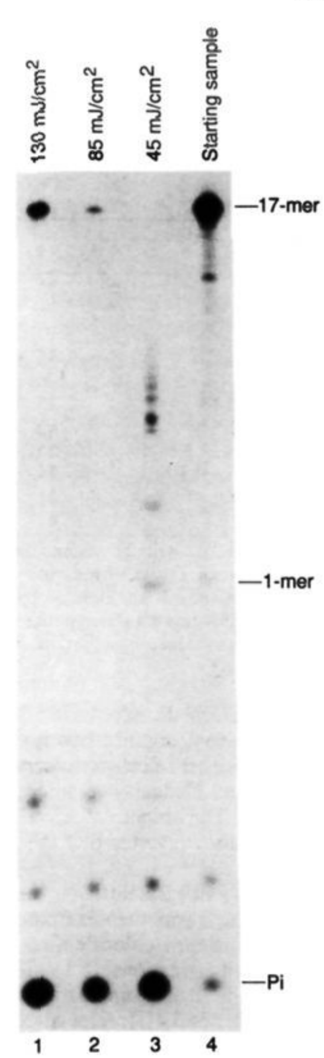

Figure 2. Polyacrylamide gel electrophoretic analysis of a vaporized oligonucleotide. The vaporized radioactive materials on the filter papers shown in Figure 1 are excised and extracted with two 150-μL portions of water, and the resulting solutions are concentrated and then loaded onto a 20% polyacrylamide gel:[6] lane 1, 130 mJ/cm^2; lane 2, 85 mJ/cm^2; lane 3, 45 mJ/cm^2; lane 4, starting oligonucleotide. The gel is electrophoresed at 1000 V for 2 h, and then the positions of the bands are determined by autoradiography. Authentic inorganic phosphate and mononucleotide are run in adjacent lanes.

(i) less molecular dATP is obtained; (ii) more dAMP is produced; (iii) more phosphate and diphosphate are formed; and (iv) less tripolyphosphate is observed (not shown; less than 4%). These trends are consistent with photochemical activation of the P–O–P bonds at intermediate and low vaporization power. The incident photon fluence ($\sim 2 \times 10^{17}$ photons cm^{-2} s^{-1}) is high enough that this activation can proceed through a two-photon excitation of the 274-nm electronic absorption band of the phosphate[11] or through an excitation of the adenine base with subsequent energy transfer to the phosphate bonds. Alternatively, the photon energy may degrade to thermal energy before vaporization occurs. This would result in a photothermal mechanism for cleaving the weak phosphodiester bond at low laser powers. At the highest powers, the P–O–P bonds are still activated, but the energy is most likely quenched by the high number of subsequent collisions.

These results strongly suggest that fragile, single-stranded DNA molecules can be molecularly vaporized out of a rhodamine 6G thin film using laser pulse energies greater than 85 mJ/cm^2. At lower energies the phosphodiester bonds cleave, presumably through photochemical activation. Finally, recent studies in our laboratory suggest that single strands as long as 1000 bases can be vaporized intact.[12]

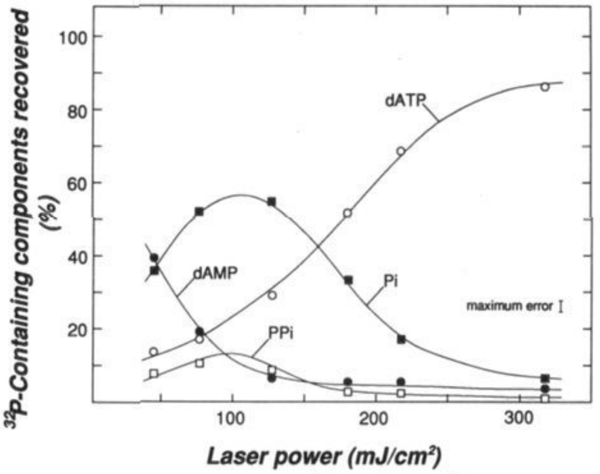

Figure 3. Analysis of vaporized [α-^{32}P]dATP. [α-^{32}P]ATP (60 pmol, 3000 Ci/mmol) is dissolved in 20 μL of water containing 10% methanol and 10 mg/mL rhodamine 6G. The thin film is vaporized from a fresh spot for each power level. The vaporized radioactive materials are eluted and adjusted so that each has 20000 cpm/μL. Two microliters are spotted onto a glass-backed PEI-cellulose F TLC plate (EM Science) and are eluted with a solution of 0.6 M LiCl in 1.0 M formic acid. The amount of radioactivity present in each spot is determined by using an Ambis radioactivity image scanner: (○) dATP, (●) dAMP, (□) pyrophosphate, (■) phosphate.

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[11] The visible/ultraviolet spectra of sodium phosphate, pyrophosphate, and polytriphosphate were obtained on a Hewlett-Packard 8452A diode array spectrophotometer. In essence, two electronic absorptions were observed for each sample, a strong feature at 198 nm and a weak feature at 274 nm.

(12) Romano, L. J.; Levis, R. J., manuscript in preparation. These recent experiments provide further evidence for molecular vaporization. These studies show that there is a considerable difference between the autoradiographic band intensities for single-stranded DNA mixtures that have been either vaporized or directly loaded onto a gel. For example, a comparison of the ratio of the 20-mer to 75-mer intensities for the two samples indicated that the intensity of the 75-mer band was reduced by 90% in the vaporized sample relative to the starting sample. Spallation would be expected to generate materials on the filters having band intensity distributions identical with those of the starting sample.

Reactions of Sulfinylated Radicals. Solvent Effect and Efficient Stereoselectivity Enhancement by Complexation of the Sulfinyl Group with Lewis Acids

Philippe Renaud* and Marco Ribezzo

Université de Lausanne, Institut de Chimie Organique
2 rue de la Barre, CH-1005 Lausanne, Switzerland

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Control of the stereoselectivity of radical reactions[1] is an important problem to solve in order to generalize the application of these reactions in preparative organic synthesis.[2] Very little is known about controlling the stereochemical outcome of radical reactions by external factors like solvent[3] or coordinating species. In the course of our studies on the reactions of sulfinylated radicals, we have decided to address this particular problem. We report herein a unique case of stereoselectivity enhancement of a radical reaction based on complexation of the radical intermediate with metals and Lewis acids.

The use of sulfoxides as chiral auxiliaries for radical reactions has recently attracted much attention. Cyclization of acyclic radicals has been reported.[4-7] A cyclic radical generated from

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(1) (a) Giese B. *Radicals in Organic Synthesis: Formation of Carbon-Carbon Bonds*; Pergamon: Oxford, 1988. (b) Curran, D. P. *Synthesis* **1988**, 417, 489.

(2) Giese, B. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 969.

(3) The first case of a solvent effect in this context was reported by Giese in ref 2, p 971.

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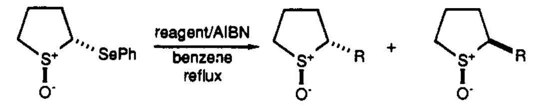
Table I. Reaction of **1** with Different Reagents in Refluxing Benzene



1 **2-4**

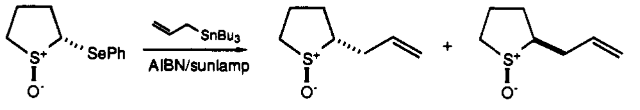
product	R	reagent	yield,[a] %	trans/cis
2	$CH_2{=}CHCH_2$	allyltributylstannane[b]	35	6.0:1
3	$CH_2CH_2SiMe_3$	vinyltrimethylsilane, tributyltin hydride[c]	25[d]	4.0:1
4	D	tributyltin deuteride[b]	88	1.1:1

[a] Isolated yield. [b] A solution of **1** (2 mmol), Bu_3SnR (2.5 mmol), and AIBN (20 mg) in 5 mL of benzene. [c] A 10-fold excess of vinyltrimethylsilane. [d] Thiolane-1-oxide was isolated as a single side product.

a sulfinamide was also studied, showing that solvent may affect stereoselectivity.[8] We have chosen to investigate, as a model system for the present study, reactions of the 1-oxo-thiolan-2-yl radical. In such a simple five-membered-ring cyclic radical, the stereoselectivity was expected to be governed only by steric effects.

The selenylated sulfoxide **1** was prepared from thiolane 1-oxide (2 equiv of LDA, 1 equiv of $(PhSe)_2$) and was used to generate the radical.[9] We first looked at the reaction of this radical with different substrates in refluxing benzene (Table I). The radical reacted with allyltributylstannane and vinyltrimethylsilane from the less hindered face (anti to the $S^+–O^-$ bond), leading preferentially to the trans-substituted isomers[10] (trans/cis, 6.0:1 and 4.0:1, respectively). The deuteration of the radical derived from **1** afforded **4** (88% yield) with very low selectivity (trans/cis, 1.1:1). This result reflects the smaller size of the tributyltin deuteride relative to the olefins. The effect of temperature was also examined for the allylation reaction. When it was run at 15 °C (300-W sunlamp irradiation), **2** was obtained with only a slight increase of selectivity (trans/cis, 6.2:1, 72% yield).

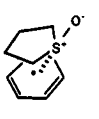
Table II. Reaction of **1** with Allyltributylstannane/AIBN at 15 °C in Different Solvents and in the Presence of Salts and Lewis Acids[a]



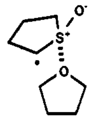
1 **2**

solvent	complexating agent	yield,[b,c] %	*trans*-**2**/*cis*-**2**[d]
benzene		72	6.6:1
THF		58	6.7:1
propionitrile		79	10:1
CH_2Cl_2		86	14:1
EtOH		76	14:1
THF	LiCl, 0.5 M	25	16:1
THF	$ZnBr_2$, 0.5 M	62	34:1
THF	$BF_3{\cdot}OEt_2$, 1.1 equiv	55	41:1
CH_2Cl_2	$Eu(dpm)_3$, 0.5 M	54	35:1
CH_2Cl_2	Bu_4NClO_4	81	14:1
propionitrile	$LiClO_4$, 0.5 M	82	50:1

[a] A solution of **1** (2 mmol), allyltributylstannane (2.5 mmol), and AIBN (20 mg) in 5 mL of solvent was irradiated with a 300-W sunlamp at 15 °C for 24 h. Crude **2** was isolated by filtration through silica gel. [b] Isolated yield. [c] Unreacted starting material was isolated as a single side product. [d] Determined by GC (SE 30, packed column) and DB-1 (capillary column).



I



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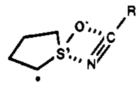
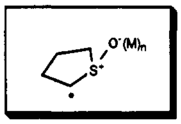


III



IV: M = Li^+, Zn^{2+}, $BF_3{\cdot}OEt_2$, $Eu(dpm)_3$

The solvent effect for the allylation reaction was investigated next (Table II). The standard reaction conditions used were irradiation with a 300-W sunlamp of a 0.4 M solution of **1** containing 1.5 equiv of allylstannane and a catalytic amount of AIBN. THF (trans/cis, 6.7:1) and benzene (trans/cis, 6.6:1) gave very similar results. Better selectivities were obtained in propionitrile (trans/cis, 10:1), methylene chloride (trans/cis, 14:1), and ethanol (trans/cis, 14:1). The lower selectivity observed for the reaction in benzene is attributed to complexation of the benzene with the positive end of the $S^+–O^-$ dipole[11] (I). Similar complexation effects may exist with nucleophilic solvents like THF (II) and with PCN (III). No such solvent organization is expected from dichloromethane, and the higher selectivity observed in that solvent confirmed this hypothesis. Alcohols may interact with sulfoxides by hydrogen bonding.[12] The absence of selectivity enhancement relative to dichloromethane suggested that the complexation was weak in the ethanol case.[13,14]

The effect of salts and Lewis acids[15] on the stereoselectivity of the reaction leading to **2** was then examined (Table II). In THF, the addition of lithium chloride (0.5 M) allowed enhancement of the selectivity (trans/cis, 16:1). The effect was even stronger with zinc bromide (0.5 M) and boron trifluoride etherate (1.1 equiv) (trans/cis, 34:1 and 41:1, respectively). However, the yield stayed relatively low (25–62%), and unreacted starting material was recovered. The addition of $Eu(dpm)_3$ (1.1 equiv), a Lewis acid often used as a shift reagent for determining the structure of substituted cyclic sulfoxides by NMR,[10b] led to good stereoselectivity enhancement (trans/cis, 35:1). The best selectivity was observed for the reaction in propionitrile containing lithium perchlorate (0.5 M) (trans/cis, 50:1) with a good 82% isolated yield. Finally, we observed no stereoselectivity enhancement in dichloromethane when tetrabutylammonium perchlorate (a noncoordinating salt) was present (trans/cis, 14:1). The dramatic increase of anti attack relative to the $S^+–O^-$ bond, which was observed in all solvents investigated when the reaction was run in the presence of lithium salts and Lewis acids,[16] is explained by formation of complexes of lithium cations[17] or other Lewis acids

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(13) Use of ethanol and trifluoroethanol enhanced very effectively the selectivity of the sulfinylated radical reactions studied by Waldner et al.[6]

(14) In benzene, the effect of concentration was investigated in the range 0.02–0.4 M for the radical precursor **1**. No influence on the stereoselectivity was observed, ruling out the importance of aggregation.

(15) We have checked that the reactions proceeded effectively by a radical mechanism for all the investigated Lewis acids, by showing that no reaction occurred without irradiation.

(16) A mixture of isomers of **2** (trans/cis, 6:1) was recovered unchanged after irradiation under the reaction conditions, showing that neither isomerization nor decomposition of the cis isomer occurred.

(17) Recently, lithium perchlorate was shown to enhance the rate of Diels–Alder reactions: (a) Grieco, P. A.; Nunes, J. J.; Gaul, M. D. *J. Am. Chem. Soc.* **1990**, *112*, 4595. This effect was attributed to the Lewis acidity of lithium ion: (b) Forman, M. A.; Dailey, W. P. *J. Am. Chem. Soc.* **1991**, *113*, 2761.

with the oxygen atom of the sulfinyl group (IV).[12] Even the deuteration reaction, which was shown to be almost completely unselective in refluxing benzene (Table I) gave **4** as a 6.2:1 trans/cis mixture of isomers when it was run in propionitrile containing lithium perchlorate (0.5 M) at 15 °C.

In conclusion, we have demonstrated that the stereoselectivity of reactions of sulfinylated radicals was influenced by the nature of the solvent and to a higher degree by complexating agent. For instance, lithium perchlorate, a very mild Lewis acid, allowed very efficient selectivity enhancement in propionitrile.

Acknowledgment. Funding from the Fonds National Suisse de la Recherche Scientifique is gratefully acknowledged.

Synthesis and X-ray Structural Characterization of the First Unbridged Diplatinum(III) Compound: Bis[bis(1-imino-1-hydroxy-2,2-dimethylpropane)trichloroplatinum(III)]

Renzo Cini,[†] Francesco P. Fanizzi,[‡] Francesco P. Intini,[‡] and Giovanni Natile*,[‡]

Dipartimento di Chimica, Università di Siena
Pian dei Mantellini 44, I-53100 Siena, Italy
Dipartimento Farmaco-Chimico, Università di Bari
Trav. 200 Re David 4, I-70125 Bari, Italy

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It is known that there is significant intermetallic bonding in Pt^{III}–Pt^{III} complexes.[1] However, the presence of bridging ligands such as sulfate,[2] orthophosphate,[3] pyrophosphite,[4] carboxylate,[5] 2-pyridonate,[6] and 2-pyrimidonate[7] was considered crucial in stabilizing the oligomers and influencing the metal–metal distance. In this context the isolation of a platinum(III) complex without bridging-ligand restraints would be useful for investigating the role of the intermetallic interaction and its fate upon redox, ligand-substitution, and photochemical processes.

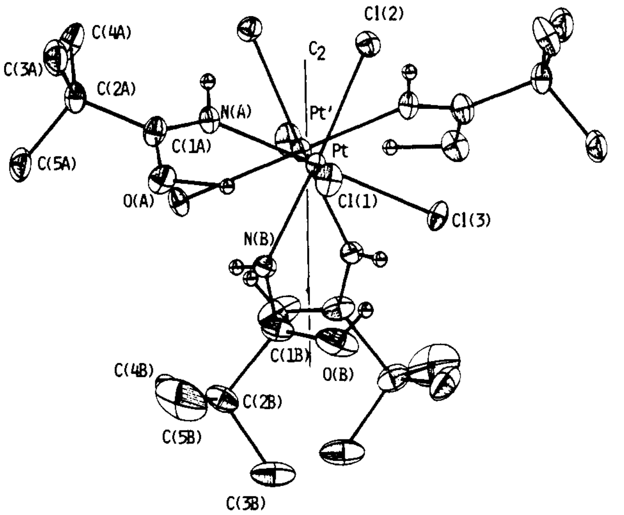

Figure 1. ORTEP drawing of the dimeric molecule of **1**, showing also the labeling scheme. Ellipsoids enclose 30% probability. The view is almost parallel to the Pt–Pt axis. Only the H atoms bound to N and O atoms are reported. Selected bond distances are as follows (Å): Pt–Pt′, 2.694 (1); Pt–Cl(1), 2.458 (3); Pt–Cl(2), 2.306 (3); Pt–Cl(3), 2.328 (3); Pt–N(A), 2.019 (11); Pt–N(B), 2.037 (8).

This work reports on the first example of unbridged Pt^{III}–Pt^{III} dimer, $[Pt^{III}_2Cl_6\{HN{=}C(OH)C(CH_3)_3\}_4]$ (**1**), obtained by reaction of *cis*-$[Pt^{II}Cl_2\{HN{=}C(OH)C(CH_3)_3\}_2]$ (**2**),[8] with chlorine in CH_2Cl_2 solution. Complex **1** is formed immediately in ca. 60% yield after mixing of the reactants [together with some *cis*-$[Pt^{IV}Cl_4\{HN{=}C(OH)C(CH_3)_3\}_2]$ (**3**)],[9] it is rather stable in solution containing chlorine (where it is oxidized in a few days to **3**), and it can be crystallized from carbon tetrachloride/pentane to give dark red crystals. In the absence of chlorine, compound **1** readily disproportionates ($^1/_2$ h) into **2** and **3**.

The single-crystal X-ray diffraction study[10] gives important structural information on the separation and mutual rotation of the two platinum subunits.

The crystal lattice consists of discrete $[Pt_2Cl_6\{HN{=}C(OH)C(CH_3)_3\}_4]$ molecules (Figure 1). The Pt–Pt bond axis is orthogonal to a crystallographic 2-fold rotation axis. The intermetallic bond distance [2.694 (1) Å] is in agreement with the values found in $K_4[Pt_2Cl_2(\mu\text{-}P_2O_5H_2)_4]$ and other pyrophosphite four-bridged dimers.[4] It is much longer than those found in other

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[†] Dipartimento di Chimica, Università di Siena.

[‡] Dipartimento Farmaco-Chimico, Università di Bari.

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(8) Compound **2** was prepared from *cis*-$[PtCl_2\{NCC(CH_3)_3\}_2]$. The nitrile complex was dissolved in dichloromethane and treated with excess powdered potassium hydroxide. After a few minutes, the solvent was evaporated; the solid residue containing the amidato species ($K_2[PtCl_2\{NHCOC(CH_3)_3\}_2]$) and the excess potassium hydroxide was dissolved in cold water and treated with excess of HCl, and compound **2** precipitated as a light green solid. The compound was characterized by elemental analyses and ^1H NMR and IR spectra. The cis configuration was also confirmed by comparing the spectral data of **2** with those of the trans isomer obtained by a similar procedure from *trans*-$[PtCl_2\{NCC(CH_3)_3\}_2]$.

(9) Compound **3** was characterized by elemental analyses and ^1H NMR and IR spectra. The cis configuration was also confirmed by comparing the spectral data of **3** with those of the trans isomer obtained by oxidation with chlorine of *trans*-$[PtCl_2\{HN{=}C(OH)C(CH_3)_3\}_2]$.

(10) Crystal data for $C_{20}H_{44}N_4O_4Cl_6Pt_2$: M = 1007.5, orthorhombic, space group *Pbcn* (No. 60), with a = 11.359 (3) Å, b = 20.054 (5) Å, c = 15.028 (2) Å, V = 3423 Å^3, Z = 4, D_{calcd} = 1.955 g cm^{-3}, μ(Mo Kα) = 87.5 cm^{-1}, Mo Kα radiation with graphite monochromator, T = 22 °C. Intensities collected on a CAD4 Enraf-Nonius diffractometer, $\omega/2\theta$ scan method, scanning range $5° < 2\theta < 50°$. Lorentz polarization and empirical absorption (ψ scan) were correction applied. The structure was solved by Patterson and Fourier methods and refined by full-matrix least squares on the basis of 1939 independent reflections with $F > 3\sigma(F)$. Difference maps based on the anisotropic full-matrix least-squares refinement on F including Pt, Cl, N, O, and C atoms revealed the positions of eight H atoms. They were included in the final full-matrix least-squares cycles with isotropic thermal parameters. Final R and R_w indices converged to 0.039 and 0.043, respectively.

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