Oxidative Additions of E−E Bonds (E = Chalcogen) to Group 10 Metals: "Tunable" Cleavage of Se−Se Bonds by Pt(0) Complexes

Vincenzo G. Albano,*[,†] Magda Monari,[†] Ida Orabona,[‡]
Achille Panunzi,*[,‡] and Francesco Ruffo[‡]

Dipartimento di Chimica "G. Ciamician"
Università di Bologna, Via Selmi 2, I-40126 Bologna, Italy
Dipartimento di Chimica, Università di Napoli "Federico II"
Complesso Universitario di Monte S. Angelo
via Cintia, I-80126 Napoli, Italy

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Oxidative addition and reductive elimination reactions are of utmost importance in organometallic chemistry,[1] and the knowledge of the factors ruling these processes is extremely useful. A comprehensive study can be carried out only in the presence of "tunable" equilibria involving detectable concentrations of both reagents and products. In fact, in these cases fine variations of electronic or steric properties have measurable effects on equilibrium and hence can be rationalized. On the other hand, very few examples of reversible and tunable addition−elimination reactions are known,[2] since these are in most cases totally shifted toward either the reagents or the products. Furthermore, equilibrium is often prevented by the occurrence of other processes, such as ligand loss,[3] insertion,[4] or competing eliminations.[5]

We have recently shown[2c,e,6] that three-coordinate platinum(0) complexes of the type [Pt(N,N-chelate)(olefin)] (**I**) readily undergo addition by a variety of electrophiles A−B to give five-coordinate type **II** products, according to eq 1:

$$[\mathrm{Pt(N,N\text{-}chelate)(olefin)}]\ (\mathbf{I}) + \mathrm{A{-}B} = [\mathrm{Pt(A)(B)(N,N\text{-}chelate)(olefin)}]\ (\mathbf{II}) \quad (1)$$

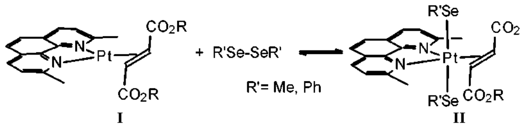
where (N,N-chelate = 2,9-Me_2-1,10-phenanthroline; A−B= X−SnR_nX_{3-n}, X−HgR, Cl−GeR_nCl_{3-n}, Cl−PbR_2Cl; X = halides, R = alkyls). These reactions have been revealed to be particularly suitable for the study of addition−elimination processes. In fact, sterically crowded nitrogen chelates (e.g., dmphen= 2,9-Me_2-1,10-phenanthroline) stabilize the five-coordinate 18 e^- products (**II**) toward further rearrangements.[7] Furthermore, both electronic and steric features of the complexes can be finely varied by an accurate choice of the olefin ligand. Thus, several trends concerning the reversible oxidative addition of organo-tin[2c−e] and -mercury[2c] halides have been rationalized in detail.

Table 1. Thermodynamic Parameters for the Addition of R′Se−SeR′ Electrophiles to Complexes of Type **I** at 295 K in $CDCl_3$

type **I** complex	electrophile	pK_{add}[a]	ΔH_{add}[b]	ΔS_{add}[c]
[Pt(dmphen)(iPr-fu)]	MeSe−SeMe	−3.4	−15.0 ± 0.3	−36 ± 1
[Pt(dmphen)(Et-fu)]	MeSe−SeMe	−3.3	−15.5 ± 0.6	−38 ± 2
[Pt(dmphen)(Me-fu)]	MeSe−SeMe	−3.0	−13.5 ± 0.6	−31 ± 2
[Pt(dmphen)(MePh-fu)]	MeSe−SeMe	−2.8		
[Pt(dmphen)(Ph-fu)]	MeSe−SeMe	−2.7		
[Pt(dmphen)(ClPh-fu)]	MeSe−SeMe	−2.5		
[Pt(dmphen)(Me-fu)]	PhSe−SePh	*d*		
[Pt(dmphen)(ClPh-fu)]	PhSe−SePh	*d*		

[a] The estimated errors are less than ±0.2. [b] In kcal·mol^{-1}. [c] In cal·mol^{-1}·K^{-1}. [d] The addition is quantitative.

Scheme 1



Herein, we communicate the first example of tunable oxidative addition of an E−E bond (E = Se) to platinum(0) complexes. When a yellow chloroform solution of a fumaric ester complex of type **I** is treated with a 100% molar excess of either MeSe−SeMe or PhSe−SePh (Scheme 1), the color of the reacting mixture rapidly turns orange-red. Analytically pure products of type **II**, which are the first saturated species containing Pt(II)−SeR fragments,[8] can be crystallized by careful addition of *n*-pentane. NMR spectra in $CDCl_3$ of the five-coordinate compounds disclose that an equilibrium is established in solution because the products are partially dissociated into the reactants. The corresponding pK_{add} constants can be evaluated by integrating suitable separated peaks in the proton NMR spectrum at 295 K. Six fumaric esters have been employed, i.e., dimethylfumarate (Me-fu), diethylfumarate (Et-fu), diisopropylfumarate (^{i}Pr-fu), diphenylfumarate (Ph-fu), di(4-methylphenyl)fumarate (MePh-fu), and di(4-chlorophenyl)-fumarate (ClPh-fu). A clean relationship between the extent of the addition and the electronic properties of the olefins has been found. The equilibrium constants for the addition of MeSe−SeMe to type **I** complexes (Table 1) decrease with increasing electron-withdrawing properties of the coordinated olefins. The razionalization is in terms of lowering of the electronic density on the metal centers and, consequently, of its basicity.

The ΔS_{add} values, on the other hand, are negative according to the stoichiometry of the addition and reflect the trend of molecular crowding within the alkyl fumaric esters (Me-fu, Et-fu, and ^{i}Pr-fu). More precisely, the ΔS_{add} for the Me-fu precursor is less negative than that measured for the Et-fu or the ^{i}Pr-fu analogues (Table 1). This relates to the conformational freedoms of the −COOR appendages in the Pt(0) precursors, which undergo increasing motion restrictions in the five-coordinate derivatives as the R groups grow bigger. The ΔH_{add} values have been used for an unprecedented evaluation of the Pt−Se bond energy. By assuming that $\Delta H_{add}(av)^9 = 2\Delta H_{Pt-Se} - \Delta H_{Se-Se}$,[10] a value of −33 kcal/mol was found for ΔH_{Pt-Se}. On changing the hydrocarbyl group bonded to Se pronounced effects are observed on the equilibrium. While the addition of MeSe−SeMe to the Pt(0) precursors used in this work produces tunable equilibria, PhSe−

[†] University of Bologna.

[‡] University of Napoli.

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(9) ΔH_{add}(av) is the average value among those reported in Table 1.

(10) A value of −51 kcal/mol was adopted for ΔH_{Se-Se}, which is the average of several calculated values taken from the following: Maung, N.; Williams, J. O.; Wright, A. C. *THEOCHEM* **1998**, *453*, 181−189.

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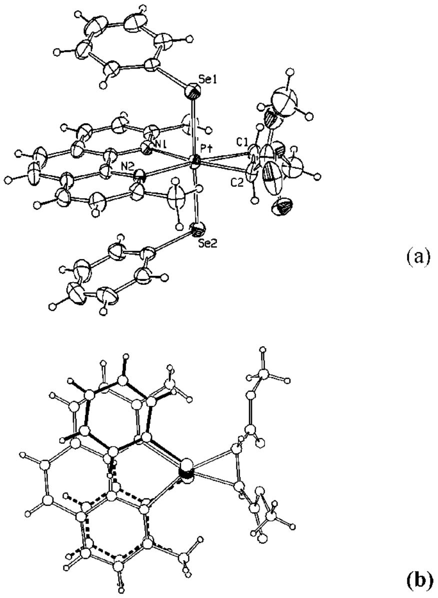

Figure 1. (a) ORTEP drawing of the molecule [Pt(SePh)$_2$(dmphen)-(Me-fu)]. Selected bond lengths (Å) and angles (deg): Pt−C(1) 2.090, Pt−C(2) 2.092(4), C(1)−C(2) 1.438(6), Pt−N(1) 2.181, Pt−N(2) 2.192-(3), Pt−Se(1) 2.5197, Pt−Se(2) 2.5142(5); Pt−Se−C 105.3 (av). (b) View down the SePtSe axis showing the ring overlaps.

SePh completely adds even to the less basic [Pt(dmphen)(ClPh-fu)]. This result can be attributed only in part to the electronic properties of the SeMe and SePh ligands. A determining contribution to the stability of the SePh derivatives, as pointed out by the solid-state structure of [Pt(SePh)$_2$(dmphen)(Me-fu)] (see hereafter), derives from stabilizing interactions between phenyl groups and pyridine rings. According to NMR spectra, these interactions are strong enough to be retained in solution, as demonstrated by the shift of the PhSe− protons of type **II** products at higher field (δ 6.35−5.95) with respect to those of the PhSe−SePh molecule.

The X-ray diffraction study of the representative species [Pt(SePh)$_2$(dmphen)(Me-fu)][12] has also been prompted by its close similarity to the platinum(IV) derivatives [PtMe$_2$(SePh)$_2$(bipy)][11] and [PtMe$_2$(SePh)$_2$(1,10-phen)],[13] whose structures were previously described. The molecular geometry is depicted in Figure 1a,b and exhibits the expected coordination of the SePh ligands in the axial sites, while the equatorial plane is defined by the olefin double bond and the chelate dmphen ligand. The phenyl rings are oriented away from the −COOMe groups of the fumarate ligand and approximately overlap, from opposite sides, both pyridinic rings of dmphen [average interplanar angle 17.3°]. The molecule would conform to an idealized C_2 symmetry was it not for the conformations of the −COOMe groups. The orientations of the phenyl rings with respect to the dmphen ligand are similar to those found in the two reported polymorphs of [Pt(Me)$_2$(SePh)$_2$(1,10-phen)][11,13] and indicate specific interactions between the ring dipoles. It is worth noting the stereochemical resemblance of this molecule to that of the just cited dimethylplatinum(IV) derivative,[11,13] despite the different oxidation states of Pt. The similarity seems to be more than formal and points to a description of the platinum−fumarate bond to the limit of a metallacyclopropane ring.

In conclusion, an unprecedented addition−elimination equilibrium has been discovered. This finding is of interest because organic chalcogenides −ER are attracting a great deal of attention as ligand fragments,[14] and the close similarity between products of type **II** and the intermediates invoked in the Pd-catalyzed addition of E−E bonds (E = chalcogen) to unsaturated hydrocarbons.[15] The equilibrium can be tuned by varying electronic and steric properties of the ligands, according to trends which have found reasonable explanation. Extension of this study to other dichalcogenides is in progress, although to date, no O−O, S−S, and Te−Te bond has been found to establish tunable equilibria with precursors of type **I**. The same held true when the additions were performed[11,13] on Pt(II) species yielding Pt-(IV) products, thus confirming the rarity of tunable equilibria in addition−elimination reactions.

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Supporting Information Available: Preparation and spectroscopic data for the products and tables of crystallographic data, atomic coordinates, isotropic and anisotropic thermal parameters, and bond lengths and angles for [Pt(SePh)$_2$(dmphen)(Me-fu)] (PDF) as well as CIF data. This material is available free of charge via the Internet at http://pubs.acs.org.

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