Inorganica Chimica Acta, 181 (1991) 7–9 7

Inorganica Chimica Acta
LETTER

The destructive oxidation of a rhodium(II) dimer: crystal and molecular structure of [Rh(Ph)(SbPh$_3$)$_2$Cl$_2$(CH$_3$CN)]

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(Received November 15, 1990; revised January 14, 1991)

Recently several unusual reactions between triarylphosphine ligands and metal–metal bonded dimers have been reported. For example a number of compounds are now known in which orthometallated triphenylphosphine ligands bridge across a rhodium–rhodium single bond [1–6]. Also the interaction of triarylphosphine ligands and ruthenium(II/III) centres pre-coordinated by amidate ligands has been shown to result in the cleavage of phosphorus–carbon bonds and the formation of novel ruthenium(III/III) dimers [7, 8]. In this report we describe the characterisation of a new monomeric rhodium(III) compound formed during the destructive oxidation of the metal–metal bonded dimer [Rh$_2$(HNCOCH$_3$)$_4$(SbPh$_3$)$_2$]. This reaction involves antimony–carbon bond cleavage and is clearly related to those already described for ruthenium.

Results and discussion

In the course of investigations into the redox chemistry of a range of axially ligated [Rh$_2$(RNCOR′)$_4$] compounds we carried out a quantitative scale electrosynthesis on the compound [Rh$_2$(HNCOCH$_3$)$_4$(SbPh$_3$)$_2$]. In contrast to the cyclic voltammetric experiment, the results of which were consistent with the reversible interconversion of the neutral rhodium(II/II) species and its rhodium(II/III) cation [9], the bulk electrosynthesis, carried out at a potential of +2.00 V (versus Ag/AgCl) in CH$_2$Cl$_2$ solvent under a dinitrogen atmosphere in the presence of an excess of SbPh$_3$ over a period of 20 min, in which time the current decayed to zero, led to the formation of the monomeric rhodium(III) compound [Rh(Ph)(SbPh$_3$)$_2$Cl$_2$(CH$_3$CN)] in near quantitative yield. Crystals were obtained by cooling the electrosynthetic solution to 0 °C for several days.

Crystal structure determination

An orange single crystal of C$_{44}$H$_{38}$NCl$_2$RhSb$_2$ ($M_r = 998$, monoclinic, $a = 13.772(4)$, $b = 13.536(3)$, $c = 21.999(4)$ Å, $\beta = 95.81°$, $U = 4080$ Å^3, space group $C2/c$, $Z = 4$, $D_c = 1.63$ g cm^{-1}, μ(Mo Kα) = 18.8 cm^{-1}, $\lambda = 0.71073$ Å, $F(000) = 1960$), of approximate dimensions 0.15×0.15×0.35 mm, was used to collect 3925 data (3585 unique) in the range $5 \leq 2\theta \leq 50°$ on a Nicolet R3mV diffractometer equipped with a graphite monochromated molybdenum X-ray tube. The data were corrected for Lorentz and polarisation effects, and an empirical absorption correction was applied. The crystallographic asymmetric unit contains one half of the formula unit. The position of the unique rhodium atom, which sits on the two-fold axis at $\frac{1}{2},y,\frac{1}{4}$, was derived from direct methods and the remaining non-hydrogen atoms found by iterative application of least-squares refinement and difference-Fourier synthesis. The two-fold axis bisects the phenyl ring and is coincident with the carbon and nitrogen atoms of the acetonitrile molecule, the hydrogen atoms of which are as a consequence disordered. In the latter stages of refinement the non-hydrogen atoms were refined anisotropically, while hydrogen atoms were omitted from the refinement. The final least-squares refinement included

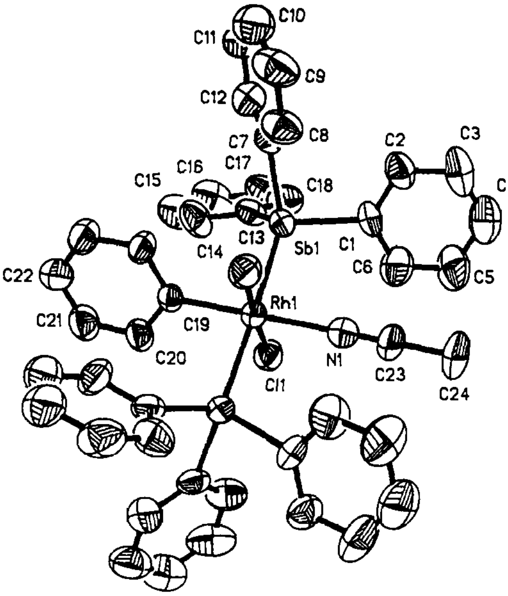

Fig. 1. Thermal ellipsoid plot of [Rh(Ph)(SbPh$_3$)$_2$Cl$_2$(CH$_3$CN)]. Atoms are represented by thermal vibration ellipsoids at the 50% level, and the atom numbering scheme is defined.

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TABLE 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$)

	x	y	z	U_{eq}
Rh(1)	5000	2731(1)	2500	44(1)
Cl(1)	3449(2)	2668(2)	2879(1)	60(1)
Sb(1)	3997(1)	2758(1)	1448(1)	46(1)
C(1)	3441(7)	1332(8)	1192(5)	49(4)
C(2)	3529(9)	955(9)	624(6)	71(5)
C(3)	3239(12)	−36(11)	496(8)	100(7)
C(4)	2859(12)	−600(12)	926(9)	103(8)
C(5)	2734(11)	−197(11)	1505(8)	95(7)
C(6)	3025(10)	767(11)	1621(7)	82(6)
C(7)	4636(8)	3134(8)	642(5)	55(4)
C(8)	5954(10)	2728(11)	552(6)	74(5)
C(9)	5564(9)	2930(13)	0(7)	96(7)
C(10)	5474(12)	3549(13)	−437(7)	93(7)
C(11)	4547(13)	3937(11)	−347(6)	91(7)
C(12)	4121(10)	3728(10)	201(6)	78(5)
C(13)	2721(8)	3639(9)	1330(5)	54(4)
C(14)	2773(10)	4623(10)	1522(6)	77(5)
C(15)	1927(11)	5220(11)	1442(6)	85(6)
C(16)	1053(11)	4823(13)	1167(7)	92(7)
C(17)	1016(10)	3818(13)	987(6)	91(7)
C(18)	1859(9)	3234(11)	1074(5)	71(5)
C(19)	5000	4229(11)	2500	41(5)
C(20)	4577(8)	4763(8)	2954(5)	58(4)
C(21)	4552(9)	5806(10)	2945(6)	71(5)
C(22)	5000	6322(14)	2500	85(8)
N(1)	5000	1153(11)	2500	55(5)
C(23)	5000	321(14)	2500	83(9)
C(24)	5000	−798(15)	2500	135(13)

Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor.

TABLE 2. Bond lengths (Å)

Rh(1)–Cl(1)	2.371(3)	Rh(1)–Sb(1)	2.573(1)
Rh(1)–C(19)	2.027(14)	Rh(1)–N(1)	2.137(15)
Rh(1)–Cl(1A)	2.371(3)	Rh(1)–Sb(1A)	2.573(1)
Sb(1)–C(1)	2.131(10)	Sb(1)–C(7)	2.119(11)
Sb(1)–C(13)	2.118(11)	C(1)–C(2)	1.366(17)
C(1)–C(6)	1.383(18)	C(2)–C(3)	1.419(20)
C(3)–C(4)	1.361(25)	C(4)–C(5)	1.411(26)
C(5)–C(6)	1.381(21)	C(7)–C(8)	1.422(17)
C(7)–C(12)	1.397(17)	C(8)–C(9)	1.404(19)
C(9)–C(10)	1.391(22)	C(10)–C(11)	1.412(24)
C(11)–C(12)	1.421(20)	C(13)–C(14)	1.397(17)
C(13)–C(18)	1.374(16)	C(14)–C(15)	1.414(20)
C(15)–C(16)	1.399(21)	C(16)–C(17)	1.416(24)
C(17)–C(18)	1.403(20)	C(19)–C(20)	1.406(14)
C(19)–C(20A)	1.406(14)	C(20)–C(21)	1.413(17)
C(21)–C(22)	1.396(16)	C(22)–C(21A)	1.396(16)
N(1)–C(23)	1.125(24)	C(23)–C(24)	1.515(28)

The atoms labelled ‘A’ are generated by crystal symmetry.

TABLE 3. Bond angles (°)

Cl(1)–Rh(1)–Sb(1)	84.1(1)
Sb(1)–Rh(1)–C(19)	89.2(1)
Sb(1)–Rh(1)–N(1)	90.8(1)
Cl(1)–Rh(1)–Cl(1A)	175.9(2)
C(19)–Rh(1)–Cl(1A)	92.1(1)
Cl(1)–Rh(1)–Sb(1A)	96.0(1)
C(19)–Rh(1)–Sb(1A)	89.2(1)
Cl(1A)–Rh(1)–Sb(1A)	84.1(1)
Rh(1)–Sb(1)–C(7)	121.7(3)
Rh(1)–Sb(1)–C(13)	118.7(3)
C(7)–Sb(1)–C(13)	100.0(4)
Sb(1)–C(1)–C(6)	118.9(9)
C(1)–C(2)–C(3)	119.1(12)
C(3)–C(4)–C(5)	120.1(15)
C(1)–C(6)–C(5)	121.9(14)
Sb(1)–C(7)–C(12)	119.7(9)
C(7)–C(8)–C(9)	118.2(11)
C(9)–C(10)–C(11)	120.1(14)
C(7)–C(12)–C(11)	118.7(13)
Sb(1)–C(13)–C(18)	119.8(9)
C(13)–C(14)–C(15)	119.4(12)
C(15)–C(16)–C(17)	119.7(14)
C(13)–C(18)–C(17)	120.0(13)
Rh(1)–C(19)–C(20A)	120.9(7)
C(19)–C(20)–C(21)	121.0(11)
C(21)–C(22)–C(21A)	120.1(17)
N(1)–C(23)–C(24)	180.0(1)
Cl(1)–Rh(1)–C(19)	92.1(1)
Cl(1)–Rh(1)–N(1)	87.9(1)
C(19)–Rh(1)–N(1)	180.0(1)
Sb(1)–Rh(1)–Cl(1A)	96.0(1)
N(1)–Rh(1)–Cl(1A)	87.9(1)
Sb(1)–Rh(1)–Sb(1A)	178.4(1)
N(1)–Rh(1)–Sb(1A)	90.8(1)
Rh(1)–Sb(1)–C(1)	111.8(3)
C(1)–Sb(1)–C(7)	99.5(4)
C(1)–Sb(1)–C(13)	101.9(4)
Sb(1)–C(1)–C(2)	121.1(8)
C(2)–C(1)–C(6)	119.9(11)
C(2)–C(3)–C(4)	120.8(16)
C(4)–C(5)–C(6)	118.1(15)
Sb(1)–C(7)–C(8)	118.6(8)
C(8)–C(7)–C(12)	121.7(11)
C(8)–C(9)–C(10)	121.1(14)
C(10)–C(11)–C(12)	120.0(13)
Sb(1)–C(13)–C(14)	118.9(8)
C(14)–C(13)–C(18)	121.3(11)
C(14)–C(15)–C(16)	119.7(14)
C(16)–C(17)–C(18)	119.8(13)
Rh(1)–C(19)–C(20)	120.9(7)
C(20)–C(19)–C(20A)	118.2(14)
C(20)–C(21)–C(22)	119.8(12)
Rh(1)–N(1)–C(23)	180.0(1)

The atoms labelled ‘A’ are generated by crystal symmetry.

229 parameters for 1985 ($I \geqslant 3\sigma(I)$) variables. The last cycle did not shift any parameter by more than 0.02 times its estimated standard deviation and gave $R=0.0463$, $R_w=0.0476$ (weighting scheme $w^{-1}=\sigma^2(F)+0.00062F^2$). A final difference-Fourier contained no peaks above 0.95 e Å^{-3}. Calculations were performed with the SHELXTX PLUS program package [10]. The structure is presented in Fig. 1, fractional

atomic coordinates in Table 1, and bond lengths and inter-bond angles in Tables 2 and 3, respectively.

The coordination about the rhodium(III) ion is that of a distorted octahedron. The metal adopts an all *trans* arrangement with respect to the chloride and triphenylantimony ligands, and the sigma bound phenyl ring is located *trans* to the coordinated acetonitrile molecule. The angles between adjacent atoms in the coordination sphere lie in the range 84.1(1)–96.0(1)°. The smallest of these angles is that between a chloride ligand and an antimony atom, as is the largest angle. The rhodium–carbon and rhodium–nitrogen bonds are precisely colinear as a consequence of crystal symmetry. The rhodium–antimony bond, 2.573(1) Å, is *c.* 0.1 Å shorter than that observed in the rhodium(II/II) dimer [$Rh_2(HNCOPh)_4(SbPh_3)_2$] [11], as was to be expected. The metal–chlorine distance, 2.371(3) Å, is closely similar to that found with other d^6 metal ions and a *trans* dichloride geometry, e.g. [$RuCl_2py_4$], 2.406(1) Å [12]; [$RhCl_2(py)_2(\{C_6H_4\}NHpy)$], 2.358(2) Å [13]. The sigma bound phenyl ring is essentially planar (maximum deviation 0.018 Å) and is rotated away from an orientation which would eclipse two of the four ligands in the equatorial plane of the metal ion (torsion angle C(20)–C(19)–Rh(1)–Cl(1) 35.0°). The closer approach of the phenyl ring to the chloride ligands gives rise to the greater deviation from linearity of the Cl–Rh–Cl angle, 175.9(2)°, than of the Sb–Rh–Sb angle, 178.4(1)°. The Rh(1)–N(1) bond length, 2.14(1) Å, is greater than that commonly found for acetonitrile ligands bound *trans* to neutral nitrogen donor ligands [14], but is entirely consistent with coordination *trans* to a sigma bound carbon atom, which of course exhibits a greater *trans* directing influence.

The mechanism by which the rhodium dimer [$Rh_2(HNCOCH_3)_4(SbPh_3)_2$] is transformed into this monomeric rhodium(III) compound is obscure. The chloride ligands clearly come from the dichloromethane solvent. The acetonitrile is most likely formed *in situ*, possibly by radical attack on the coordinated acetamidate ligands. In any event, the dinuclear structure, which was undoubtedly present prior to electrolysis, is completely disrupted and the acetamidate ligands are lost. This generates solvated rhodium(III) ions which then simply undergo reaction with whatever ligands are available in solution. While the presence of the phenyl group might at first seem surprising there is already a precedent for Sb–C bond cleavage in the chemistry of the related dinuclear ruthenium compounds [$Ru(HNCOR)_4Cl$] [7, 8].

Acknowledgements

We thank Johnson Matthey plc for generous loans of rhodium trichloride and the SERC for provision of the X-ray equipment.

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