulated by the kind of metal (Cr, Mo, or W) the same general trends are found in all compounds. The axial metal–carbonyl bonds are without exception some 2–4 pm shorter than the equatorial ones (Table 5). The equatorial $\text{M}-\text{CO}$ entities tend to bend towards the tin center with the $\text{Sn}-\text{M}-\text{C}_{\text{eq}}$ angles somewhat smaller than 90° throughout, and consequently the $\text{C}_{\text{ax}}-\text{M}-\text{C}_{\text{eq}}$ angles somewhat larger than 90° (Table 5). The torsion angles α [$\text{C}_{\text{CO}(\text{eq})}-\text{M}-\text{M}-\text{C}_{\text{CO}(\text{eq})}$, Figure 7] are as well similar within each class of compounds (**1a–1c**, **1d–1f**, **1g**, and **1h**). While for **1a–1c** a more eclipsed orientation with $\alpha \approx 24^\circ$ is found to be preferred, a more staggered conformation is observed for **1d–1f** (α ca. 40°) and for **1g** and **1h** ($\alpha \approx 44^\circ$) (Table 5).

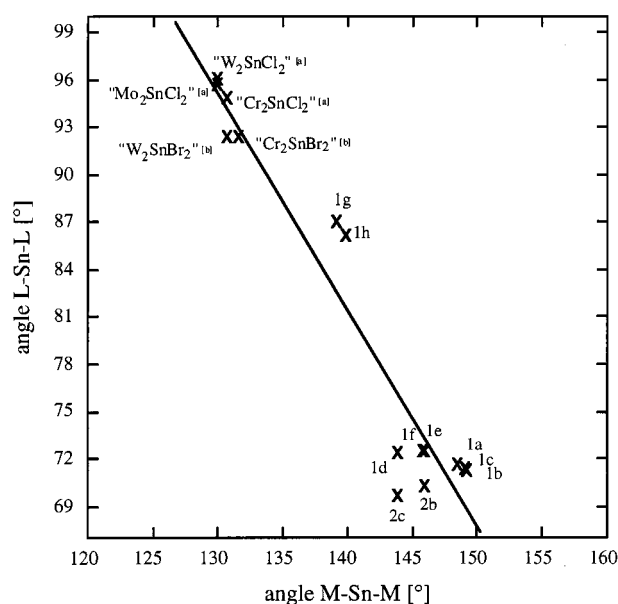
Figure 7. Newman projection of a compound of type **1**; view along the $\text{M}-\text{M}$ axis



The $\text{Sn}-\text{N}$ distances observed for **1a–1f** are close to their mean value of 229 pm within a few pm in all these compounds (Table 5). The quality of the data obtained for the tungsten compound **1c** is too low (Tables 10 and 11) to warrant a detailed discussion of individual differences; the same applies to the tungsten compound **1h**. A comparison of the 2,2'-bipyridine adduct **1g** and the bis-pyridine adduct **1f** suggests a somewhat weaker $\text{Sn}-\text{N}$ interaction in **1g** ($\text{Sn}-\text{N}$: 232.0 pm) than in **1a** ($\text{Sn}-\text{N}$: 228.5 pm) (Table 5). The most apparent difference between the three classes of compounds (**1a–1c**, **1d–1f**, **1g**, and **1h**) is found in the angular distribution around the tin center: the $\text{M}-\text{Sn}-\text{M}$ angles are close to 149° for the 2,2'-bipyridine adducts (Table 5) while they average at around 145° for the 1,10-phenanthroline adducts (Table 5). For the bis-pyridine adducts they are definitely smaller with values around 139° (Table 5).

The trend observed for the $\text{M}-\text{Sn}-\text{M}$ angles is counterbalanced by an opposite trend in the $\text{N}-\text{Sn}-\text{N}$ angles (Table 5, Figure 8): with 2,2'-bipyridine as the ligand this angle is constant at 71.3° (Table 5) within the limits of error for all three compounds **1a–1c**; with 1,10-phenanthroline (**1d–1f**) the angle stays at 72.4° (Table 5). For the bis-pyridine derivatives **1g** and **1h** angles of 86.5° (Table 5) are observed being again practically identical for the two compounds in this class. The rather small $\text{N}-\text{Sn}-\text{N}$ angles observed for **1a–1c** and **1d–1f** are thus obviously a consequence of the chelate binding mode. While in the compounds **1g** and **1h** the two separate pyridine donors are

Figure 8. Correlation between the angles around the tin center



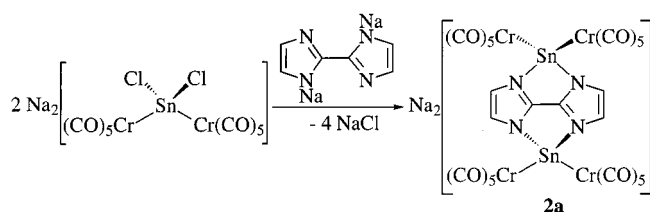
[a] Values for the chloride compounds $[\{(\text{CO})_5\text{M}\}_2\text{SnCl}_2]^{2-}$ ($\text{M} = \text{Cr, Mo, W}$) are taken from ref. [3] – [b] Values for the bromide compounds $[\{(\text{CO})_5\text{M}\}_2\text{SnBr}_2]^{2-}$ ($\text{M} = \text{Cr, W}$) are taken from ref. [4].

free to occupy the individually optimal positions, for the chemically related dianions $[\{(\text{CO})_5\text{M}\}_2\text{SnHal}_2]^{2-}$ ($\text{M} = \text{Cr, Mo, W}$; $\text{Hal} = \text{Cl}$ [3]; $\text{M} = \text{Cr, W}$; $\text{Hal} = \text{Br}$ [4]), where two halide donors bind to the tin center, the angles $\text{Hal}-\text{Sn}-\text{Hal}$ are around 94° so that it is probable to assume that an angle of around 90° is characteristic for an unstrained $\text{L}-\text{Sn}-\text{L}$ arrangement in this type of compound. The trend apparent from the structures of **1a–1h** that a small $\text{N}-\text{Sn}-\text{N}$ angle is accompanied by a large $\text{M}-\text{Sn}-\text{M}$ angle is also apparent from the fact that the $\text{M}-\text{Sn}-\text{M}$ angles observed for $[\{(\text{CO})_5\text{M}\}_2\text{SnHal}_2]^{2-}$ are close to 131° [3] [4]. The corresponding data for quite a number of compounds of the general formula $[\{(\text{CO})_5\text{M}\}_2\text{SnL}_2]^n$ ($n = 0$, $\text{L}_2 = 2,2'$ -bipyridine, 1,10-phenanthroline, 2 pyridine, 2,2'-bipyrimidine; $n = -2$, $\text{L} = \text{Cl, Br}$) are collected in the diagram of Figure 8 which illustrates the correlation between $\text{M}-\text{Sn}-\text{M}$ and $\text{L}-\text{Sn}-\text{L}$ angles in this type of compounds.

d) Compounds 2 Containing Biimidazolato or 2,2'-Bipyridine Chelating Ligands

Since the bidentate chelate ligands 2,2'-bipyridine and 1,10-phenanthroline form the stable mononuclear adducts **1** bis-bidentate chelate bases should give dinuclear compounds. When disodium biimidazolato, $\text{C}_6\text{H}_4\text{N}_4\text{Na}_2$, is treated with $[\text{Na}(\text{THF})_x]_2[\{(\text{CO})_5\text{Cr}\}_2\text{SnCl}_2]$ [3] [4] the dinuclear tin(0) compound **2a** is obtained (Scheme 1).

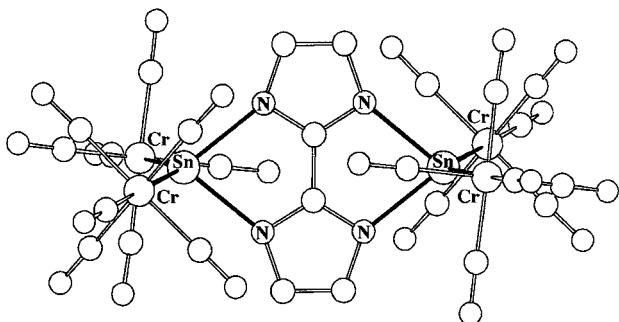
2a is separated from the reaction mixture by chromatographic workup. Crystals suitable for X-ray analysis are obtained by addition of 12-Crown-4 to a THF solution of **2a** followed by vapor diffusion from THF/diethyl ether/petroleum ether (boiling range $40-60^\circ\text{C}$).

Scheme 1. Reaction of $\text{Na}_2[\{(\text{CO})_5\text{Cr}\}_2\text{SnCl}_2]$ with disodium biimidazole

The IR- ν_{CO} spectrum in THF is consistent with the presence of $[(\text{CO})_5\text{Cr}]$ groups (Table 4)^[7]; in comparison with the IR- ν_{CO} spectra of **1a** and **1d** the absorption pattern observed for **2a** shows two additional resonances apparent as shoulders. The somewhat reduced local symmetry or some coupling between the individual $[(\text{CO})_5\text{Cr}]$ chromophores may be the reason for this^[7]. Relative to the absorptions observed for the neutral species **1a** and **1d** the center of gravity of the ν_{CO} -band pattern is shifted to slightly lower energies as expected.

The ^1H - and ^{13}C -NMR data of **2a** (see Experimental Section) are consistent with the ligand acting as a bis-bidentate chelate bridge.

A value of $\delta = 1149$ is observed for the ^{119}Sn -NMR resonance (Table 4) of **2a**. The ^{119}Sn -NMR shift is thus about 200 ppm upfield from the shifts observed for **1a** and **1d** and is close to the value observed for $[\text{Ph}_4\text{P}]_2[\{(\text{CO})_5\text{Cr}\}_2\text{SnCl}_2]$ ($\delta = 924$)^[4]. Even though no temperature-dependent ^{119}Sn -NMR data of **2a** could be obtained, the relatively strong high-field shift of the ^{119}Sn -NMR signal of **2a** suggests that there is no dynamic coordination/de-coordination equilibrium active for this compound.

Figure 9. Molecular structure of the dianion of **2a**

The X-ray analysis of **2a** (Tables 6 and 12, Figure 9) which is a centrosymmetric molecule in the solid state reveals the general type of bonding as inferred from the spectral data. The individual trends already discussed for compounds **1** are equally well seen in the structure of **2a** (Table 6). With respect to the diagram (Figure 8) correlating the bond angles $\text{M}-\text{Sn}-\text{M}$ and $\text{N}-\text{Sn}-\text{N}$ **2a** is an outlier with values of 135° and 77° , respectively (Table 6) being found for **2a**. It is not clear whether it is the steric encumbrance in the dinuclear tin species **2a** or some peculiarity

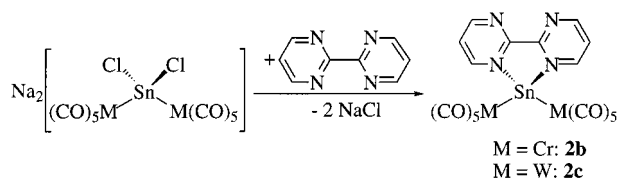
connected with the biimidazolato bridging ligand which causes this deviation.

Table 6. Selected bond lengths [pm], bond angles $^\circ$, and torsion angles $^\circ$ of compounds **2a–2c**^[a]

$[(\{(\text{CO})_5\text{M}\}_2\text{Sn})_x(\text{N}^-\text{N})^x]^{2-}$	2a · (12-Crown-4) M = Cr; x = 2; n = -2	2b M = Cr; x = 1; n = 0	2c M = W; x = 1; n = 0
M–Sn	260.1(1) 262.1(2)	265.2(2) 265.7(3)	275.2(1) 275.4(1)
M–C _{CO(ax)} ^[b]	183.2(9)	187(1)	196(2)
M–C _{CO(eq)} ^[b]	188.3(9)	191(3)	205(2)
Sn–N	229.2(5) 226.9(5)	236.0(6) 236.9(7)	231(1) 234(1)
M–Sn–M	135.26(4)	146.05(5)	143.90(4)
N–Sn–N	77.2(2)	70.2(2)	69.6(4)
M–Sn–N	112.8(1) 106.2(1) 107.1(1) 102.1(1)	101.2(2) 104.7(2) 101.3(2) 107.9(2)	99.8(3) 101.6(3) 106.4(3) 108.1(3)
Sn–N–C _{ipso} ^[b]	109.6(4)	118.4(5)	119.1(9)
Sn–M–C _{CO(ax)} ^[b]	177.1(3)	179.1(5)	175.0(4)
Sn–M–C _{CO(eq)} ^[b]	86.7(2)	88.8(8)	87.4(5)
C _{CO(eq)} –M–C _{CO(ax)} ^[b]	93.3(4)	91.2(8)	92.6(7)
C _{CO(eq)} –M–C _{CO(eq)} ^[b]	89.8(3) 173.3(3)	89(1) 172(1)	89.9(7) 174.2(7)
N–C–C–N torsion angle α ^[c]	0 33	6(1) 6	2(2) 10

^[a] Estimated standard deviations in units of the least significant figures given in each case are quoted in parentheses. – ^[b] Average values; the standard deviations refer to the largest individual esd in each set. – ^[c] α refers to the torsion angle $\text{C}_{\text{CO}(\text{eq})}-\text{M}-\text{M}-\text{C}_{\text{CO}(\text{eq})}$ as defined in Figure 7.

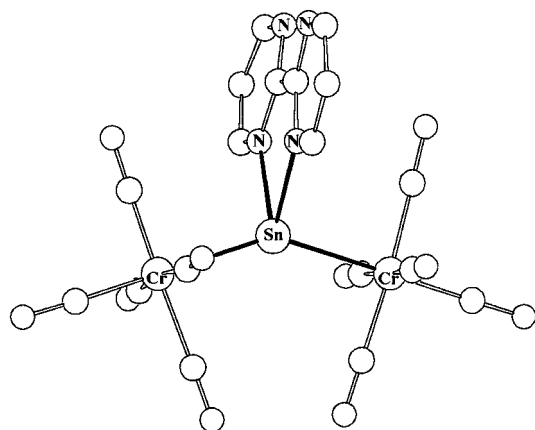
Procedures analogous to the one which leads to the dinuclear compound **2a** with biimidazole as the ligand gave, under the workup procedures applied to obtain compounds **1**, only the mononuclear species **2b** and **2c** with 2,2'-bipyrimidine (bpmd) as the potential bis-bidentate chelate ligand (Scheme 2).

Scheme 2. Reaction of $\text{Na}_2[\{(\text{CO})_5\text{M}\}_2\text{SnCl}_2]$ (M = Cr, W) with 2,2'-bipyrimidine

The IR- ν_{CO} data of **2b** and **2c** are in excellent qualitative accord with the corresponding data of compounds **1** (Table 4).

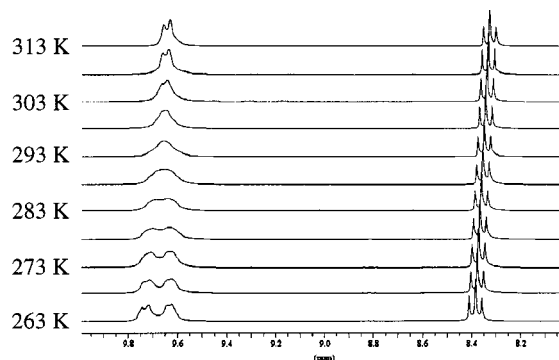
The mononuclearity of **2b** and **2c** is unequivocally proofed by X-ray analyses for both compounds (Tables 6 and 12, Figure 10). While the quality of the diffraction data obtained for the tungsten compound **2c** does not warrant a detailed discussion of individual geometric parameters the structure analysis of **2b** is of standard accuracy.

Since 2,2'-bipyridine is a direct analogue of 2,2'-bipyrimidine a comparison of structures **1a** and **2b** should be informative. Many of the general trends discussed for com-

Figure 10. Molecular structure of **2b**

pounds **1** are as well observed for compounds **2** (Tables 5 and 6). The fact that the Cr–Sn bond is more than 3 pm longer than the one observed in **1a** (Table 5) has no explanation at the moment because at the same time the Sn–N distances in **2b** [236.5 (7) pm, Table 6] are definitely longer than the Sn–N bonds in the 2,2'-bipyridine derivative **1a** [228.5 (3) pm, Table 5]. Nevertheless, the angles characterizing the coordination at the tin center are very similar for both compounds as are the angles relevant to describe the coordination of the chromium centers in both compounds (Tables 5 and 6, Figure 9).

In contrast to the mononuclear structure of **2b** and **2c** the proton-NMR signals observed for these compounds at ambient temperature show a pattern (Figure 11) which indicates at least C_{2v} symmetry for the ligand surroundings while only C_s symmetry is possible with the static structure found in the solid state (Figure 10).

Figure 11. Temperature-dependent ^1H -NMR spectrum of **2c**

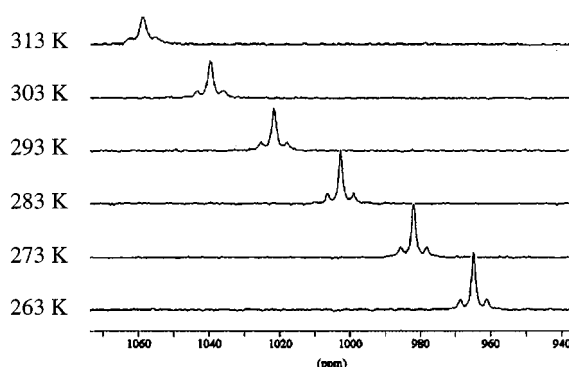
In the static structure the protons H_a and H_c (see insert, Table 2) have definitely different environments, while they give rise to only one broad signal at 298 K (Figure 11, $\delta \approx 9.6$). By variable-temperature NMR measurements (Figure 11) it is shown that upon cooling two doublets evolve from this envelope which are clearly resolved at 263 K (Figure 11). The appearance of the spectra at low temperatures thus corresponds to the static C_s -symmetric structure as is observed in the solid state (Figure 10). At higher temperatures the broad envelope observed at 298 K sharpens and a clear

doublet is apparent at 313 K (Figure 11) indicating C_{2v} symmetry in the time average. The process which gives rise to this temperature dependence is then one which equilibrates all the four donor positions of the 2,2'-bipyridine ligand in **2c**.

According to the discussions made in the previous parts of this paper the most probable equilibration pathway is the one where one Sn–N bond is opened thus allowing the now uncoordinated pyrimidyl residue to rotate. Reoordination of this pyrimidyl entity necessarily leads to the equilibration of its donor functions. With the same type of process operating for the other pyrimidyl part of the chelate ligand all four donor positions are equilibrated on the time average. The coalescence temperature for this process as observed for **2c** (Figure 11) is around 288 K corresponding to an activation barrier of around 61 ± 1 kJ/mol^[22]. The same type of ^1H -NMR observation is made for **2b** with a coalescence temperature of 293 K. The activation energy (64 ± 1 kJ/mol) is the same within the limits of error as the one found for **2c**. These energies refer to a process different from the one discussed in connection with the dynamic behavior of **1**: the process discussed there for 2,2'-bipyridine or 1,10-phenanthroline derivatives, respectively, involved nothing but a wagging motion of the chelate ligands with one of the nitrogen donors remaining tightly bound and the other one just shifting away from the tin by some 50 pm (Sn...N ca. 284 pm) without completely losing the contact to its tin neighbor (type C, Figure 4). In the case of **2b** and **2c** this contact is completely lost by a full 180° rotation of the ring. Such a rotation is not possible for 1,10-phenanthroline and the observation that the 1,10-phenanthroline derivative **1e** behaves quite like the 2,2'-bipyridine derivative **1a** (vide supra) lends quite some credit to the interpretation of the dynamic processes in these cases. For **2b** and **2c** one Sn–N bond is completely broken and EHT calculations performed on $[(\text{CO})_5\text{Cr}]_2\text{Sn}(\text{bipy})$ (**1a**) as a model compound suggest that quite some additional energy is needed for this process of completely breaking the bond.

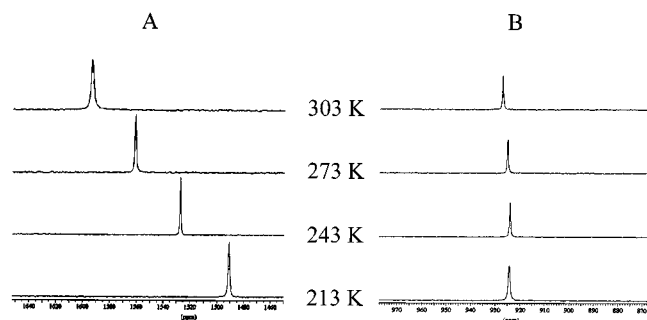
The ^{13}C -NMR data of **2b** and **2c** are formally in accord with the static structure as observed in the solid state (Figure 10) and individual signals are observed for every type of chemically different carbon atoms (Table 3). This is due to the different time window of ^1H - and ^{13}C -NMR spectroscopy and especially to the large difference in resonance frequency of C_a and C_c (Table 3)^[23]. At 313 K the resonances of C_a and C_c have just started to fade away yet without a time averaged signal being apparent. Further heating is precluded by the low boiling point of the $[\text{D}_6]$ acetone solvent used.

The type of dynamic process as discussed for the 2,2'-bipyridine and 1,10-phenanthroline adducts **1** should likewise be apparent for **2b** and **2c** (Figure 12). In these cases the weakening of one of the two Sn–N bonds at each tin center should be a low lying pre-equilibrium step with reference to the complete bond breaking and rotation process which is evident by the coalescence experiments discussed above. If no further deep energy minima are met along the reaction coordinate of bond breaking and ring rotation –

Figure 12. Temperature-dependent ^{119}Sn -NMR spectrum of **2c**

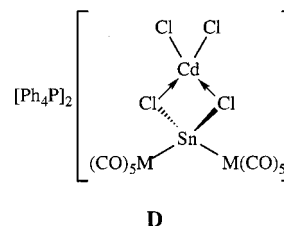
as is evident by the ^1H -NMR data – this additional dynamic process will not mirror itself into the temperature dependence of the ^{119}Sn -NMR spectrum and this is what is indeed observed. Fitting equation 1 as discussed for **1a** and **1e** to the shift values observed at different temperatures (Figure 12) for **2c** leads to the values $\delta_B = 800$, $\delta_C = 3600$ and $\Delta G = 6$ kJ/mol with B and C referring to the use of the symbols in Figure 4. These values are in good agreement to the ones obtained for **1a** and **1e**.

Observations made for $\{[(\text{CO})_5\text{M}]_2\text{SnCl}_2\}^{2-}$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) lend some additional credit to the above reasoning: the ^{119}Sn -NMR resonances of the salt $[\text{Ph}_4\text{P}]_2\{[(\text{CO})_5\text{Cr}]_2\text{SnCl}_2\}^{[4]}$ occurs at $\delta = 924$ with a only slight temperature dependence as generally induced by solvation processes (Figure 13, B).

Figure 13. Comparison of the temperature dependence of the ^{119}Sn -NMR resonances of $[\text{Na}(\text{solv})_x]_2\{[(\text{CO})_5\text{Cr}]_2\text{SnCl}_2\}$ (A) and $[\text{Ph}_4\text{P}]_2\{[(\text{CO})_5\text{Cr}]_2\text{SnCl}_2\}$ (B)

The disodium salt of the same dianion on the other hand shows a ^{119}Sn -NMR resonance which is strongly temperature dependent (Figure 13, A). The shift values observed between 213 K and 303 K span a range between $\delta = 1593$ and $\delta = 1490$. The IR- ν_{CO} absorptions of these two salts are different as well^[4] with the absorption pattern observed for the disodium salt occurring at higher energies as compared to the one of the $[\text{Ph}_4\text{P}]$ salt^[4]. A clue as to what the reason for these differences might be comes from the following observation: when THF solutions of the $[\text{Ph}_4\text{P}]_2\{[(\text{CO})_5\text{M}]_2\text{SnCl}_2\}$ are treated with an equimolar amount of CdCl_2 the infrared band pattern changes to the one characteristic for the disodium salts

$[\text{Na}(\text{THF})_x]_2\{[(\text{CO})_5\text{M}]_2\text{SnCl}_2\}$: $\nu_{\text{CO}}(\text{THF})$: $\text{M} = \text{Cr}$: 2040 w, 2007 s, 2000 sh, 1920 vs, 1895 sh cm^{-1} , Figure 2; $\text{M} = \text{Mo}$: 2051 vw, 2025 s, 1949 sh, 1929 vs, 1901 s; $\text{M} = \text{W}$: 2052 w, 2027 m, 1926 vs, 1894 s). The ^{119}Sn -NMR spectrum of solution of $[\text{Ph}_4\text{P}]_2\{[(\text{CO})_5\text{W}]_2\text{SnCl}_2\} \cdot \text{CdCl}_2$ for example taken at 300 K shows a signal at $\delta = 1250$, very similar to the one observed for the disodium salt ($\delta = 1268$). It is plausible to assume that CdCl_2 will interact with the SnCl_2 part of the dianion by association with the chlorine functions to produce an adduct of type **D** (Figure 14)

Figure 14. Possible form of an association between $[\text{Ph}_4\text{P}]_2\{[(\text{CO})_5\text{M}]_2\text{SnCl}_2\}$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) and CdCl_2 

Several forms of association are of course conceivable with the extreme of a complete separation of the adduct into the two anions $[\text{CdCl}_3]^-$ and $\{[(\text{CO})_5\text{Cr}]_2\text{SnCl}\}^-$. The observed shift in the IR- ν_{CO} absorptions (vide supra) fits into this idea as does the observation that the ^{119}Sn -NMR spectra of $[\text{Ph}_4\text{P}]_2\{[(\text{CO})_5\text{M}]_2\text{SnCl}_2 \cdot \text{CdCl}_2\}$ are strongly temperature-dependent while the ones of $[\text{Ph}_4\text{P}]_2\{[(\text{CO})_5\text{M}]_2\text{SnCl}_2\}$ are not. Fitting the NMR data of $[\text{Ph}_4\text{P}]_2\{[(\text{CO})_5\text{W}]_2\text{SnCl}_2 \cdot \text{CdCl}_2\}$ to an equilibrium of this type leads to a ΔG value of 5 kJ/mol for the relevant process and values of $\delta_B = 1000$ and $\delta_C = 3200$ with respect to Equation 1. These values are not to different from the ones estimated for a comparable equilibrium in the case of compounds **1** and **2**.

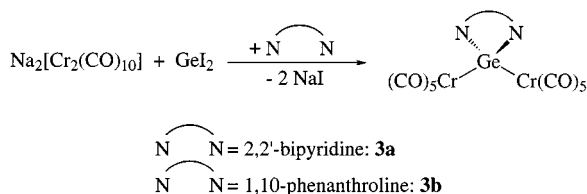
If THF solutions of $[\text{Ph}_4\text{P}]_2\{[(\text{CO})_5\text{M}]_2\text{SnCl}_2\}$ are treated with equimolar amounts of CoCl_2 , FeCl_2 , or MnCl_2 the IR- ν_{CO} absorption pattern shifts accordingly with the resulting spectrum being equal to the one observed when CdCl_2 is used as the halide abstractor and altogether equal to the one observed for THF-solutions of $[\text{Na}(\text{THF})_x]_2\{[(\text{CO})_5\text{M}]_2\text{SnCl}_2\}$. When, on the other hand, solutions of $\text{Na}_2\{[(\text{CO})_5\text{M}]_2\text{SnCl}_2\}$ in THF are treated with a large excess of [2.2.2]-Cryptand the IR- ν_{CO} absorption pattern as well as the ^{119}Sn -NMR resonances shift to the value characteristic for $[\text{Ph}_4\text{P}]_2\{[(\text{CO})_5\text{M}]_2\text{SnCl}_2\}^{[4]}$: the encrypted sodium ion can no longer act as a halide abstractor. Any attempts to isolate the product $\{[(\text{CO})_5\text{M}]_2\text{SnCl}\}^-$ formed by halide abstraction from $\{[(\text{CO})_5\text{M}]_2\text{SnCl}_2\}^{2-}$ have failed so far. The isolation of $[\text{Ph}_4\text{P}]_2[\text{Zn}_2\text{Cl}_6]^{[24]}$ from the reaction of $[\text{Ph}_4\text{P}]_2\{[(\text{CO})_5\text{Cr}]_2\text{SnCl}_2\}$ and ZnCl_2 does however show that chloride abstraction is in fact occurring with the ZnCl_2 reagent.

e) Analogous Compounds with Germanium and Lead

The germanium analogue **3a** of **1a** is prepared from the reaction of $\text{Na}_2[\text{Cr}_2(\text{CO})_{10}]$ with GeI_2 in the presence of

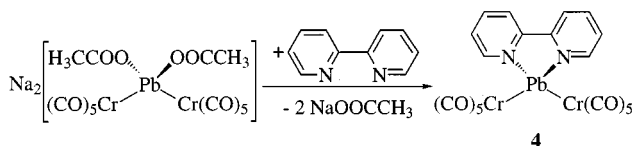
2,2'-bipyridine. The same procedure when performed with 1,10-phenanthroline instead of 2,2'-bipyridine as the chelating ligand leads to **3b** the germanium analogue of **1d** (Scheme 3).

Scheme 3. Reaction of $\text{Na}_2[\text{Cr}_2(\text{CO})_{10}]$ with GeI_2 in the presence of a chelate ligand



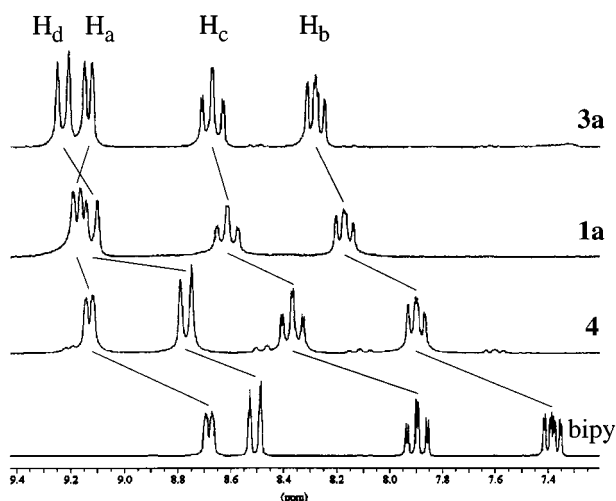
The lead analogue **4** of **1a** is accessible by the reaction of $[\{(\text{CO})_5\text{Cr}\}_2\text{Pb}(\text{OOCCH}_3)_2]^{2-}$ [4] with 2,2'-bipyridine (Scheme 4).

Scheme 4. Reaction of the disodium salt $[\{(\text{CO})_5\text{Cr}\}_2\text{Pb}(\text{OOCCH}_3)_2]^{2-}$ with 2,2'-bipyridine



All three compounds are characterized by IR- ν_{CO} , ^1H -NMR, and ^{13}C -NMR spectroscopy (Tables 2–4). The NMR shifts observed relative to the resonances of the free ligands clearly indicate a chelate type coordination in each case (Tables 2 and 3). The ^1H -NMR pattern observed for the resonances of the 2,2'-bipyridine ligands in the series of the germanium, tin, and lead compounds (**3a**, **1a**, and **4**) are compared to the ^1H -NMR pattern observed for the free ligand in Figure 15.

Figure 15. Comparison of the ^1H -NMR spectra of $[\{(\text{CO})_5\text{Cr}\}_2\text{E}(\text{bipy})]$ (E = Ge: **3a**; E = Sn: **1a**; E = Pb: **4**) with the ^1H -NMR spectrum of free 2,2'-bipyridine



It is seen that the low-field shift upon coordination is smallest for the lead compound **4** and largest for the germanium compound **3a** (Table 2, Figure 15). This may be taken as an indication of the continuously stronger interaction between the main group center and the 2,2'-bipyridine

ligand going from lead to germanium. An interesting special feature apparent from Figure 15 is that the signals originating from H_a and H_d change their relative position with respect to one another when going from the tin (**1a**) to the germanium compound **3a**. This type of observation had already been made with other coordination compounds of 2,2'-bipyridine and 1,10-phenanthroline and has prompted to some tentative explanations^[20].

Table 7. Selected bond lengths [pm], bond angles [°], and torsion angles [°] of compounds **3a–4**^[a]

$[\{(\text{CO})_5\text{Cr}\}_2\text{EL}_2]$	3a/1 E = Ge L ₂ = bipy	3a/2 E = Ge L ₂ = bipy	3b E = Ge L ₂ = phen	4 E = Pb L ₂ = bipy
Cr–E	247.1(3) 247.2(3)	247.9(3) 249.6(3)	247.5(1)	265.8(2) 265.8(2)
Cr–C _{CO(ax)} ^[b]	186(1)	186(1)	184.5(7)	187.0(2)
Cr–C _{CO(eq)} ^[b]	187(1)	187(1)	187.8(8)	189.7(2)
E–N	206.1(9) 204.3(9)	204.6(9) 205(1)	206.9(4)	244(1) 241(1)
Cr–E–Cr	133.26(9)	136.64(1)	137.94(5)	155.47(8)
N–E–N	76.7(3)	76.8(4)	78.1(2)	67.4(4)
Cr–E–N	103.7(3) 108.8(3) 112.1(3) 107.8(3)	105.5(3) 108.8(3) 103.7(3) 108.5(3)	104.4(1) 108.0(1)	100.7(3) 99.4(3) 99.4(3) 101.2(3)
E–N–C _{ipso} ^[b]	118.1(8)	117.8(8)	115.0(4)	120.2(9)
E–Cr–C _{CO(ax)} ^[b]	174.7(5)	174.7(5)	177.9(2)	175.8(5)
E–Cr–C _{CO(eq)} ^[b]	88.9(5)	88.9(5)	88.0(2)	88.3(5)
C _{CO(eq)} –Cr–C _{CO(ax)} ^[b]	91.2(6)	91.2(6)	92.0(3)	91.8(7)
C _{CO(eq)} –Cr–C _{CO(eq)} ^[b]	90.0(6) 176.3 (7)	90.0(6) 176.3(7)	89.9(3) 175.7(7)	90.0(7) 175.0(7)
N–C–C–N	7(1)	4(1)	0	16(1)
torsion angle α ^[c]	19	40	42	25

^[a] Estimated standard deviations in units of the least significant figures given in each case are quoted in parentheses. – ^[b] Average values; the standard deviations refer to the largest individual esd in each set. – ^[c] α refers to the torsion angle $\text{C}_{\text{CO}(\text{eq})}-\text{M}-\text{M}-\text{C}_{\text{CO}(\text{eq})}$ as defined in Figure 7.

The structures of **3** and **4** have been determined by X-ray crystallography (Tables 7 and 13). The overall geometry closely corresponds to the one observed for the other 2,2'-bipyridine and 1,10-phenanthroline compounds described in this paper. The structures will therefore be discussed with implicit reference to Figure 2 which shows the general structural pattern with respect to the $[\{(\text{CO})_5\text{Cr}\}_2\text{Sn}(\text{L}_2)]$ analogues **1a** and **1d**. The crystal of **3a** contains two crystallographically independent molecules designated as **3a/1** and **3a/2** in Table 7. The only very minor deviations in the scalar properties of the two crystallographically independent species **3a** (Table 7) demonstrate that the structures are to a very large extent determined by the inner molecular potential and not strongly influenced by the outer forces caused by the potential imposed onto the molecules by the crystal lattice. On the other hand the torsion angles characterizing the skew of the arrangement of the equatorial carbonyl groups of the $[(\text{CO})_5\text{Cr}]$ entities relative to each other is different in the two individual molecules of **3a** (Table 7). This means that the corresponding torsional mode is a very soft one as expected. The Ge–N distances observed in **3a** (205 pm) are significantly shorter than the ones found in its

analogue [$\{\text{Cp}'(\text{CO})_2\text{Mn}\}_2\text{Ge}(\text{bipy})$] ($\text{Ge}-\text{N}$: 211.5 pm)^[5]. The same trend is observed for the 1,10-phenanthroline compound **3b** (**3b** has crystallographic C_2 symmetry) with an $\text{Ge}-\text{N}$ distance of 206.9 pm versus the equivalent distance in [$\{\text{Cp}'(\text{CO})_2\text{Mn}\}_2\text{Ge}(\text{phen})$] of 216.8 pm^[6]. The $\text{Pb}-\text{N}$ distances in the lead compound **4** fit to this trend as well. Due to absorption effects the structure analysis is not very accurate but it is still beyond doubt that the $\text{Pb}-\text{N}$ distances in **4** (243 pm, Table 7) are significantly shorter than the ones found in [$\{\text{Cp}'(\text{CO})_2\text{Mn}\}_2\text{Pb}(\text{bipy})$] ($\text{Pb}-\text{N}$: 255.7 pm)^[5]. An explanation for this trend based on the different π -donor capabilities of [$\text{Cp}'(\text{CO})_2\text{Mn}$] versus [$(\text{CO})_5\text{Cr}$] has already been given above. Yet another trend is seen when comparing the data collected in Tables 5 and 7: the $\text{M}-\text{E}-\text{M}$ angle systematically increases along the series of germanium, tin, and lead compounds. This trend is as well apparent from the data known for the [$\text{Cp}'(\text{CO})_2\text{Mn}$] analogues of **1a**, **3a**, and **4**^{[5][6]} and their iso-electronic cationic analogues [$\{\text{Cp}'(\text{CO})_2\text{Mn}\}_2\text{E}(\text{bipy})$]⁺ ($\text{E} = \text{As}$ ^[25], Sb ^[25], Bi ^[26]).

f) Cyclic voltammetry of Compounds **1a–3b**

Cyclic voltammetric data have been obtained (see Experimental Section) for all compounds but **4** and are listed in Table 8.

Table 8. Cyclic voltammetric data^[a]

	Reduction		Oxidation	
1a	−1.16 rev.	−1.70 qrev.	+0.84 qrev.	+1.17 irrev.
1b	−1.22 rev.	−1.80 rev.	+0.70 irrev.	+1.08 irrev.
1c	−1.20 rev.	−1.76 rev.	+0.86 irrev.	+1.10 irrev.
1d	−1.16 irrev.	—	+0.84 qrev.	—
1e	−1.21 irrev.	−2.00 irrev.	+0.68 irrev.	—
1f	−1.20 irrev.	—	+0.83 irrev.	+1.09 irrev.
1g	−1.40 irrev.	−2.16 irrev.	+0.56 irrev.	+0.85 rev.
1h	−1.43 irrev.	—	+0.57 irrev.	+0.97 irrev.
2a	—	—	+0.54 irrev.	+0.89 irrev.
			+0.67 irrev.	
2b	−0.86 rev.	−1.87 qrev.	+0.85 qrev.	—
2c	−0.92 rev.	−1.81 qrev.	+0.89 irrev.	+1.08 irrev.
3a	−1.09 rev.	−1.70 rev.	+0.78 irrev.	+0.85 qrev.
3b	−1.09 irrev.	—	+0.79 irrev.	+0.89 qrev.
4	—	—	—	—

^[a] Pt/SCE electrode/ $n\text{Bu}_4\text{NPF}_6/\text{CH}_3\text{CN}$; see Experimental Section.

A first reductive electron transfer occurs in the region between −0.8 and −1.4 V. Although the redox processes are only in part fully reversible a comparison of the observed potentials is revealing. For a given set of ligands reductions are found at closely similar values independent of the $[(\text{CO})_5\text{M}]$ groups to which the main-group center is bonded (compare: **1a–1c**, $\text{L}_2 = \text{bipy}$, −1.2 V; **1d–1f**, $\text{L}_2 = \text{phen}$, −1.2 V; **1g–1h**, $\text{L}_2 = 2 \text{ py}$, −1.4 V; **1a–1c**, $\text{L}_2 = \text{bpmd}$, −0.9 V). Furthermore, the potential at which reduction occurs does appear to be independent of the kind of main-group center (compare: **1a**, Sn, $\text{L}_2 = \text{bipy}$, −1.2 V; **3a**, Ge, $\text{L}_2 = \text{bipy}$, −1.1 V). These observations indicate that the LUMO in all the compounds is ligand centered. Even the second reduction waves (Table 8) conform to this statement. Although some of the comparisons made are not

completely sound on a thermodynamic basis due to partially irreversible electron transfer processes (Table 8) the trends are altogether clear. A reliable comparison can be made for **1a** ($\text{L}_2 = \text{bipy}$) and **2b** ($\text{L}_2 = \text{bpmd}$) because in each case the first reduction is fully reversible with the second one being quasireversible. It is observed that the first reduction of **1a** is by 30 kJ/mol more difficult than the first reduction of **2b**. The difference in electron affinity of the 2,2'-bipyridine versus the 2,2'-bipyrimidine ligand is mirrored by these data which again is in favour of the conclusion that the LUMO is ligand centered in each case.

While the reduction is thus ligand-centered the oxidation of the compounds **1a–3b** appears to be metal-centered: independent of the ligand but slightly dependent on the metal the oxidation waves are observed in the range of 0.7–1.0 V. In most cases the first oxidation wave occurs in this range (Table 8). In the case of **1g** and **1h**, where two pyridine molecules act as the L_2 donor set, the first irreversible oxidation is found at a lower potential of around 0.6 V already while the second one is again in the range discussed above. It is assumed that the first irreversible oxidation wave refers to the species which result from **1g** and **1h** by loss of one pyridine ligand. The corresponding dissociation equilibrium is evident from NMR and has been explained above. With the biimidazolato bridging ligand, species **2a**, which undergoes no reduction in the potential range studied, three oxidation waves are observed, all of them irreversible. But the last one with 0.9 V (Table 8) again being in the range characteristic of all the other compounds where this complication by several oxidation steps does not occur. Comparison of the oxidation potentials observed for **1a** (Sn) and **3a** (Ge) shows that the observed potentials are also practically independent of the main-group center. Taken together these findings indicate that the HOMO of the compounds is metal-centered with the exception of the dianionic compound **2a**.

Concluding Remarks

It is shown that even though the cumulene-type compounds $[(\text{CO})_5\text{M}=\text{E}=\text{M}(\text{CO})_5]$ ($\text{E} = \text{Ge}, \text{Sn}, \text{Pb}$; $\text{M} = \text{Cr}, \text{Mo}, \text{W}$) are not yet known in the free state, their base adducts $[(\text{CO})_5\text{M}]_2\text{E}(\text{L}_2)$ are stable and well-characterized compounds. Their structures as determined by X-ray crystallography reveal a common bonding pattern for all the compounds of this type. By comparison of a series of compounds of the type $[(\text{CO})_5\text{M}]_2\text{Sn}(\text{L}_2)$ it is demonstrated that in an unstrained compound the angle sustained at the tin center by the donors of L_2 should be close to 90°. The $\text{M}-\text{E}-\text{M}$ angles ($\text{E} = \text{Ge}, \text{Sn}, \text{Pb}$) are in the range between 133° and 155° systematically increasing from $\text{E} = \text{Ge}$ over $\text{E} = \text{Sn}$ to $\text{E} = \text{Pb}$. From NMR-spectroscopic data of the corresponding 2,2'-bipyridine adducts $[(\text{CO})_5\text{Cr}]_2\text{E}(\text{bipy})$ it is inferred that the bonding interaction between the chelate ligand and the main-group element decreases in the series $\text{E} = \text{Ge}$ to $\text{E} = \text{Pb}$. The temperature dependence of the ^{119}Sn -NMR shifts observed for compounds **1** and **2** is consistently interpreted in terms of an equilibrium $[(\text{CO})_5\text{M}]_2\text{E}(\text{L}_2) \rightleftharpoons [(\text{CO})_5\text{M}]_2\text{E}(\text{L}) + \text{L}$. With 2,2'-bi-

pyrimidine as a spectroscopic probe in $[(\text{CO})_5\text{M}]_2\text{Sn}(\text{bpmd})$ ($\text{M} = \text{Cr}, \text{W}$) this process of partial de-coordination is more directly evident from dynamic ^1H -NMR spectroscopy.

The financial support by the *Deutsche Forschungsgemeinschaft* (SFB 247) and the *Fonds der Chemischen Industrie* is gratefully acknowledged.

Experimental Section

General: All manipulations were carried out under argon by means of standard Schlenk techniques at 20°C unless mentioned otherwise. All solvents were dried by standard methods and distilled under argon. $[\text{D}_6]\text{acetone}$ used for the NMR spectroscopic measurements was degassed by three successive “freeze-pump-thaw” cycles and dried over 4-Å molecular sieves. Silica gel (Kieselgel z. A. 0.06–0.2 mm, J. T. Baker Chemicals B.V.) used for chromatography and Kieselgur (Kieselgur, gereinigt, gegläht, Erg. B.6, Riedel de Haen AG) used for filtration were degassed at 1 mbar at 180°C for 12 h and saturated with argon. – NMR: Bruker Avance DPX 200 at 200.13 MHz (^1H), 50.323 MHz ($^{13}\text{C}\{^1\text{H}\}$), 74.631 MHz ($^{119}\text{Sn}\{^1\text{H}\}$); chemical shifts (δ) in ppm with respect to $[\text{D}_6]\text{-acetone}$ (^1H : $\delta = 2.04$; ^{13}C : $\delta = 29.8$) as internal standards and to SnMe_4 (^{119}Sn : $\delta = 0$ at 25°C), respectively, as external standard. – IR: Bruker FT-IR IFS-66; CaF_2 cells. – UV/Vis/NIR: Perkin Elmer Lambda 19; cells (0.2 cm; Hellma 110 suprasil). – MS (FAB or EI): Finnigan MAT 8400; Nibeol (4-nitrobenzyl alcohol) or TEA (triethanol amine) matrices, respectively. – Elemental analyses: microanalytical laboratory of the Organisch-Chemisches Institut, Universität Heidelberg. – Melting points: Gallenkamp MFB-595 010; the values are not corrected. – Cyclic voltammetry: Methrohm “Universal Meß- und Titriergefäß”, Methrohm GC electrode RDE 628, platinum electrode, SCE electrode, Princeton Applied Research potentiostat Model 273, 10^{-3} M in 0.1 M $n\text{Bu}_4\text{NPF}_6/\text{CH}_3\text{CN}$. – The dinuclear sodium salts of the composition $\text{Na}_2[(\text{CO})_5\text{M}]_2\text{EX}_2$ ($\text{E} = \text{Sn}$: $\text{M} = \text{Cr}, \text{Mo}, \text{W}$; $\text{X} = \text{Cl}$; $\text{E} = \text{Pb}$: $\text{M} = \text{Cr}$; $\text{X} = \text{OOCCH}_3$) were prepared by salt metathesis reaction from the corresponding stable phosphonium salts $[\text{Ph}_4\text{P}]_2[(\text{CO})_5\text{M}]_2\text{EX}_2$ as described^[4]. The biimidazole^[27] and the metallates $\text{Na}_2[\text{M}_2(\text{CO})_{10}]$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) were prepared as reported^[28]. All other chemicals were commercially obtained and used without further purification.

Bis(pentacarbonylchromium)(2,2'-bipyridine)tin, $[(\text{CO})_5\text{Cr}]_2\text{-Sn}(\text{bipy})$ (**1a**), and *Bis(pentacarbonylchromium)(1,10-phenanthroline)tin*, $[(\text{CO})_5\text{Cr}]_2\text{Sn}(\text{phen})$ (**1d**): $\text{Na}_2[(\text{CO})_5\text{Cr}]_2\text{SnCl}_2$ (310 mg; 0.5 mmol) was dissolved in THF (30 ml) and solid 2,2'-bipyridine (78 mg; 0.5 mmol) or solid 1,10-phenanthroline (90 mg; 0.5 mmol), respectively, was added in one portion. The clear orange solution turned deep red immediately. After stirring for 30 min, the solvent was removed in vacuo. The resulting red oil was dissolved in THF (3 ml) and chromatographed on silica gel (20 cm; $\varnothing = 3$ cm; diethyl ether). Elution with diethyl ether gave two bands. The first yellow band was identified by IR spectroscopy to be $[\text{Cr}(\text{CO})_6]^{[29]}$. The second pink band was also characterized by spectroscopic comparison (IR^[30], ^1H -, and ^{13}C -NMR spectra) and found to be $[(\text{CO})_4\text{Cr}(\text{bipy})]$ or $[(\text{CO})_4\text{Cr}(\text{phen})]$, respectively. A third red-brown band which contained the compound **1a** or **1d** was eluted with THF. The resulting solution was taken to dryness leaving **1a** (230 mg; 71%) or **1d** (230 mg; 68%), respectively, as red

solids. Single crystals of **1a** and **1d** were obtained within 3 d by applying the method described below.

Bis(pentacarbonylmolybdenum)(2,2'-bipyridine)tin, $[(\text{CO})_5\text{Mo}]_2\text{-Sn}(\text{bipy})$ (**1b**), and *Bis(pentacarbonylmolybdenum)(1,10-phenanthroline)tin*, $[(\text{CO})_5\text{Mo}]_2\text{Sn}(\text{phen})$ (**1e**): A yellow solution of $\text{Na}_2[(\text{CO})_5\text{Mo}]_2\text{SnCl}_2$, obtained by salt metathesis reaction of $[\text{Ph}_4\text{P}]_2[(\text{CO})_5\text{Mo}]_2\text{SnCl}_2$ (1340 mg; 1 mmol) with $\text{Na}[\text{BPh}_4]$ (684 mg; 2 mmol)^[4], was filtered through Kieselgur (3 cm) into a Schlenk tube which already contained solid 2,2'-bipyridine (156 mg; 1 mmol) or solid 1,10-phenanthroline (180 mg; 1 mmol), respectively. The resulting deep red solution was filtered through Kieselgur (3 cm) and taken to dryness. The resulting red oil was redissolved in THF (3 ml) and slowly chromatographed (max. 50 drops/min) on silica gel (20 cm; $\varnothing = 3$ cm; diethyl ether). Two bands were obtained by elution with diethyl ether. The first yellow band was identified by IR spectroscopy to be $[\text{Mo}(\text{CO})_6]^{[29]}$. The second pink band was also characterized by spectroscopic comparison (IR^[30], ^1H -, and ^{13}C -NMR spectra) and found to be $[(\text{CO})_4\text{Mo}(\text{bipy})]$ or $[(\text{CO})_4\text{Mo}(\text{phen})]$, respectively. A third red-brown band, containing the compound **1b** or **1d**, was eluted with THF. From the red-brown solution 310 mg (41%) of **1b** or 290 mg (38%) of **1d**, respectively, were obtained by removing the solvent in vacuo. Applying the method described below gave single crystals of **1b** and **1d** within 3 d.

Bis(pentacarbonyltungsten)(2,2'-bipyridine)tin, $[(\text{CO})_5\text{W}]_2\text{-Sn}(\text{bipy})$ (**1c**), and *Bis(pentacarbonyltungsten)(1,10-phenanthroline)tin*, $[(\text{CO})_5\text{W}]_2\text{Sn}(\text{phen})$ (**1f**). – **Method A:** The disodium salt $\text{Na}_2[(\text{CO})_5\text{W}]_2\text{SnCl}_2$ (442 mg; 0.5 mmol) was dissolved in THF (30 ml). Solid 2,2'-bipyridine (78 mg; 0.5 mmol) or solid 1,10-phenanthroline (90 mg; 0.5 mmol), respectively, was added in one portion. The orange solution turned deep red immediately. After stirring for 30 min, the solvent was evaporated in vacuo. The oily red residue was redissolved in THF (3 ml) and chromatographed on silica gel (20 cm; $\varnothing = 3$ cm; diethyl ether). Elution with diethyl ether gave two bands. The first yellow band was found to contain $[\text{W}(\text{CO})_6]$, the second pink band contained $[(\text{CO})_4\text{W}(\text{bipy})]$ or $[(\text{CO})_4\text{W}(\text{phen})]$, respectively. These compounds were characterized by comparison of spectroscopic data^{[29][30]} (IR, ^1H -, and ^{13}C -NMR spectra). **1c** or **1f** were eluted with THF as a third red-brown band. The resulting solution was taken to dryness leaving 310 mg (67%) of **1c** or 350 mg (71%) of **1f**, respectively, as red microcrystalline powders.

Method B: To a stirred orange solution of the disodium metallate $\text{Na}_2[\text{W}_2(\text{CO})_{10}]$ (347 mg; 0.5 mmol) in ethanol (30 ml) was added solid SnCl_2 (95 mg; 0.5 mmol) in one portion. The solution turned deep red immediately. After stirring for 30 min, the solution was filtered through Kieselgur (3 cm). By addition of solid 2,2'-bipyridine (78 mg; 0.5 mmol) or solid 1,10-phenanthroline (90 mg; 0.5 mmol), respectively, the corresponding chelate complex precipitated. After additional stirring for 30 min, the red solid was separated from the mother liquor by filtration, washed with ethanol (2×5 ml) and diethyl ether (2×5 ml), and taken to dryness. Yields: **1c**: 260 mg (57%); **1f**: 270 mg (56%).

Single crystals of **1c** or **1f** were obtained within 3 d by applying the method described below.

Bis(pentacarbonylchromium)bis(pyridine)tin, $[(\text{CO})_5\text{Cr}]_2\text{-Sn}(\text{py})_2$ (**1g**), and *Bis(pentacarbonyltungsten)bis(pyridine)tin*, $[(\text{CO})_5\text{W}]_2\text{Sn}(\text{py})_2$ (**1h**): To a stirred orange solution of $\text{Na}_2[(\text{CO})_5\text{Cr}]_2\text{SnCl}_2$ (620 mg; 1 mmol) or $\text{Na}_2[(\text{CO})_5\text{W}]_2\text{SnCl}_2$ (884 mg; 1 mmol), respectively, was added pyridine (316 mg; 4 mmol) in one portion. No colour change of the solution was observed upon the addition. After 30 min of stirring, the solution was

Table 9. Selected analytical data

	m.p. / °C	MS; m/z (%) [fragment]	UV / nm (THF) λ_{max} (ε)	mol. formula (mol. mass)	elemental analysis
1a	236 (dec.)	-	288 (32000); 448 (900)	$\text{C}_{20}\text{H}_8\text{Cr}_2\text{N}_2\text{O}_{10}\text{Sn}$ (659.0)	calcd. C 36.45 H 1.22 N 4.25 found C 36.64 H 1.40 N 4.22
1b	211 (dec.)	747 (100) [M^+]	306 (48600); 353 (13000, sh); 408 (4000); 485 (3500)	$\text{C}_{20}\text{H}_8\text{Mo}_2\text{N}_2\text{O}_{10}\text{Sn}$ (746.9)	calcd. C 32.17 H 1.08 N 3.75 found C 32.10 H 1.42 N 3.75
1c	145 (dec.)	-	287 (28700); 417 (3200); 464 (1100, sh)	$\text{C}_{20}\text{H}_8\text{N}_2\text{O}_{10}\text{SnW}_2$ (922.7)	calcd. C 25.92 H 1.09 N 3.02 found C 27.30 H 1.09 N 2.81
1d	228	683(18) [M^-]	280 (40000); 449 (1800, br)	$\text{C}_{22}\text{H}_8\text{Cr}_2\text{N}_2\text{O}_{10}\text{Sn}$ (683.9)	calcd. C 38.69 H 1.18 N 4.10 found C 37.37 H 2.06 N 3.99
1e	195 (dec.)	-	294 (26800); 307 (24400); 352 (7200, sh); 404 (3600); 478 (2900)	$\text{C}_{22}\text{H}_8\text{Mo}_2\text{N}_2\text{O}_{10}\text{Sn}$ (770.9)	calcd. C 34.28 H 1.05 N 3.63 found C 34.35 H 1.20 N 3.71
1f	212 (dec.)	946 (85) [M^-]	423 (3200); 485 (3000)	$\text{C}_{22}\text{H}_8\text{N}_2\text{O}_{10}\text{SnW}_2$ (946.7)	calcd. C 27.91 H 0.85 N 2.96 found C 28.03 H 0.90 N 2.96
1g	141 (dec.)	-	298 (17000); 378 (2600, sh)	$\text{C}_{20}\text{H}_{10}\text{Cr}_2\text{N}_2\text{O}_{10}\text{Sn}$ (661.0)	calcd. C 36.34 H 1.52 N 4.24 found C 35.97 H 2.47 N 3.51
1h	100 (dec.)	-	305 (16000); 405 (2300, sh)	$\text{C}_{20}\text{H}_{10}\text{N}_2\text{O}_{10}\text{SnW}_2$ (924.7)	calcd. C 25.98 H 1.09 N 3.03 found C 26.00 H 1.17 N 3.03
2a	178 (dec.)	-	293 (21000); 362 (1900, sh)	$\text{C}_{58}\text{H}_{68}\text{Cr}_4\text{N}_4\text{Na}_2\text{O}_{36}\text{Sn}_2$ (1888.5)	calcd. C 36.89 H 3.63 N 2.97 found C 34.45 H 3.57 N 2.47
2b	249 (dec.)	606 (28) [($\text{M} - 2\text{CO}$) $^-$]	285 (26000, sh) 331 (6800); 442 (2000)	$\text{C}_{18}\text{H}_6\text{Cr}_2\text{N}_4\text{O}_{10}\text{Sn}$ (660.9)	calcd. C 32.71 H 0.92 N 8.48 found C 32.76 H 1.06 N 8.44
2c	175 (dec.)	-	286 (24800); 345 (8300, sh); 419 (2600, sh); 469 (1500, sh)	$\text{C}_{18}\text{H}_6\text{N}_4\text{O}_{10}\text{SnW}_2$ (924.7)	calcd. C 23.38 H 0.65 N 6.06 found C 24.22 H 1.10 N 5.97
3a	255	613 (25) [M^-]	295 (60000); 426 (4400); 520 (1700, sh)	$\text{C}_{20}\text{H}_8\text{Cr}_2\text{GeN}_2\text{O}_{10}$ (612.9)	calcd. C 39.20 H 1.32 N 4.57 found C 39.34 H 1.83 N 4.48
3b	205 (dec.)	637 (25) [M^-]	291 (61400); 424 (5000)	$\text{C}_{22}\text{H}_8\text{Cr}_2\text{GeN}_2\text{O}_{10}$ (636.9)	calcd. C 41.49 H 1.27 N 4.40 found C 41.58 H 1.60 N 4.43
4	245 (dec.)	746 (5) [($\text{M} - 2\text{H}$) $^-$]	298 (13900); 310 (12000); 432 (2100)	$\text{C}_{20}\text{H}_8\text{Cr}_2\text{N}_2\text{O}_{10}\text{Pb}$ (747.5)	calcd. C 32.14 H 1.08 N 3.75 found C 32.17 H 1.27 N 3.71

Table 10. Crystal-structure data for **1a–1d**

compound	1a	1b	1c	1d · THF
formula	$\text{C}_{20}\text{H}_8\text{Cr}_2\text{N}_2\text{O}_{10}\text{Sn}$	$\text{C}_{20}\text{H}_8\text{Mo}_2\text{N}_2\text{O}_{10}\text{Sn}$	$\text{C}_{20}\text{H}_8\text{N}_2\text{O}_{10}\text{SnW}_2$	$\text{C}_{22}\text{H}_8\text{Cr}_2\text{N}_2\text{O}_{10}\text{Sn}$
molecular mass [g]	658.970	746.850	922.670	682.990
crystal dimensions [mm]	$0.30 \times 0.30 \times 0.30$	$0.40 \times 0.20 \times 0.10$	$0.30 \times 0.30 \times 0.30$	$0.20 \times 0.30 \times 0.35$
crystal system	orthorhombic	orthorhombic	orthorhombic	triclinic
space group (No.)	Pbca (61)	Pbca (61)	Pbca (61)	$P\bar{1}$ (2)
<i>a</i> [pm]	1260.5 (3)	1281.4 (3)	1278.4 (3)	1132.1 (6)
<i>b</i> [pm]	1650.3 (5)	1655.7 (5)	1652.7 (5)	1141.6 (6)
<i>c</i> [pm]	2158.5 (5)	2198.6 (5)	2192.8 (5)	1194.7 (6)
α [°]	90.00 (0)	90.00 (0)	90.00 (0)	81.03 (2)
β [°]	90.00 (0)	90.00 (0)	90.00 (0)	82.85 (2)
γ [°]	90.00 (0)	90.00 (0)	90.00 (0)	77.21 (2)
cell volume [10^6 pm^3]	4490 (2)	4665 (2)	4633 (2)	1481 (1)
molecular units / cell	8	8	8	2
density (calculated) [g cm^{-3}]	1.950	2.127	2.646	1.693
absorption coefficient [cm^{-1}]	21.15	21.27	110.36	16.17
temperature [K]	200	200	200	200
no. rflns. for cell parameter refinement	25	37	30	25
scan range	$4.5^\circ \leq 2\theta \leq 45.0^\circ$	$4.4^\circ \leq 2\theta \leq 49.0^\circ$	$4.4^\circ \leq 2\theta \leq 49.0^\circ$	$4.7^\circ \leq 2\theta \leq 44.0^\circ$
scan speed [$^\circ \text{ min}^{-1}$]	$8.0 < \dot{\omega} < 60.0$	$\dot{\omega} = 10$	$\dot{\omega} = 10$	$8.0 \leq \dot{\omega} \leq 60.0$
no. rflns. measured	2932	3861	3853	3844
no. unique rflns.	2932	3861	3853	3620
no. rflns. observed	2520	3105	2775	3452
observation criterion	$2\sigma(I)$	$2\sigma(I)$	$2\sigma(I)$	$2\sigma(I)$
no. parameters refined	317	317	312	381
residual electron density [$\cdot 10^{-6} \text{ e pm}^{-3}$]	0.43 / -0.70	0.65 / -0.73	1.15 / -1.54	1.31 / -1.74
R_I / R_w [%] (refinement on F^2)	3.1 / 8.4	3.6 / 10.4	4.3 / 10.0	4.0 / 13.0

filtered through Kieselgur (3 cm) and the solvent was evaporated in vacuo. The yellow oily residue was redissolved in THF (3 ml)

and chromatographed slowly on silica gel (20 cm; $\varnothing = 3$ cm; diethyl ether). A yellow band was eluted with diethyl ether containing

Table 11. Crystal-structure data for **1e–1h**

compound	1e · THF	1f · THF	1g	1h · THF
formula	C ₂₂ H ₈ Mo ₂ N ₂ O ₁₀ Sn	C ₂₂ H ₈ N ₂ O ₁₀ SnW ₂	C ₂₀ H ₁₀ Cr ₂ N ₂ O ₁₀ Sn	C ₂₀ H ₁₀ N ₂ O ₁₀ SnW ₂
molecular mass [g]	770.880	946.700	660.990	924.690
crystal dimensions [mm]	0.40 × 0.50 × 0.50	0.20 × 0.30 × 0.30	0.50 × 0.40 × 0.40	0.50 × 0.40 × 0.40
crystal system	triclinic	triclinic	triclinic	triclinic
space group (No.)	P $\bar{1}$ (2)	P $\bar{1}$ (2)	P $\bar{1}$ (2)	P $\bar{1}$ (2)
a [pm]	1129.6 (2)	1133.4 (5)	895.5 (1)	931.4 (6)
b [pm]	1136.3 (1)	1141.7 (3)	1003.8 (2)	1028.2 (6)
c [pm]	1206.4 (1)	1212.1 (2)	1433.6 (2)	1464.9 (9)
α [°]	82.69 (1)	82.79 (2)	86.16 (1)	86.36 (2)
β [°]	81.27 (1)	81.18 (3)	76.46 (1)	77.54 (2)
γ [°]	77.61 (1)	77.36 (2)	68.55 (1)	67.46 (2)
cell volume [10 ⁶ pm ³]	1487.7 (3)	1505.5 (9)	1165.8 (3)	1265 (3)
molecular units / cell	2	2	2	2
density (calculated) [g cm ⁻³]	1.864	2.230	1.883	2.428
absorption coefficient [cm ⁻¹]	17.22	85.04	20.36	101.10
temperature [K]	200	200	200	200
no. rflns. for cell parameter refinement	28	18	34	25
scan range	4.8° ≤ 2 θ ≤ 48.0°	3.4° ≤ 2 θ ≤ 42.0°	4.4° ≤ 2 θ ≤ 52.0°	4.3° ≤ 2 θ ≤ 44.0°
scan speed [° min ⁻¹]	$\dot{\omega}$ = 11	7.0 ≤ $\dot{\omega}$ ≤ 60.0	$\dot{\omega}$ = 11	8.0 ≤ $\dot{\omega}$ ≤ 60.0
no. rflns. measured	4926	3449	4894	3570
no. unique rflns.	4660	3235	4584	3104
no. rflns. observed	4467	2793	4385	2875
observation criterion	2 σ (<i>I</i>)	2 σ (<i>I</i>)	2 σ (<i>I</i>)	2 σ (<i>I</i>)
no. parameters refined	413	371	356	317
residual electron density [$\cdot$ 10 ⁻⁶ e pm ⁻³]	1.13 / - 1.15	1.34 / - 1.20	0.68 / - 1.31	2.02 / - 2.84
<i>R</i> _I / <i>R</i> _w [%] (refinement on F ²)	3.2 / 9.1	3.6 / 12.9	2.6 / 8.5	4.6 / 13.2

[Cr(CO)₆] or [W(CO)₆], respectively (identified by comparison of IR spectroscopic data^[29]). A second yellow band, eluted with diethyl ether, consisted of a mixture of [Cr(CO)₆] and [(CO)₅Cr(py)] or [W(CO)₆] and [(CO)₅W(py)], respectively, as identified by IR spectroscopy^{[29][30]}. With THF a third yellow band was obtained consisting of pure **1g** or **1h**, respectively. Evaporation of the solvent left **1g** and **1h** as yellow oils. Yield: **1g**: 100 mg (15%); **1h**: 140 mg (15%). Single crystals of **1g** and **1h** were obtained within 8 d by applying the method given below.

Bis[bis(12-crown-4)sodium] tetrakis(pentacarbonylchromium)-(biimidazolato)distannate(0), [Na-(12-crown-4)₂]₂[{(CO)₅Cr}₂-Sn(biim)₂Sn{(CO)₅Cr}₂] (**2a**): Na₂[(CO)₅Cr]₂SnCl₂] (310 mg; 0.5 mmol) was dissolved in THF (30 ml). Upon addition of solid disodium biimidazolato [45 mg; 0.25 mmol; obtained by heterogenous reaction of biimidazole (34 mg; 0.25 mmol) and NaH (14 mg; 0.6 mmol) in THF without further purification] no colour change was observed. After 30 min, the yellow solution was filtered through Kieselgur (3 cm). 12-Crown-4 (90 mg; 0.5 mmol) was added to the reaction mixture. Evaporation of the solvent in vacuo left 760 mg (80%) of **2a** as a yellow-brown solid. Applying the method described below gave single crystals of **2a** within 14 d.

2a·(12-crown-4)₂: ¹H NMR ([D₆]acetone, 25°C): δ = 7.22 (s, 4 H, imidazolato-H), 3.65 [s, 64 H, CH₂-(12-crown-4)]. – ¹³C NMR ([D₆]acetone, 25°C): δ = 230.0 (CO_{ax}), 222.5 (CO_{eq}), 144.0 (C-2, biimidazolato), 127.1 (C-4 and C-5, biimidazolato), 62.5 (CH₂, 12-crown-4).

Bis(pentacarbonylchromium)(2,2'-bipyrimidine)tin, [(CO)₅-Cr]₂Sn(bpmd)] (**2b**), and *Bis(pentacarbonylchromium)(2,2'-bipyrimidine)tin*, [(CO)₅W]₂Sn(bpmd)] (**2c**): Na₂[(CO)₅Cr]₂SnCl₂] (620 mg; 1 mmol) or Na₂[(CO)₅W]₂SnCl₂] (884 mg; 1 mmol), respectively, was dissolved in THF (50 ml). Upon the addition of

solid 2,2'-bipyrimidine (79 mg; 0.5 mmol) the orange solution turned deep red immediately. The solvent was evaporated in vacuo after stirring the solution for 30 min. The red oily residue was dissolved in THF (3 ml) and chromatographed on silica gel (20 cm; Ø = 3 cm; diethyl ether). Two bands were obtained by elution with diethyl ether. The first yellow band was identified by comparison of IR spectra^[29] and found to be [Cr(CO)₆] or [W(CO)₆], respectively. The second pink band was identified to be [(CO)₄Cr(bpmd)] or [(CO)₄W(bpmd)], respectively, by comparison of their IR spectra with the IR spectra of the corresponding 2,2'-bipyridine complexes (vide supra)^[30]. With THF a third red-brown band was eluted which contained **2b** or **2c**, respectively. Evaporation of the solvent left **2b** and **2c** as red solids. Yield: **2b**: 150 mg (45%); **2c**: 170 mg (36%). Single crystals of **2b** and **2c** were obtained within 12 d by applying the method described below.

Bis(pentacarbonylchromium)(2,2'-bipyridine)germanium, [(CO)₅-Cr]₂Ge(bipy)] (**3a**), and *Bis(pentacarbonylchromium)(1,10-phenanthroline)germanium*, [(CO)₅Cr]₂Ge(phen)] (**3b**): To a stirred, orange solution of Na₂[Cr₂(CO)₁₀] (430 mg; 1 mmol) in THF (50 ml) was added solid GeI₂ (326 mg; 1 mmol) in one portion. After 5 min of stirring, solid 2,2'-bipyridine (156 mg; 1 mmol) or solid 1,10-phenanthroline (180 mg; 1 mmol), respectively, was added and the deep red solution was filtered through Kieselgur (3 cm). After 30 min of stirring, the solvent was evaporated. The solid residue was redissolved in THF (3 ml) and chromatographed on silica gel (20 cm; Ø = 3 cm; diethyl ether). Elution with diethyl ether gave two bands. The first yellow band was identified by IR spectroscopy to be [Cr(CO)₆]^[29]. The second pink band was found to consist of [(CO)₄Cr(bipy)] or [(CO)₄Cr(phen)], respectively, by comparison of IR^[30], ¹H-, and ¹³C-NMR spectra. The compounds **3a** and **3b** were eluted with THF as the third red-brown band. Evaporation of the solvent left the compounds as red microcrystalline powders. Yields:

Table 12. Crystal-structure data for **2a–2c**

compound	2a · 12-Crown-4	2b	2c
formula	C ₅₈ H ₆₈ Cr ₄ N ₄ Na ₂ O ₃₆ Sn ₂	C ₁₈ H ₆ Cr ₂ N ₄ O ₁₀ Sn	C ₁₈ H ₆ N ₄ O ₁₀ SnW ₂
molecular mass [g]	188.520	660.960	924.660
crystal dimensions [mm]	0.30 × 0.20 × 0.10	0.30 × 0.20 × 0.20	0.30 × 0.30 × 0.20
crystal system	triclinic	monoclinic	monoclinic
space group (No.)	P $\bar{1}$ (2)	C2/c (15)	C2/c (15)
a [pm]	996.1 (2)	2977 (4)	3358.5 (6)
b [pm]	1415.2 (5)	950 (1)	1228.9 (2)
c [pm]	1581.7 (7)	1792 (2)	1253.9 (2)
α [°]	114.95 (2)	90.00 (0)	90.00 (0)
β [°]	95.86 (3)	92.22 (2)	93.20 (1)
γ [°]	103.08 (2)	90.00 (0)	90.00 (0)
cell volume [10 ⁶ pm ³]	1919 (1)	5064 (11)	5167 (2)
molecular units / cell	1	8	8
density (calculated) [g cm ⁻³]	1.634	1.734	2.443
absorption coefficient [cm ⁻¹]	12.89	18.77	99.02
temperature [K]	188	295	200
no. rflns. for cell parameter refinement	31	30	34
scan range	2.9° ≤ 2 θ ≤ 52.0°	2.7° ≤ 2 θ ≤ 50.0°	4.8° ≤ 2 θ ≤ 53.0°
scan speed [° min ⁻¹]	$\dot{\omega}$ = 15	$\dot{\omega}$ = 10	$\dot{\omega}$ = 14
no. rflns. measured	7659	4542	5449
no. unique rflns.	7213	4451	5359
no. rflns. observed	4617	2731	3777
observation criterion	2 σ (<i>I</i>)	2 σ (<i>I</i>)	2 σ (<i>I</i>)
no. parameters refined	546	389	337
residual electron density [-10 ⁻⁶ e pm ⁻³]	0.57 / - 0.61	0.66 / - 0.64	1.64 / - 1.36
<i>R</i> _j / <i>R</i> _w [%] (refinement on F ²)	5.6 / 15.0	5.2 / 14.8	5.1 / 13.7

3a: 150 mg (25%); **3b**: 160 mg (25%). Single crystals of **3a** and **3b** suitable for X-ray structural analyses were obtained within 7 d by the method described below.

Bis(pentacarbonylchromium) (2,2'-bipyridine)lead, [$\{(\text{CO})_5\text{Cr}\}_2\text{Pb}(\text{bipy})\}$] (**4**): The disodium salt Na₂[\mathbf{2}(\text{CO})₅Cr]₂Pb(OOCCCH₃)₂] (694 mg; 0.5 mmol) was dissolved in dichloromethane (30 ml) and solid 2,2'-bipyridine (78 mg; 0.5 mmol) was added in one portion. The orange solution turned deep red immediately. After 30 min of stirring, the solution was taken to dryness. The oily red residue was dissolved in THF (3 ml) and chromatographed slowly (max. 50 drops/min) on silica gel (20 cm; Ø = 3 cm) with diethyl ether. The first yellow band was identified by spectroscopic comparison (IR spectra) to be [Cr(CO)₆]^[29]. A second red band consisted of a mixture of **4** and [(CO)₄Cr(bipy)] (identified by comparison of spectroscopic data^[30]). A third red band contained pure **4**. The ethereal solution was taken to dryness leaving **4** as a red microcrystalline powder. Yield: **4**: 170 mg (45%). To grow single crystals of **4** the method described below was applied.

Procedure of Growing Single Crystals of 1–4: A concentrated THF solution (5 ml) of the chelate complex **1–4** was shared out between three test tubes (Ø = 1 cm) which were brought into a Schlenk tube (250 ml). Diethyl ether (30 ml), which was in the tube, was allowed to diffuse through the gas-phase into the THF solutions (3 h). After this period of time, the diethyl ether was replaced by petroleum ether (boiling range 40–60°C; 50 ml). Vapor diffusion of the petroleum ether (boiling range 40–60°C) gave single crystals of **1–4** suitable for X-ray structure analyses.

X-ray Structure Determinations: The measurements for **1–4** were carried out with a Siemens P4 four-circle diffractometer with graphite-monochromated Mo-*K*_α radiation. The intensities of three check reflections (measured every 100 reflections) remained con-

stant throughout the data collection, thus indicating crystal and electronic stability. All calculations were performed using the SHELXT PLUS software package. The structures were solved by direct methods with the SHELXS-86 program and refined with the SHELX93 program^[31]. The program XPM^[32] was used for the graphical handling of the data. Absorption corrections (ψ scan, $\Delta\psi = 10^\circ$) were applied to the data. The structures were refined in fully or partially anisotropic models by full-matrix least-squares calculations. Hydrogen atoms were introduced at calculated positions. Tables 10–13 compile the data for the structure determinations. Peculiarities about the structures are as follows: **1c**: In this tungsten-containing compound one carbon atom of an equatorial carbonyl group could only be refined isotropically. **1d**: The crystal analyzed contained one THF per molecule **1d** with one of the THF carbon atoms refined isotropically in a disordered position (occupation: 0.6:0.4). **1e**: The crystal used contained one THF per molecule as well; again one of the THF carbon atoms was found in a split position (occupation: 0.7:0.3; anisotropic refinement). **1f**: All atoms of the solvent molecule THF included in the unit cell of **1f** showed some disorder (occupation: 0.6:0.4) and thus were refined only isotropically. **2a**: One of the crown ether molecules showed disorder. **2b**: The equatorial carbonyl groups at one chromium atom had to be refined in split positions ($\Delta\alpha \approx 25^\circ$, with α defined as shown in Figure 7; occupation: 0.52:0.48). **2c**: The crystal analyzed contained 0.4 THF per unit cell with the oxygen atom showing some disorder (occupation: 0.5:0.5). Further details of the crystal-structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository numbers CSD-408203 (**1a**), -408201 (**1b**), -408206 (**1c**), -408197 (**1d**), -408204 (**1e**), -408196 (**1f**), -408205 (**1g**), -408207 (**1h**), -408198 (**2a**), -408209 (**2b**), -408199 (**2c**), -408231 (**3a**), -408202 (**3b**), -408200 (**4**).

Table 13. Crystal-structure data for **3a–4**

compound	3a	3b · THF	4
formula	C ₄₀ H ₁₆ Cr ₄ Ge ₂ N ₄ O ₂₀	C ₂₂ H ₈ Cr ₂ GeN ₂ O ₁₀	C ₂₀ H ₈ Cr ₂ N ₂ O ₁₀ Pb
molecular mass [g]	1225.750	636.890	747.470
crystal dimensions [mm]	0.30 × 0.30 × 0.20	0.30 × 0.30 × 0.30	0.20 × 0.30 × 0.30
crystal system	monoclinic	orthorhombic	orthorhombic
space group (No.)	P2 ₁ /c (14)	Pnna (52)	Pbca (61)
a [pm]	869.6 (1)	1445.2 (1)	1272.2 (3)
b [pm]	4226.2 (5)	1727.8 (5)	1638.9 (5)
c [pm]	1295.1 (4)	1178.6 (1)	2178.4 (5)
α [°]	90.00 (0)	90.00 (0)	90.00 (0)
β [°]	107.52 (1)	90.00 (0)	90.00 (0)
γ [°]	90.00 (0)	90.00 (0)	90.00 (0)
cell volume [10 ⁶ pm ³]	4539 (2)	2943.0 (9)	4542 (2)
molecular units / cell	4	4	8
density (calculated) [g cm ⁻³]	1.794	1.577	2.186
absorption coefficient [cm ⁻¹]	23.16	17.99	83.94
temperature [K]	293	295	200
no. rflns. for cell parameter refinement	30	45	25
scan range	3.4° ≤ 2θ ≤ 45.0°	4.2° ≤ 2θ ≤ 50.0°	4.5° ≤ 2θ ≤ 50.0°
scan speed [° min ⁻¹]	ω = 10	ω = 13	ω = 10
no. rflns. measured	6390	5057	4455
no. unique rflns.	5937	2600	4455
no. rflns. observed	3198	1471	2692
observation criterion	2 σ (I)	2 σ (I)	2 σ (I)
no. parameters refined	631	201	318
residual electron density [· 10 ⁻⁶ e pm ⁻³]	0.49 / - 0.69	0.52 / - 0.33	2.05 / - 2.13
R _I / R _w [%] (refinement on F ²)	5.8 / 15.6	4.7 / 12.4	6.2 / 17.4

☆ Dedicated to Professor Heinrich Nöth on the occasion of his 70th birthday.

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