Inorganica Chimica Acta 362 (2009) 4517–4525

Contents lists available at ScienceDirect

Inorganica Chimica Acta

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

Structure, bonding, and ligand-based reactions of zwitterionic boratoiridium(I) complexes with oxazolinyl scorpionate ligands

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ARTICLE INFO

Article history:
Received 31 January 2009
Received in revised form 28 May 2009
Accepted 2 June 2009
Available online 13 June 2009

Dedicated to Prof. Swiatoslaw Trofimenko.

Keywords:
Iridium compounds
Scorpionate
Oxazoline

ABSTRACT

New tris(4,4-dimethyl-2-oxazolinyl)phenylboratoiridium(I) scorpionate-type compounds $[\mathrm{Ir(To^M)L_2}]$ ($\mathrm{L_2} = \eta^4$-$\mathrm{C_8H_{12}}$ and $\mathrm{(CO)_2}$) and electrophiles form adducts that contain a bidentate $\mathrm{IrTo^M}$-coordination and an *N*–electrophile interaction of the third oxazoline instead of the oxidative addition product. The adduct with lithium chloride gives a unique heterobimetallic Li–*O*-oxazoline-*N*–Ir bridging structure that has been identified through X-ray crystallography. Density functional theory calculations provide thermodynamic data, orbital symmetries, and orbital energies that explain the formation of the observed iridium(I) products.

1. Introduction

Oxidative addition reactions of monovalent Rh and Ir scorpionates yield racemic [M(Tp)R(X)L] compounds (Tp = tris(pyrazolyl)borate, Chart 1 [1]; M = Rh, Ir; R = hydrocarbyl; X = hydride, halide; L = neutral ligand) that contain a stereogenic metal center [2]. The configuration of the metal stereocenter and peripheral stereocenters on the hydrocarbyl R group could be controlled by chiral ligands. However, few diastereoselective C–H bond activation reactions have been reported with TpRh(I)- or TpIr(I)-type compounds. Notable examples include the diastereoselective activation of a fused menthylpyrazole group on an optically active Tp ligand [3], and cyclometalation of a diisopropylamine ligand that gives racemic $[\mathrm{Tp^{Me2Cl}}\overline{\mathrm{RhH(NH(^iPr)CHMeC}}\mathrm{H_2})]$ ($\mathrm{Tp^{Me2Cl}} = \mathrm{HB(4\text{-}Cl\text{-}3,5Me_2N_2C_3)_3}$) in high diastereoselectivity (>95%) [4]. Stereoselective C–H bond oxidative additions could be an important component of hydrocarbon functionalization mediated by scorpionate compounds [5], providing impetus for investigating oxidative addition reactions of new chiral scorpionate compounds, as well as comparing related optically active and achiral ligands.

Therefore, we recently prepared the optically active scorpionate compounds $[\mathrm{Ir(To^P)L_2}]$ ($\mathrm{To^P}$ = tris(4*S*-isopropyl-2-oxazolinyl)phenylborate, Chart 1; $\mathrm{L_2} = \eta^4$-$\mathrm{C_8H_{12}}$ or $\mathrm{(CO)_2}$) to study stereoselective oxidative addition reactions [6]. However, reactions of $[\mathrm{Ir(To^P)L_2}]$ and the electrophiles MeOTf and MeI provide *N*-methylated oxazolinium species $[\mathrm{Ir(\kappa^2\text{-}To^P\text{-}Me)L_2}]^+$ rather than oxidative addition products. Interestingly, reactions of Group 9 Tp-type scorpionates with protons show either metal- or ligand-based reactivity [7]. For example, mixtures of $[\mathrm{TpRh(CO)_2}]$ and $[\mathrm{HOEt_2}][\mathrm{BF_4}]$ give a pyrazolyl-protonated rhodium(I) product, whereas the heavier iridium congener forms an iridium(III)-hydride [7]. Additionally, a tetrahedral tris(carbene)boratocobalt(II) chloride complex reacts with $\mathrm{H^+}$ to give a protonated carbene [8]. In contrast, $[\mathrm{Tp^*Rh(CO)_2}]$ ($\mathrm{Tp^*} = \mathrm{HB(N_2C_3HMe_2)_3}$) and MeI react to give the acetyl compound $[\mathrm{Tp^*Rh(CO)(COMe)I}]$ via the unobserved Rh(III) oxidative addition product [9]. Likewise, the cationic compound $[\mathrm{Rh(tris\text{-}ox)(\eta^4\text{-}C_8H_{12})}]^+$ is oxidized by $\mathrm{CsBr_3}$ to give $[\mathrm{RhBr_3(tris\text{-}ox)}]$ (tris-ox = 1,1,1-tris(4*S*-isopropyl-2-oxazolinyl)ethane) [10].

Tris(oxazolinyl)boratoiridium(I) compounds were further explored to clarify their reactivity in the context of this Group 9 scorpionate chemistry. In this contribution, achiral $\mathrm{To^MIr(I)}$ compounds ($\mathrm{To^M}$ = tris(4,4-dimethyl-2-oxazolinyl)phenylborate) and their interactions with electrophiles are reported. Although enantiopure $\mathrm{IrTo^P}$-based compounds are amorphous as determined by linewidths of solid state CPMAS NMR experiments [6], the achiral $\mathrm{IrTo^M}$ compounds described here are crystalline and therefore amenable to X-ray diffraction studies for structural analysis. Interestingly, the reaction of $\mathrm{Li[To^M]}$ and $[\mathrm{Ir(\mu\text{-}Cl)(\eta^4\text{-}C_8H_{12})}]_2$ produces an unusual heterobimetallic complex that contains a $[\mathrm{Li\text{–}(\mu\text{-}To^M)\text{–}Ir}]$ interaction through N–Ir, N–Li, and O–Li bonds. The N–Ir interactions are persistent in solution, as verified by ^{15}N NMR chemical shift data obtained using ^{1}H–^{15}N heteronuclear multiple bond cor-

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doi:10.1016/j.ica.2009.06.017

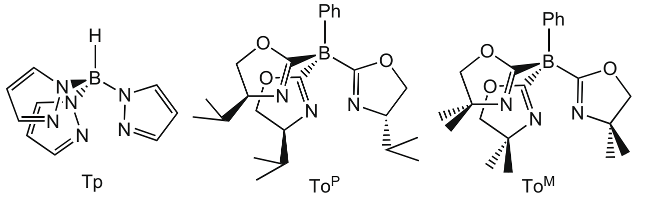


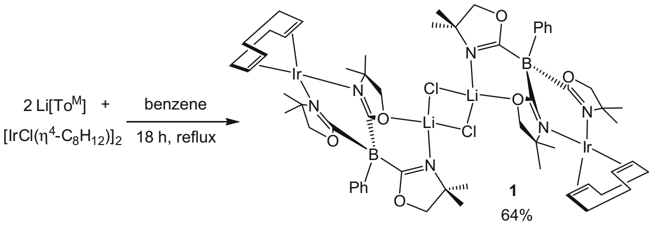
Chart 1.

relation (HMBC) experiments. Additionally, the X-ray data is compared with model structures obtained from density functional theory (DFT) calculations. These computational studies indicate that the observed *N*-methylated and *N*-protonated oxazolinium species are the thermodynamic products and thus favored in comparison to the oxidative addition products $[Ir(E)(To^M)L_2]^+$ (E = H, Me).

2. Results and discussion

2.1. Synthesis and characterization of tris(2-oxazolinyl)boratoiridium(I) compounds

The compound $[(\eta^4\text{-}C_8H_{12})Ir(\mu\text{-}\kappa^2\text{-}N1,N2\text{-}To^M\text{-}\kappa^2\text{-}N3,O2)Li(\mu\text{-}Cl)]_2$ (**1**; *N*1, *N*2, *N*3, and *O*2 designate nitrogen- and oxygen-centers in oxazoline rings 1, 2, and 3) is obtained upon heating a benzene solution of $Li[To^M]$ [11] and 0.5 equiv. of $[Ir(\mu\text{-}Cl)(\eta^4\text{-}C_8H_{12})]_2$ to reflux for 18 h (Eq. (1)).



(1)

The solid state structure of **1** was established by X-ray crystallography as an interesting heterobimetallic dimer in which the $[To^M]$ anion is a bridging bidentate ligand for one iridium and one lithium center (Fig. 1). The pseudo-square planar iridium centers are coordinated by nitrogen from two oxazoline rings and by 1,5-cyclooctadiene. The nitrogen of the third oxazoline ring interacts with a lithium cation, and that four-coordinate lithium center is also bonded to the oxygen of the second oxazoline ring. Thus, that oxazoline interacts with both iridium and lithium in a Li–*O*-oxazoline-*N*–Ir bridging structure. The final two coordination sites of the lithium cation are taken by two inversion-related chloride ions that bridge to the symmetry-equivalent lithium cation in the other half of the dimer. This configuration gives a $(LiCl)_2$ planar parallelogram (<Li1–Cl1–Li1#, 78.0(4)°; <Cl1–Li1–Cl1#, 102.0(4)°; the <Li1–Cl1–Li1#–Cl1# dihedral angle is 0°), and the crystallographic inversion center that relates the two halves of the dimer is located at the center of the parallelogram. The Ir–N distances are identical within error (Ir1–N1, 2.107(5) and Ir1–N2, 2.107(6) Å) indicating that the lithium-oxygen interaction does not affect the iridium–nitrogen bond distances. In this crystalline phase, all three oxazoline groups are unique and **1** is C_1-symmetric, whereas in solution two oxazoline rings are related by a mirror plane (see NMR discussion below).

The structure of **1** contains the first crystallographically characterized *O*-coordinated oxazoline, and it is further highlighted by a unique heterobimetallic M-*N*-oxazoline-*O*-M′ bridging interaction. A few examples of *O*-coordinated oxazole-metal interactions (particularly benzoxazole, **A** in Fig. 2) have been proposed, and a europium(III) compound *O*-coordinated by 2-(2′-pyridyl)-1,3-benzoxazole has been crystallographically characterized [12]. The configuration of divalent cobalt, nickel, copper, and zinc *O*-coordinated benzoxazole compounds was assigned using their metal–oxygen stretching frequencies (ν_{M-O}) in the far infrared [13], and EPR studies supported oxygen binding in a related copper(II) complex [14]. The dimeric [Pd(oxalato)(benzoxazole)]$_2$ apparently involves a unique Pd–*N*-benzoxazole-*O*–Pd bridging structure (structure **B** in Fig. 2) based on its ν_{M-O} and ν_{M-N} [15]. In oxazoline coordination chemistry, oxygen–metal interactions are less common. A trimeric lithium compound 2-(2′-lithiophenyl)-4,4-dimethyl-2-oxazoline was proposed to contain an oxygen–lithium interaction, although *N*-coordination was not excluded [16]. Recently, a zirconium(IV)-mediated oxazoline ring opening was suggested to involve a Zr–O interaction [17].

We have not found analogous examples of M-(μ-Tp)-M′ or M-(μ-pyrazolyl)-M′ structures from intact classic scorpionates in the literature, although functionalized scorpionates have recently provided heterobimetallic structures useful for building coordination networks, investigating M···M′ electronic interactions, and developing new catalytic reactions [18].

The structure of **1** is particularly interesting in the context of salt metathesis reactions of polydentate anionic ligands. Presumably the reaction of optically active $Li[To^P]$ and 0.5 $[IrCl(\eta^4\text{-}C_8H_{12})]_2$ that yields LiCl-free $[Ir(To^P)(\eta^4\text{-}C_8H_{12})]$ [6] proceeds through structures in which oxazoline groups bond simultaneously with both metal centers before the eventual extrusion of LiCl. Likewise, reactions of KTp and metal halides likely involve unobserved heterobimetallic intermediates. Thus, compound **1** may be viewed as an intermediate in salt metathesis reactions of polydentate ligand anions and metal halides. In the case of achiral $Li[To^M]$, the salt elimination is not completed under the reaction conditions, by refluxing in tetrahydrofuran, by heating in non-polar solvents (to precipitate LiCl), or by Soxhlet extraction. However, ligand substitution reactions and stronger electrophiles than Li^+ will induce LiCl extrusion (see below).

Although **1** is C_1-symmetric in the solid state, solution state NMR data (in benzene-d_6, methylene chloride-d_2, and tetrahydrofuran-d_8) are consistent with C_s-symmetry. In the ^1H NMR spectrum of **1** in tetrahydrofuran-d_8, the oxazoline methyl resonances appeared as three singlet resonances at 1.18, 1.24 and 1.46 ppm, and three resonances assigned to ring methylene moieties were observed as a singlet (3.5 ppm, 2 H) and two coupled diastereotopic doublets (4.18 and 4.26 ppm, 4 H, $^2J_{HH}$ = 7.7 Hz) from one unique and two equivalent oxazoline rings, respectively. The spectrum for a C_1-symmetric structure (not observed in solution) would contain six singlet resonances and six doublets for oxazoline CH_3 and CH_2 groups. Thus, two of the three oxazolines are related by a mirror plane that is coincident with the third oxazoline ring. A ^1H–^{15}N HMBC experiment helped identify the solution state coordination mode of the $[To^M]$ ligand in **1**; two ^{15}N NMR resonances at −145.9 and −181.4 ppm (referenced to nitromethane and acquired in tetrahydrofuran-d_8) correspond to one unique and two equivalent oxazoline nitrogen, respectively. The latter resonance was assigned to the iridium-coordinated oxazoline nitrogen based on its crosspeaks with the two diastereotopic doublets in the ^1H NMR spectrum. The chemical shift of the former ^{15}N NMR resonance (−145.9 ppm) is 18 ppm upfield from that of uncoordinated 4,4-dimethyl-2-oxazoline (−127.9 ppm) and substantially downfield from the two oxazoline nitrogen that are coordinated to iridium (−182 ppm, 36 ppm difference).

These NMR data contrast the solution structures of **1** and the optically active, LiCl-free derivative $[Ir(To^P)(\eta^4\text{-}C_8H_{12})]$; in the latter, the three 4*S*-isopropyloxazoline groups are equivalent due to a