Organometallic Selenolates, 8[◇]

The Reaction of Potassium Polyselenides with [CpW(CO)$_3$Cl] in DMF Formation and Crystal Structure of [CpW(CO)$_3$SeC(O)NMe$_2$] and {[CpW(CO)$_3$]$_2$Se$_4$}

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The reactions of the potassium polyselenides "K_2Se_6" and "K_2Se_8" with [CpW(CO)$_3$Cl] and 18-crown-6 in DMF lead to a mixture of the selenido complexes {[CpW(CO)$_3$]$_2$Se$_4$} **1** and [(18-crown-6)K]$^+$[CpW(Se$_4$)$_2$]$^-$ **3** and the Se−bonded selenocarbamato complex [CpW(CO)$_3$SeC(O)NMe$_2$] **2** in yields depending on the selenium content of the used potassium polyselenides ("K_2Se_6" or "K_2Se_8"). A similar reaction in THF produces {[CpW(CO)$_3$]$_2$Se$_4$} as the main product. X-ray structures of **1** and **2** were determined. In **1** the Se$_4$-chain is bonded in a μ^2-η^1 fashion, with corresponding W−Se bond lengths of 264.0(1) and 264.3(1) pm. The Se−Se bond lengths lie in the range 232 to 237 pm. The first example of an η^1 Se-bonded selenocarbamato ligand is observed in the crystal structure of **2**, with a W−Se bond length of 263.1(1) pm. The ^{77}Se-NMR data are compared with the corresponding data of related complexes.

The synthesis of oligoselenido complexes via reactions of alkali-metal polyselenides with appropriate transition metal complexes is widely applicable and the resulting oligoselenido complexes are of particular interest because of their potential use as solid state precursors and the versatile binding modes of Se_n^{2-} [1]. However, the synthesis of organoselenolato complexes using the same route is restricted to accessible organic selenolates or diselenides[2]. For this reason, there is still a need for new synthetic methods that can avoid this difficulty. Recently, we described the formation of organometallic selenolates via selenium insertion into the alkali-metal−transition-metal bonds of appropriate carbonylates such as MM′Cp(CO)$_3$ (M = Li, Na, K; M′ = Mo, W) and MMn(CO)$_5$[3]. The resulting selenolates react with a variety of organic electrophiles to form the corresponding organoselenolato complexes, whereas oxidation with O_2 in the presence of SiO_2 leads to oligoselenido complexes[4]. Here we report on the reaction of the potassium polyselenides "K_2Se_6" and "K_2Se_8" with CpW(CO)$_3$Cl in DMF, producing the organoselenolato complex [CpW(CO)$_3$SeC(O)NMe$_2$] and the tetraselenido complexes {[CpW(CO)$_3$]$_2$Se$_4$} and [(18-crown-6)K]$^+$[CpW(Se$_4$)$_2$]$^-$.

Results and Discussion

Potassium polyselenides can be easily prepared by reducing elemental selenium with KBEt$_3$H in DMF at 150°. The resulting nearly black solutions contain formally "K_2Se_6" or "K_2Se_8", if an appropriate Se/KBEt$_3$H ratio is used[5]. The exact composition of such polyselenides is very difficult to predict, since complicated equilibria can be observed in solution[6]. Thus a reaction of such polyselenides with metal halide complexes can lead to various products depending on the metal center, the solvent and the temperature.

When [CpW(CO)$_3$Cl] is stirred overnight with a DMF solution of "K_2Se_6" in the presence of 18-crown-6, three products can be separated: {[CpW(CO)$_3$]$_2$Se$_4$} **1** (10%), [CpW(CO)$_3$SeC(O)NMe$_2$] **2** (40%), and the salt [(18-crown-6)K]$^+$[CpW(Se$_4$)$_2$]$^-$ **3** (9%).

The reaction mechanism is not clear, since the formyl group of DMF must be deprotonated in the initial step of the formation of **2**. A few reports concerning the synthesis of η^1-bonded selenocarbamato complexes have been published in which [Me$_2$NH$_2$][SeC(O)NMe$_2$] or CSe_2 in the presence of Me$_2$NH are required as the starting materials[7]. However, these alternative routes are not widely applicable and can lead also to the chelated η^2-derivatives.

If "K_2Se_8" is employed instead of "K_2Se_6", **3** is the main product and only traces of **1** and **2** are produced. The reason for this difference seems to be the high stability of $M(Se_4)_n^{2-}$ complexes (M = Zn, Cd, Hg, Ag, Au, Mo, W, Pd, Rh, Ir, Ru, Ni, Pt, Mn) that contain five-membered MSe_4 rings[8]. However, if THF is used as the solvent in the reaction of "K_2Se_6" with [CpW(CO)$_3$Cl], **1** is formed as the main separable product (35%) together with some decomposition products. A more straightforward synthesis of **1** has been developed recently in our laboratory. It comprises the insertion of three seleniums into the Li−W bond of LiWCp(CO)$_3$ and subsequent oxidation with O_2 in the presence of SiO_2[4].

[◇] Part 7: Ref.[1]

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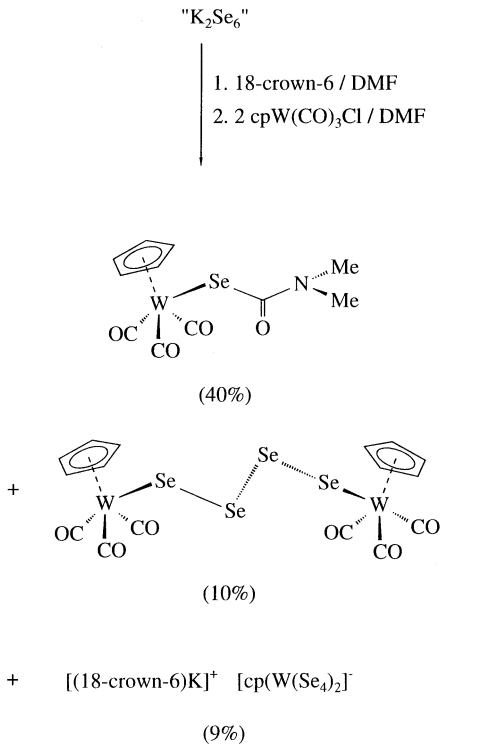
Scheme 1. The reaction of "K_2Se_6" with $[CpW(CO)_3Cl]$ and 18-crown-6 in DMF



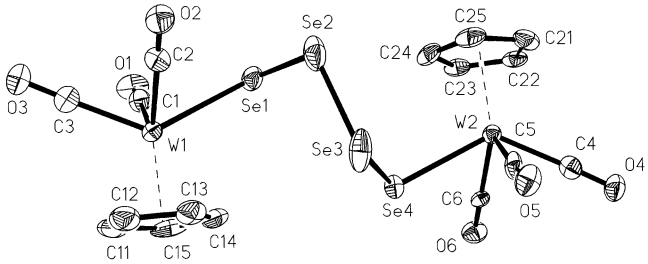
The ^{77}Se-NMR data of **1**, **2**, and **3** are consistent with their structures and comparable with related complexes. The ^{77}Se-NMR spectrum of **1** has been already described and seems to be typical of oligoselenido complexes with μ^2-η^1 bonded selenium chains in which the metal-bonded selenium atom is usually shifted highfield[4]. The chemical shifts in the ^{77}Se-NMR spectra are strongly influenced by electronic and steric effects and cannot always be interpreted by simple means. Thus, the spectrum of **3** shows a completely different pattern. The metal-bonded selenium atoms are deshielded; ^{183}W satellites and a corresponding ^{77}Se-^{183}W coupling constant of 80 Hz are observed. There are only few reported $^1J(^{77}Se\text{-}^{183}W)$ coupling constants and the values range from 35 Hz in $[CpW(CO)_3SeC(O)Ph]$[9] to 112 Hz in the $W_3Se_9^{2-}$ anion[8b]. Recently the cp* derivative $[(\sigma\text{-}C_5Me_5)(CO)_5WSeMe]$ has been published with a $^1J(^{77}Se\text{-}^{183}W)$ value of 49 Hz[10]. Unfortunately, for **2**, no ^{183}W satellites could be observed because of the broadness of the signal, but the chemical shift of −136.1 ppm is in good accordance with the data of related complexes[3a][3b][3c][3d][3e][3f].

Crystal Structures of $\{[CpW(CO)_3]_2Se_4\}$ (1) and $[CpW(CO)_3SeC(O)NMe_2]$ (2)

The crystal structure of **1** is presented in Figure 1. It consists of two $cpW(CO)_3$ moieties, which are bridged by an Se_4 chain in a μ^2-η^1 fashion. This structural motif is rare and the only reported examples are $[Cp_2Hf(\mu\text{-}O)(\mu\text{-}Se_4)HfCp_2]$ and $[Au_2(\mu\text{-}Se_2)(\mu\text{-}Se_4)]^-$[11].The conformation of the Se_4 group in **1** can be described by its torsion angles [W1−Se1−Se2−Se3: 75.51(6)°; Se1−Se2−Se3−Se4: 51.81(7)°, Se2−Se3−Se4−W2: 78.70(6)°] as a helical chain with corresponding bond angles at selenium ranging from 104.53(6) to 110.69(5)°. In the triselenido complex $\{[CpW(CO)_3]_2Se_3\}$, comparable absolute values of the torsion angles were observed [W1−Se1−Se3−Se2: 83.12(7)°; Se1−Se3−Se2−W2: 88.31(7)°][4]. The W−Se bond lengths, W1−Se1 263.99(11) pm and W2−Se4 264.29(10) pm, are comparable with the W−Se bond lengths in $\{[CpW(CO)_3]_2Se_3\}$ (263.2(1), 265.1(1) pm). Similar bond lengths were also found in a series of organoselenolato tungsten complexes and they are attributable to W−Se single bonds (vide infra). The W-bonded Se_2 moieties display Se−Se bond lengths of 232.1(2) and 232.2(2) pm, whereas the central Se−Se bond Se2−Se3 [236.7(2) pm] is 4.5 pm longer, indicating that this bond should display a more pronounced reactivity.

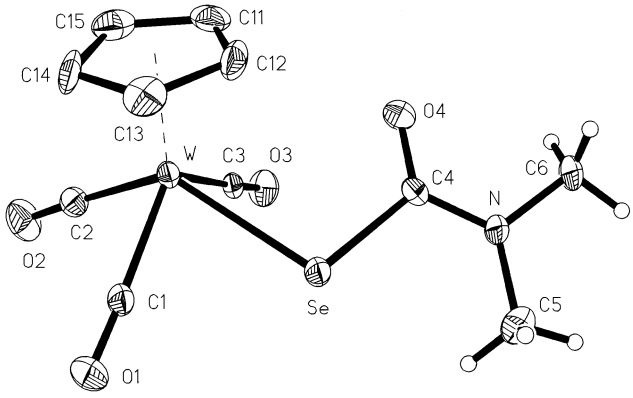
The crystal structure of **2** is presented in Figure 2. The atoms W, C4, O4, N, C5, and C6 are approximately coplanar (mean deviation 1.3 pm); the selenium atom lies 20

Figure 1. Molecular structure of $\{[CpW(CO)_3]_2Se_4\}$ (**1**) (50% probability ellipsoids, H atoms omitted for clarity)[a]



[a] Selected bond lengths [pm] and angles [°]: W1−Cp (ring center) 201.0, W1−Se1 263.99(11), Se1−Se2 232.1(2), Se2−Se3 236.7(2), Se3−Se4 232.2(2), Se4−W2 264.29(10), W2−Cp (ring center) 200.6; C1−W1−Se1 75.1(3), C2−W1−Se1 75.9(3), C3−W1−Se1 130.2(3), W1−Se1−Se2 110.69(5), Se1−Se2−Se3 104.53(6), Se2−Se3−Se4 105.49(6), Se3−Se4−W2 109.65(5), C4−W2−Se4 129.3(3), C5−W2−Se4 75.3(2), C6−W2−Se4 74.7(3).

Figure 2. Molecular structure of $[CpW(CO)_3SeC(O)NMe_2]$ (**2**) (50% probability ellipsoids, cp hydrogens omitted for clarity)[a]



[a] Selected bond lengths [pm] and angles [°]: W−Cp (ring center) 200.6, W−Se 263.08(8), Se−C4 196.1(6), C4−N 133.6(8), N−C5 146.3(8), N−C6 146.7(8); C1−W−Se 74.3(2), C2−W−Se 129.4(2), C3−W−Se 75.6(2), W−Se−C4 103.8(2), Se−C4−N 114.5(4), O4−C4−N 123.8(6), Se−C4−O4 121.7(5), C4−N−C5 124.4(5), C4−N−C6 118.0(5), C5−N−C6 117.3(5).

pm out of this plane. The W−Se bond length of 263.08(8) pm is comparable with other W−Se bond lengths in organoselenolato tungsten complexes with terminal selenolato ligands {e.g. 258.8(2) pm in $[(\eta^7\text{-}C_7H_7)(CO)_2WSePh]$[12]; 263(2) pm in $[CpW(CO)_3SeCH_2CHCH_2]$[3d] and 262.3(1) pm in $[CpW(CO)_3SeCH_2Ph]$[3a]}, whereas complexes with bridging selenolato groups display considerably shorter W−Se bond lengths {e.g. 251.3(5) pm in $[W_2Cl_4(\mu\text{-}SePh)(\mu\text{-}Cl)(dppm)_2]$[13] and 254.9(1) pm in $[PPh_4]_2[Cl_3W(\mu\text{-}SeCl)(\mu\text{-}SePh)_2WCl_3]$[14]}. The selenium atom displays a slightly distorted tetrahedral angle of 103.8(2)°.

Experimental Section

All manipulations were carried out under a dry nitrogen atmosphere using conventional Schlenk techniques. − NMR: Bruker AC 200 (^{1}H 200 MHz, ^{13}C 50.3 MHz, ^{77}Se 38.2 MHz). The spectra were recorded using $CDCl_3$ or C_6D_6 as solvents. Standards: ^{1}H, ^{13}C TMS internal; ^{77}Se Me_2Se external. − IR: Biorad FTS 165. − MS: Finnigan MAT 8430. − *N,N*-Dimethylformamide (DMF) was distilled under nitrogen prior to use. Tetrahydrofuran (THF) was dried over sodium in nitrogen atmosphere. $KBEt_3H$ (1 M in THF), Se, and 18-crown-6 were purchased from Aldrich and used as received. $[CpW(CO)_3Cl]$ was prepared according to the literature method[15].

Reaction of "K_2Se_6"/18-Crown-6 with $[CpW(CO)_3Cl]$ in DMF: 2.7 ml of a solution of $KBEt_3H$ (1 M in THF, 2.7 mmol) were added to 20 ml of DMF. After 10 min of stirring, 0.64 g of Se (8.1 mmol) were added, and the mixture was refluxed for 2 h. After cooling to room temperature, 0.71 g of 18-crown-6 (2.7 mmol) were added to the deep green solution, which was then combined with a solution of 1 g of $[CpW(CO)_3Cl]$ in 20 ml of DMF over a period of 10 min via a syringe. Stirring for 18 h afforded a dark green reaction mixture, which was evaporated to dryness. The residue was extracted three times with 50-ml portions of diethyl ether, leaving a black residue. The work-up procedure of the red organic extract comprised removal of the solvent in vacuo and column chromatography (SiO_2, 20 × 4 cm, CH_2Cl_2/acetone, 95:5, as eluent). The first red band was characterized as $\{[CpW(CO)_3]_2Se_4\}$ **1**[4]. The second orange band corresponds to $[CpW(CO)_3SeC(O)NMe_2]$ **2**. The black precipitate was treated with 10 ml of CH_2Cl_2/acetone, 9:1. The crude mixture was then filtered and column chromatography in the same solvent mixture (SiO_2, 20 × 4 cm) afforded $[(18\text{-crown-}6)K]^+[CpW(Se_4)_2]^-$ **3** in the deep green band accompanied by a small amount of immobile brown impurities.

1: Yield 0.122 g (10%), m.p. 126°C. The spectroscopic data were consistent with those previously described[4].

2: Yield: 0.520 g (40%), m.p. 138°C. − ^{1}H NMR (C_6D_6): δ = 2.65 (s, 3 H, CH_3), 2.87 (s, 3 H, CH_3), 4.9 (s, 5 H, C_5H_5). − ^{13}C NMR (C_6D_6) δ = 36.4 (s, CH_3), 39.8 (s, CH_3), 93.1 (s, C_5H_5), 164.8 (s, μ-CO), 213.9, 226.2 (s, CO). − ^{77}Se NMR (C_6D_6): δ = −136.1 (s). − IR (CH_2Cl_2): $\tilde{\nu}$ = 2029, 1951, 1925 (CO), 1626 (μ−CO). − MS (70 ev); *m/z* (%): 457 (88) [M^+ − CO], 429 (43) [M^+ − 2 CO], 401 (100) [M^+ − 3 CO]. − $C_{11}H_{11}NO_4SeW$ (484.0): calcd. C 27.30, H 2.29, N 2.89; found C 27.31, H 2.38, N 2.84.

3: Yield: 0.140 g (9% on Se), m.p. 153°C. − ^{1}H NMR ($CDCl_3$): δ = 3.47 (s, 24 H, CH_2), 5.02 (s, 5 H, C_5H_5). − ^{13}C NMR ($CDCl_3$): δ = 70.1 (s, CH_2), 94.6 (s, C_5H_5). − ^{77}Se NMR ($CDCl_3$): δ = 486.1 (s, Se-*Se*-*Se*-Se), 866.3 [s, ^{183}W satellites, $J(^{77}Se\text{-}^{183}W)$ 80 Hz, W-*Se*). − MS (70 ev); *m/z* (%): 303 (100) [M^+]. − $C_{17}H_{29}KO_6Se_8W$ (1184.0): calcd. C 17.25, H 2.47; found C 17.41, H 2.46.

Reaction of "K_2Se_6"/18-Crown-6 with $[CpW(CO)_3Cl]$ in THF: A similar reaction in THF employing the same quantities of Se, 18-crown-6, and $[CpW(CO)_3Cl]$ led to the formation of **1** as the main product in 40% yield, together with insoluble inorganic tungsten selenides.

Reaction of "K_2Se_8"/18-Crown-6 with $[CpW(CO)_3Cl]$ in DMF: The reaction was performed as described above using 0.85 g of Se (10.8 mmol). After evaporating to dryness, the black residue was washed three times with 25 ml portions of diethyl ether. In contrast to the reaction with "K_2Se_6", the organic extract contained only traces of **1** and **2**. The remaining black precipitate was treated as described above, yielding 0.48 g **3** (30%), accompanied by immobile brown impurities.

Crystal Structure Determinations[16]: Suitable crystals of **1** and **2** were obtained by layering CH_2Cl_2 solutions with hexanes (ambient temperature), mounted on glass fibers in inert oil and transferred to the cold gas stream of the diffractometer (Siemens P4, −100°C) equipped with an LT-2 low-temperature attachment. Mo-K_α radiation (λ = 0.71073 Å, graphite monochromator) was used to collect the intensity data in the ω-scan mode. Cell constants were refined from setting angles of 62 reflections in the 2 Θ range 8−23°. Absorption corrections based on ψ-scans were applied. The crystallographic program system used was SHELXL-93[17]. Both structures were solved by direct methods and refined by full-matrix least-squares procedures on F^2. All non-H atoms were refined anisotropically; hydrogen atoms were included using a riding model or as rigid methyls. The final difference Fourier maps were featureless; in the case of **1**, the highest peak of 1.95 e Å^{-3} is located near the

Table 1. X-ray structure analyses, details of solution and refinement

Compound	**1**	**2**
Empirical formula	$C_{16}H_{10}O_6Se_4W_2$	$C_{11}H_{11}NO_4SeW$
Formula weight [g mol^{-1}]	981.78	484.02
Crystal system	triclinic	monoclinic
Space group (No.)	$P\bar{1}$ (2)	$P2_1/n$ (14)
a [pm]	654.96(6)	653.4(2)
b [pm]	1266.46(12)	3272.9(5)
c [pm]	1299.99(10)	668.4(1)
α [°]	86.198(6)	
β [°]	79.570(6)	112.75(2)
γ [°]	84.402(8)	
V [Å^3]	1054.1(2)	1318.2(5)
$\rho_{calc.}$ [g cm^{-3}]	3.09	2.44
Z	2	4
F (000) [e]	876	896
μ [cm^{-1}]	178.4	115.3
Crystal size [mm]	0.50 × 0.15 × 0.10	0.32 × 0.30 × 0.08
2 Θ_{max} [°]	50	50
T [°C]	−100	−100
Measured reflections	3929	2879
Unique reflections	3707	2315
R_{int}	0.0244	0.0324
No. of parameters	253	165
No. of restraints	122	86
min/max Transmission	0.38/1.00	0.37/0.96
R (*F*), F > 4σ (*F*)[a]	0.0346	0.0254
R_w (F^2), all refl.[b]	0.0846	0.0564
Weighting parameters (*a,b*)	0.0921, 0	0.031, 0
S [c]	0.97	0.99
max. Δ/σ	< 0.001	< 0.001
ρ_{fin} (max/min) [e Å^{-3}]	1.95/−1.83	0.98/−1.02

[a] $R(F) = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$. − [b] $wR(F^2) = [\Sigma\{w(F_o^2-F_c^2)^2\}/\Sigma\{w(F_o^2)^2\}]^{0.5}$; $w^{-1} = (F_o^2) + (aP)^2 + bP$, where $P = [F_o^2 + 2F_c^2]/3$ and *a* and *b* are constants adjusted by the program. − [c] $S = [\Sigma\{w(F_o^2-F_c^2)^2\}/(n-p)]^{0.5}$, where *n* is the number of data and *p* the number of parameters.

W atom. Additional crystallographic data are presented in Table 1. Selected bond lengths and angles are listed in the Figure captions.

[1] [1a] M. A. Ansari, J. A. Ibers, *Coord. Chem. Rev.* **1990**, *100*, 223−266. − [1b] D. Coucouvanis, *Acc. Chem. Res.* **1991**, *24*, 1−8. − [1c] L. C. Roof, J. W. Kolis, *Chem. Rev.* **1993**, *93*, 1037−1080. − [1d] M. G. Kanatzidis, S. P. Huang, *Coord. Chem. Rev.* **1994**, *130*, 509−621.

[2] J. Arnold, *Progr. Inorg. Chem.* **1995**, *43*, 353−417.

[3] [3a] W. Eikens, P. G. Jones, C. Kienitz, C. Thöne, *J. Chem. Soc., Dalton Trans.* **1994**, 3329−3330. − [3b] W. Eikens, S. Jäger, P. G. Jones, C. Thöne, *J. Organomet. Chem.* **1996**, *511*, 67−75. − [3c] W. Eikens, S. Jäger, P. G. Jones, J. Laube, C. Thöne, *Chem. Ber.* **1996**, *129*, 1275−1279. − [3d] P. G. Jones, J. Laube, C. Thöne, *Inorg. Chem.* **1997**, *36*, 2097−2102. − [3e] P. G. Jones, J. Laube, C. Thöne, *Acta Crystallogr.* **1997**, *C53* 1539−1542. − [3f] T. M. Klapötke, M. Broschag, *Compilation of reported ^{77}Se NMR Chemical Shifts − up to the year 1994*, John Wiley & Sons, Chichester, **1996**, pp. 12−13.

[4] P. G. Jones, C. Thöne, *Inorg. Chem.* **1996**, *35*, 6625−6626.

[5] J. A. Gladysz, J. L. Hornby, J. E. Garbe, *J. Org. Chem.* **1978**, *43*, 1204−1208.

[6] F. Weller, J. Adel, K. Dehnicke, *Z. Allg. Anorg. Chem.* **1987**, *548*, 125−132.

[7] [7a] G. Nagao, K. Tanaka, T. Tanaka, *Inorg. Chim. Acta* **1980**, *42*, 43−48. − [7b] K. Tanaka, K. Ueda, T. Tanaka, *Inorg. Nucl. Chem.* **1981**, *43*, 2029−2032. − [7c] E. Román, D. Catheline, D. Astruc, *J. Organomet. Chem.* **1982**, *236*, 229−236.

[8] [8a] 69 crystal structures of $M(Se_4)_n$ derivatives are included in the CCDC data base (April 1997); F. H. Allen, O. Kennard, *Chem. Des. Autom. News* **1993**, *8*, 31 − 37. − [8b] For $W(Se_4)_n$ derivatives see: R. W. M. Wardle, S. Bhaduri, C.-N. Chau, J. A. Ibers, *Inorg. Chem.* **1988**, *27*, 1747−1755.

[9] S. Jäger, P. G. Jones, C. Thöne, unpublished work.

[10] C. M. Bates, C. P. Morley, *J. Organomet. Chem.* **1997**, *533*, 197−200.

[11] [11a] N. Albrecht, E. Weiss, *J. Organomet. Chem.* **1988**, *355*, 89−98. − [11b] S.-P. Huang, M. G. Kanatzidis, *Inorg. Chem.* **1991**, *30*, 3572−3575.

[12] A. Rettenmaier, K. Weidenhammer, M. L. Ziegler, *Z. Anorg. Allg. Chem.* **1981**, *478*, 91−100.

[13] J. A. M. Canich, F. A. Cotton, K. R. Dunbar, L. R. Falvello, *Inorg. Chem.* **1988**, *27*, 804−811.

[14] J. M. Ball, P. M. Boorman, J. F. Fait, H. B. Kraatz, J. F. Richardson, D. Collison, F. E. Mabbs, *Inorg. Chem.* **1990**, *29*, 3290−3293.

[15] [15a] T. S. Piper, G. Wilkinson, *J. Inorg. Nucl. Chem.* **1956**, *3*, 104−124. − [15b] C. E. Coffey, *J. Inorg. Nucl. Chem.* **1963**, *25*, 179−185.

[16] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: int. code +44 (1223) 336-033, e-mail: deposit@chemcrys.cam.ac.uk) on quoting the deposition number 100769.

[17] G. M. Sheldrick, *SHELXL-93*, *Program for Crystal Structure Refinement*, University of Göttingen, F. R. G., **1993**.

[97238]