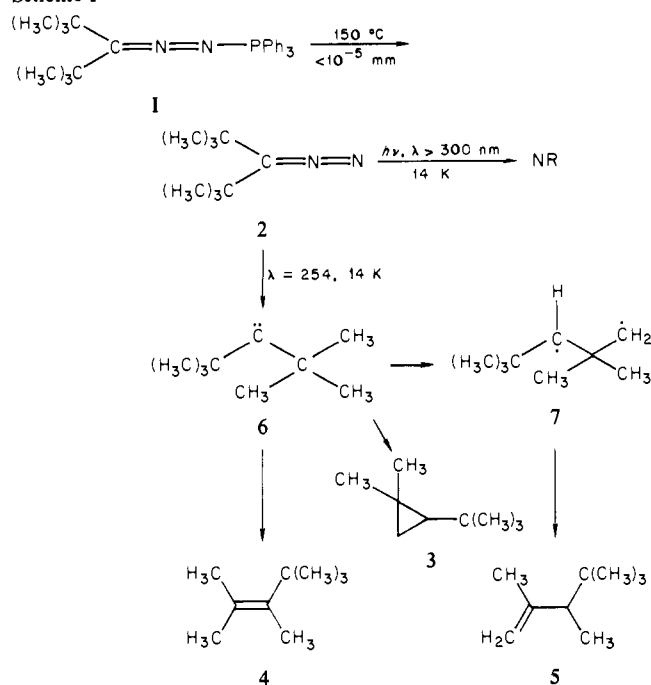


Scheme I



adduct, **1** (Scheme I), under reduced pressure. Irradiation at long wavelengths ( $\lambda > 300$  nm) produced no change, but irradiation at 254 nm, followed by collection and separation (GLPC), allowed the isolation of three major products in a 5:3:2 ratio. These were identified as 1,1-dimethyl-2-tert-butylcyclopropane (**3**), 2,3,4,4-tetramethyl-2-pentene (**4**), and 2,3,4,4-tetramethyl-1-pentene (**5**), respectively. Monitoring of the progress of the photolysis by infrared spectroscopy showed that the composition of the product mixture was fairly constant. The three major products (**3–5**) accounted for all of the major bands observed at low temperatures. The azine was not formed under these conditions.<sup>4a</sup> Products **3** and **4** represent classic reactivity of a carbene such as **6**. The origin of **5** is not obvious. Hydrogen atom transfers (via a tunneling mechanism) have precedent under these conditions.<sup>6</sup> Conceivably, **7**, thus formed, could rearrange to **5** and possible also represent a source of **3**.

The gradual warming after the photolysis was uneventful with the exception of the disappearance, at temperatures  $>100$  K, of a moderately intense band observed at  $1290\text{ cm}^{-1}$ . The band was determined to be associated with a primary photoproduct by monitoring its intensity during the early stages of photolysis. This band was also present when **2** was irradiated while matrix isolated in argon.<sup>7</sup> Subsequent irradiation of **2** in an outgassed 2-methyltetrahydrofuran glass at 20 K revealed the characteristic ESR spectrum of a triplet. The observation of a stable ESR signal at 20 K indicates that the triplet is the molecule's ground state or is within a few cal/mol of the ground state. Although stable at low temperatures, the ESR spectrum disappeared irreversibly at temperatures in excess of 70 K. The zero-field parameters ( $|D/\hbar c| = 0.689 \pm 0.005\text{ cm}^{-1}$  and  $|E/\hbar c| = 0.039 \pm 0.002\text{ cm}^{-1}$ ) fully support the assignment of the triplet spectrum as di-tert-butylcarbene (**6**). The  $|D/\hbar c|$  parameter is at least a factor of 5 larger than expected for a triplet biradical such as twisted tetra-tert-butylethylene.<sup>8</sup> We did not detect any triplet biradical spectra upon scanning the appropriate spectral region between 2500 and 41 000 G, specifically the product of 1,3 hydrogen

migration,<sup>7,9</sup> The  $|D/\hbar c|$  parameter of di-tert-butylcarbene is comparable to that observed by Wasserman for  $\text{CF}_3-\dot{\text{C}}-\text{CF}_3$  ( $0.7444\text{ cm}^{-1}$ ).<sup>10</sup> The parameter is, as expected, much larger than the  $|D/\hbar c|$  values of aryl- and diarylcarbenes. Recent calculations suggest that di-tert-butylcarbene should have a singlet ground state.<sup>11</sup> We suspect that the tert-butyl groups force the bond angle (vide infra) open sufficiently to raise the singlet above the triplet.

The zero-field parameters indicate that this carbene is not linear. The  $|E/D|$  ratio predicts a bond angle about the central carbon of  $\sim 143^\circ$ . This value is surprisingly similar to the value of  $138^\circ$  found in triplet methylene and of  $140^\circ$  found for  $\text{CF}_3-\dot{\text{C}}-\text{CF}_3$ .<sup>10</sup> Clearly, even with the bulky tert-butyl groups present, the historical proposal<sup>12,13</sup> that triplet carbenes are linear has not proven correct. Further structure-stability correlations and kinetic measurements are in progress to clarify why this highly congested carbene should show this surprising resistance to rearrangement.

**Acknowledgment.** J.E.G. gratefully acknowledges partial financial support from the Research Corp. and a University of Toledo Faculty Research Award, the technical assistance of Mary Johnson and useful discussions with K. N. Houk. Partial support of this work by N.S.F. Grant No. CHE-7900896 is gratefully acknowledged by M.S.P.

**Registry No.** **1**, 56956-22-0; **2**, 54396-68-8; **6**, 81158-97-6.

(9) Buchwalter and Closs have observed a localized triplet biradical spectrum 1,3-cyclopentadienyl with  $|D/\hbar c| = 0.084$ : Buchwalter, S. L.; Closs, G. L. *J. Am. Chem. Soc.* **1975**, *97*, 3857.

(10) (a) Wasserman, E.; Yager, W.; Kuck, W. *Chem. Phys. Lett.* **1970**, *7*, 409. (b) Wasserman, E.; Barash, L.; Yager, W. *J. Am. Chem. Soc.* **1965**, *87*, 4974.

(11) Mueller, P. H.; Rondon, N. G.; Houk, K. N.; Harrison, J. F.; Hooper, D.; Willen, B. H.; Liebman, J. F. *J. Am. Chem. Soc.* **1981**, *103*, 5049.

(12) Kirmse, W. "Carbene Chemistry", 1st ed.; Academic: New York, 1964, p 7.

(13) Exact bond angles from zero-field parameters are suspect. A better determination of this quantity awaits carbon-13 labeling.

## Anodic Oxidation of Heterocumulenes in Acetonitrile

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Studies on the electrochemical oxidation of organic compounds containing an allenic-type bond are rare. Recently we reported on the oxidation of allenic hydrocarbons in methanol<sup>1</sup> and in acetonitrile.<sup>2</sup> The present communication reports, for the first time, on the anodic oxidation of cumulenes possessing an  $\text{N}=\text{C}=\text{y}$  bond in which  $\text{y} = \text{N}$ ,  $\text{O}$ , or  $\text{S}$ . All compounds studied undergo  $\alpha$  cleavage predominantly, similar to what was previously reported for the anodic oxidation of ketones<sup>3</sup> and alkyl halides.<sup>4</sup>

Dicyclohexylcarbodiimide (**1**), di-tert-butylcarbodiimide (**2**), cyclohexyl isocyanate (**3**), and cyclohexyl isothiocyanate (**4**) were potentiostatically oxidized at the Pt anode in acetonitrile-LiClO<sub>4</sub> solutions, by employing a three-compartment cell with Ag/0.1 N AgNO<sub>3</sub> as the reference electrode. The oxidation of **1**, **2**, and **4** was terminated when the current dropped to its background value, generally after passing  $\sim 1$  F/mol. The reaction of **3** was arbitrarily terminated after passing 1 F/mol, because of a high background current. In all the former cases pulses to 0 V (for 0.5 s every 35 s) were required to maintain a decent current since

(1) Zinger, B.; Becker, J. Y. *Electrochim. Acta* **1980**, *25*, 791; *Tetrahydrofuran*, in press.

(2) Becker, J. Y.; Zinger, B. *J. Chem. Soc., Perkin Trans. 2*, in press.

(3) Becker, J. Y.; Miller, L. L.; Siegel, T. M. *J. Am. Chem. Soc.* **1975**, *97*, 849.

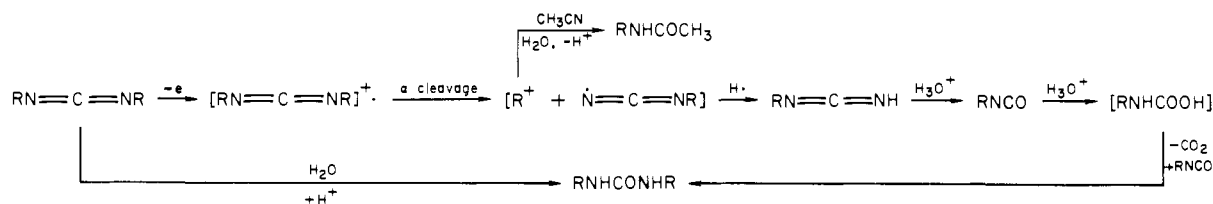
(4) Becker, J. Y. In "The Chemistry of the Functional Groups"; Patai, S., Ed., Supplement D; "The Chemistry of Halides, Pseudohalides and Azides"; Patai, S., Rappoport, Z., Eds.; Wiley: New York; in press, and references therein.

(6) Senthilnathan, V. P.; Platz, M. S. *J. Am. Chem. Soc.* **1981**, *103*, 5503.

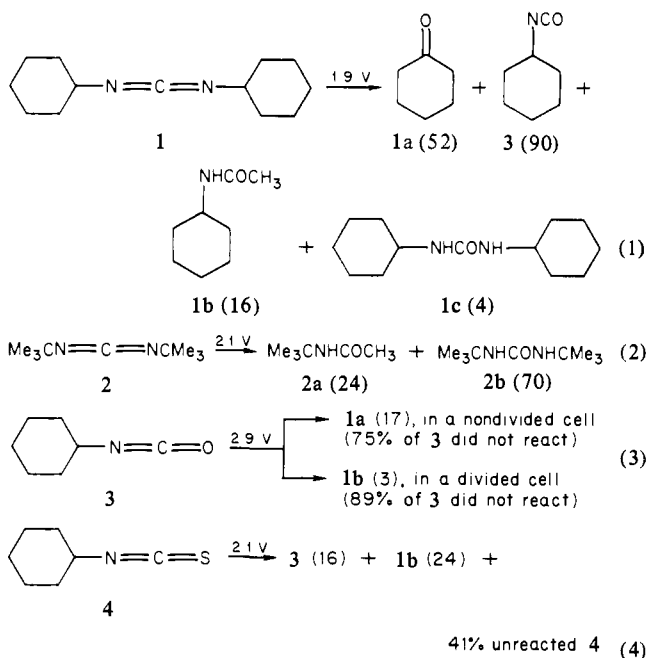
(7) Since nitrous oxide shows a strong band at  $1290\text{ cm}^{-1}$  and it could have been formed by irradiation with our lamp if air (nitrogen and oxygen) had leaked into the system, it is significant to note that the characteristic nitrous oxide band near  $2240\text{ cm}^{-1}$  was absent.

(8) The possibility of this being tetra-tert-butylethylene is also ruled out by the  $1290\text{ cm}^{-1}$  band, which appears even when **2** is irradiated while matrix isolated in argon.

Scheme I



the anode was coated by an insulating film. Reaction equations 1–4 demonstrate the outcome from the oxidation of substrates

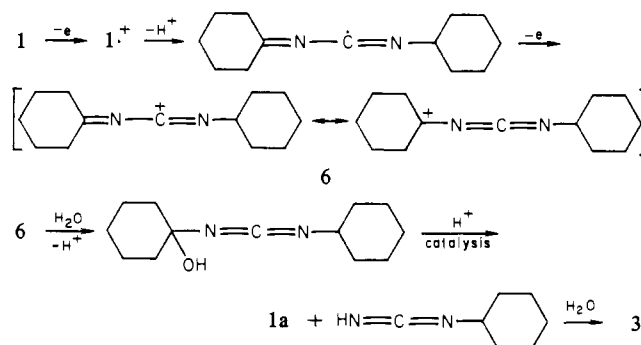


1–4 (numbers in parentheses account for chemical yields in percent).<sup>5</sup>

The HOMO of allenic hydrocarbons consists of  $\pi$  electrons of one of the double bonds, depending on the substituents attached to them. The electrooxidation of these compounds in methanol<sup>1</sup> resulted in the formation of products due to 2-e, 4-e, and 6-e oxidation, whereas in acetonitrile<sup>2</sup> they underwent only 2-e oxidation yielding products that retained one of the two double bonds. Since in the case of "heteroallenes" the HOMO may consist of both  $\pi$  and nonbonding electrons of a heteroatom, these compounds are expected to produce products also via other route(s) than those described for allenes. Indeed, most of the products obtained from the oxidation of 1–4 may be rationalized by assuming that a cleavage at the  $\alpha$  position to the allenic bond takes place. As a result a C–N bond breaks, a cleavage that has been previously reported for the electrochemical oxidation of *N*-alkoxyurea derivatives<sup>6</sup> and carbamates<sup>7</sup> as well as for the ozonolysis of carbodiimides.<sup>8</sup> Such an  $\alpha$ -cleavage process did not occur at all in the anodic oxidation of allenic hydrocarbons.<sup>1,2</sup>

In parallel to the oxidation of 1 and 2, controlled experiments were carried out in acetonitrile in the presence of 2% HClO<sub>4</sub>. The findings show that only trace amounts of 1c were detected (by GLC) from 1 and 21% of 2b was formed from 2. Consequently, because of the possible formation of hydrolytic products and because of the necessity to pulse throughout the electrolyses, the interpretation of the *n* value becomes hazardous. To elucidate

Scheme II



the mechanism for the formation of products 1a–1c, 3, 2a, and 2b one may postulate (Scheme I) that an initial uptake of an electron from a substrate followed by  $\alpha$ -N–C bond cleavage affords both carbenium ion and carbodiimide radical (5) type intermediates. The former may react with CH<sub>3</sub>CN and then H<sub>2</sub>O to give an acetamide derivative. Radical 5 may abstract a hydrogen atom from the solvent or a substrate molecule to form RNCO and urea type products, after consecutive hydrolyses. The urea derivative may be formed also by invoking an acid-promoted hydrolysis of 1 and 2 to produce 1c and 2b, respectively. Controlled experiments show<sup>9a</sup> that Me<sub>3</sub>CNCO undergoes fast hydrolysis in acidic solutions to yield 2b. On the other hand, the slow hydrolysis of 3 explains its survival throughout the reaction period, as well as the low yield of 1c from the electrochemical process. Since 1 possesses  $\alpha$  hydrogens, one may invoke an  $\alpha$  deprotonation (Scheme II)<sup>9b</sup> to explain the formation of both 1a and 3 from 1. The fact that radical products (e.g., succinonitrile) were not observed in this reaction may support this hypothesis.

The oxidation potential of 3 is higher by almost 1 V compared to that of 4. The same trend was observed in the gas phase, e.g., the ionization potentials of MeNCO and MeNCS are 10.67 and 9.37 eV, respectively.<sup>10</sup> Since the oxidation of 3 takes place at a potential well into the background, in the breakdown region of the solvent–electrolyte mixture, it is not surprising that it is very slightly electrolyzed and that most of it has been recovered after passing 1 F/mol. The characterization of both products 1a (from 3) and 1b (from 3 and 4) again hints for an  $\alpha$ -cleavage type process, as described in both schemes.

The ease of electron uptake from 4 relative to 3 may be attributed to the contribution of the nonbonding electrons of the sulfur atom to the HOMO of the molecule. Apparently, the formation of product 3 from the oxidation of 4 also supports the involvement of the sulfur atom in the anodic process. Interestingly, a loss of NCS group in the anodic process mimics the mass spectroscopic one for aromatic and not for aliphatic isothiocyanates since the latter undergo mainly  $\beta$ - and McLafferty-type cleavages.<sup>11</sup>

(5) Products were isolated and compared with authentic samples, both for identification and estimation of yields (by means of GLC).

(6) Ozaki, S.; Masui, M. *J. Chem. Soc. Perkin Trans. 2* 1980, 1022.

(7) Shono, T.; Hamaguchi, H.; Mutsumara, Y. *J. Am. Chem. Soc.* 1975, 97, 4264.

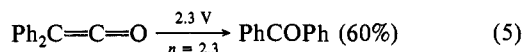
(8) Kolsaker, P.; Jøraanostad, O. *Acta Chem. Scand. Sect. B* 1975, B29, 7.

(9) (a) It has been found that upon introducing Me<sub>3</sub>CNCO at a given concentration in a CH<sub>3</sub>CN–1% HClO<sub>4</sub> mixture, a complete hydrolysis to 2b took place after 2 h, whereas under the same conditions 3 was hydrolyzed only partly after 5 h. (b) A referee is acknowledged for suggesting this.

(10) Craddock, S.; Ebsworth, E. A. V.; Murdoch, J. D. *J. Chem. Soc., Faraday Trans. 2* 1972, 68, 86.

(11) Budzikiewicz, H.; Djerassi, C.; Williams, D. H. "Mass Spectrometry of Organic Compounds"; Holden-Day, San Francisco, CA, 1967; Chapter 11, pp 420–427.

It is noteworthy that a different heterocumulene, namely diphenylketene, was anodically oxidized in acetonitrile and afforded benzophenone as the sole product (eq 5). Clearly, no molecular



oxygen is involved in the formation of the product since the same result was obtained when the reaction was carried out under nitrogen atmosphere.

Further mechanistic studies as well as MO calculations on various heteroallenes and their corresponding radical cations are in progress in our laboratory.

Registry No. 1, 538-75-0; 2, 691-24-7; 3, 3173-53-3; 4, 1122-82-3; 1a, 108-94-1; 1b, 1124-53-4; 1c, 2387-23-7; 2a, 762-84-5; 2b, 5336-24-3; diphenyl ketene, 525-06-4; benzophenone, 119-61-9.

### Mixed-Metal Cluster of Isocyanide Containing a Mercury Atom in the Center of a Trigonal-Prismatic Platinum Framework. $\text{Hg}[\text{Pt}_3(2,6\text{-Me}_2\text{C}_6\text{H}_3\text{NC})_6]_2$

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Metal clusters are of interest as plausible models of the surface of heterogeneous catalysts.<sup>1</sup> Carbonyl clusters with various kind of nuclearity are well-known, whereas there are few examples of metal clusters containing isocyanides as a sole ligand. Muetterties et al. have reported the synthesis and properties of a four-metal-atom cluster,  $\text{Ni}_4[(\text{CH}_3)_3\text{CCN}]_7$ .<sup>2</sup> Recently we established the crystal structure of an isocyanide cluster containing seven platinum atoms,  $\text{Pt}_7(2,6\text{-Me}_2\text{C}_6\text{H}_3\text{NC})_{12}$ .<sup>3</sup> We here describe the synthesis and characterization of a unique mixed-metal cluster having platinum and mercury atoms.

A mixture of dichlorobis(2,6-xylyl isocyanide)platinum(II) (0.6 g, 1.14 mmol) and 2,6-xylyl isocyanide (0.05 g, 0.38 mmol) was treated with Na-Hg in THF at room temperature under a nitrogen atmosphere. After 4 h, the resulting dark green solution was chromatographed on deactivated alumina under nitrogen atmosphere, and two bands were observed. The first elution with benzene gave dark green solution. After removal of the solvent, the green crystals (0.157 g) resulting from crystallization of the residue from benzene-hexane were formulated as  $\text{HgPt}_6(2,6\text{-Me}_2\text{C}_6\text{H}_3\text{NC})_{12}$ , **1**.<sup>4</sup> The mother liquor changed from dark green to reddish brown after removal of **1**. Further crystallization from the mother liquor gave known brown crystals **2** (0.07 g) formulated as  $\text{Pt}_7(2,6\text{-Me}_2\text{C}_6\text{H}_3\text{NC})_{12}$ .<sup>3</sup> The second elution from benzene- $\text{CH}_2\text{Cl}_2$  eluted a pale yellow solution, from which a pale yellow crystalline solid having the formula  $\text{Pt}(2,6\text{-Me}_2\text{C}_6\text{H}_3\text{NC})_5$ , **3** (0.01 g),<sup>5</sup> was obtained.

(1) (a) Muetterties, E. L. *Bull. Soc. Chim. Belg.* **1976**, *85*, 451-470. (b) Muetterties, E. L.; Rhodin, T. N.; Band, E.; Brucker, C. F.; Pretzer, W. R. *Chem. Rev.* **1979**, *79*, 91-137.

(2) Thomas, M. G.; Pretzer, W. R.; Beier, B. F.; Hirsekorn, F. J.; Muetterties, E. L. *J. Am. Chem. Soc.* **1977**, *99*, 743-748.

(3) Yamamoto, Y.; Aoki, K.; Yamazaki, H. *Chem. Lett.* **1979**, 391-392.

(4) Mp 207-209 °C(dec). Anal. Calcd for  $\text{C}_{108}\text{H}_{108}\text{N}_{12}\text{Pt}_6\text{Hg}$ : C, 44.04; H, 3.70; N, 5.71; Pt, 39.74; Hg, 6.81. Found: C, 44.14; H, 3.72; N, 5.76; Pt, 39.62; Hg, 7.04.

(5) Mp 254-256 °C(dec); IR (Nujol) 2168, 2176 ( $\text{N}=\text{C}$ ), 1614, 1584 ( $\text{C}=\text{N}$ )  $\text{cm}^{-1}$ , NMR ( $\text{CDCl}_3$ )  $\delta$  2.26 (b s, 6,  $\text{CH}_3$ ), 2.59 (s, 2,  $\text{CH}_3$ ), 2.65 (s, 2,  $\text{CH}_3$ ), 2.84 (s,  $\text{CH}_3$ ), 5.8-7.5 (aromatic protons); UV ( $\text{CH}_2\text{Cl}_2$ ) 307 (sh), 280 (sh) nm. The structure was tentatively assigned to *cis*-bis(2,6-xylyl isocyanide)tris(2,6-xylylimino)platinacyclobutane. Single crystals of **3** belong to the orthorhombic system,  $a = 22.702$  (5) Å,  $b = 22.197$  (5) Å,  $c = 18.543$  (10) Å, and  $V = 9343$  (6) Å<sup>3</sup>. The data revealed systematic extinctions consistent with  $P_{\text{nam}}$  and  $P_{\text{na}21}$ . However, the intensity is going down rapidly with increasing angles and also shows pseudo C center position. The resultant Fourier map using the Pt atom shows C center distribution. Because of the low quality of data and the pseudosymmetry, the analysis was unsuccessful.

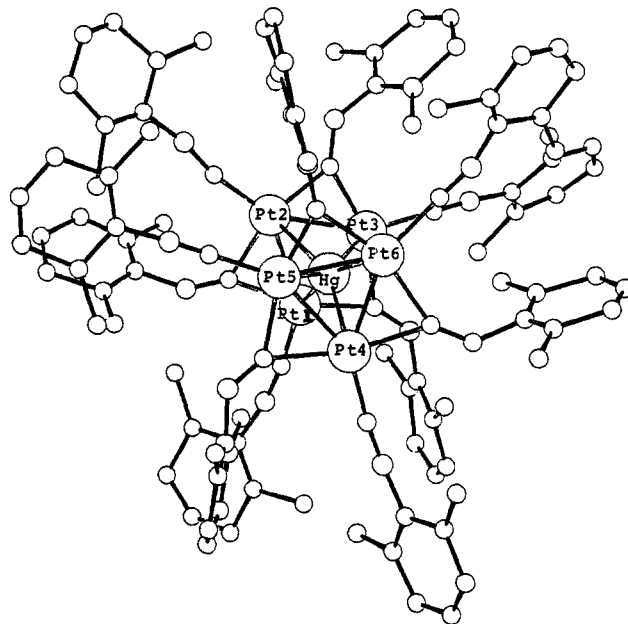


Figure 1. Crystal structure of  $\text{Hg}[\text{Pt}_3(2,6\text{-Me}_2\text{C}_6\text{H}_3\text{NC})_6]_2$ .

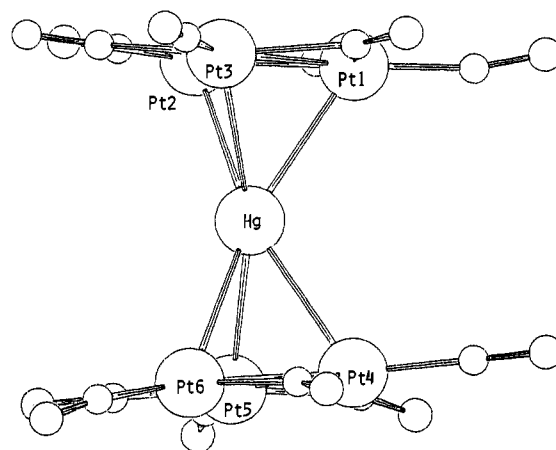


Figure 2. Crystal structure of  $\text{Hg}[\text{Pt}_3(2,6\text{-Me}_2\text{C}_6\text{H}_3\text{NC})_6]_2$ . 2,6-Xylyl groups are omitted for clarity.

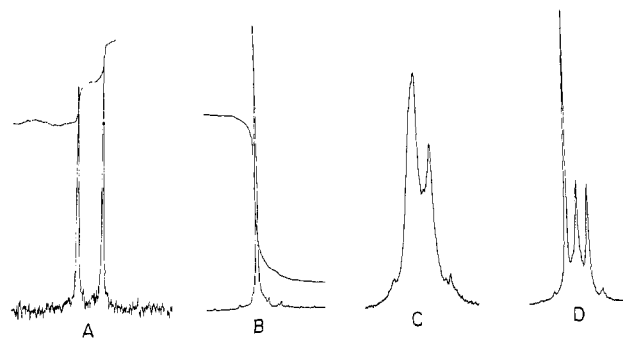


Figure 3.  $^1\text{H}$  NMR spectra of  $\text{Hg}[\text{Pt}_3(2,6\text{-Me}_2\text{C}_6\text{H}_3\text{NC})_6]_2$  in  $\text{C}_6\text{D}_6$  (A, 23 °C) and of a mixture of  $\text{Hg}[\text{Pt}_3(2,6\text{-Me}_2\text{C}_6\text{H}_3\text{NC})_6]_2$  and 2,6- $\text{Me}_2\text{C}_6\text{H}_3\text{NC}$  [B (23 °C), C (-20 °C), D (-74 °C)] in  $\text{CD}_2\text{Cl}_2$  ( $\text{Hg}[\text{Pt}_3(2,6\text{-Me}_2\text{C}_6\text{H}_3\text{NC})_6]_2$  (40 mg) and 2,6- $\text{Me}_2\text{C}_6\text{H}_3\text{NC}$  (8 mg)).

Crystals of **1** belong to the monoclinic space group *Cc*. Unit cell data are  $a = 27.2961$  (0) Å,  $b = 15.8173$  (1) Å,  $c = 24.5133$  (0) Å,  $\beta = 102.37$  (2)°, and  $Z = 4$ . The 4252 reflections having  $I \geq 3\sigma(I)$  and  $2\theta < 45^\circ$  were collected on a Rigaku four-circle diffractometer by the  $\omega$ - $2\theta$  scan technique, with  $\text{Mo K}\alpha$  radiation. The positions of the Hg and Pt atoms were located through a direct method (MULTAN) and the remaining atoms by standard difference Fourier syntheses. The final *R* value was 0.0481 (the Hg and Pt atoms were refined with anisotropic thermal parameters and