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

Received May 13, 1991

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.

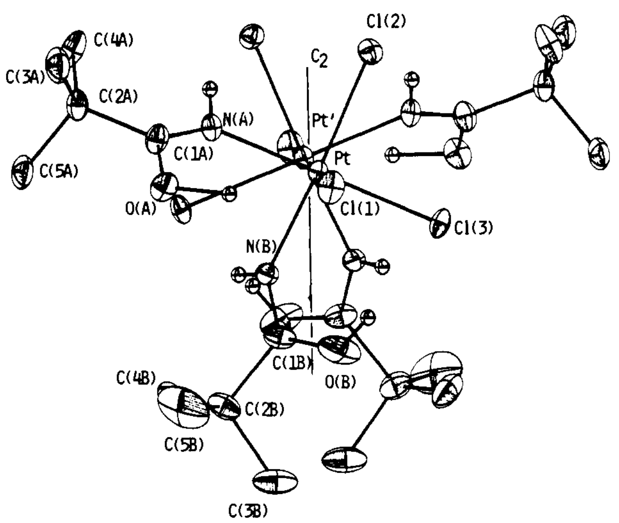

Figure 1. ORTEP drawing of the dimeric molecule of **1**, showing also the labeling scheme. Ellipsoids enclose 30% probability. The view is almost parallel to the Pt–Pt axis. Only the H atoms bound to N and O atoms are reported. Selected bond distances are as follows (Å): Pt–Pt′, 2.694 (1); Pt–Cl(1),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

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.

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

---

† Dipartimento di Chimica, Università di Siena.

‡ Dipartimento Farmaco-Chimico, Università di Bari.

(1) (a) Roundhill, D. M.; Gray, H. B.; Che, C.-M. *Acc. Chem. Res.* **1989**, *22*, 55. (b) Cotton, F. A.; Walton, R. A. *Multiple Bonds Between Metal Atoms*; Wiley: New York, 1982. (c) Zipp, A. P. *Coord. Chem. Rev.* **1988**, *84*, 47. (d) Woollins, J. D.; Kelly, P. F. *Coord. Chem. Rev.* **1985**, *65*, 115. (e) O'Halloran, T. V.; Lippard, S. J. *Isr. J. Chem.* **1985**, *25*, 130.

(2) (a) Muraveiskaya, G. S.; Kukina, G. A.; Orlova, V. S.; Evstaf'eva, O. N.; Porai-Koshits, M. A. *Dokl. Akad. Nauk SSSR* **1976**, *226*, 76. (b) Cotton, F. A.; Falvello, L. R.; Han, S. *Inorg. Chem.* **1982**, *21*, 2889. (c) Bancroft, D. P.; Cotton, F. A.; Falvello, L. A.; Han, S.; Schwotzer, W. *Inorg. Chim. Acta* **1984**, *87*, 147.

(3) (a) El-Mehdawi, R.; Fronczek, F. R.; Roundhill, D. M. *Inorg. Chem.* **1986**, *25*, 1155. (b) Conder, H. L.; Cotton, F. A.; Falvello, L. R.; Han, S.; Walton, R. A. *Inorg. Chem.* **1983**, *22*, 1887. (c) Cotton, F. A.; Falvello, L. R.; Han, S. *Inorg. Chem.* **1982**, *21*, 1709. (d) Appleton, T. G.; Hall, J. R.; Neale, D. W.; Ralph, S. F. *Inorg. Chim. Acta* **1983**, *77*, L149. (e) Cotton, F. A.; Han, S.; Conder, H. L.; Walton, R. A. *Inorg. Chim. Acta* **1983**, *72*, 191.

(4) (a) Che, C.-M.; Schaefer, W. P.; Gray, H. B.; Dickson, M. K.; Stein, P. B.; Roundhill, D. M. *J. Am. Chem. Soc.* **1982**, *104*, 4253. (b) Che, C.-M.; Mak, T. C. W.; Gray, H. B. *Inorg. Chem.* **1984**, *23*, 4386. (c) Stein, P. B.; Dickson, M. K.; Roundhill, D. M. *J. Am. Chem. Soc.* **1983**, *105*, 3489. (d) Che, C.-M.; Herbstein, F. H.; Schaefer, W. P.; Marsh, R. E.; Gray, H. B. *J. Am. Chem. Soc.* **1983**, *105*, 4604. (e) Alexander, K. A.; Bryan, S. A.; Fronczek, F. R.; Fultz, W. C.; Rheingold, A. L.; Roundhill, D. M.; Stein, P. B.; Watkins, S. F. *Inorg. Chem.* **1985**, *24*, 2803.

(5) (a) Bellitto, C.; Flamini, A.; Gastaldi, L.; Scaramuzza, L. *Inorg. Chem.* **1983**, *22*, 444. (b) Bellitto, C.; Bonamico, M.; Dessy, G.; Fares, V.; Flamini, A. *J. Chem. Soc., Dalton Trans.* **1986**, 595. (c) Schagen, J. D.; Overbeek, A. R.; Schenk, H. *Inorg. Chem.* **1978**, *17*, 1938. (d) Kuyper, J.; Vrieze, K. *Transition Met. Chem.* (*London*) **1976**, *1*, 208. (e) Steele, B. R.; Vrieze, K. *Transition Met. Chem.* (*London*) **1977**, *2*, 169.

(6) (a) Hollis, L. S.; Lippard, S. J. *J. Am. Chem. Soc.* **1981**, *103*, 6761. (b) Hollis, L. S.; Lippard, S. J. *Inorg. Chem.* **1982**, *21*, 2116. (c) Hollis, L. S.; Lippard, S. J. *Inorg. Chem.* **1983**, *22*, 2605. (d) Hollis, L. S.; Roberts, M. M.; Lippard, S. J. *Inorg. Chem.* **1983**, *22*, 3637. (e) O'Halloran, T. V.; Roberts, M. M.; Lippard, S. J. *Inorg. Chem.* **1986**, *25*, 957. (f) Bancroft, D. P.; Cotton, F. A.; Falvello, L. R.; Schwotzer, W. *Inorg. Chem.* **1986**, *25*, 763. (g) Bancroft, D. P.; Cotton, F. A. *Inorg. Chem.* **1988**, *27*, 1633 and 4022.

(7) (a) Lippert, B.; Shöllhorn, H.; Thewalt, U. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1983**, *38B*, 1441. (b) Lippert, B.; Schöllhorn, H.; Thewalt, U. *Inorg. Chem.* **1986**, *25*, 407. (c) Lippert, B.; Schöllhorn, H.; Thewalt, U. *J. Am. Chem. Soc.* **1986**, *108*, 525. (d) Faggiani, R.; Lippert, B.; Lock, C. J. L.; Speranzini, R. A. *J. Am. Chem. Soc.* **1981**, *103*, 1111. (e) Goodgame, D. M. L.; Rollins, R. W.; Skapski, A. C. *Inorg. Chim. Acta* **1984**, *83*, L11. (f) Schöllhorn, H.; Eisenmann, P.; Thewalt, U.; Lippert, B. *Inorg. Chem.* **1986**, *25*, 3384.

(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.

0002-7863/91/1513-7805$02.50/0

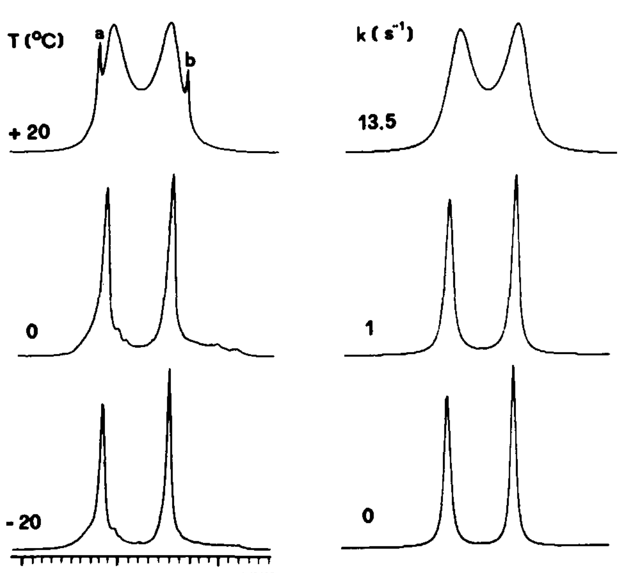

Figure 2. Experimental (left) and simulated (right) NMR spectra for *t*-Bu protons as a function of temperature for compound **1** in CD_2Cl_2; **a** and **b** mark the resonances of compounds **3** and **2**, respectively.

Pt^{III} complexes with either two (>0.10–0.15 Å) or four bridging ligands (>0.20–0.23 Å).[2,3,5-7]

The coordination sphere of Pt, including the intermetallic bond, is almost octahedral. The four equatorial sites are occupied by two cis chloride ions and two nitrogen atoms from the amide ligands; a third chloride ion occupies the apical position.

The Pt–Cl(eq) distances, 2.306 (3) and 2.328 (3) Å, are comparable to those found in $K_2[PtCl_4]$ and $K_2[PtCl_6]$ [2.316 (2)[11] and 2.323 (1) Å,[12] respectively]. The much longer Pt–Cl(ax) distance, 2.458 (3) Å, is indicative of a high *trans influence* exerted by the Pt^{III}–Pt^{III} bond. The corresponding distances were 2.407 (2) Å in $K_4[Pt_2Cl_2(\mu\text{-}P_2O_5H_2)_4]$,[4d] 2.448 (4) Å in $(Et_4N)_2[Pt_2Cl_2(\mu\text{-}PO_4H_2)_2(\mu\text{-}PO_4H)_2]\cdot H_2O$,[3e] and 2.444 (2) and 2.429 (4) Å in $[Pt_2(\mu\text{-}C_5H_4NO)_2Cl_2(NH_3)_4](NO_3)_2$.[6d]

The Pt–N distances average 2.028 (10) Å, in the range of square-planar Pt^{II} and octahedral Pt^{IV} complexes.[6d,13]

The amide ligands are in the iminol tautomeric form, the hydrogens on the oxygen and on the nitrogen atoms having been located from the difference Fourier synthesis. The same tautomeric form was reported for *trans*-$[PtCl_2\{HN{=}C(OH)C(CH_3)_3\}_2]$ and appears to be a common feature of platinum–amide complexes.[14] The C–N bond lengths [1.24 (1) and 1.26 (1) Å] and the coplanarity of H(N), N, Pt, and C(1) atoms also agree with an sp^2 hybridization of the N atoms. There are intramolecular hydrogen bonds between the apical chlorine ligand and one oxygen atom of a platinum subunit [Cl(1)···O(A) = 2.95 Å] and between the equatorial chlorine and the nitrogen atoms of twin subunits [N(A)···Cl(2′) = 3.18 Å and N(B)···Cl(3′) = 3.11 Å].

The complex adopts one of the two possible staggered conformations, placing the farthest away the amide ligands of the two platinum subunits; the values of the torsion angles about the Pt–Pt vector (ω) are close to 45°. This conformation was not allowed in platinum(III) dimers containing bridging ligands, for which the maximum value of ω was 26°.[1a,6c] The amide ligands are in equivalent pairs, and a 90° rotation of the two platinum subunits about the Pt–Pt vector interchanges the ligand positions and converts the complex into its enantiomeric form. Both enantiomers are found in the crystal.

The ^1H NMR spectrum shows two sets of signals of equal intensity for the amide ligands. Each set has resonances assignable to OH, NH, and $C(CH_3)_3$ protons, supporting the iminol bonding mode of all ligands. A line broadening was observed as a function of temperature, but the experiment had to be stopped well before coalescence because of the thermal lability of the compound (Figure 2). The fit to a unimolecular exchange process gave an approximate activation energy of 15.7 ± 0.5 kcal mol^{-1}. We suggest that complex **1** has in solution the same structure found in the solid and that the rotation about the Pt–Pt vector (which would lead to equivalence of the amide ligands by interchange of their positions) is slow on the NMR time scale. The barrier to rotation consists of the contribution of the steric repulsion between the two platinum subunits, which is built up in the eclipsed conformation, as well as the contribution of the intramolecular hydrogen bond disruptions.

The amide ligands appear to play a critical role in favoring the association of platinum units in oligomers. Considering this feature, the presence of amidate type bridging groups in several platinum oligomers, including the platinum blues,[15] appears not to be fortuitous.

Acknowledgment. This work was supported by the Ministero della Università e della Ricerca Scientifica e Tecnologica (MURST) and the Italian National Research Council (CNR).

Supplementary Material Available: Elemental analyses and ^1H NMR and IR data of compounds, complete structural data, listing of positional and thermal parameters for all atoms, distances, and angles for **1**, and an ORTEP drawing of **1** showing a perspective different from that in Figure 1 (8 pages); listing of observed and calculated structure factors for **1** (9 pages). Ordering information is given on any current masthead page.

---

(11) Mais, R. H. B.; Owston, P. G.; Wood, A. M. *Acta Crystallogr.* **1972**, *B28*, 393.

(12) Williams, R. J.; Dillon, D. R.; Milligan, W. O. *Acta Crystallogr.* **1973**, *B29*, 1369.

(13) Hartley, F. R. *The Chemistry of Platinum and Palladium*; Applied Science Publishers: London, 1973. Belluco, U. *Organometallic and Coordination Chemistry of Platinum*; Academic Press Inc.: London, 1974.

(14) Brown, D. B.; Robin, M. B.; Burbank, R. D. *J. Am. Chem. Soc.* **1968**, *90*, 5621. Brown, D. B.; Burbank, R. D.; Robin, M. B. *J. Am. Chem. Soc.* **1969**, *91*, 2895.

(15) (a) Barton, J. K.; Szalda, D. J.; Rabinowitz, H. N.; Waszcjzak, J. W.; Lippard, S. J. *J. Am. Chem. Soc.* **1979**, *101*, 1434. (b) Ginsberg, A. P.; O'Halloran, T. V.; Fanwick, P. E.; Hollis, L. S.; Lippard, S. J. *J. Am. Chem. Soc.* **1984**, *106*, 5430. (c) O'Halloran, T. V.; Mascharak, P. K.; Williams, I. D.; Roberts, M. M.; Lippard, S. J. *Inorg. Chem.* **1987**, *26*, 1261 and references cited therein. (d) Sakai, K.; Matsumoto, K. *J. Am. Chem. Soc.* **1989**, *111*, 3074 and references cited therein. (e) Micklitz, W.; Müller, G.; Huber, B.; Riede, J.; Rashwan, F.; Heinze, J.; Lippert, B. *J. Am. Chem. Soc.* **1988**, *110*, 7084 and references cited therein.

Asterane-like Compounds from 2,2,4,4-Tetramesityl-1,3-diphospha-2,4-disilabicyclo[1.1.0]butane

Alan D. Fanta, Matthias Driess, Douglas R. Powell, and Robert West*

Department of Chemistry, University of Wisconsin
Madison, Wisconsin 53706

Received May 6, 1991

In an earlier report we described the reaction of tetramesityldisilene with white phosphorus in toluene at 40 °C to give the bicyclic title compound **1**.[1] Compound **1** behaved as a Lewis base toward transition metals, forming the tungsten carbonyl complexes $\mathbf{1}\cdot W(CO)_5$ and $\mathbf{1}\cdot 2[W(CO)_5]$. In the previous communication the reaction of **1** with $(Ph_3P)_2PtC_2H_4$ was also described, leading to a compound $(Mes_2Si)_2P_2Pt(PPh_3)_2$, (**2**). At the time, it was not certain whether the product had the dative-bonded propellane structure **2b** or the tricyclo[1.1.1]pentane (asterane) structure **2a** in which the P–P bond is broken. An X-ray crystal structure determination has now shown that the asterane structure is

---

(1) Driess, M.; Fanta, A. D.; Powell, D. R.; West, R. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1038.