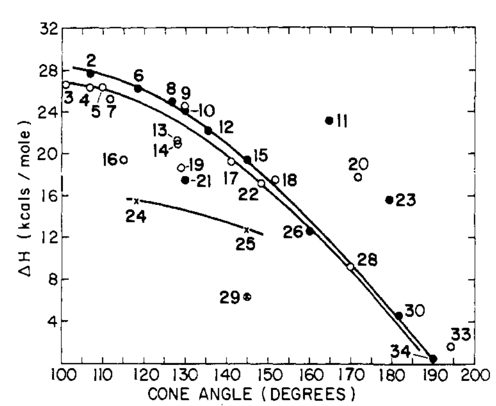
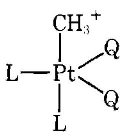
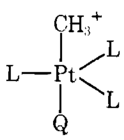


Figure 1. Heat evolved per mole of *trans*-[$CH_3PtQ_2(THF)$](PF_6) in the reactions with excess L as a function of ligand cone angle: ●, phosphine; ○, phosphite; ×, arsine, and ⊗, stibine. Ligand numbers refer to Table I.

$$2\textit{trans}\text{-}[CH_3PtQ_2(NCR)]^+ + L \longrightarrow \textit{trans}\text{-}[CH_3PtQL(NCR)]^+ + [CH_3PtQ_3]^+ + NCR \quad (2)$$

Small phosphorus ligands (cone angles less than ~120°) give rapid exchange of free and coordinated ligands at 25°. Five-coordinate complexes whose structures depend on L are observed in the low temperature limit spectra below −80°. The ABM_2 and A_3M spectra observed for L= $P(OMe)_3$ and $P(OCH_2)_3CCH_2CH_2CH_3$, respectively, indicate the trigonal bipyramidal structures **2** and **3**.


2


3

Values of ${}^1J$(Pt-Q) in *trans*-[CH_3PtQ_2L]$^+$ reflect a strengthening of the Pt-Q bond as the phosphorus ligand L increases in size (L = $P(OCH_2)_3CPr$, 2490 Hz; $P(OPh)_3$, 2530; $P(O\text{-}o\text{-}tolyl)_3$, 2554; $P(O\text{-}o\text{-}C_6H_4\text{-}i\text{Pr})_3$, 2562).

Further ${}^{31}P$ and ${}^1H$ NMR studies are in progress.

Acknowledgments. We are indebted to Dr. W. Partenheimer of the Clarkson Institute of Technology for getting us started in calorimetry. We are also very grateful to Dr. L. W. Gosser of this department for gifts of phosphorus and phosphite ligands.

References and Notes

(1) C. A. Tolman, *J. Am. Chem. Soc.*, **92**, 2956 (1970); C. A. Tolman, W. C. Seidel, and L. W. Gosser, *J. Am. Chem. Soc.*, **96**, 53 (1974).
(2) W. Partenheimer, *Inorg. Chem.*, **11**, 743 (1972), and W. Partenheimer and E. F. Hoy, *Inorg. Chem.*, **12**, 2085 (1973), report the only calorimetric studies on group 5 donor reactions of which we are aware.
(3) Many of the complexes have been isolated and characterized in previous studies: (a) H. C. Clark and J. D. Ruddick, *Inorg. Chem.*, **9**, 1226 (1970); (b) M. H. Chisholm and H. C. Clark, *ibid.*, **10**, 1711 (1971); (c) H. C. Clark and L. E. Manzer, *ibid.*, **10**, 2699 (1971); (d) *ibid.*, **11**, 503 (1972); (e) M. H. Chisholm, H. C. Clark, and L. E. Manzer, *ibid.*, **11**, 1269 (1972).
(4) The cone angle gives a quantitative measure of steric effects in phosphorus ligands and has been described in detail in ref 1 and 2.
(5) M. H. Chisholm, H. C. Clark, L. E. Manzer, J. B. Stothers, and J. E. H. Ward, *J. Am. Chem. Soc.*, **95**, 8574 (1973).
(6) The trans influence may be measured by a number of methods including NMR. For a recent review see: T. G. Appleton, H. C. Clark, and L. E. Manzer, *Coord. Chem. Rev.*, **10**, 335 (1973).
(7) The nitrile complex with NCR = $p\text{-}NCC_6H_4OCH_3$ was used in some of the ${}^{31}P$ studies in place of THF because it is a stable, easily handled crystalline solid.

Leo E. Manzer,* Chadwick A. Tolman
Contribution No. 2215, Central Research Department
Experimental Station, E. I. du Pont de Nemours and Co.
Wilmington, Delaware 19898

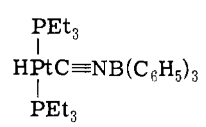
Received November 18, 1974

Linkage Isomerism of the Cyanide Ligand in a Platinum(II) Complex

Sir:

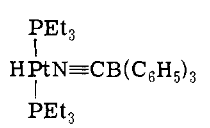
Linkage isomerism is common in complexes containing SCN^- as a ligand.[1] In many cases both the M-SCN and M-NCS isomers have been isolated and characterized.[2] The cyanide ion CN^- is potentially capable of ambidentate bonding although the vast majority of cyanide complexes contain cyanide bonded to metal through the pair of electrons on the carbon atom.[3] A few complexes have been characterized in which the cyanide is bridging between two metal atoms, e.g., Cu-CN-Cu.[3b,4] Recently a new class of compounds, *trans*-$HPt(PEt_3)_2CN{\rightarrow}$(Lewis acid), have been reported.[3a,5]

We now report the preparation of a novel pair of complexes, (I and II) containing ambidentate cyanide. These are the first examples of linkage isomerism of the cyanide ligand in a platinum(II) compound, where both isomers have been isolated and characterized.



$$\begin{array}{l} PEt_3 \\ | \\ HPtC{\equiv}NB(C_6H_5)_3 \\ | \\ PEt_3 \end{array}$$

I



$$\begin{array}{l} PEt_3 \\ | \\ HPtN{\equiv}CB(C_6H_5)_3 \\ | \\ PEt_3 \end{array}$$

II

Isomer I was isolated from the reaction of *trans*-$HPt(PEt_3)_2CN$ with triphenylborane in toluene as an air-stable white crystalline solid (mp 110–111°). The second isomer was prepared by the reaction of *trans*-$HPt(PEt_3)_2Cl$ with sodium cyanotriphenylborane in tetrahydrofuran and was obtained as a white crystalline solid (mp 106–107°). Both complexes are air stable although the reaction involving triphenylborane must be performed under an atmosphere of nitrogen.

The 220-MHz ${}^1H$ NMR spectra of the two complexes are similar in the range τ 0–10 and show resonances typical of mutually trans triethylphosphine ligands. The high field spectra show resonances at τ 27.69 and 28.15 for isomers I and II, respectively. Each appears as a triplet due to coupling with the two equivalent ${}^{31}P$ nuclei confirming the trans configuration. The magnitude of ${}^1J$(Pt-H) is very different for the two isomers. Isomer I has a value of ${}^1J$(Pt-H) = 852 Hz, slightly larger than that found in *trans*-$PtHCN(PEt_3)_2$ (778 Hz).[6] This results from a weakening of the metal cyanide bond on coordination to a Lewis acid.[7] The value of ${}^1J$(Pt-H) for isomer II is 1061 Hz, very similar to that found for N-bonded thiocyanate in *trans*-$PtH(NCS)(PEt_3)_2$[6] (1086 Hz). The infrared spectra of both complexes show a strong peak at 2192 cm^{-1} due to ν(C≡N) and a weak peak at 2082 and 2236 cm^{-1} for isomers I and II respectively, due to ν(Pt—H). Although the vibrations are probably coupled the higher value of ν(Pt—H) for N-bonded compared with C-bonded cyanide is consistent with the weaker trans influence[8] of the N-bonded isomer.

The ${}^{11}B$ NMR spectra obtained at 28.88 MHz are diagnostic of the mode of coordination. For comparison with I and II we have also run the ${}^{11}B$ NMR of *trans*-$PtH(PEt_3)_2CN{\rightarrow}B(CH_2C_6H_5)_3$[5] (III). Resonances are observed at 17.5, 27.5, and 25.1 ppm downfield from trimethylborate with line widths of 800, 225, and 675 Hz for compounds I, II, and III, respectively. The much broader lines are associated with the compounds containing Pt-C and N-B bonds, the broadening presumably resulting from interaction of the ${}^{11}B$ nuclear spin (I = 3/2, 80.4% natural abundance) with the ${}^{14}N$ nuclear spin (I = 1, 99.6% natural abundance).

Isomer II is readily converted, thermally, to its more thermodynamically stable isomer, I. For example, a benzene solution of II was refluxed under nitrogen for 5 hr to give I in quantitative yield. At room temperature there appears to be no interconversion of the two isomers, in the solid state, over a period of months.

Acknowledgments. We would like to thank Dr. A. D. English for obtaining the ^{11}B NMR spectra.

References and Notes

(1) (a) J. L. Burmeister, *Coord. Chem. Rev.*, **1**, 205 (1966); (b) *ibid.*, **3**, 225 (1968); (c) A. H. Norbury and A. I. P. Sinha, *Q. Rev., Chem. Soc.*, **24**, 69 (1970); (d) R. A. Bailey, S. L. Kozak, T. W. Michelsen, and W. N. Mills, *Coord. Chem. Rev.*, **6**, 407 (1971).
(2) Y. S. Wong, S. Jacobson, P. C. Chieh, and A. J. Carty, *Inorg. Chem.*, **13**, 284 (1974), and references therein.
(3) (a) P. Rigo and A. Turco, *Coord. Chem. Rev.*, **13**, 133 (1974); (b) D. F. Shriver, *Struct. Bonding (Berlin)*, **1**, 32 (1966).
(4) F. R. Fronczek and W. P. Schaefer, *Inorg. Chem.*, **13**, 727 (1974).
(5) L. E. Manzer and G. W. Parshall, *J. Chem. Soc., Chem. Commun.*, submitted for publication.
(6) J. Powell and B. L. Shaw, *J. Chem. Soc.*, 3879 (1965).
(7) L. E. Manzer and C. A. Tolman, *J. Am. Chem. Soc.*, this issue.
(8) For a recent review see T. G. Appleton, H. C. Clark, and L. E. Manzer, *Coord. Chem. Rev.*, **10**, 335 (1973).

Leo E. Manzer*
Contribution No. 2214, Central Research Department
Experimental Station, E. I. du Pont de Nemours and Co.
Wilmington, Delaware 19898

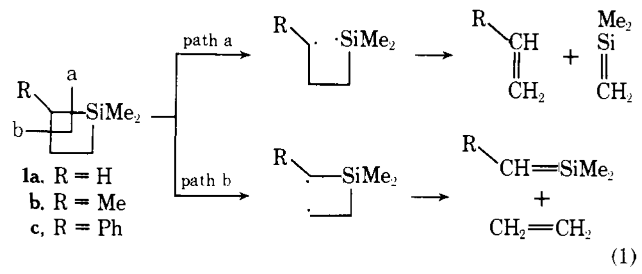
William C. Seidel
Polymer Intermediates Department
E. I. du Pont de Nemours and Co.
Orange, Texas 77630

Received December 9, 1974

Silicon–Carbon (p_π–p_π) Multiply Bonded Intermediates. The First Thermal Generation and Reactions of 2-Substituted 1,1-Dimethyl-1-silaethenes [$Me_2Si{=}CHR$]

Sir:

Although silicon-carbon (p_π–p_π) multiply bonded intermediates have been the subject of considerable attention in recent years,[1] thermally generated tri- or tetrasubstituted silaethenes have never been reported.[2] Generation of 2-substituted 1-silaethenes from thermolysis of the appropriately substituted silacyclobutanes (eq 1) and an investigation of their chemistry would answer two important questions.

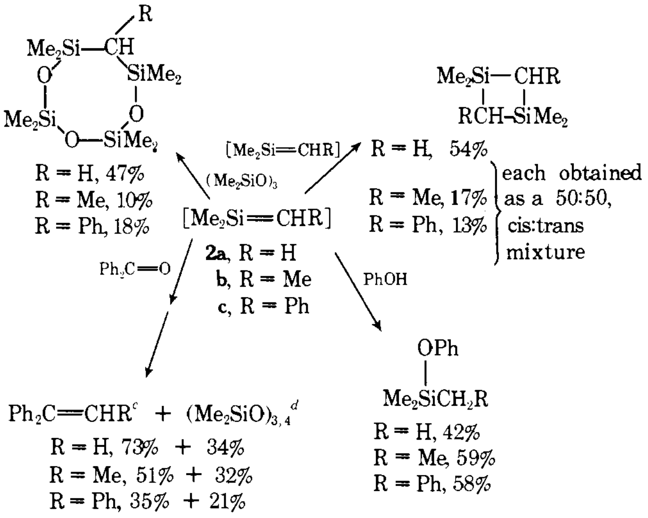


(1)

First, what is the initial step in the thermal decomposition of silacyclobutanes? Although gas phase kinetic data from the thermolysis of **1a** exclude a simultaneous rupture of Si-C and C-C bonds,[1a] the strength of the Si-C bond relative to that of the C-C bond is not known to a sufficient accuracy to predict which bond would break first.

Second, is the general chemical behavior of [$R_2Si{=}CHR$] intermediates similar to that already recorded[1] for [$R_2Si{=}CH_2$]? Information of this type is needed to answer the following question. Would isolation and study of a silaethene stabilized by substitution at both silicon and carbon provide a generally accurate picture of the properties of silaethenes in general or would such substitution drastically alter their properties?

Scheme I. Isolated Yields of the 1:1 Adducts from the Reaction of [$Me_2Si{=}CHR$][a] with Organic Substrates[b]



[a] Generated by thermolysis of the corresponding 2-substituted silacyclobutane. [b] [$Me_2Si{=}CHR$] generated in the presence of at least a two-fold molar excess of substrate. [c] Via a pseudo-Wittig reaction, see ref 1d. [d] From tri- and tetramerization of the [$Me_2Si{=}O$] produced in the pseudo-Wittig reaction, see ref 1d.

We wish to report the first thermal generation and also the reactions of two carbon-substituted silaethenes, 1,1,2-trimethyl-1-silaethene [$Me_2Si{=}CHMe$] (**2b**) and 1,1-dimethyl-2-phenyl-1-silaethene [$Me_2Si{=}CHPh$] (**2c**). Intermediates **2b** and **2c** were generated by gas phase thermolysis at 530–611° of the corresponding 2-substituted silacyclobutanes **1b** and **1c**[3] using a nitrogen flow system in a manner completely analogous to that reported for 1,1-dimethylsilacyclobutane (**1a**).[1d] Using otherwise identical reaction conditions it was observed that while **1a** and **1b** required approximately the same thermolysis temperature of 611° for complete decomposition, **1c** decomposed completely at 530°. The isolated products indicated that the predominant decomposition products of **1b** and **1c** were intermediates **2b** and **2c**, respectively, (minor amounts of **2a** were produced in all of these reactions and are discussed below). These observations provide evidence in support of C_2-C_3 bond scission as the initial step of thermal silacyclobutane decomposition (path b, eq 1). Although an initial Si-C_4 bond scission could account for the observed products, the reduction in E_a for **1c**, relative to **1a**, by ca. 6-8 kcal/mol by a substituent one atom removed from the bond undergoing scission appears unlikely.

The greatly diminished effect of a 2-methyl relative to a 2-phenyl substituent on the silacyclobutane activation barrier is in accord with an expected greater stabilization of the diradical intermediate by a phenyl group.

Scheme I summarizes the reactions of intermediates **2b** and **2c** with a variety of substrates together with the analogous reactions previously reported for intermediate **2a**.[1d,1h] Also included in Scheme I are the previously unknown reactions of silaethenes **2a–c** with ($Me_2SiO)_3$ in which the six-membered cyclotrisiloxane ring is expanded by one Si-C unit. This insertion reaction, similar to that of silanones [$R_2Si{=}O$] with $(Me_2SiO)_3$,[6] appears to be general for silaethenes and should be of considerable mechanistic interest and synthetic utility.