

Note

Contents lists available at ScienceDirect

# Journal of Organometallic Chemistry



journal homepage: www.elsevier.com/locate/jorganchem

# Hexacoordinate triphenylantimony(V) complex with tridentate bis-(3,5-di-*tert*-butyl-phenolate-2-yl)-amine ligand: Synthesis, NMR and X-ray study

# Andrey I. Poddel'sky<sup>a,\*</sup>, Nikolay V. Somov<sup>b</sup>, Yury A. Kurskii<sup>a</sup>, Vladimir K. Cherkasov<sup>a</sup>, Gleb A. Abakumov<sup>a</sup>

<sup>a</sup> G.A. Razuvaev Institute of Organometallic Chemistry, Russian Academy of Sciences, Tropinina 49, 603950 Nizhniy Novgorod, GSP-445, Russia
<sup>b</sup> Nizhniy Novgorod State University, Physical Faculty, Building 3, Gagarina Avenue 23, 603950 Nizhniy Novgorod, Russia

#### ARTICLE INFO

Article history: Received 16 May 2008 Received in revised form 28 July 2008 Accepted 5 August 2008 Available online 11 August 2008

Keywords: Antimony(V) ONO ligands NMR spectroscopy EPR spectroscopy X-ray diffraction

# 1. Introduction

The chemistry of organoantimony compounds has been an area of extensive research for more than four decades [1]. The reason to investigate these compounds is their application in the organic synthesis and catalysis [2], as the potential agents in biochemistry and medicine [3]. Recently, some antimony(V) complexes with catecholate/o-amidophenolate, (Cat)SbPh3/(AP)SbPh3, ligands were found to bind the molecular oxygen in a reversible manner [4] that suggests their potentiality in different oxidation processes and modeling biological systems [5]. Such unique ability of these complexes is liable to the presence of redox-active catecholate/oamidophenolate ligand coupled with the heavy antimony atom having: (i) a large spin-orbital interaction constant, and (ii) a free coordination site to coordinate superoxide anion formed from O<sub>2</sub>. The mechanism of this interaction discussed in [4a,c] includes the step of the one-electron oxidation of dianionic Cat/AP ligand by dioxygen that imposes a limitation on the first redox-potential range of ligand. In work [6], we have shown that triphenylantimony(V) catecholates with electron withdrawing groups are inert toward molecular oxygen. On the other hand, triphenylantimony(V) 4,6-di-tert-butyl-N-aryl-o-amidophenolates (AP)SbPh<sub>3</sub> show the high dioxygen reactivity forming the stable spiroendoperoxides

#### ABSTRACT

The oxidative addition reaction of 4,6-di-*tert*-butyl-*N*-(2-hydroxy-3,5-di-*tert*-butyl-phenyl)-*o*-iminobenzoquinone (**IBQ**) to triphenylantimony(III) proceeds with the migration of hydroxyl-proton to a nitrogen atom to form tridentate O,N,O'-coordinated bis-(3,5-di-*tert*-butyl-phenolate-2-yl)-amine ligand. In accordance with <sup>1</sup>H, <sup>13</sup>C, DEPT NMR data, the new hexacoordinate complex [bis-(3,5-di-*tert*-butyl-phenolate-2-yl)-amine]triphenylantimony(V), [(AP-AP)H]SbPh<sub>3</sub> (**1**) in solution has a *C<sub>s</sub>* symmetry plane leading to the equivalence of two O,N-chelate *o*-aminophenolato moieties. The molecular structure of **1** · acetone was studied by a single-crystal X-ray. Compound **1** was found to be air-stable both in solid and in solution. Its oxidation by PbO<sub>2</sub> leads to paramagnetic [4,6-di-*tert*-butyl-*N*-(3,5-di-*tert*-butyl-phenolate-2-yl)-*o*-iminobenzosemiquinolato]triphenylantimony(V), [(AP-ISQ)]SbPh<sub>3</sub> (**2**).

© 2008 Elsevier B.V. All rights reserved.

[4a,c]. The modification of AP ligand with an insertion of third coordinating hydroxy group, as we will show in the present paper, causes the distinctive structure and, as a result, behaviour of triphenylantimony(V) complex formed. Here we are describing the synthesis and structure of new triphenylantimony(V) complex with O,N,O'-coordinated tridentate bis-(3,5-di-*tert*-butyl-phenolate-2-yl)-amine ligand.

# 2. Experimental

# 2.1. Synthesis

All reagents were grade. Solvents were purified following standard methods [7]. The ligand 4,6-di-*tert*-butyl-*N*-(2-hydroxy-3,5di-*tert*-butyl-phenyl)-*o*-iminobenzoquinone (**IBQ**) was prepared according literature procedure [8].

Hexacoordinate [bis-(3,5-di-*tert*-butyl-phenolate-2-yl)-amine]triphenylantimony(V) (**1**) was prepared from triphenylstibine and **IBQ** in hexane solution. The sample of SbPh<sub>3</sub> (0.353 g, 1.0 mmol) was dissolved in deaerated dry hexane (20 ml) and to this colorless solution the hexane solution (30 ml) of **IBQ** (0.423 g, 1.0 mmol) was added dropwise. Deep blue–violet color of solution (the color of initial IBQ) gradually disappeared reaching lilac coloration. After storing at 0 °C for a day, the colorless residue was collected, filtered off. Recrystallization of this crude product from another hexane portion gave colorless microcrystalline powder in 95% yield. Compound **1** is air-stable.

<sup>\*</sup> Corresponding author. Tel.: +7 831 462 76 82; fax: +7 831 462 74 97. *E-mail address:* aip@iomc.ras.ru (A.I. Poddel'sky).

<sup>0022-328</sup>X/\$ - see front matter  $\odot$  2008 Elsevier B.V. All rights reserved. doi:10.1016/j.jorganchem.2008.08.002

Elemental Anal. Calc. for C<sub>46</sub>H<sub>56</sub>NO<sub>2</sub>Sb: C, 71.13; H, 7.27; Sb, 15.68; N, 1.80. Found: C, 71.19; H, 7.25; Sb, 15.37; N, 1.85%.

IR data (nujol, v, cm<sup>-1</sup>): 3307 m, 1605 w, 1570 w, 1530 w, 1481 s, 1433 s, 1410 m, 1362 m, 1334 w, 1301 s, 1281 s, 1263 m, 1237 w, 1202 w, 1181 w, 1165 w, 1123 w, 1076 m, 1071 m, 1061 m, 1023 w, 997 w, 983 s, 934 w, 904 m, 893 w, 871 m, 854 w, 835 s, 809 w, 780 m, 762 w, 748 m, 727 s, 693 s, 671 m, 656 w, 644 w, 598 w, 586 w, 525 w, 512 w, 478 w, 459 m, 449 w.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, *δ*, ppm): 1.21 (s, 18H, 2 *t*Bu), 1.29 (s, 18H, 2 *t*Bu), 5.49 (s, 1H, N–H), 7.03 and 7.13 (both d, both 2H, arom. C<sub>6</sub>H<sub>2</sub>,  ${}^{4}J_{H,H}$  = 2.26 Hz), 7.08–7.28 (mult., 4H, *o*-H of 2 Ph), 7.32–7.42 (mult., 6H, *m*- and *p*-H of 2 Ph), 7.42–7.50 (mult., 3H, *m*- and *p*-H of 1 Ph) and 7.98–8.08 (mult., 2H, *o*-H of 1 Ph).

<sup>13</sup>C NMR (CDCl<sub>3</sub>, *δ*, ppm): 29.39 (2C(CH<sub>3</sub>)<sub>3</sub>), 31.57 (2C(CH<sub>3</sub>)<sub>3</sub>), 34.11 (2C(CH<sub>3</sub>)<sub>3</sub>), 35.13 (2C(CH<sub>3</sub>)<sub>3</sub>), 117.87, 122.58, 127.95, 128.29, 129.10, 129.60, 134.45, 134.67, 137.13, 138.24, 140.72, 144.64, 150.79.

<sup>13</sup>C DEPT NMR (CDCl<sub>3</sub>,  $\delta$ , ppm): 29.39 (2C(CH<sub>3</sub>)<sub>3</sub>), 31.57 (2C(CH<sub>3</sub>)<sub>3</sub>), 117.87, 122.58, 127.95, 128.29, 129.10, 129.60, 134.45, 134.67.

#### 2.2. Physical measurements

IR spectra were monitored in the 400–4000 cm<sup>-1</sup> range by a FSM 1201 Fourier-IR spectrometer in nujol. X-band EPR spectral investigations were performed on Bruker ER 200 D-SRC spectrometer with ER041 MR microwave bridge, ER 4105 DR double resonator and ER 4111 VT variable temperature unite. <sup>1</sup>H, <sup>13</sup>C, <sup>13</sup>C DEPT NMR-spectra were registered using Bruker AVANCE DPX-200 spectrometer (with a TMS as internal reference and CDCl<sub>3</sub> as solvent).

The crystals of **1** suitable for X-ray diffraction analysis were grown using a prolonged recrystallization of **1** from acetone as the acetone solvate  $1 \cdot C_3 H_6 O$ .

Intensity data were collected on Oxford Diffraction (Gemini S) diffractometer with graphite monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å) in the  $\phi - \omega$  scan mode ( $\omega = 0.3^{\circ}$ , 10 s on each frame). The crystal structure was solved and refined by WINGX v1.70.01 program [9]. All non-hydrogen atoms were refined with anisotropic correction. The one/some part of H atoms were placed in calculated positions and refined in the "riding-model" ( $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm carbon})$  Å<sup>2</sup> for aromatic hydrogen and  $1.5U_{\rm eq}({\rm carbon})$ Å<sup>2</sup> for alkyl hydrogen), and the another part were located from Fourier synthesis and refined isotropically [9].

# 3. Results and discussion

# 3.1. Synthesis and characterization

Ligand 4,6-di-*tert*-butyl-*N*-(2-hydroxy-3,5-di-*tert*-butyl-phenyl)-*o*-iminobenzoquinone (**IBQ**) was prepared by a previously reported method [8] from 3,5-di-*tert*-butyl-*o*-benzoquinone and 4,6di-*tert*-butyl-*o*-aminophenol. Its reaction with triphenylstibine in hexane solution gives pale lilac solution. After a cooling of resulting solution the colorless powder was obtained. In accordance with previous experience [4,6] one can expect the formation of O,N,O'coordinated *o*-amidophenolato derivative of triphenylantimony(V) containing hydroxy-group coordinated to central antimony atom (Scheme 1). But we have found this product to be triphenylantimony(V) complex **1** with O,N,O'-coordinated bis-(3,5-di-*tert*-butylphenolate-2-yl)-amine dianion (Scheme 1).

IR spectrum of **1** in nujol contains the band of stretching vibrations of N–H group at 3307 cm<sup>-1</sup>. <sup>1</sup>H NMR spectrum of **1** reveals proton of NH group at  $\delta$  = 5.49 ppm (Fig. 1). According to the NMR spectral data, complex **1** in solution has a symmetrical structure with a symmetry plane. Fig. S1 of Supplementary information



Scheme 1. Complex 1 is soluble in THF, toluene, but weakly soluble in alkanes.



Fig. 1. The <sup>1</sup>H NMR spectrum of complex 1 (CDCl<sub>3</sub>, 200 MHz).



Scheme 2.

represents <sup>13</sup>C NMR and <sup>13</sup>C DEPT NMR spectra of **1** with the correlation of signals to the specified carbon atoms. The <sup>1</sup>H–<sup>1</sup>H COSY spectrum in the region 6.92–8.20 ppm useful for the signal assignment is depicted in Fig. S2.

The protons of four *tert*-butyl groups give rise to two singlets at  $\delta$  = 1.21 and 1.29 ppm in the <sup>1</sup>H NMR spectrum of **1** indicating their pair equivalence. Four aromatic protons of aminophenolate fragments appear as two doublets centered at  $\delta$  = 7.03 and 7.13 ppm (with <sup>4</sup>J<sub>H,H</sub> = 2.26 Hz). The <sup>1</sup>H and <sup>13</sup>C NMR show the equivalency of two phenyl groups, while third phenyl differs from those ones.

Unlike *o*-amidophenolate complexes [4a,c], complex **1** was found to be air-stable: it left unchanged on the exposition to air within several weeks. Even its oxidation with lead(IV) oxide proceeds slowly and leads to the loss of amine hydrogen by this complex to yield paramagnetic compound **2** (Scheme 2). X-band EPR spectrum of **2** toluene solution (Fig. 2) is a multiplet with  $g_{iso} = 2.0039$ . The hyperfine structure (HFS) is caused by unpaired electron splitting on nitrogen (<sup>14</sup>N, *I* = 1, 99.64%), two pairs of protons (<sup>1</sup>H, *I* = 1/2, 99.99%) of paramagnetic ligand, and magnetic antimony nuclei (<sup>121</sup>Sb, *I* = 5/2, 57.25%,  $g_N = 1.34550$ ; <sup>123</sup>Sb, *I* = 7/ 2, 42.75%,  $g_N = 0.72876$ ). Due to moderate linewidth (>3 G) and a substantial number of magnetic nuclei involved, the precise HFS constant determination is difficult, but the estimated from computer simulation HFS constants are  $A_N$  (1N)  $\approx$  7.1 G,  $A_H$  (2H)  $\approx$ 3.1 G,  $A_H$  (2H)  $\approx$  1.5 G, A (<sup>121</sup>Sb)  $\approx$  12.2 G, A (<sup>123</sup>Sb)  $\approx$  6.6 G. The HFS on two protons' pairs with approximately two times less than





in other *o*-iminobenzosemiquinonato radical complexes [10] evidences the unpaired electron delocalization over both aromatic cycle fragments of ligand (Scheme 2).

The air-stability of complex **1** is explained by the following reasoning: (i) Cat and AP antimony(V) complexes reacting with molecular oxygen [4] have a free coordination site of central antimony atom to coordinate -O-O group; (ii) they can form the stable *o*-semiquinonato (*o*-iminosemiquinonato) radical-anion as required by the mechanism proposed [4a]. In the case of **1**, antimony atom has no vacant coordination site and  $[(AP-AP)H]^{2-}$  ligand cannot form stable delocalized radical-anionic structure without being deprotonated that is confirmed by EPR experiment with the oxidation of **1** with lead(IV) oxide.

## 3.2. X-ray structure

Crystals of **1** suitable for a single crystal structural analysis were grown from acetone as the acetone solvate  $1 \cdot C_3H_6O$ . Table 1

Crystallographic data of  $\boldsymbol{1}\cdot C_3H_6O$ 

Empirical formula	C <sub>49</sub> H <sub>62</sub> NO <sub>3</sub> Sb
Formula weight	834.75
Temperature, K	298(2)
Wavelength, Å	0.71073
Crystal system	Triclinic
Space group	ΡĪ
Unit cell dimensions	
a (Å)	10.1118(8)
b (Å)	13.5373(13)
<i>c</i> (Å)	18.3274(19)
α (°)	79.614(8)
β(°)	75.726(8)
γ (°)	69.369(8)
Volume, Å <sup>3</sup>	2263.3(4)
Ζ	2
$D_{\text{calc}}, \text{ mg/m}^3$	1.225
Absorption coefficient, mm <sup>-1</sup>	0.649
F(000)	876
Crystal size, mm <sup>3</sup>	$0.16 \times 0.08 \times 0.05$
$\theta$ Range for data collection (°)	2.95-28.28
Completeness to $\theta$ = 28.28 (%)	99.7
Reflections collected	11204
Independent reflections	6356 [R <sub>int</sub> = 0.0374]
Absorption correction	SADABS
Maximum and minimum transmission	0.9775; 0.9305
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data/restraints/parameters	11204/0/491
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0293, wR_2 = 0.0492$
R indices (all data)	$R_1 = 0.0662, wR_2 = 0.0550$
Goodness-of-fit on F <sup>2</sup>	0.777
Largest difference in peak and hole, $e^{A^{-3}}$	0.746 and -0.315

Table 2	
Selected bond distances (Å) and	bond angles (°) in $\boldsymbol{1}\cdot(CH_3)_2CO$

Sb(1)-O(1)	2.0491(12)	O(1)-Sb(1)-O(2)	82.19(5)
Sb(1)-O(2)	2.0739(11)	O(1)-Sb(1)-C(13)	89.36(6)
Sb(1)-N(1)	2.3229(16)	O(2)-Sb(1)-C(13)	90.38(6)
Sb(1)-C(13)	2.107(2)	O(1)-Sb(1)-C(19)	164.17(6)
Sb(1)-C(19)	2.1574(19)	O(2)-Sb(1)-C(19)	87.69(6)
Sb(1)-C(25)	2.1592(17)	C(13)-Sb(1)-C(19)	102.91(8)
O(1) - C(1)	1.333(2)	O(1)-Sb(1)-C(25)	90.25(6)
O(2) - C(7)	1.337(2)	O(2)-Sb(1)-C(25)	168.29(6)
O(3) - C(47)	1.209(2)	C(13)-Sb(1)-C(25)	98.50(7)
N(1)-C(6)	1.462(2)	C(19)-Sb(1)-C(25)	97.66(7)
N(1)-C(12)	1.458(2)	O(1)-Sb(1)-N(1)	76.49(5)
C(1) - C(2)	1.415(2)	O(2)-Sb(1)-N(1)	74.02(5)
C(1) - C(6)	1.386(2)	C(13)-Sb(1)-N(1)	160.07(6)
C(2) - C(3)	1.381(3)	C(19)-Sb(1)-N(1)	89.06(7)
C(3) - C(4)	1.385(3)	C(25)-Sb(1)-N(1)	95.58(6)
C(4) - C(5)	1.390(2)	C(12)-N(1)-C(6)	113.54(14
C(5) - C(6)	1.374(2)	C(12)-N(1)-Sb(1)	104.62(10
C(7) - C(8)	1.415(2)	C(6)-N(1)-Sb(1)	107.20(11
C(7)-C(12)	1.387(2)	C(1)-O(1)-Sb(1)	118.96(11
C(8) - C(9)	1.380(3)	C(7)-O(2)-Sb(1)	114.85(10
C(9) - C(10)	1.383(3)		
C(10)-C(11)	1.393(2)		
C(11)-C(12)	1.363(2)		

represents the crystal data collection and structure refinement data. The selected bond lengths and angles are listed in Table 2.

Central antimony atom Sb(1) adopts a slightly distorted octahedral geometry (Fig. 3). The angles between the axially positioned atoms equal to  $164.17(6)^{\circ}$ ,  $168.29(6)^{\circ}$  and  $160.07(6)^{\circ}$  (angles C(13)–Sb(1)–N(1), O(2)–Sb(1)–C(25) and O(1)–Sb(1)–C(19) correspondingly). The sums of bond angles in the plane orthogonal to the corresponding directions are  $357.79^{\circ}$ ,  $357.82^{\circ}$  and  $358.48^{\circ}$ , respectively.

The geometrical parameters in two aromatic  $tBu_2C_6H_2O$  (oaminophenolato) moieties in O,N,O'-coordinated ligand are nearly equal within the experimental error. The angle between two hypothetic planes formed by two o-aminophenolato moieties is 70.3°. Six-membered carbon cycles C(1–6) and C(7–12) are of aromatic character without the o-quinoid distortion typical for O,N-(O,O-) coordinated o-iminobenzosemiquinones [10] (o-semiquinones [11]). The oxygen-to-carbon bonds O(1)–C(1), O(2)–C(7) of 1.333(2) and 1.337(2) Å are shorter than the ordinary O–C bonds in different triphenylantimony catecholates or o-amidophenolates [4,12]. For example, these bonds are av. 1.356(2) Å and av. 1.361(2) Å in catecholates (4-MeO-3,6-DBCat)SbPh<sub>3</sub> · CH<sub>3</sub>OH and



Fig. 3. Platon view [16] of 1. The H atoms (except H(1)) are omitted for clarity.

(4,5-(MeO)<sub>2</sub>-3,6-DBCat)SbPh<sub>3</sub> · CH<sub>3</sub>CN, respectively [4b]; 1.351(4) Å in *o*-amidophenolate (AP-*i*Pr)SbPh<sub>3</sub> [4a] (4-MeO-3,6-DBCat is 4-methoxy-3,6-di-*tert*-butyl-catecholate, 4,5-(MeO)<sub>2</sub>-3,6-DBCat is 4,5-dimethoxy-3,6-di-*tert*-butyl-catecholate, and AP-*i*Pr is 4,6-di*tert*-butyl-*N*-(2,6-di-iso-propylphenyl)-*o*-amidophenolate).

The nitrogen atom N(1) is sp<sup>3</sup>-hybridized and tetracoordinated; the sum of bond angles between N(1) and non-hydrogen atoms C(6), C(12), Sb(1) is 325.36°. The significant difference in Sb–N bond length in **1** (Sb(1)–N(1), 2.3229(16) Å) and, for example, in (AP–*i*Pr)SbPh<sub>3</sub> (Sb–N, 2.041(3) Å [4a]) reflects the difference in bond nature between the neutral donor–acceptor amino-functions in **1** and the valence bound amide-group in (AP–*i*Pr)SbPh<sub>3</sub>. Noteworthy, this bond Sb(1)–N(1) in **1** is themselves the shortest among those bonds in structurally characterized antimony complexes with the related O,N,O'-ligands such as  $[\gamma^3$ -PhN(*o*-C<sub>6</sub>H<sub>4</sub>O)<sub>2</sub>]Sb}<sub>4</sub>(µ<sub>3</sub>-O)<sub>2</sub> (2.723(7) and 2.684(8) Å), {{[\gamma^3-N(*o*-



Fig. 4. The presentation of the unit cell of 1 (left) and its rotation about horizontal line to 180° (right). The H atoms (except H(1)) and carbons of *tert*-butyl groups are omitted for clarity.

The coordination of N(1) to antimony atom elongates the distances N(1)–C(6) and N(1)–C(12) with aromatic carbon rings (1.462(2) and 1.458(2) Å, respectively) compared with the usual  $C_{(aryl)}$ –NH<sub>(sp3,pyramidal)</sub> bonds (1.41–1.43 Å) [14].

The antimony-to-carbon bonds differ from each other reflecting *trans*-effect: Sb(1)–C(19) and Sb(1)–C(25) (2.1574(19) and 2.1592(17) Å) of phenyl groups *trans*-positioned toward oxygen atoms are ~0.02–0.04 Å longer than those bonds in catecholates [4b,c], while the third Sb(1)–C(13) bond (2.107(2) Å) which is *trans*-located to a donor–acceptor Sb(1)–N(1) bond lies in the common range of Sb–C<sub>(phenyl)</sub> bonds (2.10–2.13 Å).

Worthy of note is that, if complex **1** in solution has a symmetrical structure, as it shown above by NMR spectroscopy, in crystal such symmetry is broken. Antimony–oxygen bond distances differs by ~0.025 Å (see Table 2). The geometries of the five-membered chelate metallocycles SbOOCC (the chelate rings) are not planar and non-equivalent. The bend angles along the O(1)···N(1) and O(2)···N(1) lines in two parts of **1** are 6.27° and 30.93°, respectively. The corresponding dihedral angles O(1)–C(1)–C(6)–N(1) and O(2)–C(7)–C(12)–N(1) are 5.07° and 2.85°. This fact of non-equivalence may be rationalized by crystal packing effect and, in addition, by the solvation of acetone molecule to **1**.

As mentioned above, in the crystals of  $1 \cdot (CH_3)_2CO$  each complex molecule is solvated with acetone molecule coordinated to the hydrogen H(1) of NH-group (Fig. 4). The distance  $O(3) \cdots H(1)N(1)$  is 2.235(3)Å, being shorter than the sum of O and H van der Waals radii (1.5 + 1.2 = 2.7 Å) [15]. Meanwhile, the  $O(3) \cdots N(1)$  distance (3.016(3) Å) is close to the value of normal van der Waals  $O \cdots N$  contact (3.1 Å) [15].

We should note that the unit cell (Fig. 4) contain two complex **1** molecules which are enantiomers in their distortion.

#### Acknowledgements

We are grateful to the Russian Foundation for Basic Research (Grant 07-03-00819), President of Russian Federation (Grants MK-3523.2007.3 and NSh-4182.2008.3) and Russian Science Support Foundation (A.I. Poddel'sky) for financial support of this work.

#### Appendix A. Supplementary material

CCDC 686968 contains the supplementary crystallographic data for **1** · acetone. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/ data\_request/cif. Supplementary information contains <sup>13</sup>C NMR, DEPT (Fig. S1) and <sup>1</sup>H–<sup>1</sup>H COSY (Fig. S2) spectra. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2008.08.002.

#### References

 (a) C.A. McAuliffe, in: G. Wilkinson, R.D. Gillard, J.A. McCleverty (Eds.), Comprehensive Coordination Chemistry, vol. 3, Pergamon, Oxford, 1987. pp. 256–278;

- (b) W. Levason, G. Reid, Coord. Chem. Rev. 250 (2006) 2565-2594;
- (c) S.S. Garje, V.K. Jain, Coord. Chem. Rev. 236 (2003) 35-56;
- (d) S. Schulz, Coord. Chem. Rev. 215 (2001) 1–37;
- (e) H.J. Breunig, R. Rösler, Chem. Soc. Rev. 29 (2000) 403–410;
- (f) N.R. Champness, W. Levason, Coord. Chem. Rev. 133 (1994) 115–217;
- (g) C. Silvestru, I. Haiduc, Coord. Chem. Rev. 147 (1996) 117–146;
- (h) H.P.S. Chauhan, Coord. Chem. Rev. 173 (1998) 1–30.
   (a) J.P. Finet, Ligand Coupling Reactions with Heteroatomic Compounds,
- Pergamon, New York, 1998. p. 308; (b) D.V. Moiseev, A.V. Gushchin, A.S. Shavirin, Y.A. Kursky, V.A. Dodonov, J. Organomet. Chem. 667 (2003) 176;

(c) K. Matoba, S. Motofusa, C.S. Cho, K. Ohe, S. Uemura, J. Organomet. Chem. 574 (1999) 3;

- (d) C.S. Cho, K. Tanabe, O. Itoh, S. Uemura, J. Org. Chem. 60 (1995) 274;
- (e) L.-J. Zhang, X.-S. Mo, J.-Z. Huang, Y.-Z. Huang, Tetrahedron Lett. 34 (1993) 1621–1624;
- (f) A.B. Goel, H.J. Richards, J.H. Kyung, Tetrahedron Lett. 25 (1984) 391;
- (g) A.B. Goel, H.J. Richards, J.H. Kyung, Inorg. Chim. Acta 76 (1983) L95.
- [3] (a) Guo-Cang Wang, Yong-Na Lu, Jian Xiao, Lin Yu, Hai-Bin Song, Jin-Shan Li, Jing-Rong Cui, Rui-Qing Wang, Fu-Xiang Ran, J. Organomet. Chem. 690 (2005) 151–156;

(b) Siucheong Yan, Fei Li, Keyang Ding, Hongzhe Sun, J. Biol. Inorg. Chem. 8 (2003) 689–697;

(c) C. Silvestru, İ. Haiduc, Main Group Elements and Their Compounds, Narosa, New Delhi, 1996;

(d) C. Silvestru, L. Silaghi-Dumitrescu, I. Haiduc, M.J. Begley, M. Nunn, D.B. Sowerby, J. Chem. Soc., Dalton Trans. (1986) 1031;

(e) C. Silvestru, M. Curtui, I. Haiduc, M.J. Begley, D.B. Sowerby, J. Organomet. Chem. 426 (1992) 49;

- (f) C. Silvestru, C. Socaciu, A. Baba, I. Haiduc, Anticancer Res. 10 (1990) 803.
- [4] (a) G.A. Abakumov, A.I. Poddel'sky, E.V. Grunova, V.K. Cherkasov, G.K. Fukin, Yu.A. Kurskii, L.G. Abakumova, Angew. Chem., Int. Ed. 44 (2005) 2767–2771;
   (b) G.A. Abakumov, V.K. Cherkasov, E.V. Grunova, A.I. Poddel'sky, L.G. Abakumova, Yu.A. Kurskii, G.K. Fukin, E.V. Baranov, Dokl. Chem. 405 (2005) 222–225;

(c) V.K. Cherkasov, G.A. Abakumov, E.V. Grunova, A.I. Poddel'sky, G.K. Fukin, E.V. Baranov, Yu.A. Kurskii, L.G. Abakumova, Chem. Eur. J. 12 (2006) 3916–3927.

[5] (a) H. Mimoun, in: G. Wilkinson, R.D. Gillard, J.A. McCleverty (Eds.), Comprehensive Coordination Chemistry, vol. 6, Pergamon, Oxford, 1987. pp. 317-410;

(b) L.I. Simándi, Advances in Catalytic Activation of Dioxygen By Metal Complexes, Catalysis By Metal Complexes, vol. 26, Kluwer, Boston, 2003; (c) E.I. Solomon, T.C. Brunold, M.I. Davis, J.N. Kemsley, S.-K. Lee, N. Lehnert, F. Neese, A.J. Skulan, Y.-S. Yang, J. Zhou, Chem. Rev. 100 (2000) 235.

- [6] A.I. Poddel'sky, I.V. Smolyaninov, Yu.A. Kurskii, N.T. Berberova, V.K. Cherkasov, G.A. Abakumov, Russ. Chem. Bull. (2008), in press.
- [7] D.D. Perrin, W.L.F. Armarego, D.R. Perrin, Purification of Laboratory Chemicals, Pergamon. Oxford, 1980.
- [8] A.Y. Girgis, A.L. Balch, Inorg. Chem. 14 (1975) 2724.
- [9] L.J. Farrugia, J. Appl. Crystallogr. 32 (1999) 837-838.
- [10] A.I. Poddel'sky, V.K. Cherkasov, G.A. Abakumov, Coord. Chem. Rev. (2008), doi:10.1016/j.ccr.2008.02.004.
- [11] (a) C.G. Pierpont, Coord. Chem. Rev. 219-221 (2001) 415-433;
- (b) C.G. Pierpont, R.M. Buchanan, Coord. Chem. Rev. 38 (1981) 45–87.
- [12] (a) M. Hall, D.B. Sowerby, J. Am. Chem. Soc. 102 (1980) 628–632;
  (b) R.R. Holmes, R.O. Day, V. Chandrasekhar, J.M. Holmes, Inorg. Chem. 26 (1987) 163–168;
  (c) G.K. Fukin, L.N. Zaharov, G.A. Domrachev, A.Yu. Fedorov, S.N. Zaburdyaeva,

V.A. Dodonov, Russ. Chem. Bull. 48 (1999) 1722–1732;
(d) V.K. Cherkasov, E.V. Grunova, A.I. Poddel'sky, G.K. Fukin, Yu.A. Kurskii, L.G. Abakumova, G.A. Abakumov, J. Organomet. Chem. 690 (2005) 1273–1281;

- (e) G.A. Abakumov, N.N. Vavilina, Yu.A. Kurskii, L.G. Abakumova, G.K. Fukin, V.K. Cherkasov, A.S. Shavyrin, E.V. Baranov, Russ. Chem. Bull. 56 (2007) 1813–1820.
- [13] J.M. Tanski, B.V. Kelly, G. Parkin, Dalton Trans. (2005) 2442-2447.
- [14] D.R. Lide (Ed.), Handbook of Chemistry and Physics, 84th ed., CRC Press, 2003– 2004, pp. 6–9.
- [15] S.S. Batsanov, Russ. J. Inorg. Chem. 36 (1991) 3015.
- [16] A.L. Spek, PLATON A Multipurpose Crystallographic Tool, Utrecht University, 2000.