

π -Bonding in the star-type compound $[\{(\text{CO})_5\text{Cr}\}_3\text{Sn}]^{2-}$. How to rationalize its electronic absorption spectrum and its out-of-range ^{119}Sn -NMR shift of $\delta = 3924^1$

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Abstract

$[\{(\text{CO})_5\text{Cr}\}_3\text{Sn}]^{2-}$, **1**, is obtained from $\text{Na}_2[\text{Cr}_2(\text{CO})_{10}]$ or $\text{K}_2[\text{Cr}(\text{CO})_5]$ by reaction with SnCl_2 under well specified conditions on three different routes. The structure of **1** as determined for its salt $[\text{Ph}_4\text{P}]_2 \cdot \mathbf{1}$. The star-type anion **1** shows a D_{3h} arrangement of the $[\text{Cr}_3\text{Sn}]$ core. At each chromium center two equatorial carbonyl groups are close to the coordination plane of the tin center, with the remaining two roughly pointing into the direction of the idealized C_3 -axis. These 'out-of-plane' carbonyl groups are bent towards the center with $\text{Sn}-\text{Cr}-\text{C}_{\text{CO}}$ angles of ca. 82° . The unconventional C_s symmetry of the $[(\text{CO})_5\text{Cr}]$ entities thus resulting, is well-rationalized in terms of tin- π^* -CO back-bonding within the EHT model. EHT calculations also substantiate the idea that **1** is to be considered as a 4-center, 6π -system, isoelectronic, in a formal sense, to well-known π -systems of this type, like $[\text{CO}_3]^{2-}$ or $[\text{C}(\text{CH}_2)_3]^{2-}$. **1** has a prominent electronic absorption in the visible range, which is attributed to a $\pi-\pi^*$ transition from the occupied e-set of the π -system into the empty π^* LUMO of the compound. This assignment is in line with the results of CI calculations on model compounds. The most unconventional property of **1** is its ^{119}Sn -NMR resonance, which is found at $\delta = 3924$, well outside the low-field limit hitherto documented in ^{119}Sn -NMR spectroscopy. In terms of the models describing the π -bonding situation in **1**, this extreme low-field shift is not unexpected: the low-lying π^* LUMO will greatly increase the paramagnetic contribution to the shift. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Tin; Trigonal planar coordination; Chromium-tin- π -system; ^{119}Sn -NMR; Crystal structure

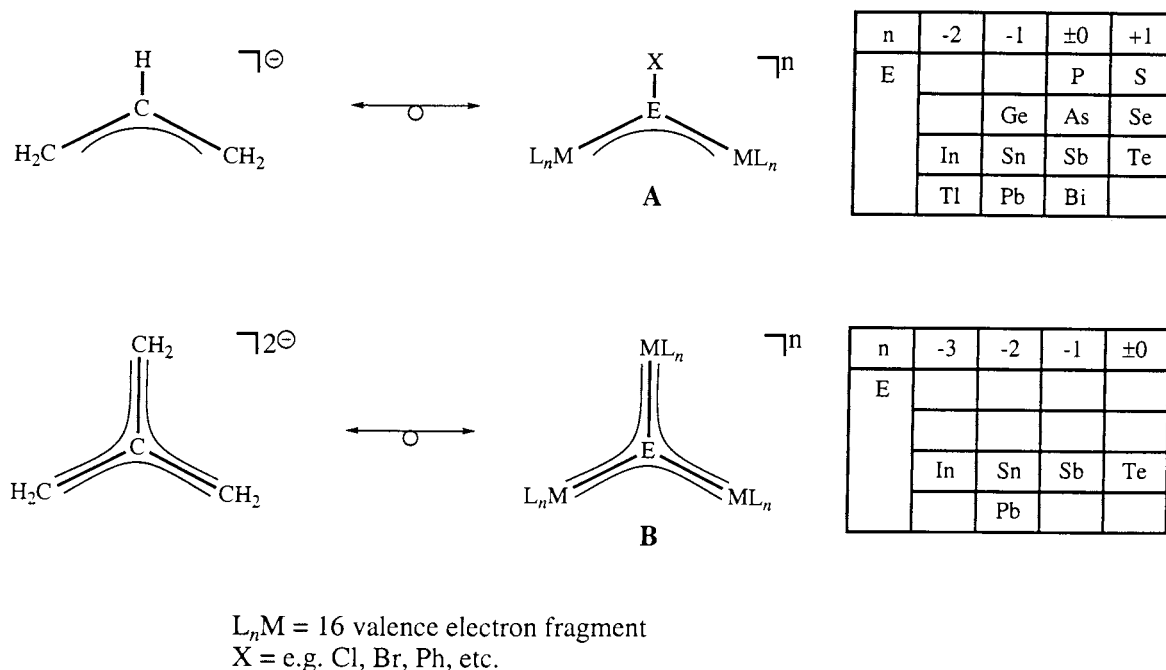
1. Introduction

π -Bonding between main group atoms, so well-established in organic chemistry, has become a topic of major concern in the chemistry of the heavier main group elements in more recent times [1]. Many of the species involving double and even triple bonding between such elements, which would have been considered as non-existent only a few decades ago, have in fact been prepared [1]. Parallel to this effervescent

renaissance of main group chemistry, the chemistry of compounds containing multiple bonds between transition metals and the heavier main group elements has become an important part of organometallic chemistry [2,3]. There are several classes of compounds which owe their very existence to π -bonding between d-type metal-centered donor orbitals and vacant p-valence orbitals of the heavier main group atoms [2,3]. Among these the broadest variety of species is obviously available for 'inidene-type' compounds, $[\text{L}_n\text{M} \cdots \text{E}(\text{X}) \cdots \text{ML}_n]^n$ (type A, Scheme 1), where filled $[\text{L}_n\text{M}]$ d-type donor orbitals of the 16 electron L_nM fragments interact with an empty p-valence orbital of the six electron bridging ligand $[\text{E}(\text{X})]^n$ so as to give a 3-center, 4π -conjugated system [2,3]. This type of compound is thus like the

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¹ Dedicated to Professor Peter Jutzi on the occasion of his 60th birthday.



Scheme 1. Organometallic 3-center, 4 π - (A) and 4-center, 6 π -systems (B) and their relation to organic prototypes.

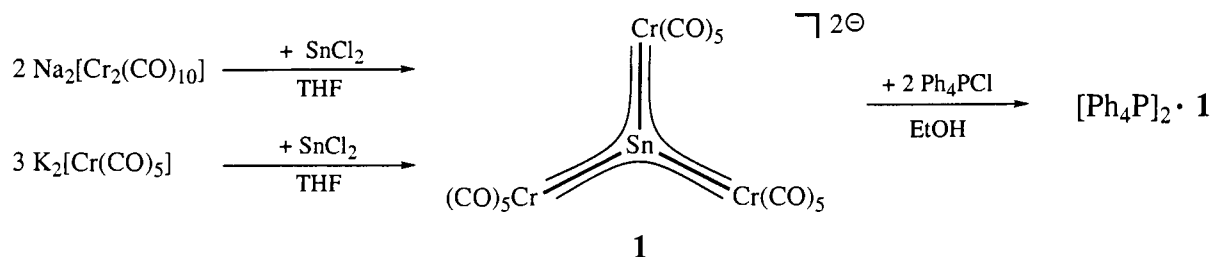
well-known 3-center, 4 π -systems of allylic or carboxylate anions, to name just a few. This analogy between type A compounds and the more conventional 3-center, 4 π -systems has been made use of from the beginning of the development of the chemistry of such species [4] and is rationalized in general terms by the concept of isolobality [5].

The π -system characterizing the bonding in these compounds is the basis of a number of peculiarities observed for them: the main group atoms are in a trigonal planar environment throughout (Scheme 1). The reactivity of the compounds is to a large extent determined by the acceptor capabilities of the low lying π^* LUMO of the compounds due to the fact that the π -interactions between the transition metal d-type orbitals and main group p-valence orbitals are much weaker than π -interactions between the carbon atoms in an organic compound [2,3]. The splitting of the π -levels is small enough to shift the π - π^* absorptions well into the visible range; a characteristic strong π - π^* absorption is generally observed for the compounds [2,3]. Yet another consequence of the low lying π^* -orbitals is an extremely strong low-field shift of the NMR signal of the main group center, wherever this is observable. With phosphorous at the center, shifts of up to $\delta(^{31}\text{P}) = 1362$ have been observed [6], which are neatly correlated with the energy required for electronic excitation [7]; the lower the energy of the π - π^* transition, the larger the paramagnetic contribution to the shift should be [8], and this is what is observed [7]. For compounds of type A containing tin as a potential NMR active center ([3]c,d) no NMR data have been

reported. It has, however, been found that $\{[\text{Cp}^*(\text{CO})_2\text{Mn}]_2\text{Sn}=\text{Mn}(\text{CO})_2\text{Cp}^*\}$, the π -bonding pattern of which is closely related to the one discussed for 'indenyl' compounds, has a ^{119}Sn -NMR shift of $\delta = 3301$, which is well out of the range observed so far for any other type of tin compound [9]. Again, the low lying π^* LUMO of this compound is the straightforward rationale of this observation.

There is another class of compounds with trigonal planar coordinated main group centers (type B, Scheme 1) the π -system of which has its analogue in well-known traditional π -systems such as nitrate, carbonate, or to go back to an organic example, in the trimethylenemethane dianion ($\text{C}\{\text{CH}_2\}_3^{2-}$) [10]. With $[L_nM]$ being a 16-electron organometallic fragment, the six electron center $[E]^n$ will be stabilized in a trigonal planar environment by the π -interaction between the d-type metal donor orbitals and the vacant p-orbital at the main group center. Species of type B are known for the heavier congeners of group 13–16 (Scheme 1) [11]. Even though the syntheses and structures of these compounds are well documented, no NMR data referring to the central atoms have yet been reported, despite the fact that both, tellurium and tin, are NMR active nuclei.

With the idea in mind that compounds of type B with their conjugated 4-center, 6 π -system should have a low lying π^* LUMO as well, we set out to prepare such a compound with tin as the NMR active nucleus in order to probe whether the predicted strong low-field shift of the ^{119}Sn -NMR signal would in fact be observed. The paper describes a number of ways to prepare



Scheme 2. Reactions of tin(II)chloride with $\text{Na}_2[\text{Cr}_2(\text{CO})_{10}]$ or $\text{K}_2[\text{Cr}(\text{CO})_5]$ and $[\text{Ph}_4\text{P}]\text{Cl}$ forming **1** and $[\text{Ph}_4\text{P}]_2 \cdot \mathbf{1}$, respectively.

$[\{(\text{CO})_5\text{Cr}\}_3\text{Sn}]^{2-}$, **1**. The X-ray analysis of $[\text{Ph}_4\text{P}]_2 \cdot \mathbf{1}$ is reported as is its ^{119}Sn -NMR shift which amounts to $\delta = 3924$ and thus marks the low-field extreme in ^{119}Sn -NMR spectroscopy.

2. Results and discussion

2.1. Syntheses and reactions

$\text{Na}_2[\text{Cr}_2(\text{CO})_{10}]$, disodiumdecacarbonyldichromate, reacts with tin dichloride, SnCl_2 , in THF to produce a dark-red solution, from which black-red **1** is precipitated by $[\text{Ph}_4\text{P}]\text{Cl}$, tetraphenylphosphoniumchloride, as its phosphonium salt $[\text{Ph}_4\text{P}]_2 \cdot \mathbf{1}$ (Scheme 2). This salt may also be prepared from $\text{K}_2[\text{Cr}(\text{CO})_5]$, dipotassiumpentacarbonylchromate, by an analogous sequence (Scheme 2).

1 is also obtained when $[\{(\text{CO})_5\text{Cr}\}_2\text{SnCl}_2]^{2-}$, bis-pentacarbonylchromiumdichlorostannate (2⁻) [12], is reacted with $\text{Na}_2[\text{Cr}_2(\text{CO})_{10}]$ and it is found that this reaction may be inverted by adding SnCl_2 to the solutions containing **1** in so far as $[\{(\text{CO})_5\text{Cr}\}_2\text{SnCl}_2]^{2-}$ is reformed under these conditions (Scheme 3).

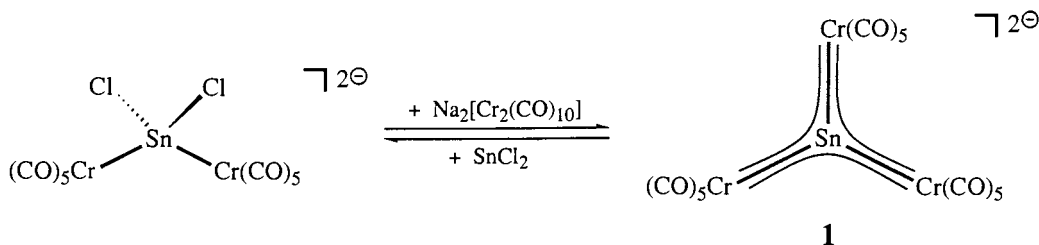
From this observation it appears that **1** is an intermediate in the reaction of $\text{Na}_2[\text{Cr}_2(\text{CO})_{10}]$ with SnCl_2 to produce $[\{(\text{CO})_5\text{Cr}\}_2\text{SnCl}_2]^{2-}$ [12]. In all literature reports referring to this transformation, the stoichiometric ratio $\text{Na}_2[\text{Cr}_2(\text{CO})_{10}]/\text{SnCl}_2$ was 1/1 [12]. Under these conditions only $[\{(\text{CO})_5\text{Cr}\}_2\text{SnCl}_2]^{2-}$ is observed since **1** is only obtained if the stoichiometric ratios are the ones inferred from the composition of **1** (Scheme 3). It might be that the primary product in each case is $[\{(\text{CO})_5\text{Cr}\}_2\text{SnCl}_2]^{2-}$, which is then transformed to **1** by $\text{Na}_2[\text{Cr}_2(\text{CO})_{10}]$. Any **1**, however, if occasionally formed under the reaction conditions, will lead to $[\{(\text{CO})_5\text{Cr}\}_2\text{SnCl}_2]^{2-}$, whenever an excess of SnCl_2 is present.

Mass spectra showing the anion **1** could not be obtained, even under FAB conditions under which, when performed with triethanolamine (TEA) as the matrix, only the fragments $[\{(\text{CO})_5\text{Cr}\}\text{Sn} \cdot \text{TEA} - 2\text{H}]^-$ ($m/z = 458$), $[\{(\text{CO})_5\text{Cr}\}\text{Sn} \cdot \text{TEA} - 2\text{H}]^-$ ($m/z = 402$), and $[\{(\text{CO})_5\text{Cr}\}_2\text{Sn} \cdot \text{TEA} - \text{C}_2\text{H}_4\text{OH} - 2\text{H}]^-$ ($m/z = 605$) are observed, all of which contain the matrix compound as a constituent.

2.2. Structure analysis

Unequivocal proof of the constitution and structure of **1** comes from X-ray analysis of $[\text{Ph}_4\text{P}]_2 \cdot \mathbf{1}$. Black-red single crystals of this salt are obtained by layering its solution in THF with ethanol. The structure of **1** is shown in Fig. 1. Table 1 contains atomic coordinates and equivalent isotropic displacement parameters, while Table 2 shows the most relevant geometric information.

The salt $[\text{Ph}_4\text{P}]_2 \cdot \mathbf{1}$ consists of discrete anions and cations. The three chromium atoms and the tin atom forming the core of the anion **1** are coplanar (maximum deviation < 11 pm); the angles Cr–Sn–Cr are all very close to 120° (Table 2). The idealized symmetry of the core is hence D_{3h} . The orientation of the $[(\text{CO})_5\text{Cr}]$ groups reduces this idealized symmetry. The absolute values of the skew angles Cr–Sn–Cr– $\text{C}_{\text{CO}}(\text{b})$, which should be either 90 or 45° and 135° , respectively, for an ideal D_{3h} orientation, are close to 110° (70°) in the observed conformation (Fig. 1, Table 2). This means that in a rough sense, the four equatorial carbon groups at each $[(\text{CO})_5\text{Cr}]$ entity can still be classified as ‘equatorial’ (**a** in Fig. 1) and ‘axial’ (**b** in Fig. 1) with respect to the $[\text{Cr}_3\text{Sn}]$ plane. In a fair approximation, analysis of the bonding pattern may thus refer to an idealized D_{3h} symmetry. It is observed (Fig. 1, Table 2) that the ‘axial’ carbonyl groups (**b** in Fig. 1) are bent towards the idealized C_3 -axis of the molecule with a mean Sn–Cr– $\text{C}_{\text{CO}}(\text{b})$ angle of only 82° , corresponding to a mean value of the $\text{C}_{\text{CO}}(\text{b})$ –Cr– $\text{C}_{\text{CO}}(\text{b})$ angle of 164° (Fig. 1, Table 2). The Sn–Cr– $\text{C}_{\text{CO}}(\text{a})$ angles on the other hand average at 89.5° with $\text{C}_{\text{CO}}(\text{a})$ –Cr– $\text{C}_{\text{CO}}(\text{a})$ angles of 177° (Table 2). With respect to these CO groups (**a**), the coordination around chromium is the normal one (the expected slight bending towards the tin center [13] lies well in the range of 86.3 – 90.2° , documented for other tin compounds containing $[(\text{CO})_5\text{M}]$ fragments ($\text{M} = \text{Cr}, \text{W}$) [12,14,15]) while the distinct bending of the other set of carbonyl groups (**b**) is unconventional and completely unexpected at first glance. It is expected [13] that bending occurs in the direction of the ligand that has a better σ -donor capacity as compared with CO. The distinctive bending of the ‘axial’ carbonyl groups (**b**) in contrast to the ‘equatorial’ ones (**a**) calls for some additional explanation.



Scheme 3. Transformation of **1** into $\{(\text{CO})_5\text{Cr}\}_2\text{SnCl}_2\}^{2-}$ and vice versa.

An MO analysis was therefore performed in order to sort out possible reasons for this deviation of the $[(\text{CO})_5\text{Cr}]$ entities from local C_{4v} symmetry.

As a model compound $\{(\text{CO})_5\text{Cr}\}\text{SnH}_2$ was chosen [16] since in this case molecular C_{2v} symmetry with one set of mutually *trans*-equatorial carbonyl groups does not, in contrast to **1**, pose any steric problem (Fig. 2). While $[(\text{CO})_5\text{Cr}]$ is most stable in its square pyramidal C_{4v} structure [13], $\{(\text{CO})_5\text{Cr}\}\text{SnH}_2$ (Fig. 2) is stabilized by bending its two 'out-of-plane' carbonyl groups (with respect to the coordination plane of the tin center) so that they approach the tin center as indicated in Fig. 2.

The EHT energy of the compound is lowered by 0.7 eV when the Sn–Cr– C_b angle is decreased from 90 to 80°. The overlap between the valence orbitals at the tin center and the chromium valence orbitals is of course not influenced by this distortion. What is affected, however, is the overlap between the valence orbitals at the 'out-of-plane' carbon atoms (C_b) and the orbitals at the other atoms. Especially noteworthy is a considerable increase of the overlap between the p_z -orbital at the tin center and the p_x -orbitals at the carbon atoms (C_b) from 0.11 to 0.15 for the angles of 90 and 80°, respectively. Parallel to this increase in overlap, the bond order between these carbon atoms (C_b) and the tin center as evaluated by a Mulliken population analysis increases from 0.18 to 0.29. The charge at the tin center is reduced by this deformation while the charge calculated at the relevant carbon and oxygen atoms is appropriately increased.

The main reason for the observed bending in terms of this EHT analysis is the following: charge accumulated at the tin center is back-donated to the π^* -orbitals of the 'out-of-plane' carbonyl groups (**b**) [18–20].

An analogous model calculation was performed for **1**. The rotational position of the $[(\text{CO})_5\text{Cr}]$ groups with respect to the torsion around the Sn–Cr bonds was left unchanged with respect to the observed solid state structure of **1**. Two sets of calculations were done, one with the 'out-of-plane' CO groups (**b**) staying at the Sn–Cr– $C_{\text{CO}}(\text{b})$ angles as observed and the other one with these angles set back to 90°. The energy of the structure as observed is calculated 0.8 eV below the structure which had the Sn–Cr– $C_{\text{CO}}(\text{b})$ angles set back to 90°. The bond order Sn– $C_{\text{CO}}(\text{b})$ (Fig. 1, Table 2) is

definitely higher (0.17) for the observed structure as compared with the idealized one (0.12). Back-bonding from the tin p_z -orbital to the 'out-of-plane' π^* -orbitals is thus the rationale for the unconventional bending of the 'out-of-plane' carbonyl groups (**b** in Fig. 1) observed for **1**.

In contrast to what is often observed for semi-bridging carbonyl groups in organometallic chemistry the Cr–C–O angles are close to their ideal values of 180° (Table 2) for all the semi-bridging, as well as for the other carbonyl groups in **1**.

The Cr–C bonds observed for the two groups of equatorial carbonyl ligands are equal within the limits of error (188–189 pm, Table 2), whereas the bonds involving the axial carbonyl ligands appear to be marginally shorter (185 pm, Table 2).

The bonds radiating from the tin center to the three chromium atoms are definitely longer (266.5 pm, Table 2) than the ones observed for stannylene complexes $\{(\text{CO})_5\text{Cr}\}\text{SnR}_2$ (256–261 pm) [17]. They are in the range observed for dinuclear compounds $\{(\text{CO})_5\text{Cr}\}_2\text{SnR}_2\}^{2-}$ (264–268 pm) [12]. The Sn–Cr bond order as calculated by the EHT approach is only ca. 0.4 for **1**. This low bond order and all of the structural observations then indicate that the π -interaction between the chromium d-orbitals and the p_z -valence orbital at the tin atom is weak.

2.3. UV/Vis spectroscopy

The UV/Vis spectrum of **1** shows an absorption band at 423 nm (THF, 25°C) at a position which is well-separated from the range where the strong absorptions of the $[(\text{CO})_5\text{Cr}]$ groups occur [21]. This band is interpreted in terms of a π – π^* transition within the 4-center, 6π -system characterizing the bonding situation in **1**.

EHT calculations on **1** give the energies of these π -orbitals as shown in Fig. 3. The symmetry labels used refer to an idealized D_{3h} conformation of **1** to which the observed structure is a close approximation. The contributions of the individual atomic orbitals, as well as the energies, are taken from the EHT calculation performed for the observed structure of **1**. The total bonding combination (a'_2) and the e-set (e') of orbitals are in the bonding range. The total antibonding combination

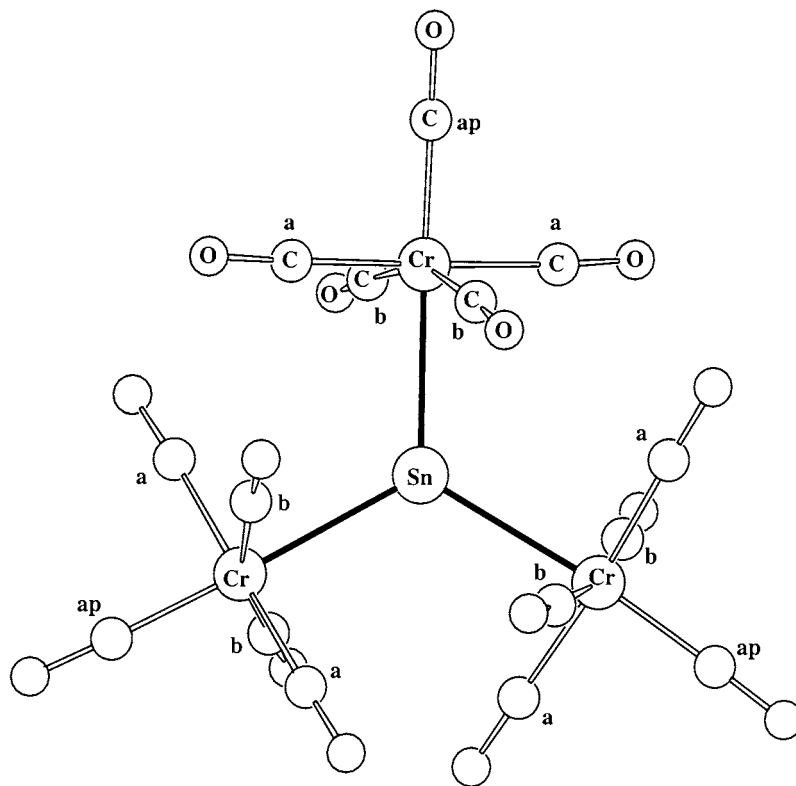


Fig. 1. Molecular structure of the dianion **1**. The carbonyl groups are labeled in groups (a, b, ap) according to their relative position with respect to the $[\text{Cr}_3\text{Sn}]$ plane.

is the LUMO of the compound, while the e-set is found at the positions (HOMO-3) and (HOMO-4). Unfortunately, parameters to do a CI calculation for the tin compound **1** were not available [22]. They were available, however, for the analogous phosphorous compound $[\{(\text{CO})_5\text{Cr}\}_3\text{P}]^-$ where formally $[\text{Sn}]^{2-}$ is replaced by $[\text{P}]^-$. For this model compound, the orientation and structure of the $[(\text{CO})_5\text{Cr}]$ groups were used as found for **1**. The P–Cr distances on the other hand were set to a value of 245 pm [23].

A CI calculation done for this model compound resulted in the prediction of the UV/Vis spectrum as shown in Fig. 4. The band at ca. 400 nm is characterized as an almost pure $\pi-\pi^*$ transition by this calculation, well-represented by a HOMO(e')–LUMO($a2''$) transition with respect to Fig. 3. In addition, the band is predicted to occur in a range that is separated from the higher energy range, where $[(\text{CO})_5\text{Cr}]$ -typical absorptions occur. Even though the absolute energy scale given by this calculation will (as well as the extinction coefficient) have some distortion and offset [24], the pattern observed should be meaningful: it is a $\pi-\pi^*$ absorption localized to the 4-center, 6π -system which gives rise to the long wavelength band [25]. The pattern observed in the real compound **1** is qualitatively similar

to the one calculated for the $[\{(\text{CO})_5\text{Cr}\}_3\text{P}]^-$ model compound. The observed extinction coefficient is roughly one order of magnitude lower than the one calculated for the model. This fits, however, to the observation that for the 3-center, 4π -system of 'inidene' compounds, strong $\pi-\pi^*$ absorptions in the range of some $10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$ are only observed with group 15 ([2]a,b, [3]g,i–k) or group 16 elements ([3]m–r) in the bridging position, while no such prominent bands are found for the anionic group 14 ([3]c,e) and group 13 analogues ([3]a). The absence of prominent $\pi-\pi^*$ absorptions of these latter compounds might have two reasons: (a) π -bonding is stronger and the $\pi-\pi^*$ separation is too large therefore, to shift the bands into the visible range, such that they are hidden under the short wavelength L_nM absorptions. (b) The oscillator strength characterizing the $\pi-\pi^*$ transitions decreases with increasing negative charge of the compounds such that the bands are no longer prominent. Even both of these effects might cooperate such as to hide the corresponding bands in 'inidene' compounds containing group 14 ([3]c,e) or 13 centers ([3]a). Taking this background into account, the assignment of the band at 423 nm observed for **1** as a $\pi-\pi^*$ absorption is a plausible one.

Table 1
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for complex **1**

Atom	x	y	z	U_{eq}^a	Atom	x	y	z	U_{eq}^a
Sn(1)	3014(1)	5962(1)	2343(1)	26(1)	C(58)	8745(7)	8003(3)	2063(3)	48(4)
Cr(1)	2061(2)	6970(1)	2782(1)	31(1)	C(59)	8467(7)	8207(3)	1502(3)	48(4)
Cr(2)	3169(2)	6029(1)	1276(1)	33(1)	C(60)	8131(6)	7725(4)	1079(2)	41(3)
Cr(3)	3502(2)	4785(1)	2893(1)	31(1)	C(61)	8074(6)	7040(3)	1217(3)	30(3)
O(10)	975(7)	7470(4)	1611(3)	43(2)	C(62)	6264(6)	6701(4)	–369(3)	34(3)
O(11)	3253(8)	6420(4)	3914(4)	52(3)	C(63)	5288(6)	6915(4)	–705(2)	52(4)
O(12)	289(7)	5909(5)	2626(4)	57(3)	C(64)	4503(5)	7185(4)	–457(3)	55(4)
O(13)	863(8)	7971(5)	3339(4)	62(3)	C(65)	4696(6)	7242(4)	126(3)	51(4)
O(14)	3988(8)	7864(5)	2749(4)	60(3)	C(66)	5672(6)	7028(4)	462(2)	44(3)
O(20)	2965(9)	6033(6)	23(4)	89(4)	C(67)	6456(5)	6757(4)	214(3)	30(3)
O(21)	3190(8)	7579(5)	1303(4)	58(3)	C(68)	6402(5)	5344(4)	854(3)	41(3)
O(22)	3335(8)	4493(5)	1207(4)	55(3)	C(69)	6246(5)	4708(4)	1074(3)	46(3)
O(23)	795(7)	5879(4)	1233(3)	45(2)	C(70)	7121(7)	4336(3)	1371(3)	49(4)
O(24)	5569(8)	6125(5)	1806(4)	70(3)	C(71)	8153(5)	4601(4)	1448(3)	48(4)
O(30)	4143(9)	3348(5)	3487(4)	68(3)	C(72)	8309(5)	5238(4)	1228(3)	32(3)
O(31)	5136(8)	5654(5)	3668(4)	69(3)	C(73)	7434(6)	5610(3)	931(3)	31(3)
O(32)	1831(7)	5054(4)	3570(4)	46(2)	P(2)	8271(2)	5953(2)	4113(1)	27(1)
O(33)	1591(8)	4338(4)	1979(4)	54(3)	C(75)	9237(5)	5086(3)	3488(3)	30(3)
O(34)	5186(8)	4517(6)	2219(4)	64(3)	C(76)	9247(5)	4544(4)	3122(3)	42(3)
C(11)	2785(10)	6619(6)	3484(5)	34(3)	C(77)	8345(6)	4131(3)	2956(3)	39(3)
C(12)	971(11)	6313(7)	2704(5)	38(3)	C(78)	7433(5)	4260(3)	3157(3)	39(3)
C(13)	1354(11)	7611(7)	3127(5)	45(3)	C(79)	7423(5)	4803(4)	3524(3)	37(3)
C(14)	3271(11)	7522(6)	2764(5)	37(3)	C(80)	8325(6)	5215(3)	3689(3)	30(3)
C(20)	3079(11)	6045(7)	509(6)	51(4)	C(81)	6977(6)	6588(3)	3194(3)	37(3)
C(21)	3144(11)	7003(7)	1300(5)	41(3)	C(82)	6513(5)	7152(4)	2885(3)	41(3)
C(22)	3275(10)	5081(7)	1241(5)	34(3)	C(83)	6856(6)	7806(3)	3062(3)	49(4)
C(23)	1684(11)	5947(6)	1230(4)	34(3)	C(84)	7662(6)	7896(3)	3549(3)	46(3)
C(24)	4670(11)	6082(7)	1593(5)	47(4)	C(85)	8125(5)	7332(4)	3858(3)	34(3)
C(30)	3885(11)	3965(8)	3263(5)	50(4)	C(86)	7782(6)	6678(3)	3680(3)	27(3)
C(31)	4505(10)	5311(6)	3379(5)	39(3)	C(87)	10361(6)	6441(4)	4291(2)	43(3)
C(32)	2478(11)	4954(6)	3325(5)	35(3)	C(88)	11344(6)	6644(4)	4625(3)	50(4)
C(33)	2335(11)	4498(6)	2320(5)	37(3)	C(89)	11537(5)	6591(4)	5208(3)	55(4)
C(34)	4515(11)	4615(6)	2451(5)	43(3)	C(90)	10745(6)	6334(4)	5457(2)	44(3)
P(1)	7673(3)	6434(2)	660(1)	28(1)	C(91)	9762(5)	6131(4)	5123(3)	33(3)
C(50)	9482(6)	6819(3)	286(3)	35(3)	C(92)	9569(5)	6184(4)	4540(3)	30(3)
C(51)	10228(5)	6733(3)	41(3)	40(3)	C(93)	6716(6)	6267(3)	4690(3)	32(3)
C(52)	10165(5)	6166(4)	–391(3)	40(3)	C(94)	6061(5)	6126(3)	5058(3)	40(3)
C(53)	9356(6)	5686(3)	–413(3)	38(3)	C(95)	6099(6)	5488(4)	5311(3)	41(3)
C(54)	8611(5)	5772(3)	–85(3)	34(3)	C(96)	6793(6)	4990(3)	5196(3)	40(3)
C(55)	8673(5)	6339(4)	265(3)	26(3)	C(97)	7449(5)	5131(3)	4829(3)	33(3)
C(56)	8352(6)	6836(3)	1779(3)	34(3)	C(98)	7410(5)	5769(3)	4576(3)	29(3)
C(57)	8688(6)	7318(4)	2202(2)	47(4)					

^a U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

2.4. Electrochemistry

As a two electron oxidation product of **1**, a stable compound with a metal–metal bond formed between two $[(\text{CO})_5\text{M}]$ groups might be expected. This type of compound is known for quite a number of isoelectronic species [26], and as a direct analogue of the potential two electron oxidation product of **1** $[\{\text{W}_2(\text{CO})_{10}\}\text{Sn}=\text{W}(\text{CO})_5]$ has been characterized ([11]c). While a two electron reduction of $[\{\text{W}_2(\text{CO})_{10}\}\text{Sn}=\text{W}(\text{CO})_5]$, which should give the isoelectronic analogue of **1**, has not yet been probed, it has been found that $[\{\text{W}_2(\text{CO})_{10}\}\text{Sn}=\text{W}(\text{CO})_5]$ has a rather Lewis acidic tin center which

eagerly coordinates THF as a two electron donor ligand [27]. Preparative oxidation of **1** to produce the chromium analogue of $[\{\text{W}_2(\text{CO})_{10}\}\text{Sn}=\text{W}(\text{CO})_5]$ has not yet been successful. Cyclovoltammetry shows, however, that **1** in the form of its $[\text{Ph}_4\text{P}]$ salt is easily oxidized with the anodic peak occurring at -0.07 V versus SCE in THF. As expected, if electrons are taken out from the nonbonding e-set of the 4-center, 6π -system (Fig. 3), oxidation is irreversible with the partially occupied e-set leading to a severe distortion of the framework such that the two electron oxidation product should have a structure similar to the one observed for $[\{\text{W}_2(\text{CO})_{10}\}\text{Sn}=\text{W}(\text{CO})_5]$ ([11]c).

Table 2
Selected bond lengths (pm), angles (°), and torsion angles (°) for complex **1**^a

Sn1–Cr1	267.0 (2)
Sn1–Cr2	265.9 (2)
Sn1–Cr3	266.6 (2)
Cr–C _{CO} (ap)	185 (1)–186 (1)
Cr–C _{CO} (a)	187 (1)–191 (1)
Cr–C _{CO} (b)	185 (1)–190 (1)
C _{CO} (ap)–O _{CO} (ap)	114 (1)–116 (1)
C _{CO} (a)–O _{CO} (a)	113 (1)–116 (1)
C _{CO} (b)–O _{CO} (b)	114 (1)–116 (1)
Sn···C _{CO} (a)	314–329
Sn···C _{CO} (b)	285–321
Cr1–Sn1–Cr2	120.01 (6)
Cr1–Sn1–Cr3	120.90 (6)
Cr2–Sn1–Cr3	118.19 (6)
Sn–Cr–C _{CO} (ap)	172.1 (4)–177.9 (4)
Sn–Cr–C _{CO} (a)	85.5 (4)–91.1 (4)
Sn–Cr–C _{CO} (b)	75.5 (4)–87.8 (4)
Cr–C _{CO} (ap)–O _{CO} (ap)	175 (1)–178 (1)
Cr–C _{CO} (a)–O _{CO} (a)	175 (1)–179 (1)
Cr–C _{CO} (b)–O _{CO} (b)	176 (1)–179 (1)
C _{CO} (ap)–Cr–C _{CO} (a)	87.6 (6)–93.2 (5)
C _{CO} (ap)–Cr–C _{CO} (b)	94.6 (6)–103.4 (6)
C _{CO} (a)–Cr–C _{CO} (b)	86.1 (5)–93.6 (6)
C _{CO} (a)–Cr–C _{CO} (a)	175.6 (5)–179.3 (5)
C _{CO} (b)–Cr–C _{CO} (b)	159.9 (5)–168.8 (5)
Cr–Sn–Cr–C _{CO} (a) ^b	27.2–31.3
	148.0–155.8
Cr–Sn–Cr–C _{CO} (b) ^b	62.1–71.3
	103.7–116.8

^a Estimated S.D. in units of the least significant figures given in each case are quoted in parentheses. ^b Absolute values.

2.5. NMR spectroscopy

¹³C-NMR: Two ¹³C-NMR resonances for the carbonyl groups are observed for **1**. The apical carbonyl groups (**ap** in Fig. 1) give rise to a signal at $\delta = 239.8$. For the equatorial CO groups (**a** and **b** in Fig. 1), just one signal is observed at $\delta = 225.2$. The shift difference between the ¹³C-NMR CO signals of the apical (**ap**) and equatorial carbonyl groups (**a** and **b**) is larger than usually observed for compounds containing [(CO)₅Cr]

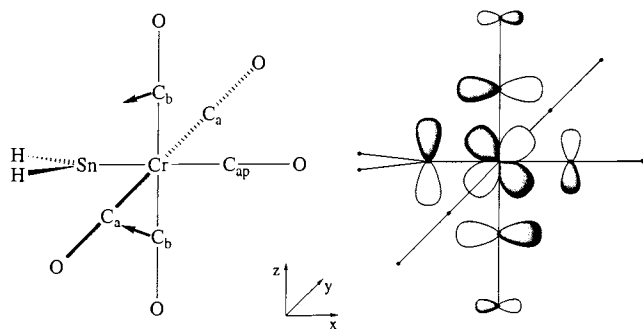


Fig. 2. EHT results on the π -bonding orbital in [(CO)₅Cr]SnH₂. Bending of the 'axial' CO groups (**b**) as indicated will stabilize the molecule.

fragments ([12]b, [15]). The observation of only one signal for the equatorial carbonyl groups means that at 25°C, i.e. at the temperature at which the spectrum was recorded, the [(CO)₅Cr] groups are free to rotate around the Sn–Cr-axes. In the solid state structure of **1** two sets of chemically different equatorial carbonyl groups are observed (**a** and **b**, respectively) on the other hand. With respect to the distinctly different Sn–Cr–C_{CO} angles (Fig. 1, Table 2) with the π^* -orbitals of the 'out-of-plane' carbonyl groups (**b**) interacting with the 'out-of-plane' p_z-orbital of the tin center (Fig. 2) it has been argued that this type of Sn–CO back-bonding stabilizes the compound (vide supra). It is clear, however, that this additional stabilization is independent of the rotational position of the [(CO)₅Cr] fragment. Overlap lost with one of the carbonyl carbon atoms during rotation will be compensated by an increase in overlap with another carbonyl group. Rotation should then be accompanied by alternately forward and backward bending of the CO groups. Taken together, rotation of the [(CO)₅Cr] groups around the Cr–Sn-axes would not be impeded by electronic reasons, but might well be slowed down by the steric repulsion between the three of these groups in **1**. At 25°C rotation is still free.

¹¹⁹Sn-NMR: With the 4-center, 6 π -system characterizing the bonding situation in **1** and with the empty π^* -orbital of the system at low energy and the occupied orbitals at rather high energy a large paramagnetic contribution to the chemical shift of the tin center in **1** is expected. The corresponding ¹¹⁹Sn-NMR resonance is in fact found at $\delta = 3924$ well beyond the low-field limit observed in ¹¹⁹Sn-NMR spectroscopy so far [9]. The simplified model of describing compounds like **1** as 4-center, 6 π -systems thus has quite some predictive power.

3. Experimental

All manipulations were carried out under an argon atmosphere by means of standard Schlenk techniques at 25°C. All solvents were dried by standard methods and distilled under argon. [D₆]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) used for chromatography and Kieselgur (Kieselgur, gereinigt, geglüht, 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 (¹³C{¹H}), 74.631 MHz (¹¹⁹Sn{¹H}), 81.015 MHz (³¹P{¹H}); chemical shifts (δ) in ppm with respect to [D₆]acetone (¹H: $\delta = 2.04$, ¹³C: $\delta = 29.8$) as internal standards; chemical

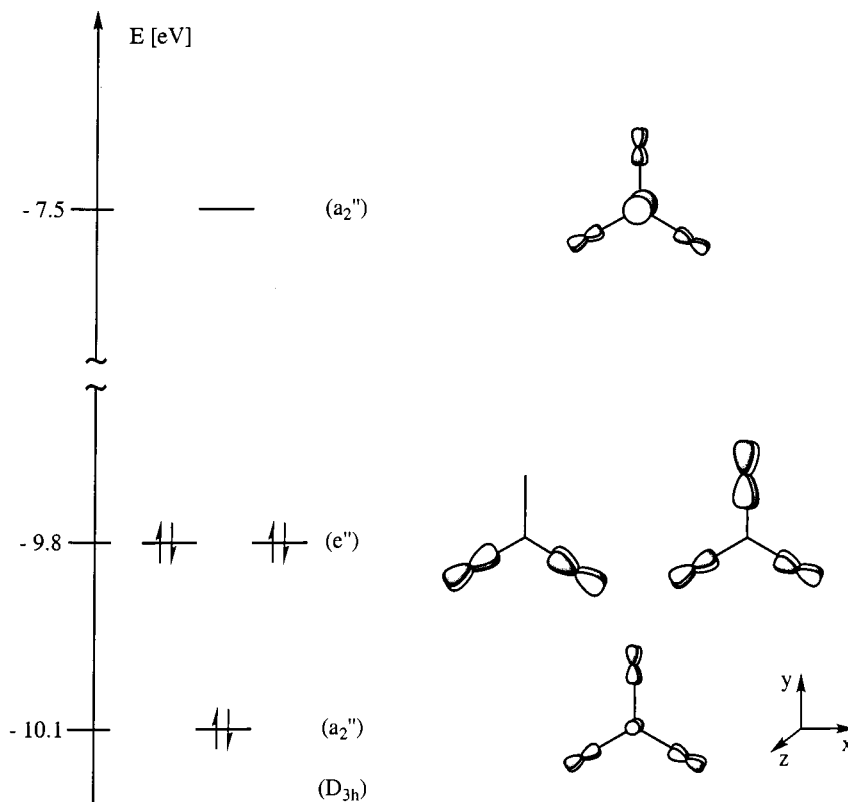


Fig. 3. π -orbitals and EHT energies of **1**.

shifts (δ) in ppm with respect to SnMe_4 (^{119}Sn : $\delta = 0$, at 25°C) and to 85% H_3PO_4 (^{31}P : $\delta = 0$) 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 (neg.-FAB): Finnigan MAT 8400; TEA (triethanolamine) matrix. Melting point: Galenkamp MFB-595 010; the m.p. is not corrected. Cyclic voltammetry: Metrohm 'Universal Meß- und Titriergefäß', Metrohm GC electrode RDE 628, platinum electrode, SCE electrode, Princeton Applied Research potentiostat Model 273, 10^{-3} M in 0.1 M $^t\text{Bu}_4\text{NPF}_6/\text{THF}$. The dinuclear sodium salt $\text{Na}_2[\{(\text{CO})_5\text{Cr}\}_2\text{SnCl}_2]$ was prepared by salt metathesis from the corresponding stable phosphonium salt $[\text{Ph}_4\text{P}]_2[\{(\text{CO})_5\text{Cr}\}_2\text{SnCl}_2]$ as described ([12]b). The metallates $\text{Na}_2[\text{Cr}_2(\text{CO})_{10}]$ [28] and $\text{K}_2[\text{Cr}(\text{CO})_5]$ ([12]a, [29]) were prepared as reported. SnCl_2 as commercially available was dehydrated by acetic anhydride [30]. All other chemicals were commercially obtained and used without further purification.

3.1. Preparation of $[\text{Ph}_4\text{P}]_2[\{(\text{CO})_5\text{Cr}\}_3\text{Sn}]$, $[\text{Ph}_4\text{P}]_2 \cdot \mathbf{1}$

3.1.1. Method A

To a stirred, orange solution of $\text{Na}_2[\text{Cr}_2(\text{CO})_{10}]$ (430 mg; 1 mmol) in THF (50 ml) solid SnCl_2 (95 mg; 0.5 mmol) was added in one portion. The solution turned deep red immediately. After stirring for 15 min, solid

$[\text{Ph}_4\text{P}]\text{Cl}$ (750 mg; 2 mmol) was added and the heterogeneous mixture was stirred for another 2 h and finally immersed in an ultrasonic bath for 15 min. After filtration through Kieselgur (3 cm) and removing the solvent in vacuo, the oily, black residue was washed with ethanol (5×30 ml) and diethylether (5×10 ml) leaving $[\text{Ph}_4\text{P}]_2 \cdot \mathbf{1}$ as a black-red microcrystalline powder. Yield: 480 mg (70%).

For further purification, $[\text{Ph}_4\text{P}]_2 \cdot \mathbf{1}$ was dissolved in THF (5 ml) and chromatographed on silica gel (20 cm; $\varnothing = 3$ cm; THF). Elution with THF gave two bands. The first, yellow band was identified by IR spectroscopic comparison and found to consist of $[\text{Cr}(\text{CO})_6]$ [31]. The second, brown band contained $[\text{Ph}_4\text{P}]_2 \cdot \mathbf{1}$. This THF fraction was concentrated to 5 ml and overlaid with ethanol (100 ml). After 7 days, single crystals of $[\text{Ph}_4\text{P}]_2 \cdot \mathbf{1}$ suitable for X-ray structure analysis were obtained. Crystalline yield: 100 mg (14%).

$[\text{Ph}_4\text{P}]_2 \cdot \mathbf{1}$: $^1\text{H-NMR}$ ($[\text{D}_6]$ acetone): δ 7.90–7.86 (m, H_{arom}). $^{13}\text{C-NMR}$ ($[\text{D}_6]$ acetone): δ 239.8 (s, C_{ap}), 225.2 (s, $\text{C}_{\text{a,b}}$), 136.2 (d, C_{para} , $^4J(^{31}\text{P}, ^{13}\text{C}) = 3$ Hz), 135.5 (d, C_{ortho} , $^2J(^{31}\text{P}, ^{13}\text{C}) = 9$ Hz), 131.2 (d, C_{meta} , $^3J(^{31}\text{P}, ^{13}\text{C}) = 13$ Hz), 118.8 (d, C_{ipso} , $^1J(^{31}\text{P}, ^{13}\text{C}) = 90$ Hz). $^{119}\text{Sn-NMR}$ ($[\text{D}_6]$ acetone, 25°C): δ 3924. $^{31}\text{P-NMR}$ ($[\text{D}_6]$ acetone): δ 24.3 ($^1J(^{13}\text{C}, ^{31}\text{P}) = 90$ Hz). IR (THF): $\tilde{\nu}_{\text{CO}} = 2053$ vw, 1990 sh, 1983 s, 1932 sh, 1909 vs, 1862 s, br cm^{-1} . M.p. 178°C (dec.). UV/Vis (THF): 423 nm ($\epsilon = 1100$ $\text{l mol}^{-1} \text{cm}^{-1}$). CV (THF/ versus SCE): Oxi-

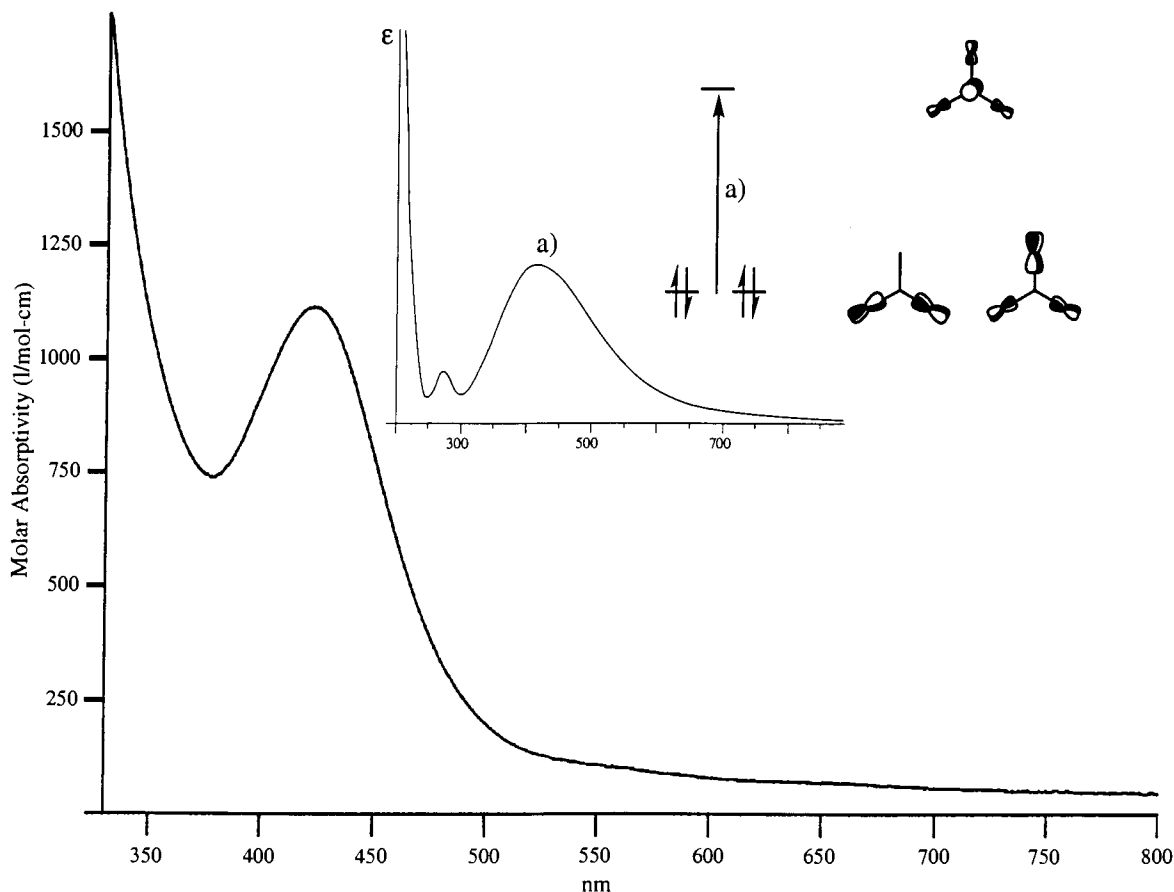


Fig. 4. UV/Vis spectrum of $[\text{Ph}_4\text{P}]_2 \cdot \mathbf{1}$ in THF. Insert: calculated UV/Vis spectrum for the model compound $[\{(\text{CO})_5\text{Cr}\}_3\text{P}]^-$ and orbital assignment.

dation -0.07 V (irrev.); reduction -1.76 V (irrev.). MS (neg. FAB, TEA), m/e (%): 605 (40) $[\{(\text{CO})_5\text{Cr}\}_2\text{Sn} \cdot \text{N}(\text{C}_2\text{H}_4\text{O})_2]^-$, 458 (100) $[\{(\text{CO})_5\text{Cr}\}_3\text{Sn} \cdot \text{TEA} - 2\text{H}]^-$, 402 (100) $[\{(\text{CO})_3\text{Cr}\}_3\text{Sn} \cdot \text{TEA} - 2\text{H}]^-$.

3.1.2. Method B

Solid SnCl_2 (63 mg; 0.33 mmol) was added to a greenish solution of $\text{K}_2[\text{Cr}(\text{CO})_5]$ (270 mg; 1 mmol) in THF (50 ml). The solution turned black-red immediately. After addition of solid $[\text{Ph}_4\text{P}]\text{Cl}$ (750 mg; 2 mmol) the reaction mixture was stirred for 2 h. After waiting for 1 h without stirring, the solution was carefully decanted from the solid and filtered through Kieselgur (3 m). The further workup was performed as described in Section 3.1.1. Yield: 380 mg (83%).

3.1.3. Method C

To a stirred, orange solution of $\text{Na}_2[\text{Cr}_2(\text{CO})_{10}]$ (215 mg; 0.5 mmol) in THF (30 ml) a solution of $\text{Na}_2[\{(\text{CO})_5\text{Cr}\}_2\text{SnCl}_2]$ (310 mg; 0.5 mmol) in THF (20 ml) was added. Again the solution turned black-red immediately. After stirring for 15 min, the workup procedure as described in Section 3.1.1 was started by addition of solid $[\text{Ph}_4\text{P}]\text{Cl}$ (375 mg; 1 mmol). Yield: 515 mg (75%).

3.2. X-ray structure determination

The measurement for $[\text{Ph}_4\text{P}]_2 \cdot \mathbf{1}$ was carried out on a Siemens P4 four circle diffractometer with graphite-monochromated Mo-K α radiation ($\lambda = 0.71073$ Å). The intensities of three check reflections (measured every 100 reflections) remained constant throughout the data collection, thus indicating crystal and electronic stability.

Formula $\text{C}_{63}\text{H}_{40}\text{Cr}_3\text{O}_{15}\text{P}_2\text{Sn}$; $M = 1373.580$ g; $0.25 \times 0.25 \times 0.10$ mm; monoclinic; space group $P2_1/c$ (No. 14); $a = 1279.7(3)$, $b = 1958.1(4)$, $c = 2438.0(5)$ pm; $\beta = 103.42(2)^\circ$; $V = 5942(2) \cdot 10^3$ pm 3 ; $Z = 4$; $\rho_{\text{calc}} = 1.535$ g cm $^{-3}$; $\mu = 10.71$ cm $^{-1}$; $T = 200$ K; 40 reflections for cell parameter refinement; scan range $4.0^\circ < 2\theta < 48.0^\circ$; scan speed $\dot{\omega} = 10^\circ$ min $^{-1}$; 9790 reflections collected; 9324 independent and 4744 observed reflections ($I \geq 2\sigma$); 422 refined parameters; $R = 0.079$; $R_w = 0.195$ (refinement on F^2); max. residual electron density 0.85 (-0.78) $\cdot 10^{-6}$ e pm $^{-3}$.

All calculations were performed using the SHELXT PLUS software package. The structure was solved by direct methods with the SHELXS-86 program and refined with the SHELX-93 program [32]. The program

XPMA [33] was used for graphical handling of the data. Absorption corrections (ψ scan, $\Delta\psi = 10^\circ$) were applied to the data. The structure was refined in fully anisotropic models by full-matrix least-squares calculations. Hydrogen atoms were introduced at calculated positions. Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany, on quoting the depository number CSD-408312 ([Ph₄P]₂⁻1).

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