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Kinetics and mechanism of oxidative addition of MeI to binuclear cycloplatinated complexes containing biphosphine bridges: Effects of ligands

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ABSTRACT

The binuclear complex $[Pt_2Me_2(bhq)_2(\mu\text{-dppf})]$, **1a**, in which bhqH = benzo{h}quinoline and dppf = 1,1′-bis(diphenylphosphino)ferrocene, was synthesized by the reaction of $[PtMe(SMe_2)(bhq)]$ with 0.5 equiv of dppf at room temperature. The reaction of Pt(II)–Pt(II) complex **1a** with excess MeI gave the Pt(IV)–Pt(IV) complex $[Pt_2I_2Me_4(bhq)_2(\mu\text{-dppf})]$, **2a**. The complexes were fully characterized using multinuclear (^1H, ^{31}P and ^{195}Pt) NMR spectroscopy and elemental analysis. The kinetic and mechanism of the reaction of complex **1a** with MeI was investigated in $CHCl_3$ and based on the data, obtained from UV–vis and low temperature ^{31}P NMR spectroscopies, a mechanism involving stepwise oxidative addition of MeI to the two Pt(II) centers is suggested. Reaction rates concerning the complex **1a**, having bhq ligand, are almost 1.4 times slower than those involving the ppy complex $[Pt_2Me_2(p\text{-}py)_2(\mu\text{-dppf})]$, ppyH = 2-phenylpyridine, reported previously (Inorg. Chem. 2008, 47, 5441). This is attributed to the stronger donor ability of the ppy ligand as compared to that of the bhq ligand as is further confirmed using density functional theory (DFT) calculations through finding approximate structures for the described complexes. A comparative kinetic study of reaction of the dimeric platinum(II) complex $[Pt_2Me_2(bhq)_2(\mu\text{-dppm})]$, **1b**, where dppm = bis(diphenylphosphino)methane, with MeI was also performed to investigate the effect of bridging biphosphine ligand on the kinetic and mechanism of the dimeric complexes with MeI. A double MeI oxidative addition was observed for which the classical S_N2 mechanism for both steps, as well as the possible intermediates, is suggested.

1. Introduction

Oxidative addition is a fundamental reaction which is the base for many applications of organometallic compounds in many homogeneous catalytic processes and organic synthesis [1–3]. Oxidative addition of carbon-halide or other bonds to monomeric organoplatinum(II) complexes, especially those containing diimine ligands, has been extensively studied [4–10]. The most common mechanism of oxidative addition of alkyl halides is the classical S_N2 mechanism involving a second-order rate law (rate = k_2[complex][halide]), although in some relatively rare cases, the reactions proceed by concerted addition *via* a three–center transition state (mostly for aryl halides) [5,11,12] or by radical mechanisms, e.g. as observed for isopropyl iodide [13]. In all of these, the addition product has the halide and organic group bound to the same metal atom, increasing the oxidation state of the metal by 2. Despite these, examples of the related oxidative addition to binuclear complexes are much rarer [14–18]. The oxidative addition to the binuclear complexes is interesting because cooperative electronic or steric effects between the two adjacent metal centers can give rise to reaction pathways or products not possible in the mononuclear analogous [19–23]. In some cases, increased steric hindrance in binuclear complexes are thought to decrease the reactivity of systems [16], but in other cases, cooperative effects between the two metal centers lead to an increase in reactivity [24,25].

On the other hand, transition metal cyclometalated complexes, in particular those involving platinum, are of interest because of their potential applications in many areas, such as chemosensors [26,27], photocatalysts [28,29], and optoelectronic devices [30,31]. Square planar cyclometalated platinum complex species have also

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been used as “building blocks” for complex systems such as dendrimers [32].

Although oxidative addition reactions on mononuclear square planar platinum(II) complexes, as a key step in many catalytic reactions, have been extensively studied, to the best of our knowledge, such reactions have rarely been studied on binuclear platinum complexes, especially complexes having two cycloplatinated centers [18]. Cyclometalated platinum(II) complexes can be highly reactive *via* oxidative addition to give the corresponding platinum(IV) products.

A series of cycloplatinated complexes containing bridging biphosphine ligands of the types $[Pt_2R_2(C{-}N)_2(\mu\text{-dppf})]$, $[Pt_2R_2(C{-}N)_2(\mu\text{-dppm})]$ and $[Pt_2R_2(C{-}N)_2(\mu\text{-dppe})]$, in which, dppf = 1,1′- bis(diphenylphosphino)ferrocene (R = Me or aryl), dppm = bis(diphenylphosphino)methane (R = aryl), dppe = bis(diphenylphosphino)ethane (R = Me or aryl) and C–N = ppy (ppyH = 2-phenylpyrine) or bhq (bhqH = benzo{h} quinoline) ligands have recently been prepared [18,33–36]. In continuation of our interest in oxidative addition reactions of cyclometalated Pt(II) complexes, in this study, we attempted to investigate influence of the nature of biphosphine bridges on the kinetic and mechanism of oxidative addition of MeI to binuclear cyclometalated methylplatinum(II) complexes $[Pt_2Me_2(bhq)_2(\mu\text{-dppf})]$, **1a**, and $[Pt_2Me_2(bhq)_2(\mu\text{-dppm})]$, **1b**. By comparing the data to those reported previously for the corresponding reaction involving the ppy analogous $[Pt_2Me_2(ppy)_2(\mu\text{-dppf})]$ [18], it was possible to describe the effect of cycloplatinated rings on rate of the related reactions.

2. Experimental

The NMR spectra were recorded on a Bruker Avance DRX 500 MHz spectrometer. The operating frequencies and references, respectively, are shown in parentheses as follows: ^{1}H (500 MHz, TMS), ^{31}P (202 MHz, 85% H_3PO_4) and ^{195}Pt (107 MHz, aqueous Na_2PtCl_4). All the chemical shifts and coupling constants are in ppm and Hz, respectively. Kinetic studies were carried out by using a Perkin–Elmer Lambda 25 spectrophotometer with temperature control using an EYELA NCB-3100 constant-temperature bath. Benzo{h}quinoline and 1,1′-bis(diphenylphosphino)ferrocene were purchased from commercial sources. $[PtMe(bhq)(SMe_2)]$ [34] and $[Pt_2Me_2(bhq)_2(\mu\text{-dppm})]$ [36] were prepared as reported.

2.1. $[Pt_2Me_2(bhq)_2(\mu\text{-dppf})]$, *1a*

1,1′-Bis(diphenylphosphino)ferrocene (275 mg, 0.5 mmol) was added to a solution of $[Pt(Me)(bhq)(SMe_2)]$, (450 mg, 1.0 mmol) in acetone (20 ml). The mixture was stirred at room temperature for 2 h. After removal of the solvent by evaporation, a yellow residue was obtained which was further purified by repeated washing with ether and cold acetone. Yield 66%, mp = 258 °C (decomp). Anal. Calcd for $C_{62}H_{50}FeN_2P_2Pt_2$: C, 56.0; H, 3.8; N, 2.1; Found: C, 55.6; H, 4.0; N, 2.4. NMR data in $CDCl_3$: $\delta(^{1}H)$ 1.17 (d, 6H, $^{2}J_{PtH} = 85.9$ Hz, $^{3}J_{PH} = 8.1$ Hz, 2 Me), 4.38 (br s, 4H, β, β′ Cp protons), 4.44 (br s, 4H, α, α′ Cp protons), (aromatic protons): 6.81 (m, 2H, $^{3}J_{PtH} = 7.7$ Hz, $^{3}J_{HH} = 2.5$ Hz, CH groups adjacent to coordinated C atoms), 7.3–8.1 (m, 32H, overlapping multiplets), 8.18 (m, 2H, $^{3}J_{PtH} = 49.2$, 2 CH groups adjacent to coordinated N atoms); $\delta(^{13}C)$ −14.5 (d, $^{1}J_{PtC} = 735$ Hz, $^{2}J_{PC} = 7$ Hz, Me ligands), 73.8 (d, $^{3}J_{PC} = 10$ Hz, β, β′ Cp carbons), 75.8 (d, $^{2}J_{PC} = 12.5$ Hz, α, α′ Cp carbons), 76.6 (d, $^{1}J_{PC} = 46$ Hz, $^{2}J_{PtC} = 31$ Hz, *ipso* Cp carbons), $\delta(^{31}P)$ 24.1 ($^{1}J_{PtP} = 2226$ Hz, 2P of dppf); $\delta(^{195}Pt)$ −2588 (d, $^{1}J_{PtP} = 2225$ Hz, 2Pt).

2.2. $[Pt_2I_2Me_4(bhq)_2(\mu\text{-dppf})]$, *2a*

An excess of MeI (50 μL) was added to a solution of complex **1a** (100 mg in 20 mL of chloroform) at room temperature. The mixture was stirred at this condition for 1 h, then the solvent was removed under reduced pressure and the residue was triturated with ether (2 × 3 mL). The product was dried under vacuum. Yield: 84 mg, 70%. Anal. Calcd for $C_{64}H_{56}I_2FeN_2P_2Pt_2$: C, 47.6; H, 3.5; N, 1.7; Found: C, 47.2; H, 3.7; N, 1.6. NMR data in $CDCl_3$: $\delta(^{1}H)$ 1.03 (d, 6H, $^{2}J_{PtH} = 60.5$ Hz, $^{3}J_{PH} = 7.6$ Hz, 2 Me ligands *trans* to P), 1.55 (d, 3H, $^{2}J_{PtH} = 71.2$ Hz, $^{3}J_{PH} = 2.9$ Hz, 1 Me ligand *trans* to N), 1.59 (d, 3H, $^{2}J_{PtH} = 72.6$ Hz, $^{3}J_{PH} = 2.9$ Hz, 1 Me ligand *trans* to N), 2.51, 2.63, 2.96 (each a br s,1H, 1H, 2H, respectively, β, β′ Cp protons), 3.44 (br s, 4H, α, α′ Cp protons), aromatic protons: 6.6–8.2 (overlapping multiplets), 9.55 (d, 1H, $J_{HH} = 5.1$ Hz, $^{3}J_{PtH} = 9$ Hz, CH group adjacent to coordinated N atom), 9.56 (d, 1H, $J_{HH} = 5.2$ Hz, $^{3}J_{PtH} = 9$ Hz, CH group adjacent to coordinated N atom); $\delta(^{31}P)$ −13.1(s, $^{1}J_{PtP} = 1012$ Hz, 1P), -13.0 (s, $^{1}J_{PtP} = 992$ Hz, 1P).

2.3. Kinetic study

In a typical experiment, a solution of complex **1a** or **1b** in $CHCl_3$ (3 ml, 3×10^{-4} M) in a cuvette was thermostated at 25 °C and a known excess of MeI was added using a micro syringe. After rapid stirring, the absorbance at corresponding wavelength was monitored with time.

3. Results and discussion

3.1. Synthesis and characterization of the new binuclear complexes

As is depicted in Scheme 1, the reaction of a solution of $[PtMe(SMe_2)(bhq)]$ in acetone, with 0.5 equiv of dppf at room temperature gave in good yield the new binuclear cyclometalated Pt(II)–Pt(II) complex $[Pt_2Me_2(bhq)_2(\mu\text{-dppf})]$, **1a**, in which bhq = deprotonated benzo{h}quinoline or dppf = 1,1′-bis(diphenylphosphino)ferrocene, by replacement of SMe_2 ligands with the P ligating atoms of dppf. Complex **1a** is an air-stable yellow solid which is stable in acetone or chloroform solution for several hours. Reaction of the complex **1a** with excess methyl iodide at room temperature led to formation of the binuclear Pt(IV)–Pt(IV) complex $[Pt_2I_2Me_4(bhq)_2(\mu\text{-dppf})]$, **2a**.

In the ^{1}H NMR spectrum of complex **1a** (see Fig. 1), the two equivalent methyl ligands, being *trans* to imine N atoms, are resonated as a doublet signal at δ 1.17 with $^{3}J_{PH} = 8.1$ Hz which is coupled to the platinum center to give satellites with $^{2}J_{PtH} = 85.9$ Hz. The 4 equivalent α and 4 equivalent β protons of the cyclopentadienyl rings are appeared as two broad singlets at δ 4.44 and 4.38, respectively. In the ^{31}P NMR spectrum of complex **1a**, the two equivalent P atoms are appeared as a singlet signal at δ 24.1 which are coupled to Pt atoms to give satellites with $^{1}J_{PtP} = 2226$ Hz. Consistent with this, in the ^{195}Pt NMR spectrum of **1a**, a doublet is observed at δ −2588 with $^{1}J_{PtP} = 2225$ Hz. The equivalency of the P atoms suggests that dppf is acting as a spacer ligand between the two PtMe(bhq) moieties and thus each P atom is coordinated to a Pt atom in a *trans* disposition to coordinating C atom of the phenyl ring of bhq ligand and each Me ligand is ought to be located *trans* to one of the coordinated N atom of bhq ligand.

In the ^{1}H NMR spectrum of complex **2a** (see Fig. 1), the relative intensity of Me ligands protons to cp protons of the dppf ligand is 12:8, confirming that the complex is a dimer. The two Me ligands locating *trans* to P are observed as overlapping doublets at δ 1.03 with $^{3}J_{PH} = 7.6$ Hz and $^{2}J_{PtH} = 61.5$ Hz. However, the two Me ligands locating *trans* to N ligating atoms are appeared as two different doublets at δ 1.55 ($^{3}J_{PH} = 2.9$ Hz) and 1.59 ($^{3}J_{PH} = 2.9$ Hz), each with