



Communication

Synthesis and X-ray investigation of novel Fe and Mn phenyltellurenyl-halide complexes: $(\text{CO})_3\text{FeBr}_2(\text{PhTeBr})$, $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{PhTeI}_2)$ and $\text{CpMn}(\text{CO})_2(\text{PhTeI})$

Yury Torubaev^{a,*}, Alexander Pasynskii^a, Pradeep Mathur^b^aN.S. Kurnakov Institute of General and Inorganic Chemistry, Russ. Acad. Sci. 119991 Moscow, GSP-1, Leninsky Prospect, 31, Russian Federation^bChemistry Department, Indian Institute of Technology, Powai, Bombay 400076, India

ARTICLE INFO

Article history:

Received 22 October 2008

Received in revised form 27 January 2009

Accepted 30 January 2009

Available online 5 February 2009

Keywords:

Metal carbonyls

Cyclopentadienyl complexes

Tellurenyl

Organotellur compounds

Iron

Manganese

ABSTRACT

New complexes of transition metals with organotellurium halide ligands are reported. Iodination of $[\text{CpMn}(\text{CO})_2]_2(\mu\text{-Ph}_2\text{Te}_2)$ leads to the Te–Te bond cleavage and formation of $\text{CpMn}(\text{CO})_2(\text{PhTeI})$. Oxidative addition of PhTeBr_3 to $\text{Fe}(\text{CO})_5$ gives the monomeric complex $(\text{CO})_3\text{FeBr}_2(\text{PhTeBr})$ which is isostructural with the recently reported $(\text{CO})_3\text{FeI}_2(\text{PhTeI})$. Insertion of phenyltellurenyl iodide (PhTeI) into the Fe–I bond of $\text{CpFe}(\text{CO})_2\text{I}$ forms $\text{CpFe}(\text{CO})_2(\text{TeI}_2\text{Ph})$. Molecular structures of the reported complexes were determined by single-crystal X-ray diffraction analysis (XRD). A considerable shortening of metal–tellurium distances is observed.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

The strong multiple bonds between transition metal (M) and non-transition group 16 elements (E) attract considerable attention [1]. Normally, such bonds are formed due to the additional π -interaction between the E lone electron pairs and the vacant *d*-orbitals of M in formally unsaturated complexes $(\text{MeC}_5\text{H}_4)\text{Cr}(\text{CO})_2\text{S}(\text{C}_5\text{H}_4\text{FeC}_5\text{H}_5)$ (Cr–S 2.136(1) Å)¹ and $[(\text{MeC}_5\text{H}_4)\text{Cr}(\text{CO})_2]_2(\mu\text{-S})$ (Cr–S 2.073 Å, Cr–S–Cr 175.6°)². The ordinary Cr–S bond distance in the dimeric saturated complex $[\text{Cp}^*\text{Cr}(\text{CO})_2\text{S}(\text{C}_5\text{H}_4\text{Mn}(\text{CO})_3)]_2$ is 2.452(1) Å³. In this work we have investigated the possibility of M–Te partial multiple bonding in formally saturated complexes by means of Te LUMO back-bonding with *d*-electrons of M.

Recently we reported the oxidative addition of PhTeI_3 to $\text{Fe}(\text{CO})_5$ to yield an unusual complex $(\text{CO})_3\text{FeI}_2(\text{PhTeI})$ ³ (**1**) which was the first example of a transition metal complex with unstable aryltellurenyl halide ligand PhTeI . Stabilization of PhTeI in **1** was achieved due to the formation of a Fe–Te bond (Te–Fe 2.5451(6) Å) which is reduced on 0.15 Å in comparison with the sum of Fe and Te covalent

radii [4] and a secondary bonding between the tellurium atom and one of the iodide ligands (Te–I (1) 3.1634(5) Å, I–Te···I 162.197(15)°). Fe–Te distance in **1** is quite close to 2.585(2) Å in $(\text{CO})_3\text{FeI}_2(\text{Ph}_2\text{Te})$ [2], so additional Te–I(1) interaction in **1** does not affect metal–tellurium bonding and the observed shortening of Fe–Te bonds in both cases is a result of Te–Fe σ -bonding and dative Fe–Te interaction with the participation of vacant *d*-orbitals of Te.

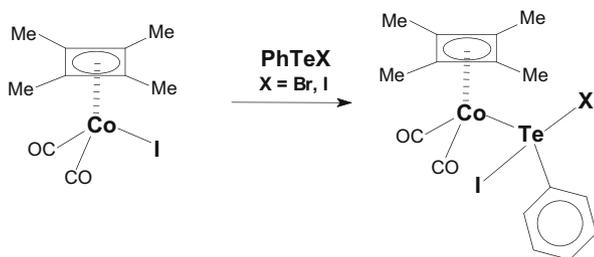
The other pattern for the interaction between PhTeX (X = Br, I) and organometallic species is the insertion of PhTeX fragment into the metal–halogen bond. In⁴ we demonstrated that treatment of $(\eta^4\text{-C}_4\text{Me}_4)\text{Co}(\text{CO})_2\text{I}$ with PhTeI gives $(\eta^4\text{-C}_4\text{Me}_4)\text{Co}(\text{CO})_2(\text{TeI}_2\text{Ph})$ (**2**) with a Co–Te bond (2.5470(7) Å) reduced on 0.09 Å as compared to the sum of Co and Te covalent radii [4] and TeI_2Ph ligand with a Te–I bonds (2.9503(6) and 2.9862(6) Å which are lengthened on average on 0.2 Å in comparison with the sum of corresponding covalent radii [4]). In **2** the shortening of Co–Te bond could be the result of Te–Co σ -bonding and dative interaction between Co atom and Te–I antibonding orbital (Scheme 1).

As part of our ongoing interest in unusual reactivity and molecular structure of metal–aryltellur–halogenide complexes and our interest in complexes with PhTeI coordinated exclusively with a metal center without any additional secondary intramolecular bonds, we have looked into the chemistry of $\text{CpMn}(\text{CO})_2(\text{PhTeI})$ (**3**). Absence of M–I bonds in **3** would suggest that additional

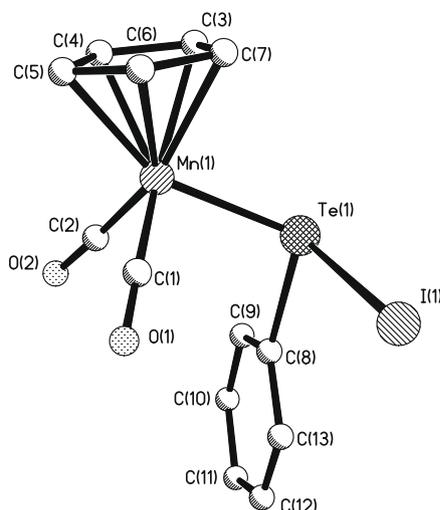
* Corresponding author. Tel.: +7 495 9543841.

E-mail address: hansmail@rambler.ru (Y. Torubaev).

¹ A. Pasynskii, I.V. Skabitsky, Yu.V. Torubaev, Zh.V. Dobrokhotova, E.V. Krasil'nikova, Russ. J. Inorg. Chem. 50 (2005) 1197.² A.A. Pasynskii, F.S. Denisov, A.N. Grechkin, I.V. Skabitsky, Yu.V. Torubaev, J.V. Dobrokhotova, G.G. Alexandrov, R.A. Lyssenko. Russ. J. Inorg. Chem. 46 (2001) 1990.³ Yu.V. Torubaev, A.A. Pasynskii, P. Mathur, Russ. J. Coord. Chem. 11 (2008) 799.⁴ Yu.V. Torubaev, A.A. Pasynskii, A.R. Galustian, P. Mathur, Russ. J. Coord. Chem., 35 (2009) 1.



Scheme 1.

Fig. 1. Molecular structure of **3**.

Scheme 2.

secondary intramolecular Te···I interactions are not possible. We have also investigated substitution of iodine atoms in **1** with bromine and of Me₄C₄Co fragment in **2** with the isoelectronic CpFe fragment.

2. Results and discussion

We have found that elemental iodine readily cleaves the Te–Te bond in [CpMn(CO)₂]₂(μ-Ph₂Te₂)⁵ to give the new complex CpMn(CO)₂(PhTeI) as dark-violet crystals (**3**) (see Fig. 1, Scheme 2).

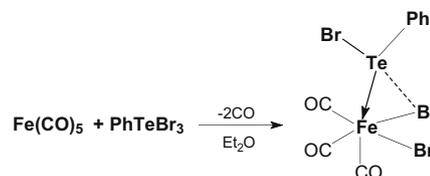
Complex **3** is the first example of PhTeI ligand bonded exclusively with metal atom in contrast with a large number of charge transfer (CT) complexes of aryltellurenyl halides with phosphines and other P-, N-, O-, S-, Se-donor ligands. It is noteworthy that in (Ph₃P)PhTeI [**3**] which is the typical example of such CT-complexes, the phosphine ligand is in *trans* position to Te–I bond so that P–Te–I angle is 179.45(5)° and Te–I distance (3.0930(9) Å) is lengthened on 0.32 Å as compared to the sum of Fe and Te covalent radii [4] while in complex **3** Mn(1)–Te(1)–I(1) angle is 105.90(4)°.

PhTeI ligand in complex **3** is attached to CpMn(CO)₂ moiety via a short Mn–Te bond (2.4267(17) Å) which is shorter than sum of Mn and Te covalent radii (2.77 Å [4]) and to our knowledge is the shortest Mn–Te distance among the structures deposited in the Cambridge Crystallographic Data Centre. Surprisingly we did not observe any intermolecular Te–I interaction in the crystal of **3**, but the Te–I distance is elongated to 2.8684(11) Å in comparison with 2.7548(5) Å in **1**.

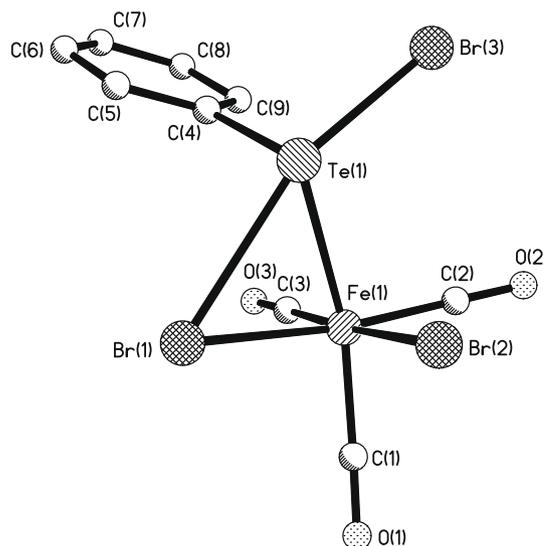
We can assume the additional π-back donation of Mn lone pairs to Te–I antibonding orbitals as a possible explanation for Mn–Te bond shortening. Mn–Te distance in **3** is close to the Mn–Te what distance is 2.486(2) Å in [CpMn(CO)₂]₂(μ-Ph₂Te₂) where the Te–Te bond was lengthened to 2.884 Å as compared to 2.705 Å in free Ph₂Te₂ [5] probably due to similar usage of the Te–Te antibonding orbitals for additional Mn → Te π-back-donation.

To investigate the effect of substitution of iodine atoms in **1** by more electronegative and smaller bromine atoms we prepared the bromine analog of **1**, complex (CO)₃FeBr₂(PhTeBr) (**4**), by treating PhTeBr₃ with Fe(CO)₅ in ether at room temperature (Scheme 3).

The stretching vibration bands of CO in the IR spectrum of **4** (2100 s, 2060 s, 2040 s cm⁻¹) are close to those for **1** (2080 s, 2040 s, 2025 s cm⁻¹) and slightly shifted into the high-frequency area due to the higher electronegativity of bromine. XRD investigation of the yellow crystals of **4** (see Fig. 2, Table 1) demonstrated that **4** is isostructural to **1**. The Te–Fe bond in **4** (2.5153(13) Å) is slightly shorter than 2.5451(6) Å in **1**. It is noteworthy that intramolecular Te–Br(1) attraction (2.9418(13) Å) results only in distortion of octahedral coordination geometry of iron center but does not affect other bonds: the Te–C (2.115(7) Å), Te–Br(3) (2.5205(13) Å) and both Fe–Br bonds are unextraordinary (2.4374(16), 2.4387(16) Å). A charge transfer (CT) type of Te–Br(1) interaction may be assumed here.



Scheme 3.

Fig. 2. Molecular structure of **4**.

⁵ A.A. Pasyanskiy, Yu.V. Torubaev; I.L. Eremenko, Russ. J. Inorg. Chem. 42 (1997) 648.

Table 1
Crystallographic data for compounds **3–5**.

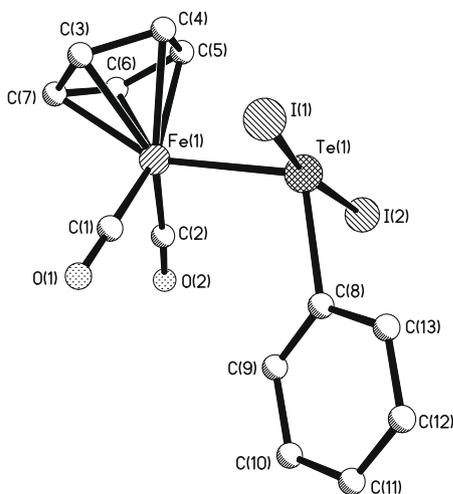
	3	4	5
Empirical formula	C ₁₃ H ₁₀ MnIO ₂ Te	C ₉ H ₅ Br ₃ FeO ₃ Te	C ₁₃ H ₁₀ FeI ₂ O ₂ Te
Formula weight	507.65	584.31	635.46
Diffractometer	Bruker APEX II CCD		
Wavelength	Mo K α , 0.71073		
Crystal system	Monoclinic		
Temperature (K)	100(2) K	296(2)	100(2)
Space group	<i>P</i> 21	<i>C</i> 2/ <i>c</i>	<i>P</i> 21/ <i>c</i>
<i>a</i> (Å)	6.4037(17)	16.750(8)	9.6807(17)
<i>b</i> (Å)	11.399(3)	10.106(5)	13.128(2)
<i>c</i> (Å)	10.128(3)	17.243(9)	13.045(2)
β	106.378(4) $^\circ$	91.525(9) $^\circ$	95.738(3) $^\circ$
Volume (Å ³)	709.3(3) E ³	2918(3)	1649.5(5)
<i>Z</i>	2	8	4
Density (calculated)	2.377 Mg/m ³	2.660 Mg/m ³	2.559 Mg/m ³
Absorption coefficient	5.112 mm ⁻¹	11.202 mm ⁻¹	6.385 mm ⁻¹
<i>F</i> (000)	468	2128	1152
Theta range for data collection	2.10–29.00 $^\circ$	2.35–29.00 $^\circ$	2.11–28.00 $^\circ$
Index ranges	$-8 \leq h \leq 8, -15 \leq k \leq 15, -13 \leq l \leq 13$	$-17 \leq h \leq 22, -10 \leq k \leq 13, -23 \leq l \leq 23$	$-12 \leq h \leq 11, -17 \leq k \leq 14, -17 \leq l \leq 17$
Reflections collected	7780	10411	11103
Independent reflections	3708 [<i>R</i> _{int}] = 0.0710]	3888 [<i>R</i> _{int}] = 0.0445]	3958 [<i>R</i> _{int}] = 0.1078]
Completeness to theta = 29.00 $^\circ$	99.8%	100.0%	99.3%
Maximum and minimum transmission	0.716 and 0.423	0.322 and 0.012	0.701 and 0.290
Absorption correction	Semi-empirical from equivalents		
Refinement method	Full-matrix least-squares on <i>F</i> ²		
Data/restraints/parameters	3708/1/1400.976	3888/0/154	3958/0/172
Goodness-of-fit on <i>F</i> ²	0.976	1.065	0.935
Final <i>R</i> indices [<i>I</i> > 2sigma(<i>I</i>)]	<i>R</i> ₁ = 0.0546, <i>wR</i> ₂ = 0.0781	<i>R</i> ₁ = 0.0481 <i>wR</i> ₂ = 0.1000	<i>R</i> ₁ = 0.0562 <i>wR</i> ₂ = 0.0779
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0883, <i>wR</i> ₂ = 0.0883	<i>R</i> ₁ = 0.0940 <i>wR</i> ₂ = 0.1164	<i>R</i> ₁ = 0.1406 <i>wR</i> ₂ = 0.0985
Largest diffraction peak and hole	1.166 and $-1.164 \text{ e} \text{ \AA}^{-3}$	1.658 and $-0.655 \text{ e} \text{ \AA}^{-3}$	1.380 and $-1.005 \text{ e} \text{ \AA}^{-3}$

The iodide, CpFe(CO)₂I interacted with PhTeI in THF to give red-orange crystals of complex CpFe(CO)₂TeI₂Ph (**5**). Its structure reveals it to be isoelectronic to the cyclobutadiene–cobalt complex **2** (Scheme 4).

IR spectrum (2035, 1990 cm⁻¹) of **5** is also similar to that of **2** (2040, 2000 cm⁻¹) and the starting CpFe(CO)₂I (2035, 2000 cm⁻¹) [6]. It is in accord with its molecular structure (see Fig. 3). Substitution of iodide ligand in CpFe(CO)₂I by PhTeI₂ fragment does



Scheme 4.

Fig. 3. Molecular structure of **5**.

not change the coordination geometry of Fe. Fe–Te bond in **5** (2.5305(17) Å) is shortened on 0.17 Å in comparison with the sum of Fe and Te covalent radii [4]. As well as in complexes **1**, **2** and **3** here we can assume the additional π -back donation of metal lone pairs to Te–I antibonding orbitals as a possible explanation for the Fe–Te bond shortening. The I–Te–I angle in **5** is close to linear (170.61(3) $^\circ$) which indicates the presence of a stereochemically active lone pair at the four-coordinate tellurium center. As in **2**, here is no intermolecular Te–I interaction in the crystal lattice of **5**.

3. Experimental

All reactions were performed using standard Schlenk techniques under dry argon. Solvents were purified, dried and distilled under in argon stream. Infrared spectra were recorded on a Spex 75 IR spectrometer in THF, diethyl ether or heptane solutions and in KBr pellets. Elemental analyses were performed on a Carlo-Erba automatic analyzer. [CpMn(CO)₂]₂(μ -Ph₂Te₂)⁵, (C₅H₅)Fe(CO)₂I [6] and PhTeBr₃ [7] were prepared using reported methods. Commercial reagent grade I₂, Ph₂Te₂ and Fe(CO)₅ were used without further purification.

3.1. Synthesis of compound **3**

Iodine (42 mg, 0.17 mmol) was added to the ink-blue solution of [CpMn(CO)₂]₂(μ -Ph₂Te₂) (140 mg, 0.18 mmol) in dry benzene (30 ml) at room temperature. Resulting ink-violet mixture was stirred for 10 min and after addition of heptane (15 ml) was concentrated under reduced pressure to the half of initial volume and kept at $-10 \text{ }^\circ\text{C}$ for 12 h to provide dark-violet crystalline precipitate. Fairly unstable in air and in solutions it contained crystals suitable for single-crystal X-ray analysis. Yield 100 mg (58%).

IR spectra (KBr, ν , cm⁻¹): 1950 s, 1885 s, 810 m, 715 m, 620 m, 580 m.

3.2. Synthesis of compound 4

Pale-yellow solution of $\text{Fe}(\text{CO})_5$ (0.07 ml, 0.5 mmol) in dry diethyl ether (5 ml) was added to the suspension of PhTeBr_3 (220 mg, 0.5 mmol) in dry diethyl ether (20 ml) at room temperature and the mixture was stirred for 30 min. Resulting dark-red solution was evaporated under reduced pressure to dryness. The residue was extracted with dry diethyl ether (20 ml) and filtered. After addition of heptane (10 ml) the solution was concentrated under reduced pressure to the half of initial volume and kept at -10°C for 12 h to provide yellow-orange crystalline precipitate. It contained crystals suitable for single-crystal X-ray analysis. Yield 100 mg (85%).

IR spectra (Et_2O , ν , cm^{-1}): 2100 s, 2040 s, 2060 s. Anal Calc. for $\text{C}_{15}\text{H}_{19}\text{FeBr}_3\text{O}_3\text{Te}$ ($M = 5,84,30$) C 18.50, H 0.86. Found: C 18.68, H 1.07.%

3.3. Synthesis of compound 5

Iodine (64 mg, 0.25 mmol) was added to an orange solution of Ph_2Te_2 (100 mg, 0.25 mmol) in dry THF (20 ml) at 0°C . The resulting black mixture was stirred for 10 min, then allowed to heat to the room temperature with $\text{CpFe}(\text{CO})_2\text{I}$ (150 mg, 0.5 mmol) added and then refluxed for 1 h. Solvent was removed under reduced pressure, residue was extracted with dry benzene (25 ml) and refluxed for 30 min. Resulting dark-red mixture was subjected to column chromatography on silica (Acrus Chem.). Pale yellow band was washed with hexane and discarded. Following orange-yellow band was eluted with CH_2Cl_2 and after addition of heptane (10 ml) was concentrated under reduced pressure to the half of initial volume and kept at -10°C for 12 h to provide red-orange crystalline precipitate. It contained crystals suitable for single-crystal X-ray analysis. Yield: 250 mg (52%).

IR spectra (KBr, ν , cm^{-1}): 2035 s, 1990 s. Anal Calc. for $\text{C}_{13}\text{H}_{10}\text{FeI}_2\text{O}_2\text{Te}$ ($M = 635.48$) C 24.57, H 1.59. Found: C 24.45, H 1.40%.

3.4. X-ray crystallography

Suitable X-ray quality crystals of **3–5** were obtained directly during preparation (see synthetic part for details). A Bruker APEX II CCD area detector diffractometer equipped with a low-temperature attachment was used for the cell determination and intensity data collection for compounds **3–5**. Structures **3–5** were solved by direct methods and refined by means of least-squares method for F^2 in anisotropic (isotropic for H atoms) approximation in SHELXTL package [8]. Positions of H atoms were calculated geometrically. Appropriate empirical absorption corrections using the programs SADABS. Relevant crystallographic data and structure refinement details are listed in Table 1. Selected distances and angles for structures **3–5** are given in Tables 2–4. CCDC 694367 (**3**), CCDC 694369 (**4**) and CCDC 694368 (**5**) contain the supplementary crystallo-

Table 2
Selected bond distances and angles for compound **3**.

Bond lengths (Å)	
Te(1)–C(8)	2.150(10)
Te(1)–Mn(1)	2.4263(17)
Te(1)–I(1)	2.8687(11)
O(2)–C(2)	1.159(11)
O(1)–C(1)	1.168(12)
Bond angles (°)	
C(8)–Te(1)–Mn(1)	106.2(2)
C(8)–Te(1)–I(1)	96.8(3)
Mn(1)–Te(1)–I(1)	105.90(4)

Table 3
Selected bond distances and angles for compound **4**.

Bond lengths (Å)	
Te(1)–C(4)	2.115(7)
Te(1)–Fe(1)	2.5153(13)
Te(1)–Br(3)	2.5205(13)
Te(1)–Br(1)	2.9418(13)
Fe(1)–Br(2)	2.4374(16)
Fe(1)–Br(1)	2.4387(16)
Bond angles (°)	
C(4)–Te(1)–Fe(1)	107.20(18)
C(4)–Te(1)–Br(3)	93.0(2)
C(4)–Te(1)–Br(1)	92.52(19)
Fe(1)–Te(1)–Br(3)	108.64(4)
Fe(1)–Te(1)–Br(1)	52.38(4)
Br(3)–Te(1)–Br(1)	161.00(3)
Br(2)–Fe(1)–Te(1)	84.39(4)
Br(1)–Fe(1)–Te(1)	72.84(4)

Table 4
Selected bond distances and angles for compound **5**.

Bond lengths (Å)	
Te(1)–C(8)	2.149(10)
Te(1)–Fe(1)	2.5305(17)
Te(1)–I(1)	2.9309(12)
Te(1)–I(2)	2.9774(12)
Bond angles (°)	
C(8)–Te(1)–Fe(1)	106.9(3)
C(8)–Te(1)–I(1)	89.6(3)
Fe(1)–Te(1)–I(1)	93.39(5)
Fe(1)–Te(1)–I(2)	95.77(4)
I(1)–Te(1)–I(2)	170.61(3)
C(8)–Te(1)–I(2)	89.7(3)

graphic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

4. Conclusions

We have demonstrated that PhTeI can be incorporated into the transition metal complexes as a monodentate ligand which is σ -donor and π -acceptor towards the metal atom. On the other hand PhTeX ($X = \text{Br}$ or I) ligand can also be involved in weak secondary interactions with halogen (Br , I) ligands at metal center or with halogenide anion but the role of these interactions is not decisive for the stabilization of PhTeI . We did not observe the cleavage of Te–I bond in PhTeX and therefore, the coordination of PhTeX with metal center appears to be more favorable. Due to the additional π -back donation from Mn lone electron pair to Te–I antibonding orbital short M–Te bonds are formed in these reactions.

Acknowledgments

We acknowledge the financial support from Russian Foundation for Basic Research (Grant 06-03-32891), Russian Academy of Sciences (Grants OX 1.5 and 8P15) and DST (India).

References

- [1] W.A. Herrmann, H. Ding, R.M. Kratzer, et al., *J. Organomet. Chem.* 549 (1997) 319.
- [2] W.-F. Liaw, M.-H. Chiang, C.-H. Lai, et al., *Inorg. Chem.* 33 (1994) 2493.
- [3] E.S. Lang, R.M. Fernandes Jr., E.T. Silveira, et al., *Z. Anorg. Allg. Chem.* 625 (1999) 1401.

- [4] B. Cordero, V. Gomez, A.E. Platero-Prats, et al., Dalton Trans. (2008) 2832.
- [5] G. Llabres, O. Dideberg, L. Dupont, Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem. 28 (1972) 2438.
- [6] G. Brauer (Ed.), Handbuch der präparativen anorganischen Chemie, sixth ed., Ferdinand Enke Verlag, Stuttgart, 1975.
- [7] W.R. McWhinnie, P. Thavornnyutikarn, J. Chem. Soc., Dalton Trans. (1972) 551.
- [8] G.M. Sheldrick, SHELXTL-97, Version 5.50, Bruker AXS Inc., Madison, WI-53719, USA, 1997.