

Fine-Tuning the Basicity of Metal Complexes: Reversible Oxidative Addition of Se–Se Bonds to Platinum(II) Precursors

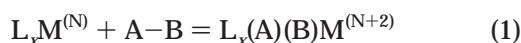
Achille Panunzi, Giuseppina Roviello, and Francesco Ruffo*

*Dipartimento di Chimica, Università di Napoli “Federico II”,
Complesso Universitario di Monte S. Angelo, Via Cintia, I-80126, Napoli, Italy*

Received May 20, 2002

Summary: The oxidative addition of diselenides to novel platinum(II) precursors affording octahedral platinum(IV) products was investigated. The properties of the substituents on Pt were finely tailored in order to prompt easy reversibility of the reaction. This allowed the achievement of the first example of equilibrium of oxidative addition of an E–E bond (E = chalcogen) to a Pt(II) precursor. The equilibrium constants could be evaluated by NMR spectroscopy, and the results were preliminarily rationalized in terms of steric and electronic factors.

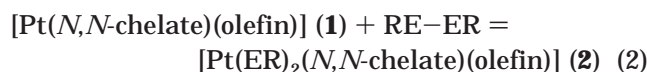
Oxidative addition and reductive elimination are pivotal reactions that intervene in several catalytic cycles and are widely used in synthesis (eq 1).¹



Although the general features that favor the oxidation of a metal according to eq 1 can be reasonably predicted, the opportunity to assess the experimental validity of these theoretical assumptions is very rare. This is mostly because the oxidative additions are generally totally shifted toward either the reagents or the products. Furthermore, the reactions are often accompanied by other rearrangements, e.g., ligands loss² or insertions,³ which prevent the establishment of equilibria. Direct information on the thermodynamics of the reaction can be achieved when the oxidative addition is reversible and involves measurable concentrations of reagents and product at equilibrium (“tuneable equilibrium”). In this rare case, any fine variation of the coordination environment can have a quantifiable effect on the equilibrium position and, hence, can be rationalized. Within this area, pioneering studies were performed by using mostly Ir(I) Vaska’s complexes.⁴ Lately,

we⁵ and other researchers^{6,7} disclosed the occurrence of tuneable equilibria in the oxidative addition of organotin or organomercury halides to Pt(0)⁵ and Pt(II)^{6,7} precursors of formula [Pt(N,N-chelate)(olefin)] (**1**) and [PtMe₂(N,N-chelate)], respectively.

More recently, we have undertaken a study of the oxidative addition of E–E bonds (E = chalcogen) to complexes of type **1** according to eq 2:⁸



The products **2** of reaction 2 are five-coordinate complexes stabilized by the presence of a nitrogen chelate with suitable steric hindrance. Within this study, we have found that the reaction is again a rare example of tuneable equilibrium, if the olefin is a fumaric ester⁸ and the acid is dimethyl diselenide, MeSe–SeMe. Instead, the reaction is totally shifted toward the products when alkenes with reduced electron-withdrawing properties (e.g., acrylic esters⁹ or ethylene⁹) are employed. A rationale of this behavior can be traced by considering that the metal-to-olefin π -back-donation decreases as the acceptor features of the alkene decrease. Accordingly, the electronic density on the metal center, and hence its basicity, grows.

On the other hand, as suggested by structural and spectroscopic properties,¹⁰ the extent of π -back-donation in complexes of type **1** is in all cases substantial. Thus, despite the formal oxidation state of platinum, these compounds exhibit a considerable Pt(II) cyclopropametalate character (**I** in Figure 1), while the other possible limit form **II** is less representative.¹¹ As a consequence, olefin Pt(0) and bis(hydrocarbyl) Pt(II) complexes are expected to display a parallel chemical behavior.

This consideration has inspired the preparation of Pt(II) species [PtR'(R'')(N,N-chelate)] (**3**) with chemical

* Corresponding author. Fax: +39-081674090. E-mail: ruffo@unina.it.

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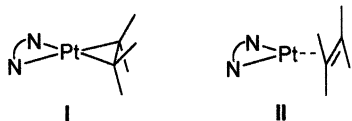
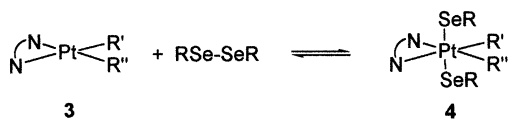
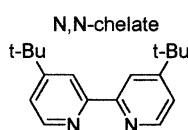
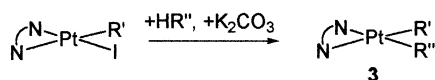


Figure 1.

Scheme 1



Scheme 2



- 3a**; R' = 4-MeO-C₆H₄, R'' = CH(CO₂Me)₂
3b; R' = 4-MeO-C₆H₄, R'' = CH(CO₂Et)₂
3c; R' = 4-MeO-C₆H₄, R'' = CH(CO₂iPr)₂
3d; R' = Me, R'' = CH(CO₂Me)₂

properties tailored to match those of type 1 Pt(0) complexes containing fumaric esters, with the expectation that an appropriate choice of R' and R'' may allow the establishment of an unprecedented tuneable equilibrium between the oxidation states II and IV according to Scheme 1.

In this preliminary report we wish to communicate the successful achievement of the target, accomplished through the "ad hoc" synthesis of new platinum(II) compounds. The tuneable oxidative addition of diphenyl diselenide¹² and dimethyl diselenide has been investigated, and the results have been usefully compared with those previously obtained with the couple Pt(0)/Pt(II).⁸

In principle, Pt(II) complexes of formula [Pt(CH₂-CO₂R'')₂(N,N-chelate)] would be the most effective candidates for mimicking fumaric ester Pt(0) precursors of type 1. However, the lack of a convenient synthesis prompted us to use the alternative preparation of mixed R',R'' platinum(II) complexes (3 in Scheme 2).

In these species, the electron-withdrawing substituents (CO₂R'') are placed on the same carbon atom. The choice of R'-R'' is aimed to disclose significant electronic and steric effects on the reaction.

The chelate was 4,4'-(t-Bu)₂-6,6'-bipyridine, which has been elegantly adopted by Puddephatt¹⁴ for assisting the solubility of Pt(II) derivatives.

Complexes of type 3 could be prepared in high yield by treating the halo precursors¹⁴ with the appropriate malonic derivative under basic conditions (Scheme 2).¹⁵⁻¹⁷ Characterization was carried out through NMR spectroscopy and elemental analysis (see Supporting

(12) Previous literature reports that diphenyl diselenide quantitatively adds to the electron-rich platinum(II) complexes [PtMe₂(N,N-chelate)] (N,N-chelate = 1,10-phen,^{13a} 2,2'-bipy^{13b}), affording the corresponding octahedral products [Pt(SePh)₂Me₂(N,N-chelate)]. The oxidation is reasonably favored by the presence of a substantial charge density on the metal precursors.

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Table 1. Equilibrium Constants (K_{add}) of the Additions of RSe-SeR Electrophiles to Complexes of Type 3 (Scheme 1)

entry	type 3 compound	RSe-SeR	product	K_{add}^a
1	3a	MeSe-SeMe	4aMe ^b	c
2	3a	PhSe-SePh	4aPh ^d	10 ± 2
3	3b	PhSe-SePh	4bPh	8 ± 2
4	3c	PhSe-SePh	4cPh	5 ± 1
5	3d	MeSe-SeMe	4dMe	5 ± 1
6	3d	PhSe-SePh	4dPh	e

^a At 293 K in CDCl₃ solutions. After several hours in solution, signals of decomposition products become detectable. ^b Attempts to isolate the product were unsuccessful. ^c No appreciable amounts of product **4aMe** at equilibrium. ^d By monitoring the addition at different temperatures (293-314 K), it was also estimated $\Delta H = 14 \pm 2$ kcal mol⁻¹ and $\Delta S = -44 \pm 6$ cal mol⁻¹ K⁻¹. ^e Quantitative addition, i.e., no appreciable amounts of **3d** and PhSe-SePh at equilibrium.

Information). The proton and carbon spectra reveal the presence of the hydrocarbyl ligands with chemical shifts and coupling constants to ¹⁹⁵Pt in line with the proposed structures. Complexes of type 3 were reacted with MeSe-SeMe or PhSe-SePh in dichloromethane (Scheme 1), and the corresponding red products (4) could be isolated in high yield.^{18,19} The equivalence of the organoselenide fragments and the chemical shifts of the Pt-Me (>1 ppm)²⁰ and -SePh (see below) protons in the ¹H NMR spectra indicated selective formation of the isomer with the organoselenide ligands mutually trans.

Remarkably, signals of the Pt(IV) products were accompanied by those of the parent compounds; that is, complexes of type 4 were partially dissociated into the reactants. Spectra were recorded at regular intervals of time until an equilibrium composition was reached.²¹ Thus, according to our preliminary assumption, tuneable equilibria were established in solution. The corresponding equilibrium constants K_{add} (Table 1) could be evaluated by integrating suitable separated peaks. An analysis of the results discloses the following significant features.

(16) A compound related to **3d** has been prepared some years ago in our laboratory for a different purpose: Albano, V. G.; Monari, M.; Orabona, I.; Ruffo, F.; Vitagliano, A. *Inorg. Chim. Acta* **1997**, *265*, 35-44.

(17) Synthesis of **3d**: a stirred solution of [PtClMe{4,4'-(t-Bu)₂-6,6'-bipy}]¹⁴ (0.20 g, 0.39 mmol) and KI (0.19 g, 1.2 mmol) in dimethylformamide (2.5 mL) was heated at 373 K for 5 min. After the orange solution was cooled at 313 K, dimethylmalonate (0.97 mmol) and anhydrous K₂CO₃ (0.11 g, 0.78 mmol) were added, and the mixture was stirred for 24 h at 313 K. The solvent and excess malonate were then removed in vacuo, and the resulting solid was extracted with chloroform. Removal of chloroform in vacuo and washing with hexane gave the product as a yellow solid (yield: 75%). Selected ¹H [¹³C] NMR data (δ , 295 K): 10.03 (d, 1H, NCH), 9.01 (d, 1H, ³J_{Pt-H} = 38 Hz, NCH), 4.20 (s, 1H, ²J_{Pt-H} = 133 Hz, [20.4 (¹J_{Pt-C} = 586 Hz)], Pt-CH), 3.59 (s, 3H, OMe), 1.09 (s, 3H, ²J_{Pt-H} = 83 Hz, Pt-Me).

(18) The octahedral products of type 4 are indicated by a letter (recalling the parent type 3 compound), followed by Me or Ph according to the substituent on Se.

(19) Synthesis of **4dPh**: a solution of diphenyl diselenide (0.20 mmol) in dichloromethane (0.5 mL) was added with stirring to a solution of **3d** (0.20 mmol) in the minimum amount of dichloromethane. After 5 min the solvent was removed in vacuo, and the oily residue grinded with ether. The orange microcrystalline solid was washed with diethyl ether and dried in vacuo (yield = 80%). Selected ¹H NMR data (δ , 295 K): 10.44 (d, 1H, NCH), 8.69 (d, 1H, ³J_{Pt-H} = 22 Hz, NCH), 6.58 (t, 2H, 4H-Ph), 6.45 (d, 4H, 2,6H-Ph), 6.35 (t, 4H, 3,5H-Ph), 4.10 (s, 1H, ²J_{Pt-H} = 93 Hz, Pt-CH), 3.81 (s, 6H, OMe), 1.85 (s, 3H, ²J_{Pt-H} = 69 Hz, Pt-Me).

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(21) This took a few minutes when the samples were exposed to light, or several hours in the dark, thus suggesting the free radical nature of the reaction.

(i) Diphenyl diselenide is a stronger oxidant than dimethyl diselenide (cf. entries 1 and 2 or 5 and 6). Two effects cooperate to stabilize the octahedral products bearing phenylselenide fragments. First, phenyl is a better electron acceptor than methyl, and this facilitates the formal reduction of selenium, which accompanies the reaction. Furthermore, an interaction between the aromatic rings of the chelate and the phenyl group on Se is established in solution, as indicated by the significant high-field shift of the Ph protons in the ^1H NMR spectrum. This type of interaction, which had been previously disclosed within related works,^{8,13,22} may play an important role in stabilizing the Pt(IV) product.

(ii) An electronic effect is also observed when the methyl on platinum is substituted for an aryl (e.g., cf. entries 2 and 6). Diphenyl diselenide quantitatively adds to the methyl precursor **3d**. On the other hand, the more effective electron-withdrawing ligand 4-MeO-C₆H₄ stabilizes the lower oxidation state, and, hence, the addition of diphenyl diselenide to **3a** is not complete ($K_{\text{add}} = 10$, entry 2).

(iii) A more subtle effect is observed when a fine variation of ligands is carried out (cf. entries 2, 3, and 4); that is, the addition becomes slightly less favored on changing the ester substituents R''' from methyl to isopropyl. This fine influence can be explained by assuming that a moderate increase of the steric hindrance perturbs the axial positions of the octahedron and, hence, disfavors the reaction.

(iv) A comparison between the behavior of related Pt(0)⁸ and Pt(II) complexes discloses a great similitude, provided a careful choice of the ligands. However, the

former ones are more easily oxidized, as expected due to their low formal charge. For instance, it was previously found⁸ that dimethyl diselenide adds to [Pt(*N,N*-chelate)(*E*-MeO₂CCH=CHCO₂Me)] with $K_{\text{add}} = 1.0 \times 10^3$, while the reaction is much more shifted toward the reactants when **3d** (entry 5) is used as Pt precursor ($K_{\text{add}} = 5$). The same Pt(0) complex reacts quantitatively with diphenyl diselenide,⁸ while a "tuneable" equilibrium is established when the electrophile is added to **3a** (entry 2). The contribution, although little, of the limit form **II** (Figure 1) is plausibly responsible for the higher basicity of the Pt(0) complexes, because in this structure the metal center is not depleted of electrons and retains the low oxidation state.

In conclusion, this preliminary investigation has disclosed the first reversible cleavage of an E-E bond (E = chalcogen) by a Pt(II) precursor,¹² which is prompted by a careful choice of the electronic and steric properties of the ligands. This result can be considered as a substantial upgrade of the knowledge⁴⁻⁸ of the thermodynamics of oxidative addition to platinum group metals. Further investigations by using modified type **3** compounds are currently in progress.

Acknowledgment. The authors thank the MURST (Programmi di Ricerca Scientifica di Rilevante Interesse Nazionale, Cofinanziamento 2000-2001) and the Centro Interdipartimentale di Metodologie Chimico-Fisiche, Università di Napoli "Federico II", for NMR facilities.

Supporting Information Available: Text giving synthetic details and characterization data for the new complexes. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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