Transition Metal Complexes of (Schiff Base)Divalent Group 14 Element Species $[(\text{salen})M]_n{=}M'(CO)_{6-n}$ (n = 1, 2; M = Ge, Sn, Pb; M′ = Cr, W)

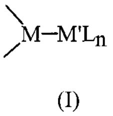
Dominique Agustin,[a] **Ghassoub Rima,**[a] **Heinz Gornitzka,**[a] **and Jacques Barrau***[a]

Keywords: Germylene / Stannylene / Plumbylene / Schiff base / Transition metal complexes of M_{14} divalent species

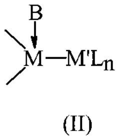
The syntheses, characterization, and reactivities of the new stable mono- and *cis*-disubstituted Group 14 metal(II) chromium and tungsten carbonyl complexes (salen)M=M′$(CO)_5$ [salen = 2,2′-*N,N*′-bis(salicylidene)ethylenediamine; M′ = Cr, M = Ge (**4**), Sn (**5**), Pb (**6**); M′ = W, M = Ge (**7**), Sn (**8**), Pb (**9**)] and $[(\text{salen})M]_2{=}M'(CO)_4$ [M′ = W, M = Ge (**10**), Sn (**11**), Pb (**12**); M′ = Cr, M = Sn (**14**), Ge (**15**)] are described. Complexes **4–9** were obtained in high yields by treatment of the M′$(CO)_5 \cdot$ THF intermediates with the stable divalent species (salen)M^{II} [M = Ge (**1**), Sn (**2**), Pb (**3**)]. Direct irradiation of mixtures of (salen)M^{II} and M′$(CO)_6$ resulted in formation of the monosubstituted compounds **4–9** together with the disubstituted species **10–12**, **14**, and **15** in ratios depending on the nature of both M and M′. Pure complexes **10–12** were obtained by two different synthetic approaches starting from the (salen)M^{II} species or the (salen)M=M′$(CO)_5$ complexes. Each of the new complexes has been characterized by ^1H- and ^{13}C-NMR, and by ^{119}Sn-NMR in the case of **5**, **8**, **11**, and **14**, as well as by IR spectroscopy in all cases. The molecular structures of **5**, **8**, **11**, and **14**, determined by X-ray structure analyses, reveal a pentacoordinated tin atom. The tin–chromium distances are among the shortest (in particular that in **5**, 2.557 Å) observed for transition metal divalent tin complexes and the tin lies about 0.99 Å above the plane defined by the O_2N_2 atoms of the salen ligand. All these complexes have been found to be unreactive towards water and organic acids. Simple phosphane monosubstitution of carbonyl in **8** using Ph_3P led to the new complex **13**. Reactions with 1,2-bis(diphenylphosphanyl)ethane and 3,5-di-*tert*-butyl-1,2-benzoquinone resulted in displacement of the divalent species from the carbonyl complexes **5** and **8**.

Introduction

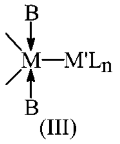
Heavier analogs of carbenes can be used as ligands in transition metal chemistry. They can play an important role in the synthesis of precursors of new materials, and various metallic analogs of carbenic complexes of transition metals have been used or postulated as catalysts in reactions involving the formation or cleavage of M–M bonds. The majority of characterized complexes involve four-coordinate M atoms with type II structures; with bulky or donor substituents, a few structures with a three-coordinate M atom (structure I) have been isolated. Only a few examples of complexes with structures of type III having a five-coordinate M atom have been observed.



(I)



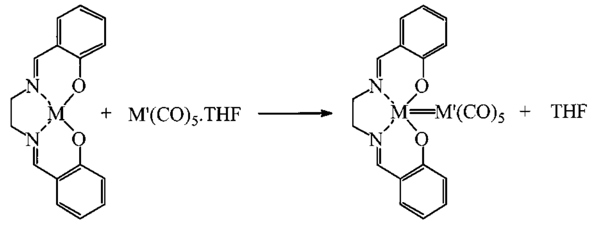
(II)



(III)

The earlier chemistry of these transition metal complexes with divalent species of Group 14 elements has been summarized in various review articles;[1–5] recent investigations concern mainly tin–Group 6 transition metal complexes.[6–14]

Recently, we reported the synthesis and characterization of new stable divalent germanium, tin, and lead homoleptic species L^2M [L^2 = 2,2′-*N,N*′-bis(salicylidene)ethylenediamine (salen), (*R,R*)-(–)-*N,N*′-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediamine, and *N*-methyl-2,2′-iminobis(8-hydroxyquinoline); M = Ge, Sn, Pb].[15] These compounds are monomeric and feature twofold N···M intramolecular coordination, which lowers the Lewis acidity of the metal atom (characteristic of the free divalent species). Nevertheless, they are efficient σ donors and can be used as monodentate ligands in transition metal chemistry. In this work, we consider the salen compounds (salen)M (M = Ge, Sn, Pb) as precursors of new $L^2M{=}M'(CO)_5$ and $(L^2M)_2{=}M'(CO)_4$ complexes (M = Ge, Sn, Pb; M′ = Cr, W). The syntheses, crystal structures, and some chemical properties of these bimetallic compounds are presented herein.



M = Ge (**1**)
Sn (**2**)
Pb (**3**)

M = Ge ; M′= Cr (**4**), W (**7**)
Sn (**5**) (**8**)
Pb (**6**) (**9**)

Scheme 1

---

[a] Hétérochimie Fondamentale et Appliquée, UPRES-A 5069 du CNRS, Université Paul-Sabatier,
118 route de Narbonne, F-31062 Toulouse Cedex, France
Fax: (internat.) + 33-5/61 55 82 04
E-mail: barrau@ramses.ups-tlse.fr

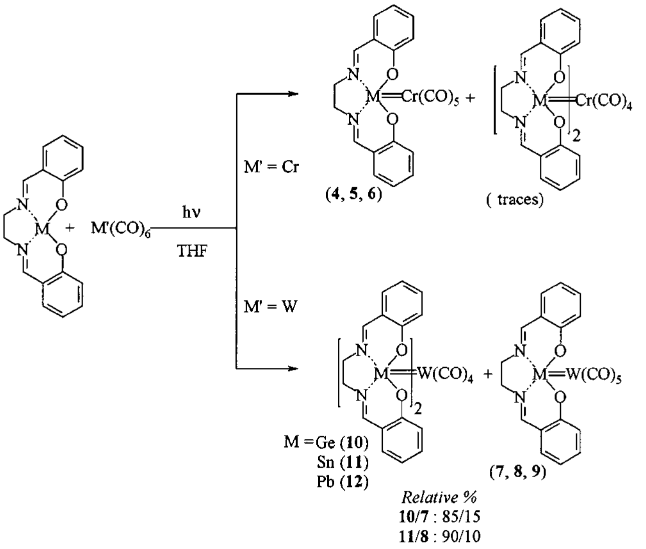
1434–1948/00/0404–0693 $ 17.50+.50/0

Results and Discussion

Synthesis of Complexes of Divalent Species (salen)M=M′(CO)$_5$ and [(salen)M]$_2$=M′(CO)$_4$ (M = Ge, Sn, Pb; M′ = Cr, W)

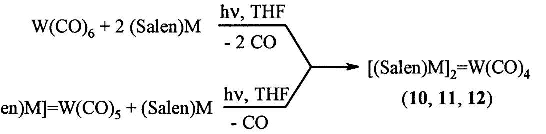
Treatment of the photochemically produced M′(CO)$_5$ · THF intermediates with the (salen)M compounds in THF led to the expected monosubstituted complexes **4–9** in high yields (Scheme 1).

These complexes were obtained as yellow-orange crystalline solids in yields in excess of 80% by recrystallization from CHCl$_3$. They were found to be soluble only in polar and protic solvents (THF, CHCl$_3$, CH$_2$Cl$_2$, DMSO, DMF, MeOH). Direct irradiation at room temperature of mixtures of the divalent compounds (salen)M and the hexacarbonyl complexes M′(CO)$_6$ (M′ = Cr, W) also resulted in the formation of the expected monometal(II) complexes in yields depending on the nature of both the Group 14 atom M and the transition metal M′ (Scheme 2). With (salen)germylene and -stannylene, the mono compounds **4** and **5** were produced in high yields when the reactions were carried out using Cr(CO)$_6$. Using W(CO)$_6$ under similar reaction conditions, substitution of more than one carbonyl was observed and the disubstituted compounds **10–12** with the ligands in a *cis* arrangement were formed alongside the monosubstituted species **7–9** (Scheme 2). Extension of this procedure to the reactions of (salen)plumbylene with Cr(CO)$_6$ and W(CO)$_6$ led to complexes **6** in 70% yield and to a mixture of **9** and **12** (30:70, as determined by ^{1}H-NMR), respectively. In contrast, attempts to prepare the (salen)M=M′(CO)$_5$ (M′ = Cr, W) complexes simply by heating mixtures of the starting materials at 80 °C for 24 h proved unsuccessful.



Scheme 2

In view of the particular sensitivity of the tungsten system and the difficulties encountered in separating the mono- and disubstituted tungsten products, we investigated alternative synthetic methods to confirm the structures of **10–12**. Thus, syntheses of pure **10** and **11** were achieved in up to 70% yield by irradiation of a mixture of (salen)M and (salen)M=W(CO)$_5$ or by irradiation of a mixture of two equivalents of (salen)M and one of W(CO)$_6$ (Scheme 3).



Scheme 3

It is interesting to note that under UV irradiation, the *cis*-[(salen)M]$_2$=M′(CO)$_4$ complexes were converted into the *trans* isomers. Such conversions have been particularly well-studied in the case of **11**; irradiation of a solution of *cis*-[(salen)Sn]$_2$=W(CO)$_4$ (**11**) for 6 h resulted in 50% conversion to *trans*-[(salen)Sn]$_2$=W(CO)$_4$ (**11′**). Crystals of **11′** suitable for X-ray structural analysis could not be obtained but its ^{1}H- and ^{13}C-NMR data, a ^{119}Sn-NMR resonance at $\delta = -374$, an IR band at $\nu_{CO} = 1999$ cm^{-1}, and mass spectroscopic data were consistent with the *trans* structure.

Such *cis*/*trans* photochemical isomerizations, as well as thermal reverse conversions, have previously been reported in the case of (carbene)$_2$=W(CO)$_4$.[16] In our case, it has not been possible to unambiguously observe reversion to the thermodynamically favoured *cis* isomer by heating a mixture of **11** and **11′** in the solid state or in solution. When a solid-state 50:50 *cis*/*trans* mixture was maintained at 180 °C for 12 h, the subsequently recorded ^{119}Sn-NMR spectrum featured only resonances due to the *cis* isomer ($\delta = -348$) and due to an unidentified product ($\delta = -410$).

Compounds **4–12** were found to be soluble in polar and protic solvents and insoluble in pentane. All these compounds proved to be stable to moisture.

Physicochemical and Structural Studies of the (salen)M=M′(CO)$_5$ and [(salen)M]$_2$=M′(CO)$_4$ Complexes (M = Ge, Sn, Pb; M′ = Cr, W)

Molecular weight determinations (cryoscopy in benzene) showed **4**, **5**, **7**, and **8** to be monomeric in solution. Compounds **4–12** have been characterized by ^{1}H-, ^{13}C-, and ^{119}Sn-NMR (for the complexes **5**, **8**, and **11**), as well as by IR spectroscopy. ^{1}H- and ^{119}Sn-NMR and IR spectroscopic data are collected in Table 1. The thermal stabilities of these complexes were found to be high; they decompose only on melting, but the germanium and tin complexes proved sufficiently volatile to allow recording of their mass spectra.

The ^{1}H-NMR spectra of complexes **4–12** show different shifts for the signals of the salen ligand relative to those seen for the divalent compounds **1–3**. The most noticeable shifts are seen in the methine proton resonances, which appear at lower field strengths as compared to those of the parent divalent species. For compounds **10–12**, NMR cannot distinguish between the two tin species complexed on the tungsten since the NMR signals of the various protons are similar and therefore non-resolvable. In all cases, as in **1–3**, the chemical shifts and splitting patterns of the CH$_2$N protons are consistent with the presence of N→M intramolecular coordination in these molecules.

Table 1. Spectroscopic data for compounds **4–12**

		4	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**
^{1}H (δ, ppm)	CH_2	3.90	4.01	3.80	3.93	3.99	3.87	3.93	3.81	4.07
	CH=N	8.32	8.42	8.24	8.25	8.73	8.27	8.17	8.43	8.03
^{119}Sn (δ, ppm) ([D$_6$]DMSO)			–137			–328			–348	
IR (Nujol, KBr, cm^{-1})	$\nu_{C=N}$	1630	1638	1620	1620	1641	1630	1620	1638	1625
	$\nu_{C=O}$	1910	1917	1915	1916	1913	1914	1892	1902	1906
		1970	1978	1976	1972	1977	1970	1980	1929	1930
		2047	2047	2048	2067	2063	2060	2009	1954	2015
								2060	2062	2060

The ^{13}C-NMR spectra of **4–12** feature signals with the characteristic chemical shifts of the carbon atoms of the salen ligand, shifted slightly downfield from those in the (salen)M compounds,[15] along with two carbonyl resonances for the monosubstituted complexes **4–9** (relative intensity 1:4) and for the disubstituted complexes **10–12** (relative intensity 1:1).

The ^{119}Sn-NMR spectra of **5**, **8**, and **11** feature singlets at δ = –137, –328, and –348, respectively, which fall within the range of shift values appropriate for pentacoordinate tin compounds; the shift variations between the signal of (salen)Sn and those of the corresponding (salen)Sn=M′(CO)$_5$ complexes reflect the electron-withdrawing effect of the M′(CO)$_5$ groups. The $^1J(^{119}\text{Sn-}^{183}\text{W})$ coupling constants are very similar to those observed in four-coordinate tin(II)–tungsten compounds.[16]

The IR spectra of compounds **4–9** show strong absorptions in the range 1620–1640 cm^{-1} attributable to the $\nu_{C=N}$ stretching frequency under the influence of the N→M intramolecular coordination; these bands are shifted toward higher frequencies by 5–20 cm^{-1} in comparison with the spectra of the free ligands but are not affected to any appreciable extent compared to those observed for the (salen)M compounds. In the metal carbonyl region, three carbonyl bands ($A''_1 + A'_1 + E$) are seen, with an intensity pattern characteristic of C_{4v} local symmetry at chromium or tungsten. Since the unique CO *trans* to the metal M is involved in the A'_1 mode, the position of this band [1970 (**4**), 1978 (**5**), 1976 cm^{-1} (**6**)] is indicative[18] of the π-acceptor ability of the (salen)M groups *trans* to the axial carbonyl. IR and ^{13}C-NMR data show that the (salen)M ligands are stronger donors of electron density, but are also π-acceptors. For complexes **10–12**, the appearance of four bands due to the CO groups is compatible with C_{2v} symmetry (*cis* geometry).

The five-coordinate environment about the M atom was confirmed structurally for **5**, **8**, and **11**. Compound **11** represents the first distannylene–tungsten complex $[L^2Sn]_2=W(CO)_4$ to be structurally characterized. Figure 1, Figure 2, and Figure 3 show solid-state structures of **5**, **8**, and **11**, respectively, together with the numbering scheme adopted. In the case of **11**, the three $CHCl_3$ solvating molecules are omitted for the sake of clarity. Crystal data of **5**, **8**, and **11** are presented in Table 6. Relevant bond lengths and angles in **5**, **8**, and **11** are given in Table 2, Table 3, and Table 4, respectively. In all three compounds, the tin resides in a distorted square-pyramidal geometry with the salen ligand occupying the base plane at Sn–N_2O_2 plane distances of 0.948 Å in **5**, 0.996 Å in **8**, and 1.005 Å and 1.024 Å in **11**. The observed σ Sn–O distances [2.039(3)–2.074(3) Å] are a little longer than classical σ Sn–O bonds (1.94–2.03 Å).[19] The lengths of the Sn←N bonds [2.230(5)–2.288(4) Å] appear to be normal. On going from **5** to **8** and **11**, these Sn–N and Sn–O distances increase as a result of the decreased inductive effect of the transition metal fragment. The tin–chromium or tin–tungsten bonds, which are shorter than typical Sn–M′ (M′ = Cr, W) single bonds,[20] are among the shortest ever observed in transition metal–divalent tin

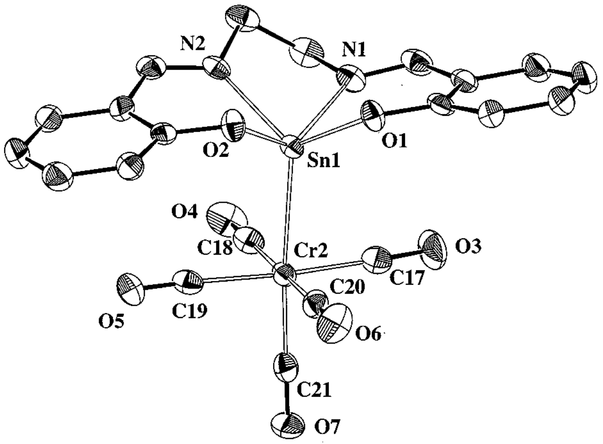


Figure 1. Solid-state structure and atom numbering scheme of (salen)Sn=Cr(CO)$_5$ (**5**)

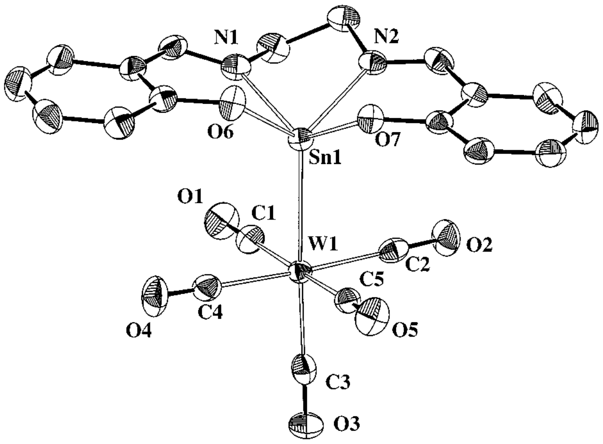


Figure 2. Solid-state structure and atom numbering scheme of (salen)Sn=W(CO)$_5$ (**8**)

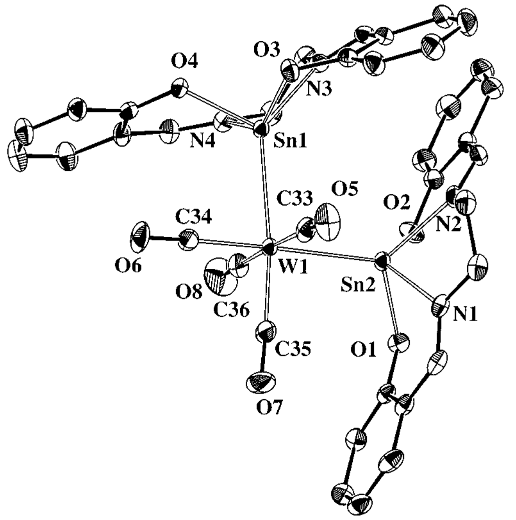


Figure 3. Solid-state structure and atom numbering scheme of $\{[(salen)Sn]_2{=}W(CO)_4\} \cdot 3\,(CHCl_3)$ (**11**); solvent molecules have been omitted for the sake of clarity

Table 4. Selected bond lengths [Å] and angles [deg] in **11**

Distances		Angles	
Sn(1)–W(1)	2.711(1)	O(4)–Sn(1)–O(3)	82.57(14)
Sn(1)–O(4)	2.062(3)	O(4)–Sn(1)–N(4)	79.43(14)
Sn(1)–O(3)	2.086(4)	O(3)–Sn(1)–N(4)	137.91(15)
Sn(1)–N(4)	2.265(4)	O(4)–Sn(1)–N(3)	108.90(14)
Sn(1)–N(3)	2.282(4)	O(3)–Sn(1)–N(3)	79.91(14)
Sn(2)–W(1)	2.703(1)	N(4)–Sn(1)–N(3)	70.65(16)
Sn(2)–O(2)	2.066(3)	O(4)–Sn(1)–W(1)	116.76(9)
Sn(2)–O(1)	2.074(3)	O(3)–Sn(1)–W(1)	115.26(11)
Sn(2)–N(2)	2.261(4)	N(4)–Sn(1)–W(1)	106.82(11)
Sn(2)–N(1)	2.288(4)	N(3)–Sn(1)–W(1)	133.06(10)
W(1)–C(35)	1.953(6)	O(2)–Sn(2)–O(1)	79.67(14)
W(1)–C(34)	1.964(6)	O(2)–Sn(2)–N(2)	81.40(16)
W(1)–C(33)	2.013(7)	O(1)–Sn(2)–N(2)	124.75(15)
W(1)–C(36)	2.028(7)	O(2)–Sn(2)–N(1)	125.58(15)
		O(1)–Sn(2)–N(1)	80.00(15)
		N(2)–Sn(2)–N(1)	70.29(17)
		O(2)–Sn(2)–W(1)	125.30(12)
		O(1)–Sn(2)–W(1)	115.03(10)
		N(2)–Sn(2)–W(1)	118.30(11)
		N(1)–Sn(2)–W(1)	109.07(10)
		Sn(2)–W(1)–Sn(1)	96.161(15)

Table 2. Selected bond lengths [Å] and angles [deg] in **5**

Distances		Angles	
Sn(1)–Cr(2)	2.578(1)	O(1)–Sn(1)–O(2)	82.27(16)
Sn(1)–O(1)	2.041(4)	O(1)–Sn(1)–N(2)	121.22(16)
Sn(1)–O(2)	2.058(4)	O(2)–Sn(1)–N(2)	80.95(16)
Sn(1)–N(2)	2.230(5)	O(1)–Sn(1)–N(1)	81.41(17)
Sn(1)–N(1)	2.260(5)	O(2)–Sn(1)–N(1)	134.07(18)
Cr(2)–C(21)	1.861(6)	N(2)–Sn(1)–N(1)	71.72(17)
Cr(2)–C(18)	1.873(7)	O(1)–Sn(1)–Cr(2)	120.85(12)
Cr(2)–C(20)	1.886(6)	O(2)–Sn(1)–Cr(2)	115.05(12)
Cr(2)–C(17)	1.894(7)	N(2)–Sn(1)–Cr(2)	117.33(11)
Cr(2)–C(19)	1.915(7)	N(1)–Sn(1)–Cr(2)	110.20(13)

Table 3. Selected bond lengths [Å] and angles [deg] in **8**

Distances		Angles	
W(1)–Sn(1)	2.712(1)	O(6)–Sn(1)–O(7)	81.02(11)
Sn(1)–O(6)	2.039(3)	O(6)–Sn(1)–N(2)	118.87(12)
Sn(1)–O(7)	2.074(3)	O(7)–Sn(1)–N(2)	79.77(11)
Sn(1)–N(2)	2.260(3)	O(6)–Sn(1)–N(1)	80.05(11)
Sn(1)–N(1)	2.261(3)	O(7)–Sn(1)–N(1)	131.39(11)
W(1)–C(3)	1.994(4)	N(2)–Sn(1)–N(1)	71.27(12)
W(1)–C(1)	2.032(4)	O(6)–Sn(1)–W(1)	123.81(9)
W(1)–C(2)	2.039(5)	O(7)–Sn(1)–W(1)	115.95(8)
W(1)–C(4)	2.040(5)	N(2)–Sn(1)–W(1)	116.83(8)
W(1)–C(5)	2.057(4)	N(1)–Sn(1)–W(1)	111.83(9)

complexes, the Sn–Cr distance [2.558(1) Å] in complex **5** being particularly short. These distances reflect a lower electron density at the tin atom in these complexes and may be indicative of double-bond character in the Sn–M′ unit (typical Sn=Cr: 2.60 Å,[7,21,22] Sn=W: 2.74 Å[10,17,23,24]). Thus, it seems that despite its tetradentate capacity the salen ligand does not cancel out the electronic deficiency at the tin atom through N···Sn intramolecular coordination thereby reducing the back-donation by the transition metal. Conversely the solid-state structures suggest that the peculiar arrangement resulting from the structure of the salen ligand maximizes the possibility of [d(M′)-d(p)(Sn)] π overlap.

The Sn–W distances in **8** [2.712(1) Å] and **11** [2.711(1) Å and 2.703(1) Å] are very similar, which shows that the strength of the π interaction between the transition metal and the tin atom is not influenced by the number of divalent species on the transition metal. In **5**, **8**, and **11**, the coordination about the Cr or W atom is almost perfectly octahedral. In each compound, the M′–C distances are very similar; the M′–C bonds *trans* to Sn are the shortest, but do not differ significantly from the M′–C equatorial bonds. This suggests that the (salen)Sn ligand is comparable to or slightly poorer than CO as a π acceptor.

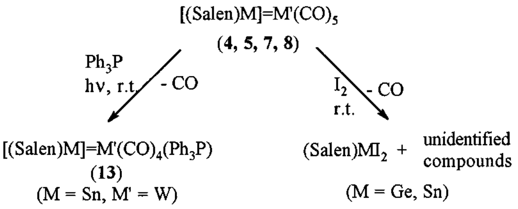
The mass spectra of complexes **4**, **5**, **7**, and **8** exhibit peaks corresponding to molecular ions M^+ [weak (**4** and **7**) or very weak (**5** and **8**) intensity] and to the characteristic fragmentations of such structures (particularly loss of carbonyl groups and of substituents on the Ge and Sn atoms).

Chemical Reactivity of the (salen)M=M′(CO)$_5$ Complexes

Due to their "transition metal–carbene-like" character, the (salen)M=M′(CO)$_5$ complexes would appear to have interesting potential in organometallic chemistry. However, as observed previously, the chemistry of the complexes $L^2M{=}M'(CO)_5$ differs markedly from that of their carbene counterparts despite the many structural similarities.

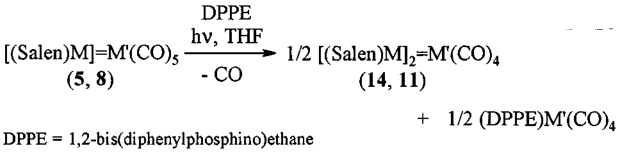
In contrast to their parent compounds (**1–3**) and various $L^2M{=}M'(CO)_5$ complexes, the (salen)M=M′(CO)$_5$ and $[(salen)M]_2{=}M'(CO)_4$ complexes **4–12** were found to be totally unreactive towards water and organic acids (Scheme 3). This lack of reactivity may be attributed to electronic and particularly steric factors, most notably about the tin atom.

With iodine, we observed the expected reactions for compounds with Group 14 metal–transition metal bonds (Scheme 4).



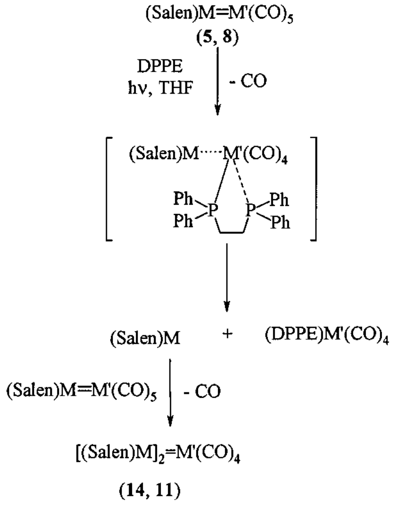
Scheme 4

Since ligands having a lone pair, such as Ph$_3$P, are able to substitute one or more of the CO groups of metal carbonyls, the monotriphenylphosphane complex of **8** (or **13**, respectively) could easily be prepared by UV irradiation (λ = 254 nm) or by heating (Scheme 4). In contrast, attempted substitution of two CO groups by the chelating ligand 1,2-bis(diphenylphosphanyl)ethane (diphos) were unsuccessful; reactions of this doubly chelating phosphane with **5** and **8** surprisingly led to the distannylene–metal carbonyl complexes **14** and **11**, respectively (Scheme 5).



Scheme 5

Since compounds **5** and **8** are stable towards UV irradiation, it seems that in these cases entry of a second phosphane group into the coordination sphere about M′ causes displacement of the (salen)Sn ligand, which reacts in situ with remaining **5** or **8** to give **14** or **11**, respectively (Scheme 6).



Scheme 6

Complex **14** could be separated from the reaction mixture in the form of orange crystals, by virtue of its low solubility in pentane. The ^{13}C-NMR spectrum and IR data relating to the ν_{CO} region were in agreement with an octahedral coordination sphere about the chromium center and a *cis* geometry. This conclusion was confirmed by an X-ray crystal structure determination (Figure 4, Table 5). The struc-

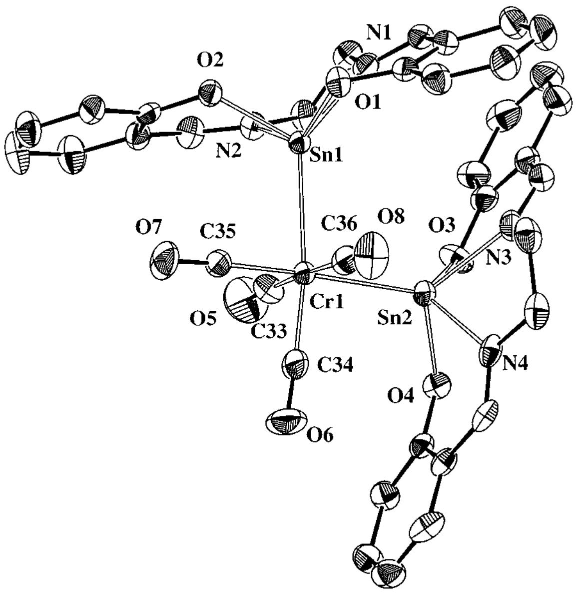
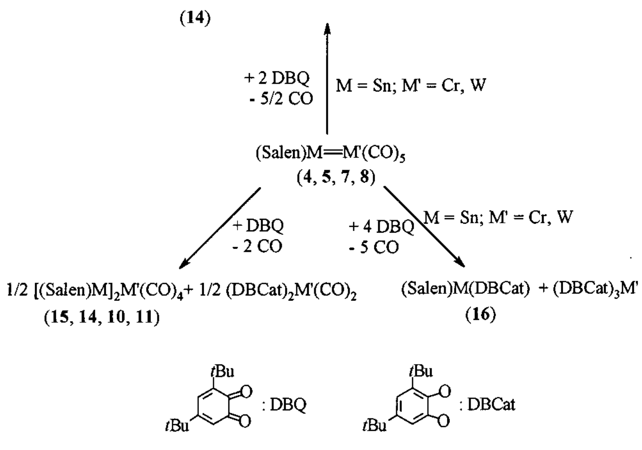


Figure 4. Solid-state structure and atom numbering scheme of {[(salen)Sn]$_2$=Cr(CO)$_4$} · 3 (CHCl$_3$) (**14**); solvent molecules have been omitted for the sake of clarity

Table 5. Selected bond lengths [Å] and angles [deg] in **14**

Distances		Angles	
Sn(1)–Cr(1)	2.568(1)	O(1)–Sn(1)–O(2)	82.08(11)
Sn(1)–O(1)	2.085(3)	O(1)–Sn(1)–N(1)	97.34(11)
Sn(1)–O(2)	2.057(3)	O(1)–Sn(1)–N(2)	137.73(13)
Sn(1)–N(2)	2.262(3)	O(2)–Sn(1)–N(1)	107.84(12)
Sn(1)–N(1)	2.288(4)	O(2)–Sn(1)–N(2)	79.49(12)
Sn(2)–Cr(1)	2.555(1)	N(1)–Sn(1)–N(2)	70.68(13)
Sn(2)–O(3)	2.071(3)	O(3)–Sn(2)–O(4)	79.48(12)
Sn(2)–O(4)	2.071(3)	O(3)–Sn(2)–N(3)	81.32(14)
Sn(2)–N(3)	2.255(4)	O(3)–Sn(2)–N(4)	125.70(13)
Sn(2)–N(4)	2.293(4)	O(4)–Sn(2)–N(3)	124.12(13)
Cr(1)–C(33)	1.875(5)	O(4)–Sn(2)–N(4)	79.80(12)
Cr(1)–C(34)	1.833(5)	N(3)–Sn(2)–N(4)	70.34(15)
Cr(1)–C(35)	1.831(5)	Sn(1)–Cr(1)–Sn(2)	96.97(3)
Cr(1)–C(36)	1.875(5)		

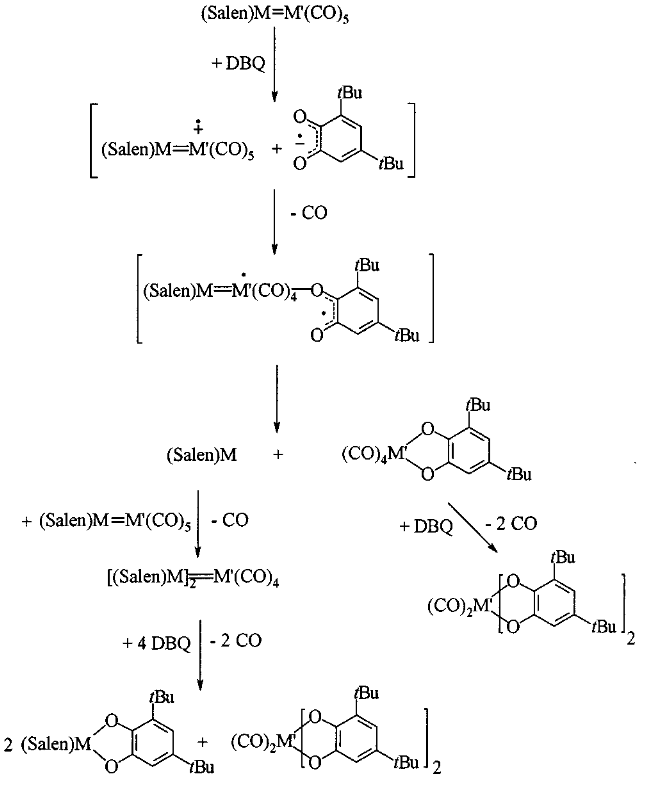


Scheme 7

ture shows similarities to that of **11**; the two *cis*-stannanediyl fragments (salen)Sn, in which the tin atoms show distorted square-pyramidal geometries, are bonded to a $Cr(CO)_4$ fragment with an octahedral environment about the chromium atom. The Cr–Sn distances [2.555(1) and 2.568(1) Å] are indicative of double-bond character in the Cr–Sn unit.

Complexes **4**, **5**, **7**, and **8** were found to react similarly with equimolar amounts of 3,5-di-*tert*-butyl-1,2-benzoquinone (DBQ), leading to **15**, **14**, **10**, and **11**, respectively, along with the $M'(CO)_2(DBCat)_2$ complexes (Scheme 7).

This reaction is consistent with a mechanism involving initial interaction of the quinone with the transition metal atom causing labilization of the M–M′ bond as a result of decreased π-back-bonding (this effect is amplified by chelate ring formation as in the case of the reaction of diphos). The resulting (salen)M ligand then primarily reacts with (salen)M=M′(CO)$_5$, leading to the bis-(divalent species)–transition metal complexes [(salen)M]$_2$=M′(CO)$_4$ rather than with the quinone to give the corresponding catecholate **16** (Scheme 8). Supporting evidence for this explanation was obtained by studying the relative reactivities of (salen)Sn towards coordination to the transition metal in (salen)Sn=Cr(CO)$_5$ and towards addition to the quinone. Starting with a 1:1:1 mixture of (salen)Sn/DBQ/(salen)Sn=Cr(CO)$_5$, the distannylene–chromium complex [(salen)Sn]$_2$=Cr(CO)$_4$ was by far the favored product (ratio 97:3). No evidence of a stable semiquinone intermediate was observed in this reaction. Using two equivalents of 3,5-di-*tert*-butyl-1,2-benzoquinone in addition to the disubstituted complexes, we observed substantial formation of the previously characterized (salen)Sn^{II}-3,5-di-*tert*-butyl-1,2-benzoquinone adduct **16**.[15]



Scheme 8

Conclusion

Several new stable mono- and *cis*-disubstituted Group 14 metal(II)–chromium and tungsten carbonyl complexes have been prepared and their reactivities towards phosphane and 3,5-di-*tert*-butyl-1,2-benzoquinone have been studied. Physicochemical and structural studies have shown that the Group 14 metal resides in a five-coordinate environment.

The Sn–M′ bond lengths observed in the tin complexes are shorter than the typical single-bond lengths and are among the shortest ever observed (in particular the Sn–Cr bond). This indicates that in these complexes, in spite of N→M intramolecular coordination, the divalent species (salen)M behave as σ-donors with π-acceptor properties. These results underline the influence of the stabilizing ligand (bound to the Group 14 element) on the magnitude of the M=M bonding interaction. In short, the (salen)Sn group, with its square-pyramidal geometry, seems to favor the π interaction between the Group 14 element and the chromium or tungsten atom.

Substitution of one CO group has been observed upon reaction with PPh_3. Interestingly, reactions with diphos and 3,5-di-*tert*-butyl-1,2-benzoquinone have been found to lead to the corresponding distannylene metal carbonyl complexes; displacement of the (salen)Sn ligand seems to be the key step in such reactions.

Experimental Section

General: All manipulations were performed under inert atmospheres of nitrogen or argon using standard Schlenk and high-vacuum-line techniques. Dry, oxygen-free solvents were employed throughout. All solvents were distilled from sodium benzophenone or P_2O_5 prior to use. ^{1}H-NMR spectra were recorded on a Bruker AC 80 spectrometer operating at 80 MHz (chemical shifts are reported in ppm relative to internal Me_4Si); ^{13}C-NMR spectra were recorded on an AC 200 spectrometer; the multiplicities of the ^{13}C-NMR signals were determined by the APT technique. ^{1}H-decoupled ^{119}Sn-NMR spectra were recorded on Bruker AC 200 or 400 instruments (chemical shifts are reported in ppm relative to external Me_4Sn). Mass spectra were obtained under electron impact (EI) or chemical ionization (CH_4) conditions at 70 eV and 30 eV, respectively using Hewlett Packard 5989 and Nermag R10-10H spectrometers. IR spectra were recorded on a Perkin–Elmer 1600 FT-IR spectrophotometer. Irradiations were carried out at room temperature using a low-pressure immersion lamp in a quartz glass immersion tube. Molecular weight determinations were carried out with a custom-built apparatus. Melting points (uncorrected) were obtained on a Leitz Biomed hot-plate microscope apparatus. Elemental analyses (C, H, N) were performed at the Microanalysis Laboratory of the Ecole Nationale Supérieure de Chimie de Toulouse.

X-ray Measurements of 5, 8, 11, and 14: Crystal data for all the structures are presented in Table 6. All data were collected at T = 173 K using an oil-coated shock-cooled crystal[25] in each case on

Table 6. Crystallographic data for compounds (salen)Sn=Cr(CO)$_5$ (**5**), (salen)Sn=W(CO)$_5$ (**8**), {[(salen)Sn]$_2$=W(CO)$_4$} · 3 (CHCl$_3$) (**11**), and {[(salen)Sn]$_2$=Cr(CO)$_4$} · 3 (CHCl$_3$) (**14**)

	5	**8**	**11**	**14**
formula	$C_{21}H_{14}CrN_2O_7Sn$	$C_{21}H_{14}N_2O_7SnW$	$C_{39}H_{31}Cl_9N_4O_8Sn_2W$	$C_{39}H_{31}Cl_9N_4O_8Sn_2Cr$
M_T	577.03	708.88	1423.96	1292.11
T [K]	173(2)	173(2)	173(2)	173(2)
crystal system	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/n$	$C2/c$	$C2/c$
a [Å]	12.213(2)	7.018(1)	22.456(4)	22.437(2)
b [Å]	16.257(3)	14.692(2)	23.240(3)	23.048(3)
c [Å]	11.691(2)	20.821(3)	18.636(3)	18.335(2)
α [°]	90	90	90	90
β [°]	115.24(2)	91.44(2)	96.38(2)	96.08(1)
γ [°]	90	90	90	90
V (Å^3)	2099.6(6)	2146.1(5)	9665(3)	9428.2(18)
Z	4	4	8	8
ρ_{calcd} [Mg/m^3]	1.825	2.194	1.957	1.821
cryst. size [mm]	0.4 × 0.4 × 0.1	0.5 × 0.3 × 0.2	0.6 × 0.5 × 0.5	0.5 × 0.3 × 0.1
μ [mm^{-1}]	1.754	6.566	3.950	1.842
F(000)	1136	1336	5472	5072
$2\varphi_{max}$ [°]	46	48	46	48
refl. collected	15265	16882	38119	38584
indep. refl.	2962	3409	6889	7500
R_{int}	0.0687	0.0426	0.0514	0.0679
absorption correct.	numerical	numerical	numerical	numerical
T_{min}, T_{max}	0.678/0.830	0.219/0.491	0.307/0.603	0.607/0.798
parameters	289	289	640	676
R [$I > 2\sigma(I)$]	0.0468	0.0220	0.0273	0.0294
$wR2$[a] (all data)	0.1086	0.0561	0.0691	0.0618
$(\Delta/\rho)_{min}$ [e.Å^{-3}]	–0.820	–0.702	–0.718	–0.596
$(\Delta/\rho)_{max}$ [e.Å^{-3}]	1.645	0.720	1.238	0.737

[a] $wR2 = \{[\Sigma w(F_c^2 - F_o^2)^2]/[\Sigma w(F_o^2)^2\}^{1/2}$.

a Stoe-IPDS diffractometer employing Mo-K_α (λ = 0.71073 Å) radiation. The structures were solved by direct methods by means of SHELXS-97[26] and refined with all data on F^2 using SHELXL-97.[27] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in geometrically ideal positions and refined using a riding model. Selected bond lengths and angles in **5**, **8**, **11**, and **14** are presented in tables 2, 3, 4, and 5, respectively. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-136101 (**5**), 136102 (**8**), 136103 (**11**), and 136104 (**14**). Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [Fax: (internat.) +44 (0)1223/336033; E-mail: deposit@ccdc.cam.ac.uk].

Synthesis of (salen)Ge=Cr(CO)$_5$ (4). – Procedure 1: A mixture of (salen)Ge[15b] (0.51 g, 1.50 mmol) and Cr(CO)$_6$ (0.33 g, 1.50 mmol) in THF (50 mL) was irradiated for 2 h, during which a red color developed. The solvent was then removed under reduced pressure and the residual solid was treated with pentane. The resulting suspension was filtered and the collected solid was dried in vacuo to afford **4** (0.64 g, 80%) as an orange powder.

Procedure 2: A solution of Cr(CO)$_6$ (0.33 g, 1.50 mmol) in THF (30 mL) was irradiated for 1.5 h. The solution was then purged of CO by passing a stream of nitrogen through it for 15 min., and then a suspension of (salen)Ge (0.51 g, 1.50 mmol) in THF (20 mL) was added. Complex **4** (0.65 g, 83%) was obtained following the same work-up procedure as outlined above; m.p. 280–285 °C (dec.). – ^{1}H NMR (CDCl$_3$): δ = 3.90 (m, 4 H, CH$_2$), 6.50–7.80 (m, 8 H, Ar), 8.32 (s, 2 H, CH=N). – ^{13}C NMR (CDCl$_3$): δ = 59.83 (CH$_2$), 117.03 (CH$_{Ar}$), 118.60 (C$_q$), 118.78 (CH$_{Ar}$), 131.60 (CH$_{Ar}$), 132.49 (CH$_{Ar}$), 161.08 (C$_q$–O), 167.88 (CH=N), 217.08 (C=O *trans*), 218.41 (C=O), 222.47 (C=O), 224.62 (C=O). – IR (Nujol, KBr): $\nu_{C=N}$ 1630; ν_{CO} 1910, 1970, 2047 cm^{-1}. – MS (EI, 70 eV): m/z = 532 [M$^{+\cdot}$], 504 [M – CO]$^+$, 476 [M – 2 CO]$^+$, 448 [M – 3 CO]$^+$, 420 [M – 4 CO]$^+$, 392 [M – 5 CO]$^+$. – $C_{21}H_{14}CrGeN_2O_7$ (531.94): calcd. C 47.37, H 2.65, N 5.26; found C 47.58, H 2.70, N 5.10.

Synthesis of (salen)Sn=Cr(CO)$_5$ (5). – Procedure 1: A mixture of (salen)Sn[15b] (0.26 g, 0.67 mmol) and Cr(CO)$_6$ (0.15 g, 0.67 mmol) in THF (50 mL) was irradiated for 2 h, during which a red color developed. After removal of the solvent, the crude product was treated with pentane and the resulting suspension was filtered. Crystallization of the collected solid from chloroform afforded **5** (0.31 g, 80%) as red-orange crystals.

Procedure 2: Following a procedure similar to that described for **4**, compound **5** (0.30 g, 83%) was obtained from (salen)Sn (0.24 g, 0.62 mmol) and Cr(CO)$_5$THF (0.17 g, 0.62 mmol); m.p. 270–280 °C (dec.). – ^{1}H NMR ([D$_6$]DMSO): δ = 4.01 (m, 4 H, CH$_2$), 6.50–7.50 (m, 8 H, Ar), 8.42 (s, 2 H, CH=N). – ^{13}C NMR ([D$_6$]DMSO): δ = 52.86 (CH$_2$), 117.77 (CH$_{Ar}$), 118.97 (C$_q$), 122.32 (CH$_{Ar}$), 134.58 (CH$_{Ar}$), 135.90 (CH$_{Ar}$), 165.65 (C$_q$–O), 169.41 (CH=N), 218.54 (C=O), 230 (C=O). – ^{119}Sn{^{1}H} NMR ([D$_6$]DMSO): δ = –149.5. – IR (Nujol, KBr): $\nu_{C=N}$ 1638; ν_{CO} 1917, 1978, 2047 cm^{-1}. – MS (EI, 70 eV): m/z = 438 [M – 5 CO]$^+$. – $C_{21}H_{14}CrN_2O_7Sn$ (577.92): calcd. C 43.60, H 2.44, N 4.85; found C 43.71, H 2.50, N 4.90.

Synthesis of (salen)Pb=Cr(CO)$_5$ (6): To a suspension of (salen)Pb[15b] (0.15 g, 0.32 mmol) in THF (30 mL) a solution of Cr(CO)$_5$ · THF (0.09 g, 0.32 mmol) in THF (20 mL) was added dropwise. The reaction mixture was stirred at room temperature for 1 h and then the solvent was evaporated under reduced pressure. The residual maroon-orange solid was washed with pentane and dried to afford **6** (0.15 g, 70%); m.p. > 300 °C (dec.). – ^{1}H NMR

([D$_6$]DMSO): δ = 3.80 (m, 4 H, CH$_2$), 6.20–7.40 (m, 8 H, Ar), 8.24 (s, 2 H, CH=N). – IR (Nujol, KBr): $\nu_{C=N}$ 1620; ν_{CO} 1915, 1976, 2048 cm^{-1}. – $C_{21}H_{14}CrN_2O_7Pb$ (665.99): calcd. C 37.84, H 2.12, N 4.21; found C 38.01, H 2.20, N 4.03.

Synthesis of (salen)Ge=W(CO)$_5$ (7): A solution of W(CO)$_5$ · THF (0.15 g, 0.35 mmol) in THF (30 mL) was added dropwise to a suspension of (salen)Ge (0.12 g, 0.35 mmol) in THF (20 mL) and the resulting mixture was stirred at room temperature for 1 h. The solvent was then removed in vacuo and the residual orange solid was washed with pentane. Filtration of the washings and drying of the collected solid gave **7** (0.22 g, 92%) in the form of orange crystals; m.p. 260–270 °C (dec.). – ^{1}H NMR (CDCl$_3$): δ = 3.93 (m, 4 H, CH$_2$), 6.72–7.60 (m, 8 H, Ar), 8.25 (s, 2 H, CH=N). – ^{13}C NMR (CDCl$_3$): δ = 57.25 (CH$_2$), 57.40 (CH$_2$), 118.74 (CH$_{Ar}$), 121.00 (CH$_{Ar}$), 131.87 (CH$_{Ar}$), 133.11 (CH$_{Ar}$), 134.70 (CH$_{Ar}$), 135.22 (CH$_{Ar}$), 138.29 (CH$_{Ar}$), 139.85 (CH$_{Ar}$), 160.92 (C$_q$–O), 167.98 (CH=N), 168.78 (CH=N), 196.37 (C=O), 198.92 (C=O). – IR (Nujol, KBr): $\nu_{C=N}$ 1620; ν_{CO} 1916, 1972, 2067 cm^{-1}. – MS (EI, 70 eV): *m*/*z* = 662 [M$^{+\cdot}$], 634 [M – CO]$^+$, 608 [M – 2 CO]$^+$, 580 [M – 3 CO]$^+$, 522 [M – 5 CO]$^+$. – $C_{21}H_{14}GeN_2O_7W$ (663.95): calcd. C 37.95, H 2.13, N 4.22; found C 38.20, H 2.29, N 4.10.

Synthesis of (salen)Sn=W(CO)$_5$ (8): A suspension of (salen)Sn (0.11 g, 0.28 mmol) in THF (20 mL) was added dropwise to a solution of W(CO)$_5$ · THF (0.12 g, 0.28 mmol) in the same solvent. The reaction mixture was stirred for a further 30 min, during which an orange color developed. The volatiles were then removed in vacuo and the residual solid product was washed with pentane and purified by crystallization from chloroform to give **8** (0.18 g, 92%) in the form of yellow crystals; m.p. 280–285 °C (dec.). – ^{1}H NMR ([D$_6$]DMSO): δ = 3.99 (m, 4 H, CH$_2$), 6.70–7.00 (m, 8 H, Ar), 8.73 (s, 2 H, CH=N). – ^{13}C NMR ([D$_6$]DMSO): δ = 52.71 (CH$_2$), 117.75 (CH$_{Ar}$), 118.87 (C$_q$), 122.32 (CH$_{Ar}$), 134.55 (CH$_{Ar}$), 135.83 (CH$_{Ar}$), 165.50 (C$_q$–O), 166.99 (CH=N), 197.06 (C=O), 201.16 (C=O). – ^{119}Sn{^{1}H} NMR ([D$_6$]DMSO): δ = –328 ($^2J_{Sn-W}$ = 1458 Hz). – IR (Nujol, KBr): $\nu_{C=N}$ 1641; ν_{CO} 1913, 1977, 2063 cm^{-1}. – MS (EI, 70 eV): *m*/*z* = 568 [M – 5 CO]$^+$. – $C_{21}H_{14}N_2O_7SnW$ (709.93): calcd. C 35.50, H 1.99, N 3.94; found C 35.70, H 2.12, N 4.00.

Synthesis of (salen)Pb=W(CO)$_5$ (9): In a similar manner, reaction of (salen)Pb (0.15 g, 0.32 mmol) with W(CO)$_5$ · THF (0.13 g, 0.32 mmol) afforded **9** (0.20 g, 79%); m.p. > 300 °C (dec.). – ^{1}H NMR ([D$_6$]DMSO): δ = 3.87 (s, 4 H, CH$_2$), 6.30–7.30 (m, 8 H, Ar), 8.27 (s, 2 H, CH=N). – IR (Nujol, KBr): $\nu_{C=N}$ 1630; ν_{CO} 1914, 1970, 2060 cm^{-1}. – $C_{21}H_{14}N_2O_7PbW$ (798.00): calcd. C 31.58, H 1.77, N 3.51; found C 31.64, H 1.92, N 3.30.

Synthesis of *cis*-[(salen)Ge]$_2$=W(CO)$_4$ (10). – Procedure 1: A mixture of (salen)Ge (0.12 g, 0.36 mmol) and W(CO)$_6$ (0.13 g, 0.36 mmol) in THF (50 mL) was irradiated for 3 h, during which a red-orange color developed. After removal of the solvent, the crude product was washed with pentane and dried to afford a mixture of **10** (85%*) and **7** (15%*) as a red-maroon powder (* relative %).

Procedure 2: A mixture of (salen)Ge (0.25 g, 0.73 mmol) and W(CO)$_6$ (0.13 g, 0.36 mmol) in THF (50 mL) was irradiated for 2.5 h, during which the solution became orange. After removal of the solvent, the crude product was washed with pentane and dried to afford pure **10** (0.65 g, 92%) as an orange powder.

Procedure 3: A mixture of **7** (0.48 g, 0.73 mmol) and (salen)Ge (0.25 g, 0.73 mmol) in THF (50 mL) was irradiated for 4 h. After removal of the solvent, the residue was washed with pentane, the washings were filtered, and the collected solid was dried to give pure **10** (0.62 g, 87%) as orange powder; m.p. 230–240 °C (dec.). – ^{1}H NMR (CDCl$_3$): δ = 3.93 (m, 8 H, CH$_2$), 6.50–7.50 (m, 16 H, Ar), 8.17 (s, 2 H, CH=N). – ^{13}C NMR (CDCl$_3$): δ = 59.79 (CH$_2$), 117.00 (CH$_{Ar}$), 116.43 (C$_q$), 117.10 (CH$_{Ar}$), 131.55 (CH$_{Ar}$), 132.45 (CH$_{Ar}$), 160.91 (C$_q$–O), 166.56 (CH=N), 196.08 (C=O), 196.38 (C=O). – IR (Nujol, KBr): $\nu_{C=N}$ 1620; ν_{CO} 1892, 1980, 2009, 2060 cm^{-1}. – MS (EI, 70 eV): *m*/*z* = 608 [M – Ge(salen) – 2 CO]$^+$, 522 [M – Ge(salen) – 5 CO]$^+$. – $C_{36}H_{28}Ge_2N_4O_8W$ (975.98): calcd. C 44.26, H 2.89, N 5.74; found C 44.50, H 2.95, N 5.68.

Synthesis of [(salen)Sn]$_2$=W(CO)$_4$ (11). – Procedure 1: A mixture of (salen)Sn (0.27 g, 0.70 mmol) and W(CO)$_6$ (0.25 g, 0.70 mmol) in THF (50 mL) was irradiated for 3 h, during which a red-maroon color developed. The volatiles were then removed in vacuo and the crude product was washed with pentane and dried to afford a mixture of **11** (90%*) and **8** (10%*) as a yellow-orange powder (* relative % as determined by ^{1}H-NMR).

Procedure 2: A mixture of (salen)Sn (0.27 g, 0.70 mmol) and W(CO)$_6$ (0.13 g, 0.35 mmol) in THF (50 mL) was irradiated for 3 h, during which the solution turned pale-orange. After removal of the solvent, the crude product was washed with pentane and dried to afford pure **11** (0.69 g, 92%) as an orange powder.

Procedure 3: A mixture of (salen)Sn (0.55 g, 1.40 mmol) and W(CO)$_6$ (0.26 g, 0.70 mmol) in THF (50 mL) was irradiated for 4 h, during which the solution again turned pale-orange. After removal of the solvent, the crude product was washed with pentane and dried to afford an orange powder consisting of a 30:70 *cis*/*trans* (**11**/**11′**) mixture, which was characterized by ^{1}H-, ^{13}C-, and ^{119}Sn-NMR and IR spectroscopy.

Procedure 4: As Procedure 2, but after irradiation for 8 h, a 50:50 mixture of **11**/**11′** was obtained from (salen)Sn (0.55 g, 1.40 mmol) and W(CO)$_6$ (0.26 g, 0.70 mmol).

Procedure 5: According to the previous procedure, pure **11** was obtained from (salen)Sn (0.27 g, 0.70 mmol) and **8** (0.49 g, 0.70 mmol); yield: 0.67 g, 90%. Crystallization from CHCl$_3$ gave **11** · 3 (CHCl$_3$) as orange crystals.

11 (*cis*): m.p. 250–260 °C (dec.). – ^{1}H NMR ([D$_6$]DMSO): δ = 3.78 (s, 4 H, CH$_2$), 6.50–7.50 (m, 16 H, Ar), 8.43 (s, 2 H, CH=N). – ^{13}C NMR ([D$_6$]DMSO): δ = 52.50 (CH$_2$), 116.94 (CH$_{Ar}$), 118.96 (C$_q$), 122.17 (CH$_{Ar}$), 134.37 (CH$_{Ar}$), 135.37 (CH$_{Ar}$), 165.69 (C$_q$–O), 169.32 (CH=N), 202.19 (C=O), 207.30 (C=O). – ^{119}Sn{^{1}H} NMR ([D$_6$]DMSO): δ = –348 ($^2J_{Sn-W}$ = 1456 Hz). – IR (Nujol, KBr): $\nu_{C=N}$ 1638; ν_{CO} 1902, 1929, 1954, 2062 cm^{-1}. – MS (EI, 70 eV): *m*/*z* = 568 [(salen)SnW$^+$]. – $C_{36}H_{28}N_4O_8Sn_2W$ (1067.94): calcd. C 40.45, H 2.64, N 5.24; found C 40.61, H 2.72, N 5.14.

11′ (*trans*): ^{1}H NMR ([D$_6$]DMSO): δ = 3.82 (s, 4 H, CH$_2$), 6.30–7.50 (m, 16 H, Ar), 8.19 (s, 2 H, CH=N). – ^{13}C NMR ([D$_6$]DMSO): δ = 51.96 (CH$_2$), 115.97 (CH$_{Ar}$), 118.96 (C$_q$), 122.06 (CH$_{Ar}$), 131.56 (CH$_{Ar}$), 132.25 (CH$_{Ar}$), 134.17 (CH$_{Ar}$), 165.82 (C$_q$–O), 167.99 (CH=N), 211.23 (C=O). – ^{119}Sn{^{1}H} NMR ([D$_6$]DMSO): δ = –374. – IR (Nujol, KBr): $\nu_{C=N}$ 1640; ν_{CO} 1999 cm^{-1}.

Synthesis of *cis*-[(salen)Pb]$_2$=W(CO)$_4$ (12). – Procedure 1: A mixture of (salen)Pb (0.15 g, 0.32 mmol) and W(CO)$_6$ (0.11 g, 0.32 mmol) in THF (50 mL) was irradiated for 3 h, during which a maroon color developed. After filtration, the volatiles were removed under reduced pressure. The residue was washed with pentane and dried in vacuo to afford a mixture of **12** (70%*) and **9** (30%*) as a red-brown powder (* relative % as determined by ^{1}H-NMR).

Procedure 2: A mixture of (salen)Pb (0.54 g, 1.14 mmol) and W(CO)$_6$ (0.20 g, 0.57 mmol) in THF (50 mL) was irradiated for 2.5 h, during which the solution turned maroon. After work-up as described in the previous procedure, **12** (0.51 g, 72%) was obtained as an orange powder.

Procedure 3: According to the previous procedure, pure **12** (0.42 g, 60%) was obtained from (salen)Pb (0.27 g, 0.57 mmol) and **9** (0.45 g, 0.57 mmol); m.p. > 300 °C (dec.). – ^{1}H NMR ([D$_6$]DMSO): δ = 4.07 (s, 4 H, CH_2), 6.25–7.35 (m, 8 H, Ar), 8.03 (s, 2 H, CH=N). – IR (Nujol, KBr): $\nu_{C=N}$ 1625; ν_{CO} 1906, 1930, 2015, 2060 cm^{-1}. – $C_{36}H_{28}N_4O_8Pb_2W$ (1244.09): calcd. C 34.72, H 2.27, N 4.50; found C 34.90, H 2.40, N 4.32.

Reactions of 4 and 7 with Iodine: To a solution of **4** (0.05 g, 0.10 mmol) or **7** (0.06 g, 0.10 mmol) in DMSO (10 mL) was added iodine (0.03 g, 0.10 mmol). CO was immediately evolved and the solution turned orange. The mixture was stirred at room temperature for 3 h. Subsequent analysis by ^{1}H- and ^{13}C-NMR and by mass spectroscopy revealed that (salen)GeI$_2$ had been produced.[15b]

Reactions of 5 and 8 with Iodine: According to the same procedure as above, reactions of **5** (0.06 g, 0.10 mmol) and **8** (0.07 g, 0.10 mmol) with iodine (0.03 g, 0.10 mmol) afforded (salen)SnI$_2$.[15b]

Synthesis of *cis*-(salen)Sn=W(CO)$_4$(PPh$_3$) (13): A solution of **8** (0.22 g, 0.31 mmol) and triphenylphosphane (0.08 g, 0.31 mmol) in THF (30 mL) was irradiated for 1.5 h. The solvent was then removed in vacuo affording a maroon-orange powder, which was washed with pentane and dried under reduced pressure to give **13** (0.26 g, 90%); m.p. 250–260 °C (dec.). – ^{1}H NMR ([D$_6$]DMSO): δ = 3.77 (s, 4 H, CH_2), 6.72–7.60 (m, 23 H, Ar), 8.44 (s, 2 H, CH=N). – ^{13}C NMR ([D$_6$]DMSO): δ = 57.95 (CH_2), 122.37 (CH_{Ar}), 124.33 (C_q), 127.62 (CH_{Ar}), 134.18 (CH_{Ar}), 134.40 (CH_{Ar}), 134.48 (CH_{Ar}), 137.41 (CH_{Ar}), 137.91 (CH_{Ar}), 139.82 (CH_{Ar}), 140.80 (CH_{Ar}), 171.16 (C_q–O), 174.77 (CH=N), 202.34 (C=O), 202.53 (C=O), 207.64 (C=O), 212.74. – $^{119}Sn\{^{1}H\}$ NMR ([D$_6$]DMSO): δ = –347.5 (d, $^{3}J_{Sn-P}$ = 2088 Hz). – $^{31}P\{^{1}H\}$ NMR ([D$_6$]DMSO): δ = –16.2 ($^{3}J_{Sn-P}$= 2088 Hz). – IR (Nujol, KBr): $\nu_{C=N}$ 1639; ν_{CO} 1876, 1977, 2011, 2055 cm^{-1}. – MS (EI, 70 eV): *m*/*z* = 502 $[Ph_3PW(CO)_2]^+$, 446 $[Ph_3PW]^+$, 386 $[(salen)Sn]^{+\cdot}$. – $C_{38}H_{29}N_2O_6PSnW$ (944.03): calcd. C 48.30, H 3.10, N 2.97; found C 48.70, H 3.30, N 2.90.

Reaction of 5 with 1,2-Bis(diphenylphosphanyl)ethane: A solution of **5** (0.22 g, 0.38 mmol) in THF (30 mL) containing 1,2-bis(diphenylphosphanyl)ethane (0.15 g, 0.38 mmol) was irradiated for 2.5 h. The solvent was then removed in vacuo, affording a maroon-orange powder, which was washed with pentane and dried under reduced pressure to give a mixture of **14** and (DPPE)Cr(CO)$_4$. The product was characterized by ^{1}H-, ^{31}P-, and ^{119}Sn-NMR and by IR. Crystallization from CHCl$_3$ gave orange crystals of **14** · 3 (CHCl$_3$). – ^{1}H NMR (CDCl$_3$): δ = 3.99 (m, 4 H, CH_2), 6.60–7.50 (m, 10 H, Ar), 8.10 (s, 2 H, CH=N). – ^{13}C NMR (CDCl$_3$): δ = 48.70 (CH_2), 118.56 (CH_{Ar}), 119.22 (Cq_{Ar}), 123.98 (CH_{Ar}), 134.37 (CH_{Ar}), 136.64 (CH_{Ar}), 164.03 (C_q–O), 166.66 (C_q–O), 170.12 (CH=N), 211.68 (CO *cis*), 218.43 (CO *cis*), 224.99 (CO *trans*). – $^{119}Sn\{^{1}H\}$ NMR (CDCl$_3$): δ = –144. – IR (CDCl$_3$, KBr): $\nu_{C=N}$ 1621, ν_{CO} 1931, 1982, 2052 cm^{-1}. – $C_{36}H_{28}CrN_4O_8Sn_2$ (935.93): calcd. C 46.16, H 3.02, N 5.98; found C 46.40, H 3.15, N 5.54.

Reaction of 8 with 1,2-Bis(diphenylphosphanyl)ethane: A solution of **8** (0.22 g, 0.31 mmol) in THF (30 mL) containing 1,2-bis(diphenylphosphanyl)ethane (0.13 g, 0.31 mmol) was irradiated for 2.5 h. The solvent was then removed in vacuo, affording a maroon-orange powder, which was washed with pentane and dried under reduced pressure to give a mixture of **11** and (DPPE)W(CO)$_4$. The product was characterized by ^{1}H-, ^{31}P-, and ^{119}Sn-NMR and by IR.

Reaction of 5 with One Equivalent of DBQ: A mixture of **5** (0.03 g, 0.05 mmol) and DBQ (0.01 g, 0.05 mmol) was dissolved in CHCl$_3$ (5 mL). The color of the solution immediately darkened. The volatiles were subsequently removed under reduced pressure. The crude product was washed with pentane and dried in vacuo to afford **14** (0.02 g, 85%)

Reaction of 7 with One Equivalent of DBQ: A mixture of **7** (0.05 g, 0.10 mmol) and DBQ (0.02 g, 0.10 mmol) was dissolved in CHCl$_3$ (5 mL). The color of the solution immediately darkened and evolution of CO was observed. After stirring for 8 h, the volatiles were removed in vacuo. The crude product was washed with pentane and dried in vacuo to afford **10** (0.04 g, 82%).

Reaction of 8 with One Equivalent of DBQ: A mixture of **8** (0.09 g, 0.12 mmol) and DBQ (0.03 g, 0.12 mmol) was dissolved in CHCl$_3$ (5 mL). The solution immediately turned dark-red. The volatiles were subsequently removed under reduced pressure and the crude product was washed with pentane and dried in vacuo to afford **11** (0.05 g, 78%).

Reaction of 8 with Two Equivalents of DBQ: A mixture of **8** (0.09 g, 0.12 mmol) and DBQ (0.06 g, 0.24 mmol) was dissolved in CHCl$_3$ (5 mL). The solution immediately turned intensely red. The volatiles were subsequently removed under reduced pressure. The crude product was washed with pentane and dried in vacuo to afford a mixture of **11** and **16** (ratio 1:2, as determined by ^{1}H-NMR).

Reaction of 8 with Four Equivalents of DBQ: A mixture of **8** (0.09 g, 0.12 mmol) and DBQ (0.12 g, 0.48 mmol) was dissolved in CHCl$_3$ (10 mL). The solution immediately turned red. The volatiles were subsequently removed in vacuo. The crude product was washed with pentane and dried in vacuo to afford **16** (0.06 g, 83%)

Reaction of 4 with DBQ: A mixture of **4** (0.03 g, 0.05 mmol) and DBQ (0.01 g, 0.05 mmol) was dissolved in CHCl$_3$ (5 mL). The color of the solution immediately darkened and the volatiles were subsequently removed in vacuo. The crude product was washed with pentane and dried in vacuo to afford **15**. – ^{1}H NMR (CDCl$_3$): δ = 4.21 (m, 4 H, CH_2), 6.40–7.70 (m, 10 H, Ar), 8.40 (s, 2 H, CH=N). – ^{13}C NMR (CDCl$_3$): δ = 54.50 (CH_2), 119.09 (CH_{Ar}), 120.89 (Cq_{Ar}), 120.13 (CH_{Ar}), 134.03 (CH_{Ar}), 136.54 (CH_{Ar}), 164.20 (C_q–O), 161.81 (C_q–O), 172.2 (CH=N), 211.70 (CO cis), 217.23 (CO). – $C_{36}H_{28}N_4O_8Ge_2Cr$ (843.97): calcd. C 51.19, H 3.34, N 6.64; found C 51.40, H 3.51, N 6.23.

---

[1] E. Brooks, H. R. Cros, *J. Organomet. Chem. Rev. A* **1970**, *6*, 227.

[2] M. Veith, O. Recktenwald, *Top. Curr. Chem.* **1982**, *104*, 1.

[3] W. Petz, *Chem. Rev.* **1986**, *86*, 1019.

[4] M. F. Lappert, R. S. Rowe, *Coord. Chem. Rev.* **1990**, *100*, 267.

[5] J. T. B. H. Jastrzebski, G. Van Koten, *Intramolecular Coordination in Organotin Chemistry; Advances in Organometallic Chemistry* **1993**, *35*, 241.

[6] H. Handwerker, C. Leis, R. Probst, P. Bissinger, A. Grohmann, P. Kiprof, E. Herdtweck, J. Blümel, N. Auner, C. Zybill, *Organometallics* **1993**, *12*, 2162.

[7] S. L. Ellis, P. B. Hitchcock, S. A. Holmes, M. F. Lappert, M. J. Slade, *J. Organomet. Chem.* **1993**, *444*, 95.

[8] D. A. Atwood, V. O. Atwood, A. H. Cowley, H. R. Gobran, *Inorg. Chem.* **1993**, *32*, 4671.

[9] N. Tokitoh, K. Manmaru, R. Okazaki, *Organometallics* **1994**, *13*, 167.

[10] M. Weidenbruch, A. Stilter, J. Schlaefke, K. Peters, H. G. von Schnering, *J. Organomet. Chem.* **1995**, *501*, 67.

[11] M. Weidenbruch, A. Stilter, K. Peters, H. G. von Schnering, *Z. Anorg. Allg. Chem.* **1996**, *622*, 534; M. Weidenbruch, A. Stilter, K. Peters, H. G. von Schnering, *Chem. Ber.* **1996**, *129*, 1565.

[12] H. Lang, M. Weinmann, W. Fresch, M. Büchner, B. Schiemenz, *Chem. Commun.* **1996**, 1299.

[13] M. Weidenbruch, A. Stilter, W. Saak, K. Peters, H. G. von Schnering, *J. Organomet. Chem.* **1998**, *560*, 125.

[14] J. Barrau, G. Rima, T. El Amraoui, *J. Organomet. Chem.* **1998**, *570*, 163.

[15] [15a] D. Agustin, G. Rima, J. Barrau, *Main Group Met. Chem.* **1997**, *20*, 791. – [15b] D. Agustin, G. Rima, H. Gornitzka, J. Barrau, *J. Organomet. Chem.* **1999**, *592*, 1.
[16] P. B. Hitchcock, M. F. Lappert, P. Pye, *J. Chem. Soc., Dalton Trans.* **1977**, 2160.
[17] A. L. Balch, E. D. Oram, *Organometallics* **1998**, *7*, 155.
[18] T. J. Marks, *J. Am. Chem. Soc.* **1971**, *93*, 7090.
[19] C. E. Holloway, M. Melnik, *Main Group Met. Chem.* **1998**, *21*, 371.
[20] M. S. Holt, W. L. Wilson, J. H. Nelson, *Chem. Rev.* **1989**, *89*, 11.
[21] K. Jurkschat, A. Tzchach, J. Meunier-Piret, M. Van Meersche, *J. Organomet. Chem.* **1988**, *349*, 143.
[22] J. T. B. H. Jastrzebski, P. A. Van der Schaaf, J. Boersma, G. Van Koten, D. Heijdenrijk, K. Goubitz, D. J. A. de Ridder, *J. Organomet. Chem.* **1989**, *367*, 55.
[23] H. P. Abicht, K. Jurkschat, A. Tzchach, K. Peters, E.-M. Peters, H. G. von Schnering, *J. Organomet. Chem.* **1987**, *326*, 357.
[24] P. Jutzi, B. Hampel, K. Stroppel, C. Krüger, K. Angermund, P. Hofmann, *Chem. Ber.* **1985**, *118*, 2789.
[25] D. Stalke, *Chem. Soc. Rev.* **1998**, *27*, 171.
[26] G. M. Sheldrick, *SHELXS-97*, Program for Crystal Structure Solution, Universität Göttingen, **1997**.
[27] G. M. Sheldrick, *SHELXL-97*, Program for Crystal Structure Refinement, Universität Göttingen, **1997**.

Received July 16, 1999
[I99248]