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Substitution reactions involving cyclometalated platinum(II) complexes: Kinetic investigations

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ABSTRACT

Substitution reaction of the labile SMe_2 ligand in the cyclometalated platinum(II) complexes of general formula $[PtAr(ppy)(SMe_2)]$, **1**, in which ppy = deprotonated 2-phenylpyridyl and Ar = p-MeC_6H_4 or p-$MeOC_6H_4$, by several N or P donor reagents were studied; the N-donors, N, are pyridine (Py) and substituted pyridines, N = 4-MePy, Py, Py-d_5, 2-MePy, 3-PhPy, 3,4-Me_2Py, 4-^{t}BuPy or 3-C(O)OMePy, and the P-donors, L, are phosphines or phosphites, L = $P(OPh)_3$, $P(O\text{-}^iPr)_3$, PPh_3, PPh_2Me and L_2 = $Ph_2PCH_2PPh_2$, bis(diphenylphosphino)methane (dppm). The products were identified by multinuclear NMR studies as [PtAr(ppy)(N)], **2**, or [PtAr(ppy)(L)], **3**, respectively. Complexes **1** have a MLCT band in the visible region which was used to easily follow the kinetics of the ligand substitution reactions by UV–vis spectroscopy. Although the complexes **1** contain two *cis* Pt–C bonds, the substitution reactions followed a normal associative mechanism. The rates of reactions were depended on the concentration and the nature of the entering group. The $\Delta H^\ddagger/\Delta S^\ddagger$ compensation plot gave a straight line suggesting the operation of the same mechanism for all entering nucleophiles.

1. Introduction

Ligand substitution reaction involving a transition metal complex is usually considered as a key step in many catalytic reactions [1]. The related reactions on square planar platinum(II) complexes have been extensively studied [2–7] and shown to proceed usually via an associative process, implying direct attack of the entering nucleophile on substrate with the formation of 18e five-coordinated intermediates [8–10]. However, to the best of our knowledge, such reactions have rarely been studied on cyclometalated platinum complexes [11–16]. Kinetic studies of ligand substitution on the cyclometalated platinum(II) complexes [Pt(N–N–C)Cl] (N–N–CH = 6-(1-methylbenzyl)-2,2′-bipyridine) [13] and $[Pt(N–C)(N)(H_2O)]$ (N–CH = *N,N*-dimethylbenzylamine, N = $pySO_3$-3) [14,15] and on the cationic complex $[Pt(N–C–N)(H_2O)]^+$ (N–CH–N = 2,6-bis((dimethylamino)methyl) phenyl) [16], each containing only one monodentate ligand for substitution, have shown that the activation mode is associative in nature. On the other hand, SMe_2 substitution reactions in the complexes $[Pt(bph)(SMe_2)_2]$ (bph = 2,2′-biphenyl dianion) and $[PtPh_2(SMe_2)_2]$, each bearing two Pt–C bondings, with reagents potentially having bidentate donor abilities such as bipyridine, phenanthroline or 1,2-(diphenylphosphino)ethane, have been shown to occur through a dissociative path [12].

Transition metal cyclometalated complexes, in particular those involving platinum, are of interest due to their potential applications in many areas, such as chemosensors [17,18], photocatalysts [19,20], and luminescent [21,22]. Square planar cyclometalated platinum complexes have also been used as “building blocks” for complex systems such as self-assembly [23], and dendrimers [24,25]. As such we prompted to study the kinetics and mechanism of the ligand substitution reactions concerning the lability of sulfur-bonded dimethylsulfide in the cyclometalated platinum(II) complexes of general formula $[PtAr(ppy)(SMe_2)]$, **1**, in which ppy = deprotonated 2-phenylpyridyl and Ar = p-MeC_6H_4 or p-$MeOC_6H_4$, with different nitrogen and phosphorous-donors. Despite the presence of two *cis*-Pt–C bondings in the starting complexes **1**, the kinetic investigations comply with the substitution reactions proceeding via an associative mechanism.

2. Results and discussion

2.1. Synthesis and characterization of the complexes

The general route used to prepare the cyclometalated organoplatinum complexes are described in Scheme 1. The reaction of 2-

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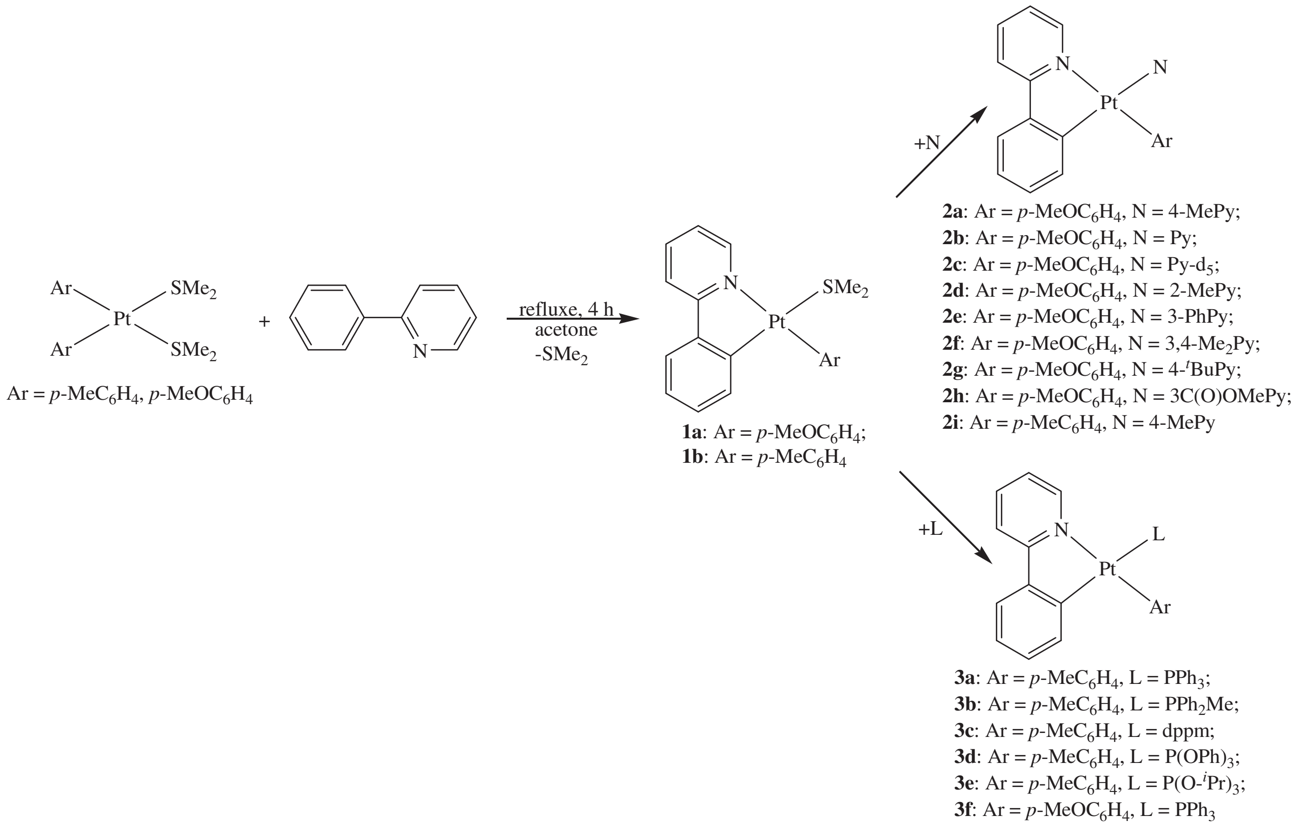

Scheme 1.

phenylpyridine (ppyH) with the starting complexes [PtAr$_2$(SMe$_2$)$_2$] (Ar = p-MeC$_6$H$_4$ or p-MeOC$_6$H$_4$) led to formation of the monoarylplatinum complexes [PtAr(ppy)(SMe$_2$)], **1**, believed to occur by coordination of the nitrogen atom of the pyridyl group followed by subsequent cyclometalation, as described elsewhere for other similar reactions involving C–H bond activation and formation of a new metal–carbon bond [26–30].

Reaction of the complexes [PtAr(ppy)(SMe$_2$)], **1** (Ar = p-MeC$_6$H$_4$ or p-MeOC$_6$H$_4$), with 1 equiv of either the nitrogen nucleophiles N (N = 4-MePy, Py, Py-d$_5$, 2-MePy, 3-PhPy, 3,4-Me$_2$Py, 4-^{t}BuPy or 3-C(O)OMePy) or the phosphorous nucleophiles L (L = PPh$_3$, PPh$_2$Me, P(OPh)$_3$, P(O-^{i}Pr)$_3$, or L$_2$ = Ph$_2$PCH$_2$PPh$_2$, dppm) proceeded via displacement of the labile SMe$_2$ ligand to give the complexes [PtAr(ppy)(N)] or [PtAr(ppy)(L)], as depicted in Scheme 1.

The complexes [Pt(p-MeOC$_6$H$_4$)(ppy)(N)], **2**, were characterized by ^{1}H NMR spectroscopy. Typically, in the ^{1}H NMR spectrum of complex [Pt(p-MeOC$_6$H$_4$)(ppy)(4-MePy)], **2a**, the methyl groups on 4-MePy and anisole ligands were observed at $\delta = 2.30$ and 3.70, respectively. A doublet signal at $\delta = 8.61$ (with $^3J_{H^mH^o} = 6.0$ Hz), that is accompanying by platinum satellites with $^3J_{PtH^o} = 24.6$ Hz, is assigned to the two equivalent H^o protons of the 4-MePy ligand. Notice that a similar doublet signal at $\delta = 8.87$ (with $^3J_{H^mH^o} = 6.3$ Hz) is assigned to the two equivalent H^o protons of the Py ligand in the ^{1}H NMR spectrum of the complex [Pt(p-MeOC$_6$H$_4$)(ppy)(Py)], **2b**, which as expected was missed in the spectrum of related deuterated complex [Pt(p-MeOC$_6$H$_4$)(ppy)(Py-d$_5$)], **2c**. This indicates that the H^o of the N ligand in complexes **2** is expected to appear close to $\delta = 8.70$ and this should not be misassigned with the signal for *ortho* hydrogen of ppy ligand (i.e. proton of C–H group locating adjacent to coordinated nitrogen atom) which seems to be overlapped under the aromatic protons. The equivalency of the two H^o of the N ligand in complexes **2** confirms that the pyridine ligands in the complexes **2** should be oriented perpendicular to the square planar geometry of the platinum centers.

The complexes [Pt(p-MeC$_6$H$_4$)(ppy)(L)], **3**, were characterized using NMR (^{1}H, ^{31}P, ^{195}Pt) spectroscopy as typically described for [Pt(p-MeC$_6$H$_4$)(ppy)(PPh$_3$)], **3a**. In the ^{31}P NMR spectrum of complex **3a**, the phosphorous atom appeared as a singlet signal at $\delta = 31.8$ which was coupled to platinum atom to give satellites with $^1J_{PtP} = 2041$ Hz. Consistent with this, in the ^{195}Pt NMR spectrum of **3a**, a doublet at -2435 with $^1J_{PtP} = 2035$ Hz was observed. In the ^{1}H NMR spectrum of complex **3a**, a singlet signal was observed at 2.10 ppm for the Me group of the *para*-tolyl ligand. The *ortho* and *meta* protons of the *para*-tolyl ligand appeared as two doublets at $\delta = 6.43$ and 6.99, respectively, each with $^3J_{H^mH^o} = 7.5$ Hz; the *ortho* protons further coupled to platinum to give satellites with $^3J_{PtH} = 65.0$ Hz. A doublet signal at $\delta = 6.50$, accompanied by platinum satellites, with $^3J_{HH} = 1.5$ Hz and $^3J_{PtH} = 12.5$ Hz was attributed to the hydrogen atom of C–H group adjacent to the coordinated C atom of ppy ligand.

2.2. Kinetics and mechanism of the reactions

As was mentioned above, reactions of the complexes [PtAr(ppy)(SMe$_2$)], **1**, with 1 equiv of either of the nitrogen or phosphorus nucleophiles proceeded via displacement of the labile SMe$_2$ ligand to give the final complexes **2** or **3**, respectively. This was typically demonstrated by monitoring the reaction of complex [Pt(p-MeOC$_6$H$_4$)(ppy)(SMe$_2$)], **1a**, with 3-PhPy in CDC1$_3$ by using ^{1}H NMR spectroscopy and the results are shown in Fig. 1S. Thus the singlet signal at 2.20 ppm with platinum satellites with $^3J_{PtH} = 25.0$ Hz due to coordinated dimethylsulfide protons was disappeared while the corresponding signal for the free SMe$_2$ ligand at 2.05 ppm was appeared.