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Synthesis and Characterization of Trigonal-Bipyramidal Platinum(II) Olefin Complexes with Chalcogenide Ligands in Axial Positions. X-ray Molecular Structures of [Pt(SMe)$_2$(dmphen)(diphenyl fumarate)], Its Cationic Dipositive Derivative [Pt(SMe$_2$)$_2$(dmphen)(diphenyl fumarate)][BF$_4$]$_2$, and Free Diphenyl Fumarate

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

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

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The oxidative addition of RE−ER molecules (E = O, R = H, C(O)Ph, C(O)Me; E = S, Se, Te, R = Me, Ph) to Pt(0) precursors [Pt(N,N-chelate)(olefin)] (**1**: N,N-chelate = e.g. 2,9-dimethyl-1,10-phenanthroline; olefin = maleic or fumaric ester) has been studied. Symmetrical cleavage of the E−E bonds affords unprecedented trigonal-bipyramidal Pt(II) complexes of the formula [Pt(ER)$_2$(N,N-chelate)(olefin)] (**2**). Products of type **2**, which have been characterized through ^{1}H and ^{13}C NMR spectroscopy, contain chalcogenide ligands in the axial positions. The reactivity of the new compounds has also been investigated. Thus, Pt−OH fragments generated by the addition of H_2O_2 are acetylated by acetic anhydride. Furthermore, S, Se, and Te coordinated to Pt are readily methylated by trimethyloxonium tetrafluoroborate, affording the first examples of dipositive coordinatively saturated platinum(II) cations (**3**). The structures of the related neutral [Pt(SMe)$_2$(2,9-dimethyl-1,10-phenanthroline)(diphenyl fumarate)] and cationic [Pt(SMe$_2$)$_2$(2,9-dimethyl-1,10-phenanthroline)(diphenyl fumarate)][BF$_4$]$_2$ compounds have been determined by X-ray diffraction together with that of the free diphenyl fumarate ligand.

Introduction

Complexes containing Pt−E bonds (E = group 16 element) have been known for a long time.[1] Nevertheless, several aspects of their chemistry are unexplored or need further investigation. For example, no coordinatively saturated Pt(II) complex with σ-bonded chalcogenides has yet been described, since the only known species are square-planar Pt(II)[2] or octahedral Pt(IV) derivatives.[3] Furthermore, the reactivity of the Pt−E bond has received substantial attention only recently.[4] For example, formation of C−E bonds from dichalcogenides and unsaturated compounds has been attained through new catalytic processes promoted by Pt or Pd complexes.[4b] A crucial step of the proposed catalytic cycle is the oxidative addition of a dichalcogenide to a low-valent metal complex with formation of an intermediate of formula [M(ER)$_2$L$_2$(unsaturated compound)].

Further impulse to gain knowledge about compounds containing Pt−E bonds stems from the recent finding that octahedral complexes bearing two σ-bonded OR

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* To whom correspondence should be addressed. E-mail: V.G.A., vgalbano@ciam.unibo.it; F.R., ruffo@unina.it.

[†] Università di Bologna.

[‡] Università di Napoli "Federico II".

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groups (R = H, C(O)Me) display interesting antitumor properties.[5] Furthermore, the biological role of selenium compounds is acknowledged and has recently been reviewed.[6]

In the recent past, the ability of N,N-ligands with "in plane" steric hindrance to stabilize the trigonal-bipyramidal (tbp)[7] geometry in 18e platinum(II) complexes of formula [Pt(X)(Y)(N,N-chelate)(olefin)] (**I**) has been disclosed.[8] Therefore, we decided to investigate the first class of 18e platinum(II) complexes containing σ-bonded chalcogenides (**2**).[9] The complexes have been obtained by oxidative addition of dichalcogenides to suitable three-coordinate precursors [Pt(N,N-chelate)(olefin)] (**1**; reaction 1 in Scheme 1).

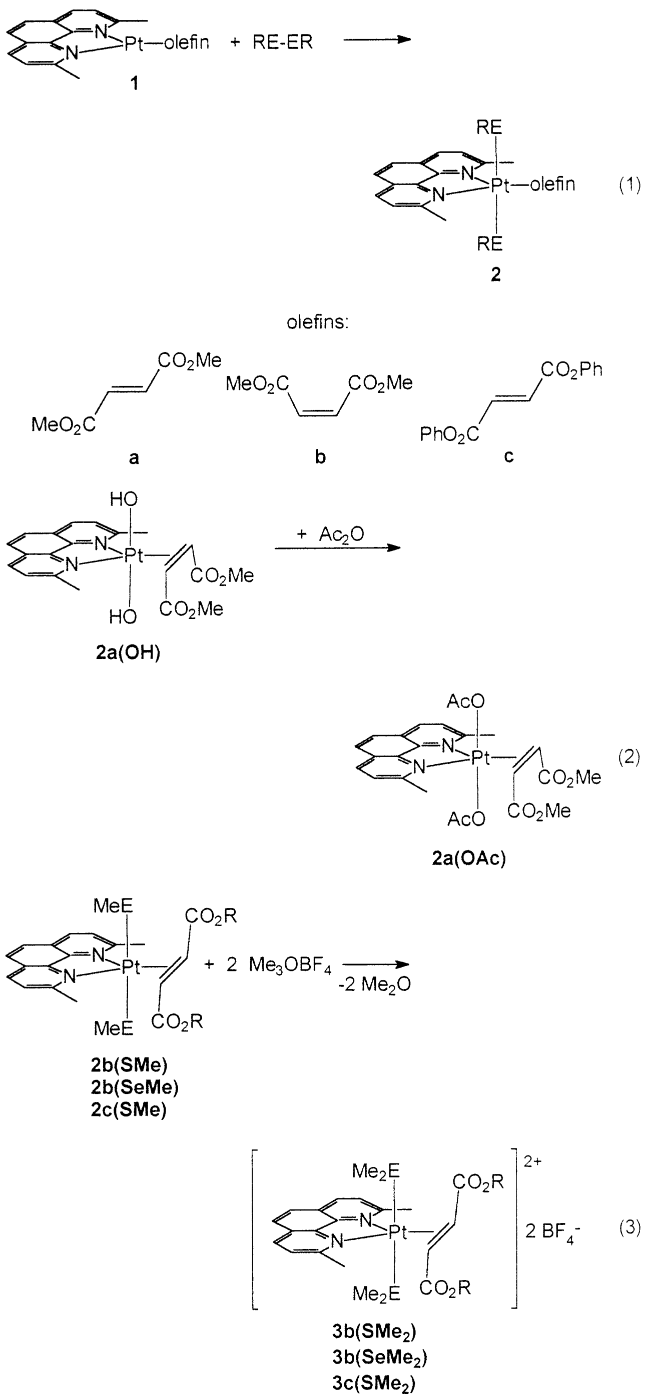
The characterization of the products, which display a tbp geometry with the anionic ligands in axial positions, has been carried out through elemental analyses and NMR and IR spectroscopy. Compounds of type **2** are reliable models of the intermediates of the abovementioned Pt-catalyzed C−E bond formation.[4] Furthermore, the availability of related Pt(IV) compounds[3] allows us to verify that the differences between compounds in very similar coordination environments but different oxidation states can be more formal than real.

The reactions of type **2** species with electrophiles have also been performed, yielding the first examples of saturated dipositive Pt(II) complexes. The molecular structures of the representative compounds [Pt(SMe)$_2$(dmphen)(diphenyl fumarate)] and [Pt(SMe$_2$)$_2$(dmphen)(diphenyl fumarate)](BF$_4$)$_2$ (dmphen = 2,9-dimethyl-1,10-phenanthroline) have been determined by X-ray diffractometry.

Results and Discussion

General Features of the Addition. Type **2** complexes have been obtained according to reaction 1 of Scheme 1. dmphen is the N,N-chelate of choice, due to its assessed peculiar ability in stabilizing the trigonal-bipyramidal geometry.[8] The olefins are dimethyl maleate, dimethyl fumarate, and diphenyl fumarate (**a**−**c** in Scheme 1). Their properties confer sufficient solubility and stability to the Pt(0) complexes without reducing the basicity. Furthermore, the symmetry of these ligands restricts the number of isomers of the products and helps to correctly formulate their structure. More precisely, if the addition proceeds with cleavage of the E−E bonds, the fumarate products are enantiomeric couples of C_2 symmetry. The 2-fold axis bisecting the equatorial ligands generates the NMR equivalence of the axial ligands, the *trans*-olefin protons, and the halves of the N,N-chelate. On the other hand, the analogous maleate products (C_s symmetry) possess a mirror symmetry bisecting the equatorial plane and, hence, the olefin protons and the halves of the chelate are equivalent, while the axial ligands are no longer equivalent.

Scheme 1



Some additions have been performed on the three-coordinate precursor [Pt(phen)(dimethyl fumarate)] (phen = 1,10-phenanthroline), containing a chelate with poor "in plane" steric hindrance. This choice is aimed at obtaining the corresponding square-planar products [Pt(ER)$_2$(1,10-phen)] by olefin loss. Unexpectedly, also in these cases five-coordinate products of type **2** have been isolated, despite the lack of steric constraints. The complexes do not show a tendency to release the olefin but are involved in a slow nonchemoselective decomposition process, which goes to completion within a few hours at room temperature. Success in isolating tbp complexes of phen is most probably due to a kinetic inertness rather than thermodynamic stability, as observed for other complexes of type **I**.[10] The products

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(7) Throughout this paper we refer to the 18e platinum complexes as five-coordinate trigonal bipyramidal. The reader should keep in mind that the alternative description as distorted octahedral is in some cases more useful.

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Table 1. Relevant ^{1}H[a] [^{13}C[b]] NMR Data for Type 2 and 3 Complexes

complex	E−R[c]	olefin[d]	other selected signals
[Pt(OH)$_2$(dmphen)(dimethyl maleate)] (**2a(OH)**)		4.27 (s, 2H, 81)	3.78 (s, 6H, OMe), 3.46 (s, 6H, Me)
[Pt(OH)$_2$(dmphen)(dimethyl fumarate)] (**2b(OH)**)		4.80 (s, 2H, 72)	3.81 (s, 6H, OMe), 3.36 (s, 6H, Me)
[Pt(AcO)$_2$(dmphen)(dimethyl maleate)] (**2a(OAc)**)		4.60 (s, 2H, 74) [38.1 (386)]	3.73 (s, 6H, OMe), 3.62 (s, 6H, Me), 1.59 (s, 3H, OAc), 1.39 (s, 3H, OAc)
[Pt(AcO)$_2$(dmphen)(dimethyl fumarate)] (**2b(OAc)**)		5.37 (s, 2H, 76) [37.5 (353)]	3.71 (s, 6H, OMe), 3.66 (s, 6H, Me), 1.49 (s, 6H, OAc)
[Pt(O$_2$CPh)(OH)(dmphen)(dimethyl fumarate)] (**2b(O$_2$CPh)(OH)**		5.37 (d, 1H), 5.15 (d, 1H) [37.1 (361), 35.0 (353)]	3.86 (s, 3H, OMe), 3.77 (s, 3H, OMe), 3.58 (s, 3H, Me), 3.37 (s, 3H, Me) [174.5, 171.0, 170.8, CO]
[Pt(SMe)$_2$(dmphen)(dimethyl maleate)] (**2a(SMe)**)	1.18 (s, 3H, 25), 0.77 (s, 3H, 27) [11.6 and 10.6]	4.22 (s, 2H, 81) [34.9 (393)]	3.79 (s, 6H, OMe), 3.41 (s, 6H, Me)
[Pt(SPh)$_2$(dmphen)(dimethyl maleate)] (**2a(SPh)**)	6.60 (m, 1H), 6.34 (m, 5H), 6.19 (d, 2H), 6.05 (t, 2H)	4.26 (s, 2H, 82) [35.9 (377)]	3.89 (s, 6H, OMe), 3.42 (s, 6H, Me)
[Pt(SMe)$_2$(dmphen)(dimethyl fumarate)] (**2b(SMe)**)	0.98 (s, 6H, 27) [11.3]	4.75 (s, 2H, 86) [30.4 (361)]	3.72 (s, 6H, OMe), 3.53 (s, 6H, Me)
[Pt(SPh)$_2$(dmphen)(dimethyl fumarate)] (**2b(SPh)**)	6.33 (t, 2H), 6.07 (m, 8H)	4.80 (s, 2H, 80) [33.6 (355)]	3.79 (s, 6H, OMe), 3.56 (s, 6H, Me)
[Pt(SeMe)$_2$(dmphen)(dimethyl maleate)] (**2a(SeMe)**)	0.92 (s, 3H, 20), 0.56 (s, 3H, 23) [−3.3 and −3.9]	4.24 (s, 2H, 79) [31.8 (388)]	3.76 (s, 6H, OMe), 3.41 (s, 6H, Me)
[Pt(SePh)$_2$(dmphen)(dimethyl maleate)] (**2a(SePh)**)	6.75 (t, 1H), 6.57 (t, 1H), 6.49 (d, 2H), 6.32 (d, 2H), 6.23 (t, 2H), 6.02 (t, 2H)	4.34 (s, 2H, 81) [32.3 (377)]	3.81 (s, 6H, OMe), 3.29 (s, 6H, Me)
[Pt(SeMe)$_2$(dmphen)(dimethyl fumarate)] (**2b(SeMe)**)[e]	0.61 (s, 6H, 25) [−3.3]	4.85 (s, 2H, 82) [30.6 (354)]	3.78 (s, 6H, OMe), 3.57 (s, 6H, Me)
[Pt(SePh)$_2$(dmphen)(dimethyl fumarate)] (**2b(SePh)**)[e]	6.35 (t, 2H), 6.10 (d, 4H), 5.95 (t, 4H)	4.81 (s, 2H, 80) [31.7 (350)]	3.80 (s, 6H, OMe), 3.56 (s, 6H, Me)
[Pt(TePh)$_2$(dmphen)(dimethyl maleate)] (**2a(TePh)**)	6.69 (t, 1H), 6.52 (t, 1H), 6.46 (d, 2H), 6.29 (d, 2H), 6.17 (t, 2H), 5.97 (t, 2H)	4.29 (s, 2H, 81) [28.7 (318)]	3.85 (s, 6H, OMe), 3.26 (s, 6H, Me)
[Pt(TePh)$_2$(dmphen)(dimethyl fumarate)] (**2b(TePh)**)	6.51 (t, 2H), 6.17 (d, 4H), 5.94 (t, 4H)	4.75 (s, 2H, 79) [29.6 (348)]	3.80 (s, 6H, OMe), 3.50 (s, 6H, Me)
[Pt(SMe)$_2$(dmphen)(diphenyl fumarate)] (**2c(SMe)**)	1.05 (s, 6H, 27) [11.2]	5.04 (s, 2H, 82) [31.8 (347)]	7.3−7.1 (m, 10 H, Ph), 3.53 (s, 6H, Me)
[Pt(SeMe)$_2$(phen)(dimethyl fumarate)]	0.90 (s, 6H, 24)	4.86 (s, 2H, 82)	3.80 (s, 6H, OMe)
[Pt(SePh)$_2$(phen)(dimethyl fumarate)]	6.44 (t, 2H), 6.15 (d, 4H), 6.04 (t, 4H)	4.80 (s, 2H, 84)	3.85 (s, 6H, OMe)
[Pt(SMe$_2$)$_2$(dmphen)(dimethyl fumarate)][BF$_4$]$_2$ (**3b(SMe$_2$)**)[f]	1.93 (s, 6H, 28), 1.49 (s, 6H, 28)	4.98 (s, 2H, 68)	3.91 (s, 6H, OMe), 3.44 (s, 6H, Me)
[Pt(SeMe$_2$)$_2$(dmphen)(dimethyl fumarate)][BF$_4$]$_2$ (**3b(SeMe$_2$)**)[f]	1.66 (s, 6H, 30), 1.35 (s, 6H, 29)	4.82 (s, 2H, 64)	3.95 (s, 6H, OMe), 3.38 (s, 6H, Me)
[Pt(SMe$_2$)$_2$(dmphen)(diphenyl fumarate)][BF$_4$]$_2$ (**3c(SMe$_2$)**)[f]	2.15 (s, 6H, 32), 1.53 (s, 6H, 30)	5.34 (s, 2H, 66)	3.70 (s, 6H, Me)

[a] At 200 or 300 MHz and 298 K. CDCl$_3$ was used as solvent (CHCl$_3$, δ 7.26 as internal standard). Abbreviations: s, singlet; d, doublet; t, triplet; m, multiplet. [b] At 50.2 or 62.9 MHz and 298 K. CDCl$_3$ was used as solvent (^{13}CDCl$_3$, δ 77 as internal standard). [c] $^{3}J_{\mathrm{Pt-H}}$ (Hz) in parentheses. [d] $^{2}J_{\mathrm{Pt-H}}$ and $^{1}J_{\mathrm{Pt-C}}$ in parentheses. [e] Data taken from ref 9. [f] In CD$_3$NO$_2$ (CD$_2$HNO$_2$, δ 4.33 as internal standard).

are reported in Table 1 with their labeling: the letters **a**−**c** indicate the olefin, while the axial fragments are specified in parentheses.

Oxidative Addition of Peroxides. The three-coordinate precursors **1a** and **1b** have been reacted with hydrogen peroxide, diacetyl peroxide, and dibenzoyl peroxide.

The additions of H$_2$O$_2$ have been conducted in THF and found to be complete within a few seconds. Addition of diethyl ether to the reaction mixture affords the pale yellow products **2a(OH)** and **2b(OH)** in good yields. The complexes are soluble in chlorinated solvents and water. The pattern of the ^{1}H NMR spectra is in agreement with the symmetry of the complexes just described. Thus, in both cases the equivalent olefin protons resonate as singlets, respectively, at δ 4.27 and 4.80. The signals are shifted upfield by ca. 2 ppm with respect to those of

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the free olefins, in the range considered diagnostic of trigonal-bipyramidal complexes containing dimethyl maleate or dimethyl fumarate.[11] The IR spectra show bands in the ranges 3520−3500 and 550−535 cm^{-1}, accounting for the O−H and Pt−O stretchings, respectively.[12]

The oxidative additions of diacetyl peroxide to **1a** and **1b** are complete within 12 h in toluene. In the ^{1}H NMR spectrum dimethyl maleate and dimethyl fumarate olefin protons resonate at δ 4.60 and δ 5.37, respectively. As expected, the axial groups are equivalent in the fumarate product **2b(OAc)**, which confirms that the addition proceeds with cleavage of the O−O bond. Obviously, the equivalence of the acetyl groups is not retained in **2a(OAc)**, and two singlets at δ 1.59 and 1.39 are found.

The addition of dibenzoyl peroxide to **1b** has also been performed. The spectrum of the product, isolated after 6 days of stirring in toluene, unexpectedly discloses the nonequivalence of the fumarate protons (two doublets at δ 5.37 and 5.15) and the halves of dmphen. This feature reveals that the axial ligands are not equivalent. Furthermore, the aromatic region is integrated for only 11 protons (6 for dmphen and 5 for one phenyl group), thus suggesting loss of one benzoate group. The ^{13}C spectrum is in keeping with this hypothesis, as only three signals in the low-field region can be attributed to as many carbonyl groups. The ensemble of results suggests that the addition of dibenzoyl peroxide is followed by hydrolysis of one Pt−OC(O)Ph bond with formation of the mixed product [Pt{OC(O)Ph}(OH)(dmphen)(dimethyl fumarate)] (**2b(O$_2$CPh)(OH)**). Attempts to isolate the dibenzoate compound by working up the reaction at earlier stages have proved unsuccessful.

It should be noted that cleavage of the M−benzoate bond has been previously found to occur quite easily when M = Pd,[3e] while stable dibenzoate compounds are isolated when the addition of dibenzoyl peroxide is performed on Pt(II) precursors of formula [Pt(hydrocarbyl)$_2$(bipy)].[3b,j]

Use of dimethyl peroxide (MeOOMe) as oxidant was also attempted. Unexpectedly, a ***violent explosion*** occurred during its preparation.[13] No further experiment was carried out.

Oxidative Addition of the Other Dichalcogenides. The three-coordinate complexes have been reacted with dichalcogenides RE−ER (E = S, Se, Te; R = Me, Ph). The reactions have been performed by adding an excess of oxidant to a chloroform solution or a toluene suspension of the Pt(0) precursors. A rapid change of color from yellow to red often signals the completion of the reaction. The products can be obtained in pure form as yellow-orange solids by addition of hexane to the reaction mixture. Only the less reactive dimethyl disulfide requires more drastic conditions, and the reactions were performed in neat electrophile. After 24 h the product is filtered from the reaction mixture and washed with diethyl ether.

The NMR spectra of the products are in line with the aforementioned expected features.[14] Again, the chemical shifts of the olefin protons fall in the range considered diagnostic for compounds of type **I**. With reference to the free alkenes, the $\Delta\delta$ value is ca. 2 ppm for both dmm and dmf, irrespective of the organoelement ligand. The high-field shift is substantially larger than that found[11] in the corresponding dichloro, dibromo, and diiodo complexes ($\Delta\delta$ < 1.5). The entity of the shift has been correlated to the extent of π-back-donation,[8] which increases as the electronic density on the metal grows. Hence, this spectral evidence suggests that organochalcogenide ligands are better donors than halides in the axial position of the trigonal bipyramid.

As expected, both olefins and −E*Me* nuclei couple to ^{195}Pt. For the alkenes, the values of $^2J_{\mathrm{Pt-H}}$ and $^1J_{\mathrm{Pt-C}}$ are within 78−82 and 350−450 Hz, respectively. On the other hand, the $^3J_{\mathrm{Pt-H}}$ satellites of the methyl signals are in the range 20−25 Hz. The −Se*Me* resonances are enriched by coupling to ^{77}Se ($^2J_{\mathrm{Se-H}}$ ca. 10 Hz).

Another spectral feature worth mentioning is the high-field shift of the phenyl protons of the −EPh ligands. A high-field shift of ca. 1.5 ppm is observed, presumably due to π-stacking of the phenyl rings with the aromatic rings of the nitrogen chelate. This interaction has been disclosed in the solid state for the representative complex **2a(SePh)**[9] and should be compared to that found in the related Pt(IV) complexes [PtMe$_2$(EPh)$_2$(N,N-chelate)].[3d,h]

On the whole, the spectral features of the complexes do not significantly change upon variation of the axial E atom.

Reactivity. The reactivity of the axial ligands in some complexes of type **2** has been explored. The hydroxyl groups in **2a(OH)** are readily acetylated in the presence of acetic anhydride (reaction 2 in Scheme 1). The identity of the product **2a(OAc)** has been confirmed by comparison with the same complex obtained independently by oxidative addition of diacetyl peroxide (see above). Esterification of Pt-bonded hydroxyl groups in the presence of a suitable electrophile has been previously reported in the case of platinum(IV) derivatives.[12] This procedure has allowed the synthesis of orally active antitumor compounds, which show significant structural analogies with **2a(OAc)** despite the different oxidation state.

The nucleophilicity of S, Se, and Te atoms in the coordinated chalcogenide ligands has been verified. Thus, complexes **2b(SMe)**, **2b(SeMe)**, and **2c(SMe)** have been reacted with 2 equiv of Me$_3$OBF$_4$ in nitromethane (reaction 3 in Scheme 1).

In all cases, the two axial heteroatoms are readily methylated with formation of the corresponding dipositive cations (**3**) containing the newly formed EMe$_2$ ligands in axial positions. As far as we know, these are the first examples of coordinatively saturated Pt(II) compounds exhibiting a dipositive net charge. The complexes can be isolated in high yield and stored for several days at 273 K without appreciable decomposition.

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[13] Hanst, P. L.; Calvert, J. G. *J. Phys. Chem.* **1959**, *63*, 104−106. The explosion occurred during dropwise addition at 273 K of 40% aqueous potassium hydroxide to the solution of dimethyl sulfate and hydrogen peroxide.

[14] The dimethyl selenide derivatives are reversibly dissociated in solution into the corresponding precursors. This equilibrium process is being investigated separately.[9]

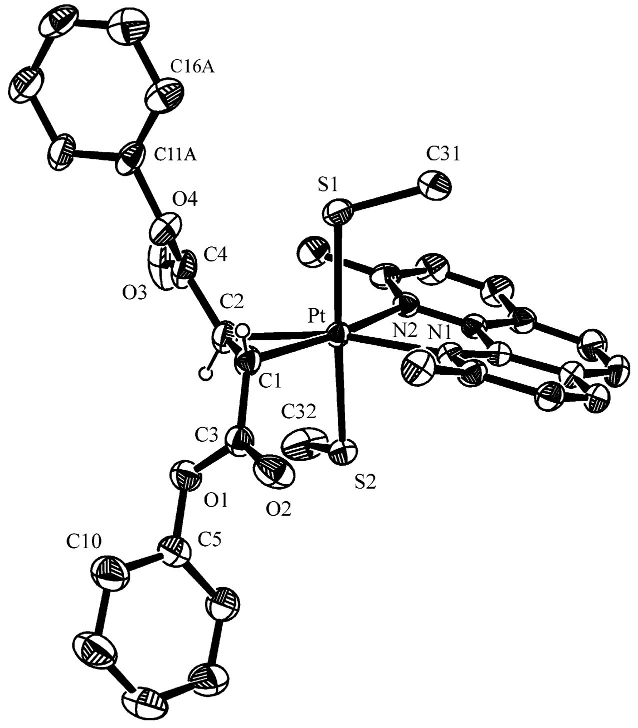

Figure 1. ORTEP drawing (30% probability thermal ellipsoids) of [Pt(SMe)$_2$(dmphen)(diphenyl fumarate)] (**2c(SMe)**) showing one of the two conformational isomers (A) present in the crystal in equal amounts. The second isomer (B) exhibits the phenyl group (C11B−C16B) bound to O(3) instead of O(4). Hydrogen atoms, except the olefinic ones, have been omitted for clarity.

The NMR spectra disclose that the products retain the C_2 symmetry. The halves of the olefin and N,N-chelate are equivalent, as are the axial ligands. Due to the presence of a prochiral olefin, the methyl groups on each E atom are diastereotopic and, hence, not chemically equivalent.

The X-ray structure of **3c(SMe$_2$)** has been determined.

X-ray Molecular Structures of [Pt(SMe)$_2$(dmphen)(diphenyl fumarate)] (2c(SMe)), Its Cationic Derivative [Pt(SMe$_2$)$_2$(dmphen)(diphenyl fumarate)][BF$_4$]$_2$ (3c(SMe$_2$)), and Free Diphenyl Fumarate. The crystals of [Pt(SMe)$_2$(dmphen)(diphenyl fumarate)] (**2c(SMe)**) contain equal amounts of two conformational isomers produced by different orientations of one −CO(O)Ph group in the fumarate ligand. Figure 1 shows the structure of one isomer, while the other contains a phenyl group attached to O(3) in place of the one shown bonded to O(4) (see Experimental Section). Although the molecule could conform to an idealized C_2 symmetry, as it does in solution on the NMR time scale, the actual conformation is asymmetric, mainly because of the unrelated orientations of the −SMe axial groups. The methyl group bonded to S1 (C(31)) is oriented above the phenanthroline rings, while that on the opposite side (C(32)) is oriented almost orthogonal to the first one. The steric pressure of the C(31) methyl induces a bending of the phenanthroline out of the coordination plane (PtNN/dmphen dihedral angle 13.5(2)°). The equatorial olefin carbons and nitrogen atoms are almost coplanar (PtNN/PtCC dihedral angle 4.9(5)°). Bond parameters of interest are reported in Table 2 together with the corresponding ones in the dication [Pt(SMe$_2$)$_2$(dmphen)(diphenyl fumarate)]$^{2+}$ (**3c(SMe$_2$)**), whose geometry is shown in Figure 2. This molecule is frozen in a single asymmetric conformation in the crystal, and again the mutual orientations of the SMe$_2$ ligands are not symmetry-related. Also, the

Table 2. Comparison of Relevant Bond Parameters in [Pt(SMe)$_2$(dmphen)(diphenyl fumarate)] (2c(SMe)) and [Pt(SMe$_2$)$_2$(dmphen)(diphenyl fumarate)]$^{2+}$ (3c(SMe$_2$)) (Distances in Å and Angles in deg)

	2c(SMe)	3c(SMe$_2$)
	Bond Distances	
Pt−C(olefin)	2.071(4)	2.067(15)
	2.095(4)	2.087(13)
	2.083 (av)	2.077 (av)
C−C(olefin)	1.444(6)	1.446(19)
Pt−S	2.378(1)	2.348(4)
	2.375(1)	2.376(4)
	2.376 (av)	2.362 (av)
S−C(methyl)	1.816(5)	1.784(11), 1.798(11)
	1.807(6)	1.792(13), 1.811(13)
	1.812 (av)	1.796 (av)
Pt−N	2.196(3)	2.184(13)
	2.198(3)	2.228(12)
	2.197 (av)	2.206 (av)
	Bond Angles	
S1−Pt−S2	177.52(4)	177.34(15)
S1−Pt−C1	90.6(1)	93.2(4)
S1−Pt−C2	92.3(1)	95.0(4)
S1−Pt−N1	92.1(1)	89.5(3)
S1−Pt−N2	91.9(1)	88.4(3)
S2−Pt−C1	91.8(1)	86.1(4)
S2−Pt−C2	89.9(1)	86.1(4)
S2−Pt−N1	86.2(1)	91.9(3)
S2−Pt−N2	86.0(1)	89.7(3)
N1−Pt−N2	75.6(1)	77.6(5)
	Torsion Angle (Fumarate)	
C−C=C−C	44.4(4)	57.6(10)

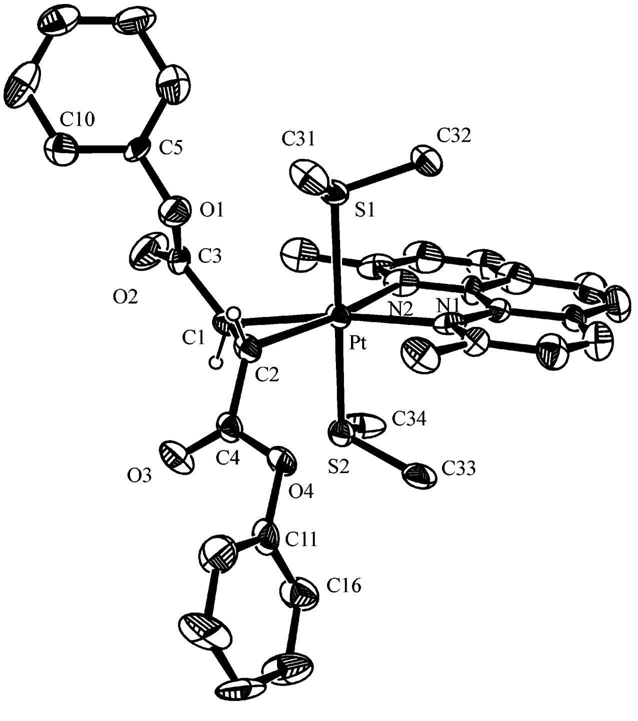

Figure 2. ORTEP drawing (30% probability thermal ellipsoids) of the dication [Pt(SMe$_2$)$_2$(dmphen)(diphenyl fumarate)]$^{2+}$ (**3c(SMe$_2$)**). Hydrogen atoms, except the olefinic ones, have been omitted.

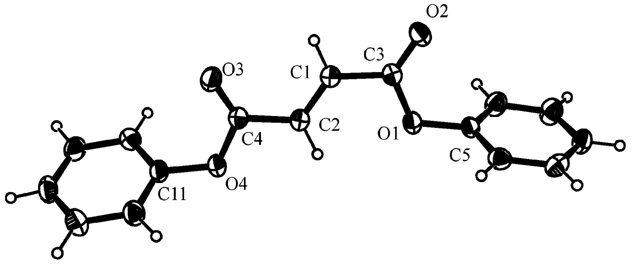

Figure 3. ORTEP drawing (30% probability thermal ellipsoids) of the solid-state structure of free diphenyl fumarate. The idealized symmetry is C_s, if the phenyl groups are ignored. Relevant distances (Å): C(1)−C(2) = 1.307(2), C(1)−C(3) = 1.479(2), C(2)−C(4) = 1.482(2), C(3)−O(2) = 1.193(2), C(4)−O(3) = 1.195(2), C(3)−O(1) = 1.341(2), C(4)−O(4) = 1.341(2), O(1)−C(5) = 1.416(1), O(4)−C(11) = 1.410(1) Å. Torsion angle (deg): C(3)−C(1)−C(2)−C(4) = 0.4(1).

−C(O)OPh groups are not superimposable by an idealized 2-fold rotation. In this molecule the methyl groups exert steric pressure on either side of the phenanthroline rings, even though in an unbalanced way. As a consequence the bending of the bidentate ligand out of the equatorial plane is much smaller (6.4(4)°). Corresponding bond parameters in the neutral and dicationic species can be analyzed on inspecting Table 2. We were expecting some shrinkage of the primarily σ bonds and stretching of those with significant π-contribution. The observed effects are small and only at the level of average values can tiny shortenings, not exceeding 0.01 Å, be observed in the dication. Very probably, packing effects tend to blur the differences that are in any way small. A molecule whose structure is comparable to the previous ones is $[Pt(SCN)_2(dmphen)(dimethyl\ maleate)]$,[15] and the bond values, although affected by higher errors, are in accord with the present ones.

Of some interest is a comparison between the geometry of the diphenyl fumarate as a free molecule and as a ligand coordinated to platinum. The solid-state structure of the ligand is illustrated in Figure 3. The molecule adopts a flat conformation, if the phenyl groups are disregarded, and the idealized symmetry is C_s. Upon coordination the C═C double bond undergoes the expected elongation (ca. 0.14 Å for both molecules) and outward bending of the C(carboxylate) atoms. The C−C═C−C torsion angles are 0.4(1), 44.4(4), and 57.6(10)° in the free ligand and neutral and dipositive complexes, respectively. The higher torsion of the carbon skeleton in the dication can be explained in terms of the metallacyclopropane bond model of the platinum−olefin interaction. A stronger C−Pt σ bond induces a more marked sp^3 rehybridization of the carbon orbitals. The equivalence of Pt−C bond distances in the neutral and dipositive species also indicates that the total bond order is substantially preserved through a different balance of its σ and π components.

Conclusions

This paper illustrates the oxidative addition of RE−ER molecules (E = O, S, Se, Te) to Pt(0) precursors of the general formula [Pt(N,N-chelate)(olefin)]. Symmetrical cleavage of the E−E bond has been observed, with formation of trigonal-bipyramidal products $[Pt(ER)_2(N,N\text{-chelate})(olefin)]$ (**2**) containing the chalcogenide ligands in axial positions. Compounds of type **2** represent the first class of coordinatively saturated Pt(II) species containing chalcogenide ligands and constitute the platinum(II) complement of previously described octahedral platinum(IV) species.[3] Furthermore, the basicity of S, Se, and Te atoms coordinated to Pt has been usefully exploited for preparing the first examples of dipositive Pt(II) cations in a trigonal-bipyramidal arrangement. Finally, we recall that, in this study, we have also found that the addition of the E−E bond to platinum(0)[9] precursors can be reversible. This very rare case[16] of equilibrium in an oxidative addition process has also been very recently extended to related platinum(II) species.[17]

Experimental Section

^1H and ^{13}C NMR spectra were recorded on Varian XL-200 or Varian Gemini-300 spectrometers. $CDCl_3$ and CD_3NO_2 were used as solvents; $CHCl_3$ (δ 7.26), $^{13}CDCl_3$ (δ 77.0) and CD_2HNO_2 (δ 4.33) were the internal standards. The following abbreviations were used for describing NMR multiplicities: s, singlet; d, doublet; dd, double doublet; t, triplet; m, multiplet. Infrared spectra were recorded on a JASCO FT-IR 430 spectrometer. Dibenzoyl peroxide, hydrogen peroxide, dimethyl disulfide, dimethyl diselenide, diphenyl disulfide, diphenyl diselenide, diphenyl ditelluride, and trimethyloxonium tetrafluoroborate were commercially available (Sigma-Aldrich). Diacetyl peroxide[18] and the Pt(0) precursors[19] were obtained according to published methods.

[Pt(OH)$_2$(dmphen)(dimethyl maleate)] (2a(OH)). Aqueous hydrogen peroxide (30%, 0.3 mL) was added to a magnetically stirred suspension of the three-coordinate precursor (0.050 g, 0.090 mmol) in tetrahydrofuran (2 mL). After stirring for 5 min at room temperature the precipitate was separated, washed with tetrahydrofuran (3 mL) and chloroform (1 mL), and dried in vacuo. Yield: 60%.

[Pt(OH)$_2$(dmphen)(dimethyl fumarate)] (2b(OH)). Aqueous hydrogen peroxide (30%, 0.3 mL) was added to a magnetically stirred suspension of the three-coordinate precursor (0.050 g, 0.09 mmol) in tetrahydrofuran (2 mL). After the mixture was stirred for 5 min at room temperature, the resulting solution was filtered and concentrated in vacuo to a small volume. Addition of diethyl ether caused crystallization of the pale yellow product, which was washed with diethyl ether and dried in vacuo. Yield: 50%.

[Pt(OAc)$_2$(dmphen)(olefin)] (2a(OAc) and 2b(OAc)). An ethereal solution of diacetyl peroxide (1 mL) was added under nitrogen to a magnetically stirred suspension of the three-coordinate precursor (0.050 g, 0.090 mmol) in dry toluene (2 mL). After the mixture was stirred for 16 h at room temperature, a yellow precipitate was separated, washed with toluene and diethyl ether, and dried in vacuo. Yield: 70−80%.

[Pt{OC(O)Ph}(OH)(dmphen)(dimethyl fumarate)] (2b-(O$_2$CPh)(OH)). To a magnetically stirred suspension of the three-coordinate precursor (0.10 g, 0.18 mmol) in toluene (5 mL) was added dibenzoyl peroxide (0.17 g, 0.72 mmol). The suspension was stirred for 7 days. The residual solid was removed by filtration and the solution concentrated to a small

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Table 3. Crystal Data and Diffraction Experimental Details for [Pt(SMe)$_2$(dmphen)(diphenyl fumarate)]·1.5CHCl$_3$ (2c(SMe)), [Pt(SMe$_2$)$_2$(dmphen)(diphenyl fumarate)][BF$_4$]$_2$ (3c(SMe$_2$)), and Diphenyl Fumarate

	$C_{32}H_{30}N_2O_4PtS_2$·1.5CHCl$_3$ (**2c(SMe)**)	$C_{34}H_{36}B_2F_8N_2O_4PtS_2$ (**3c(SMe$_2$)**)	$C_{16}H_{12}O_4$
M_r	944.84	969.48	268.26
cryst symmetry	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)	$P2_1/c$ (No. 14)
a, Å	9.128(3)	11.5573(8)	10.8898(4)
b, Å	13.748(4)	23.140(1)	7.7762(3)
c, Å	15.297(5)	14.653(1)	16.3121(6)
α, deg	77.071(1)	90	90
β, deg	78.162(1)	104.585(2)	106.639(2)
γ, deg	89.583(1)	90	90
cell vol, Å^3	1829.7(1)	3792.3(4)	1323.49(9)
Z	2	4	4
D_c, Mg m^{-3}	1.715	1.698	1.346
μ(Mo Kα), mm^{-1}	4.316	3.889	0.097
F(000)	930	1912	560
cryst size, mm	0.20 × 0.25 × 0.45	0.10 × 0.15 × 0.21	0.10 × 0.13 × 0.16
θ limits, deg	1.5−30	2.5−25	1.95−30
no. of rlfns collected	25 267	34 529	34 609
no. of unique obsd rflns ($F_o > 4\sigma(F_o)$)	10 694 ($R_{int} = 0.044$)	6659 ($R_{int} = 0.090$)	3870 ($R_{int} = 0.042$)
goodness of fit on F^2	1.040	0.961	0.891
$R1(F)$,[a] w$R2(F^2)$[b]	0.0392, 0.1048	0.0632, 0.1595	0.0426, 0.1067

[a] $R1 = \Sigma||F_o| - |F_c|/\Sigma|F_o|$. [b] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ and $P = (F_o^2 + 2F_c^2)^{1/3}$.

volume. Slow addition of hexane caused crystallization of the product, which was washed with hexane (2 mL) and dried in vacuo. Yield: 60%.

[Pt(SMe)$_2$(dmphen)(olefin)] (2a(SMe), 2b(SMe), and 2c(SMe)). The appropriate three-coordinate precursor (0.20 mmol) was suspended in dimethyl disulfide (1 mL). After the mixture was stirred for 24 h, a red solution was obtained. Addition of diethyl ether caused crystallization of a pale yellow compound, which was washed with diethyl ether (3 mL) and dried in vacuo. Yield: >90%.

[Pt(SPh)$_2$(dmphen)(olefin)] (2a(SPh) and 2b(SPh)). A solution of diphenyl disulfide (0.042 g, 0.19 mmol) in chloroform (0.5 mL) was added to a suspension of the appropriate three-coordinate compound (0.070 g, 0.13 mmol) in chloroform (0.5 mL). After the mixture was stirred for 24 h, addition of diethyl ether to the resulting red solution afforded the product as an orange solid, which was washed with diethyl ether and dried in vacuo. Yield: >90%.

[Pt(SeR)$_2$(dmphen)(olefin)] (2a(SeMe), 2b(SeMe),[9] 2a(SePh), and 2b(SePh)).[9] A solution of the appropriate diselenide (0.18 mmol) in chloroform (0.5 mL) was added to a suspension of the appropriate three-coordinate compound (0.050 g, 0.09 mmol) in chloroform (0.5 mL). After the mixture was stirred for 3 h, addition of hexane afforded the orange product, which was washed with hexane and dried in vacuo. Yield: 80−90%.

[Pt(TePh)$_2$(dmphen)(olefin)] (2a(TePh) and 2b(TePh)). Diphenyl ditelluride (0.074 g, 0.18 mmol) was added to a suspension of the appropriate three-coordinate compound (0.050 g, 0.090 mmol) in chloroform (0.5 mL). After the mixture was stirred for 3 h, a dark solution was obtained. By addition of diethyl ether the crystallization of the dark red product ensued, which was washed with diethyl ether and dried in vacuo. Yield: 85%.

[Pt(SeR)$_2$(phen)(dimethyl fumarate)] (R = Me, Ph). The appropriate diselenide (1.3 mmol) was added to a suspension of the three-coordinate compound **2b** (0.070 g, 0.013 mmol) in toluene (4 mL). After the mixture was stirred for 48 h, the precipitate was separated, washed with toluene and diethyl ether, and dried in vacuo. Yield: 70−80%.

Reaction of [Pt(OH)$_2$(dmphen)(dimethyl maleate)] (2a(OH)) with Acetic Anhydride. The complex **2a(OH)** (0.050 g, 0.090 mmol) was suspended in acetic anhydride (1 mL) and stirred in the dark at room temperature for 6 h. The yellow solution was filtered and reduced under vacuum to afford the yellow compound **2a(OAc)**, which was washed with diethyl ether (1 mL) and dried in vacuo. Yield: 65%.

[Pt(EMe$_2$)$_2$(dmphen)(olefin)][BF$_4$]$_2$ (3b(SMe$_2$), 3b(SeMe$_2$), and 3c(SMe$_2$)). A solution of trimethyloxonium tetrafluoroborate (0.060 g, 0.040 mmol) in nitromethane (0.5 mL) was added to the appropriate type **1** compound (0.020 mmol). After the mixture was stirred for 5 min, slow addition of diethyl ether to the resulting solution afforded the light yellow product, which was washed with diethyl ether and dried in vacuo. Yield: 60−70%.

X-ray Data Collection and Structure Determination of [Pt(SMe)$_2$(dmphen)(diphenyl fumarate)] (2c(SMe)), [Pt(SMe$_2$)$_2$(dmphen)(diphenyl fumarate)][BF$_4$]$_2$ (3c(SMe$_2$)), and Diphenyl Fumarate. The X-ray diffraction intensities for the three compounds were measured on a Bruker AXS SMART 2000 diffractometer, equipped with a CCD detector, using Mo Kα radiation ($\lambda = 0.710\ 73$ Å) at room temperature. Crystal data and some experimental details are given in Table 3. A full sphere of reciprocal space was scanned by 0.3° ω steps with the detector kept at 5.0 cm from the sample. The collected frames were processed for integration by using the program SAINT, and an empirical absorption correction was applied using SADABS.[20] The structures were solved by direct methods (SIR 97)[21] and subsequent Fourier syntheses and refined by full-matrix least squares on F^2 (SHELXTL).[22] The hydrogen atoms of the two complexes were included in idealized positions, except the olefinic hydrogens in the neutral [Pt(SMe)$_2$(dmphen)(diphenyl fumarate)], which were located in the Fourier map and their positions refined. The final refinement proceeded using anisotropic thermal parameters for all the non-hydrogen atoms. The H atoms were assigned isotropic thermal parameters *U*(H) set at 1.2 (1.5 for the methyl groups) times the U_{eq} value of the carrier carbon atoms**.** The solution of the structure of [Pt(SMe)$_2$(dmphen)(diphenyl fumarate)] was carried out in the centric space group $P\bar{1}$, and electron density maps disclosed most atoms, including a chloroform molecule. Complications arose for the interpreta-

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tion of the electron density peaks in the region occupied by one C(O)OPh group. Phenyl rings attached to both oxygen atoms were recognized, and more than that, one of them was superimposed to a group of out-of-plane peaks compatible with a CCl_3 group. The rationalization of the disorder was as follows: two conformational isomers of the diphenyl fumarate ligand corresponding to alternative orientations of the −C(O)-OPh fragment bonded to C(2) are present in the crystal in equivalent amounts. Where the phenyl group is bonded to O(4) (C(11A)−C(16A) as shown in Figure 1), its alternative position is occupied by a chloroform molecule in order to fill in the available space. Where the phenyl group is bonded to O(3) (not shown in Figure 1), the volume belonging to C(11A)−C(16A) is empty. The packing of the two isomers is probably ordered in the crystal, because the C(11A)−C(16A) phenyl bumps into its equivalent in a nearby molecule, indicating that contiguous molecules must belong to different isomers. Therefore, the isomers are packed in a concerted way: i.e., they are ordered in the space group *P*1 with two independent molecules. The refinement of the latter structure model was not possible because the least-squares matrix was unstable, probably because most atoms conform to a centric packing. Therefore, we had to go back to the disordered structure model in the $P\bar{1}$ space group comprising one complex and 1.5 chloroform molecules in the asymmetric unit.

The structure of $[Pt(SMe_2)_2(dmphen)(diphenyl\ fumarate)][BF_4]_2$ was solved without difficulties in the space group $P2_1/n$, and both $[BF_4]^-$ anions exhibited double images of the fluorine atoms. The standard errors of the structure model are higher than for the previous molecule because the crystal did not diffract for θ angles above 25°.

The structure of diphenyl fumarate was solved in the space group $P2_1/c$, and all non-H atoms were refined anisotropically. The hydrogen atoms were located in the electron density map and refined without positional constraints with isotropic displacement parameters. The excellent quality of the structure model allows us to use the bond parameters as reference values.

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Supporting Information Available: Tables giving elemental analyses for representative new complexes and X-ray crystallographic data for **2c(SMe)**, **3c(SMe$_2$)**, and diphenyl fumarate; these latter data are also available in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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