

# Synthesis, Structural Properties, and Reaction Chemistry of Hydrido Alkyl Diaminocarbene Complexes of Platinum(II). Cleavage of the Metal-Carbene and Metal-Alkyl Bonds and Synthesis of Formamidines and Cis Hydrido Carbene Derivatives

Rino A. Michelin\*

Istituto di Chimica Industriale, Facoltà di Ingegneria, Università di Padova, Via F. Marzolo 9, 35131 Padova, Italy

Roberta Bertani, Mirto Mozzon, and Livio Zanotto

Centro di Chimica e Tecnologia dei Composti Metallorganici degli Elementi di Transizione del CNR, Istituto di Chimica Industriale, Via Marzolo 9, 35131 Padova, Italy

Franco Benetollo

Istituto di Chimica e Tecnologia dei Radioelementi del CNR, Corso Stati Uniti 4, 35020 Padova, Italy

Gabriella Bombieri

Istituto di Chimica Farmaceutica, Università di Milano, Viale Abruzzi 42, 20131 Milano, Italy

Received August 28, 1989

Hydrido alkyl carbene complexes of the type  $\text{PtH}(\text{R}_X)[\text{C}(\text{N}(\text{CH}_2)_n\text{CH}_2)\text{NHR}](\text{PPh}_3)$  ( $n = 2$ ,  $\text{R}_X = \text{CF}_3$  (1),  $\text{CH}_2\text{CN}$  (2),  $\text{CH}_2\text{CF}_3$  (3);  $n = 4$ ,  $\text{R}_X = \text{CF}_3$  (4);  $\text{R} = p\text{-MeOC}_6\text{H}_4$ ) have been prepared by reaction of the parent isocyanide precursors  $\text{PtH}(\text{R}_X)(\text{CNR})(\text{PPh}_3)$  with azetidine or piperidine. Complexes 1-4 have cis Pt-H and Pt- $\text{R}_X$  bonds with the carbene ligand trans to hydride. They have been characterized by analytical data and their IR and  $^1\text{H}$ ,  $^{19}\text{F}$ ,  $^{31}\text{P}$ , and  $^{13}\text{C}$  NMR spectra. Compound 2 was also structurally characterized by X-ray analysis. The triclinic crystal, space group  $P\bar{1}$ , has lattice parameters  $a = 12.998$  (3) Å,  $b = 11.833$  (2) Å,  $c = 10.257$  (2) Å,  $\alpha = 100.83$  (4)°,  $\beta = 80.72$  (3)°,  $\gamma = 114.20$  (4)°, and  $Z = 2$ . The structure was refined to  $R = 0.022$  and  $R_w = 0.022$ . The coordination geometry around the Pt atom in 2 is distorted square planar. The geometry of the carbene ligand is essentially planar. The plane of the carbene intersects the platinum square plane at an angle of  $73.7$  (2)°. The molecules of 2 are associated in the solid state to give dimers through intermolecular interactions between the nitrogen atom of  $\text{CH}_2\text{CN}$  and the aminocarbene proton of an adjacent molecule. Important bond lengths are Pt-C(carbene) =  $2.069$  (4) Å, Pt-H =  $1.61$  (4) Å, Pt- $\text{CH}_2\text{CN} = 2.116$  (7) Å, and Pt-P =  $2.252$  (2) Å. The isocyanide complex  $\text{PtH}(\text{CF}_3)(\text{CNR})(\text{PPh}_3)$  reacts with excess  $\text{HNEt}_2$  in refluxing THF for 3 days to give a mixture of isomers with the carbene ligand trans to hydride (5a),  $\text{PPh}_3$  (5b), or trifluoromethyl (5c). Complexes 1-5 are stable in the solid state and in solution, and no reductive elimination of  $\text{HR}_X$  is observed in refluxing THF for several hours even in the presence of diphenylacetylene. However, complexes 2 and 3, but not 1 and 4, react with equivalent amounts of  $\text{PPh}_3$  to give *trans*-( $\text{PPh}_3$ ) $_2\text{PtH}[\text{C}(\text{NCH}_2\text{CH}_2\text{CH}_2)\text{NR}]$  (6) and formation of  $\text{CH}_3\text{CN}$  and  $\text{CH}_3\text{CF}_3$ , respectively. Isotopic experiments with N-D and Pt-D derivatives indicate that this reaction proceeds through the protonolysis of the metal-alkyl bond by the aminocarbene proton, promoted by  $\text{PPh}_3$ . Complex 6 reacts with  $\text{HBF}_4$  to give the hydrido carbene derivative *trans*-( $\text{PPh}_3$ ) $_2\text{PtH}[\text{C}(\text{NCH}_2\text{CH}_2\text{CH}_2)\text{NHR}]\text{BF}_4$  (7). Similarly the reactions of 2 with equimolar amounts of diphosphines yield (P-P) $\text{PtH}[\text{C}(\text{NCH}_2\text{CH}_2\text{CH}_2)\text{NR}]$  (P-P =  $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$  (8),  $\text{Ph}_2\text{PCH}=\text{CHPPh}_2$  (9)) and  $\text{CH}_3\text{CN}$ . Complexes 8 and 9 react with  $\text{HBF}_4$  to produce the cis hydrido carbene derivatives (P-P) $\text{PtH}[\text{C}(\text{NCH}_2\text{CH}_2\text{CH}_2)\text{NHR}]\text{BF}_4$  (10 and 11, respectively). On the other hand, complexes 1 and 4 react with diphosphines to give metal-carbene bond cleavage and formation of (P-P) $\text{PtH}(\text{CF}_3)$  and the formamidines  $\text{HC}(\text{NCH}_2\text{CH}_2\text{CH}_2)=\text{N}(\text{R})$  and  $\text{HC}[\text{N}(\text{CH}_2)_4\text{CH}_2]=\text{N}(\text{R})$ , respectively.

## Introduction

Hydrido alkyl<sup>1</sup> and carbene<sup>2</sup> complexes of transition metals are important reagents or intermediates in many stoichiometric and catalytic processes. The stabilities and

reactivities of Pt(II) hydrido alkyls  $\text{PtH}(\text{R}_H)\text{L}_2$  ( $\text{R}_H$  = alkyl, aryl; L = tertiary phosphine or  $1/2$  diphosphine) depend markedly on the metal complex geometry and the natures of the  $\text{R}_H$  and L ligands.<sup>3-5</sup> The increased thermal stability found for  $\text{PtH}(\text{R}_X)\text{L}_2$  complexes ( $\text{R}_X$  = cyanoalkyl, fluoroalkyl; L = monophosphine or  $1/2$  diphosphine) has been explained by the enhanced Pt- $\text{R}_X$  bond strength due to the presence of the electron-withdrawing cyano or fluoro groups in the alkyl chain.<sup>6</sup> The reaction chemistry for

(1) (a) James, B. R. *Homogeneous Hydrogenation*; Wiley: New York, 1973. (b) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987. (c) Janowicz, A. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1982**, *104*, 352.

(2) (a) Dötz, K. H.; Fischer, H.; Hofmann, P.; Kreissl, F. R.; Schubert, U.; Weiss, K. *Transition Metal Carbene Complexes*; Verlag Chemie: Weinheim, FRG, 1983. (b) Dötz, K. H. In *Reactions of Coordinated Ligands*; Brateman, P. S., Ed.; Plenum Press: New York, 1986; Vol. 1, Chapter 4. (c) Casey, C. P. In *Reactive Intermediates*; Jones, M., Moss, R. A., Eds.; Wiley: New York, 1981; Vol. 2. (d) Brookhart, M.; Studbaker, W. B. *Chem. Rev.* **1987**, *87*, 411. (e) Cross, J. *Catalysis* **1982**, *5*, 382. (f) *Advances in Metal Carbene Chemistry*; Schubert, U., Ed.; NATO ASI Series 269; Kluwer: Dordrecht, The Netherlands, 1989.

(3) (a) Arnold, D. P.; Bennett, M. A. *J. Organomet. Chem.* **1980**, *199*, C17. (b) Abis, L.; Santi, R.; Halpern, J. *J. Organomet. Chem.* **1981**, *215*, 263. (c) Arnold, D. P.; Bennett, M. A. *Inorg. Chem.* **1984**, *23*, 2110. (d) Bennett, M. A.; Yoshida, T. *J. Am. Chem. Soc.* **1978**, *100*, 1750.

(4) Abis, L.; Sen, A.; Halpern, J. *J. Am. Chem. Soc.* **1978**, *100*, 2915. (5) Hackett, M.; Ibers, J. A.; Whitesides, G. M. *J. Am. Chem. Soc.* **1988**, *110*, 1436.

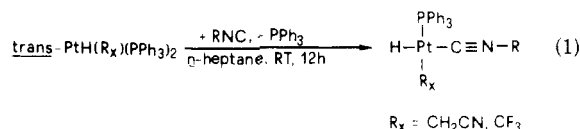
such complexes has been thoroughly investigated and includes (i) insertion of olefins into the Pt-H bond,<sup>6b</sup> (ii) thermal<sup>7</sup> and photolytic<sup>8</sup> reductive eliminations, (iii) reductive elimination by reaction with neutral ligands such as CO, PR<sub>3</sub>, diphosphine, diphenylacetylene, and RNC,<sup>9,10</sup> and (iv) reactions with electrophiles such as proton acids,<sup>11,12</sup> halogens,<sup>9</sup> and alkyl halides.<sup>9</sup>

All of the many known carbene complexes of platinum(II) contain one or two heteroatoms (N, O, or S) directly bonded to the carbene carbon.<sup>2a,13</sup> The stability of these complexes is attributed to the interaction of the carbene carbon with a lone electron pair on the heteroatom. The reaction chemistry of carbene ligands in Pt(II) complexes has been described in detail for cationic<sup>14</sup> and neutral<sup>15</sup> alkyl (alkoxy) carbene complexes. Modification of the carbene ligand in these complexes may be achieved by reactions with amines or halide ions and by acid-base reactions. In all cases the platinum-carbene bond is retained. The carbene ligands in the cationic derivatives<sup>14</sup> are also inert toward neutral ligands (PR<sub>3</sub>, CO, RNC, pyridine) and EtO<sub>2</sub>CCH=CHCO<sub>2</sub>Et, MeO<sub>2</sub>CC=CCO<sub>2</sub>Me, and MeC≡CMe (these latter ligands also under UV irradiation at 0 and 100 °C). More recently we have reported some deprotonation reactions of Pt(II) diaminocarbenes and the subsequent reactions with electrophiles to give N-functionalized carbenes<sup>16</sup> and reactions of phosphonium-substituted carbene complexes<sup>17</sup> to give platina heterocycles.<sup>18</sup> Also for these reactions no rupture of the platinum-carbene bond is observed.

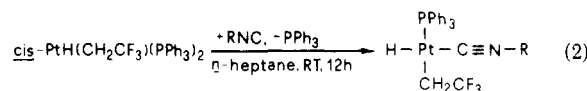
Most previous investigations on Pt(II) hydrido alkyls have features organophosphines as ancillary ligands. In this regard, the investigation about how the physical and chemical properties of Pt(II) hydrido alkyls can be affected by the presence of carbene ligands in the metal coordination sphere appears to be an unexplored field. Here we report the synthesis, structural properties, and reactivity of complexes of the type PtH(R<sub>X</sub>)(carbene)(PPh<sub>3</sub>) (R<sub>X</sub> = CH<sub>2</sub>CN, CH<sub>2</sub>CF<sub>3</sub>, CF<sub>3</sub>; carbene = diaminocarbene ligand) having adjacent Pt-H and Pt-R<sub>X</sub> bonds. The reactions of these complexes with monodentate phosphines and bidentate chelating diphosphines do not lead to reductive-elimination processes but instead to the cleavage of either the Pt-R<sub>X</sub> or Pt-carbene bonds.

## Results and Discussion

**Synthesis.** The preparation of hydrido alkyl diaminocarbene complexes of platinum(II) reported in this work takes advantage of the reactivity of *trans*-PtH(R<sub>X</sub>)(PPh<sub>3</sub>)<sub>2</sub> (R<sub>X</sub> = CH<sub>2</sub>CN,<sup>6a</sup> CF<sub>3</sub>)<sup>6c</sup> derivatives with isocyanides to afford complexes of the type PtH(R<sub>X</sub>)(CNR)(PPh<sub>3</sub>)<sub>2</sub>,<sup>6c,10</sup> having *cis* Pt-H and Pt-R<sub>X</sub> bonds with the CNR ligand *trans* to hydride (eq 1) (hereafter R =

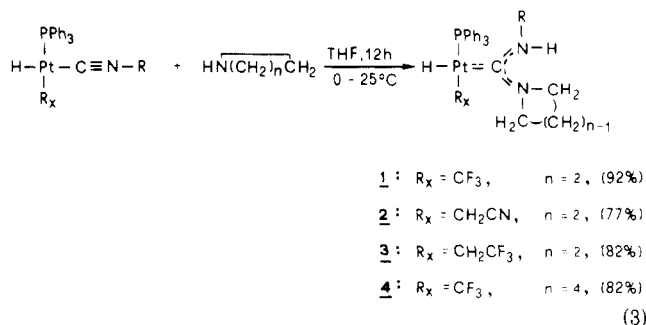


*p*-MeOC<sub>6</sub>H<sub>4</sub>). Also the reaction of the *cis* hydrido alkyl complex *cis*-PtH(CH<sub>2</sub>CF<sub>3</sub>)(PPh<sub>3</sub>)<sub>2</sub><sup>7</sup> with *p*-MeOC<sub>6</sub>H<sub>4</sub>CN in *n*-heptane gives an analogous isocyanide derivative (eq 2). For this latter reaction, no reductive elimination of



CH<sub>3</sub>CF<sub>3</sub> is observed, although *cis*-PtH(CH<sub>2</sub>CF<sub>3</sub>)(PPh<sub>3</sub>)<sub>2</sub> is known to slowly decompose at room temperature to Pt(0) species in THF and benzene solvents.<sup>7</sup>

The RNC ligand in PtH(R<sub>X</sub>)(CNR)(PPh<sub>3</sub>) species displays ν(C≡N) values in the range 2176–2179 cm<sup>-1</sup> in THF. The corresponding Δν = ν(C≡N)<sub>coord</sub> - ν(C≡N)<sub>free</sub> values are in the range 48–51 cm<sup>-1</sup>, indicating that the isocyanide is less electrophilic than that having chloride as a *trans* ligand.<sup>19</sup> However, a positive value of Δν > 40 cm<sup>-1</sup> was previously observed to indicate CNR ligand susceptibility to nucleophilic attack.<sup>20</sup> Thus, the RNC ligand in these hydrido alkyl complexes does not react with aziridine (pK<sub>a</sub> = 8.4) to form five-membered cyclic diaminocarbene derivatives<sup>19b</sup> but with stronger nucleophiles such as azetidine (pK<sub>a</sub> = 11.29) and piperidine (pK<sub>a</sub> = 11.12) to form the acyclic diaminocarbenes 1–4 (eq 3) in a manner similar to that reported for the reactions of azetidine with other Pd(II) and Pt(II) isocyanide complexes.<sup>21</sup>



Compounds 1–4 were characterized by their IR and <sup>1</sup>H and <sup>31</sup>P NMR spectra (Table I) and their <sup>13</sup>C NMR spectra (Table II). Furthermore, compound 2 was structurally characterized by X-ray diffraction analysis (see below). Complexes 1–4 show ν(Pt-H) as a medium absorption in the range 2004–2044 cm<sup>-1</sup> in Nujol mull and 2006–2040 cm<sup>-1</sup> in THF solvent, which is lower by ca. 40–50 cm<sup>-1</sup> than those found for cationic hydrido carbene complexes *trans*-[PtH(carbene)(PPh<sub>3</sub>)<sub>2</sub>][BF<sub>4</sub>] (carbene = dioxo- or

(6) (a) Ros, R.; Michelin, R. A.; Bataillard, R.; Roulet, R. *J. Organomet. Chem.* **1977**, *139*, 355. (b) *Ibid.* **1979**, *165*, 107. (c) Michelin, R. A.; Ros, R. *J. Chem. Soc., Dalton Trans.* **1989**, 1149.

(7) Michelin, R. A.; Faglia, S.; Uguagliati, P. *Inorg. Chem.* **1983**, *22*, 1831.

(8) Sostero, S.; Traverso, O.; Ros, R.; Michelin, R. A. *J. Organomet. Chem.* **1983**, *246*, 325.

(9) Ros, R.; Michelin, R. A.; Bataillard, R.; Roulet, R. *J. Organomet. Chem.* **1978**, *161*, 75.

(10) Ros, R.; Michelin, R. A.; Carturan, G.; Belluco, U. *J. Organomet. Chem.* **1977**, *133*, 213.

(11) Uguagliati, P.; Michelin, R. A.; Belluco, U.; Ros, R. *J. Organomet. Chem.* **1979**, *169*, 115.

(12) (a) Michelin, R. A.; Ros, R.; Guadalupi, G.; Bombieri, G.; Benetollo, F.; Chapuis, G. *Inorg. Chem.* **1989**, *28*, 840. (b) Michelin, R. A.; Facchin, G.; Ros, R. *J. Organomet. Chem.* **1985**, *279*, C25.

(13) (a) Cotton, F. A.; Lukehart, C. M. *Prog. Inorg. Chem.* **1972**, *16*, 487. (b) Cardin, D. J.; Cetinkaya, B.; Lappert, M. F. *Chem. Rev.* **1972**, *72*, 545. (c) Belluco, U.; Michelin, R. A.; Uguagliati, P.; Crociani, B. *J. Organomet. Chem.* **1983**, *250*, 565.

(14) Chisholm, M. H.; Clark, H. C.; Johns, W. S.; Ward, J. E.; Yasufuku, K. *Inorg. Chem.* **1975**, *14*, 900.

(15) Anderson, G. K.; Cross, R. J. *J. Chem. Soc., Dalton Trans.* **1979**, 690.

(16) Michelin, R. A.; Zanotto, L.; Braga, D.; Sabatino, P.; Angelici, R. *J. Inorg. Chem.* **1988**, *27*, 93.

(17) Michelin, R. A.; Facchin, G.; Braga, D.; Sabatino, P. *Organometallics* **1986**, *5*, 2265.

(18) Michelin, R. A.; Mozzon, M.; Facchin, G.; Braga, D.; Sabatino, P. *J. Chem. Soc., Dalton Trans.* **1988**, 1803.

(19) (a) Michelin, R. A.; Zanotto, L.; Braga, D.; Sabatino, P.; Angelici, R. *J. Inorg. Chem.* **1988**, *27*, 85. (b) Bertani, R.; Mozzon, M.; Michelin, R. A. *Inorg. Chem.* **1988**, *27*, 2809.

(20) Chatt, R. J.; Richards, R. L.; Royston, G. H. D. *J. Chem. Soc., Dalton Trans.* **1973**, 1433.

(21) Bertani, R.; Mozzon, M.; Benetollo, F.; Bombieri, G.; Michelin, R. A. *J. Chem. Soc., Dalton Trans.*, in press.

Table I. Selected IR and  $^1\text{H}$  and  $^{31}\text{P}$  NMR Spectral Data for the Complexes

| compd | IR, $\text{cm}^{-1}$ <sup>a</sup> |                  |                   | $^1\text{H}$ NMR <sup>b</sup> |                    |                   |                   |                   |                     | $^{31}\text{P}\{^1\text{H}\}$ NMR <sup>c</sup> |                      |                                |
|-------|-----------------------------------|------------------|-------------------|-------------------------------|--------------------|-------------------|-------------------|-------------------|---------------------|------------------------------------------------|----------------------|--------------------------------|
|       | $\nu(\text{CN})$                  | $\nu(\text{NH})$ | $\nu(\text{PtH})$ | $\delta(\text{PtH})$          | $^1J_{\text{HPt}}$ | $^2J_{\text{HP}}$ | $^3J_{\text{HF}}$ | $^4J_{\text{HH}}$ | $\delta(\text{NH})$ | $^3J_{\text{HPt}}$                             | $\delta$             | $^1J_{\text{PPt}}$             |
| 1     | 1545 s                            | 3346 m           | 2042 s            | -7.15 ddq                     | 896                | 19.0              | 15.0              | 3.6               | 6.47 d              | 53.2                                           | 22.10 q              | 2220 ( $^3J_{\text{PF}}$ 56.7) |
| 2     | 1549 s                            | 3267 m           | 2005 m            | -7.34 dd                      | 796                | 20.3              |                   | 3.5               | 6.64 d              | 55.4                                           | 24.20 s              | 2682                           |
| 3     | 1525 s                            | 3332 m           | 2004 m            | -7.23 dd                      | 825                | 20.7              |                   | 2.7               | 6.51 d              | 51.4                                           | 25.49 q              | 2506 ( $^4J_{\text{PF}}$ 16.6) |
| 4     | 1540 s                            | 3374 m           | 2044 m            | -8.03 ddq                     | 888                | 22.6              | 15.1              | 3.3               | d                   |                                                | 20.90 q              | 2272 ( $^3J_{\text{PF}}$ 56.4) |
| 5     | 1532 s                            | 3378 m           | 2046 m            | -8.06 ddq <sup>e</sup>        | 883                | 22.9              | 15.7              | 3.4               | d                   |                                                | 20.27 q <sup>e</sup> | 2272 ( $^3J_{\text{PF}}$ 56.3) |
|       |                                   | 3351 m           | 2020 m            | -8.87 dq <sup>f</sup>         | 711                | 25.8              | 25.6              |                   | d                   |                                                | 25.29 q <sup>f</sup> | 2760 ( $^3J_{\text{PF}}$ 7.3)  |
|       |                                   |                  |                   | -5.12 dq <sup>g</sup>         | 1223               | 184               | 16.6              |                   | d                   |                                                | h                    |                                |
| 6     | i                                 |                  | 1971 s            | -6.16 t                       | 620                | 18.6              |                   |                   |                     |                                                | 24.80 s              | 3037                           |
| 7     | 1553 s                            | 3305 m           | 2038 m            | -6.97 td                      | 645                | 14.5              |                   | 3.3               | d                   |                                                | 24.18 s              | 2902                           |
| 8     | 1499 s                            |                  | 1982 m            | -2.39 dd                      | 1212               | 179 <sup>j</sup>  |                   |                   |                     |                                                | 47.95 d <sup>i</sup> | 1720 ( $^2J_{\text{PP}}$ 5.0)  |
|       |                                   |                  |                   |                               |                    | 14.8 <sup>k</sup> |                   |                   |                     |                                                | 48.76 d <sup>m</sup> | 2354                           |
| 9     | 1510 s                            |                  | 2007 m            | -2.28 dd                      | 1241               | 185 <sup>j</sup>  |                   |                   |                     |                                                | 58.04 d <sup>i</sup> | 1810 ( $^2J_{\text{PP}}$ 11.4) |
|       |                                   |                  |                   |                               |                    | 15.8 <sup>k</sup> |                   |                   |                     |                                                | 60.31 d <sup>m</sup> | 1955                           |
| 10    | 1552 s                            | 3302 m           | 1976 s            | -1.53 dd                      | 1134               | 172 <sup>j</sup>  |                   |                   | 8.16 d              | 74.5                                           | 47.92 d <sup>i</sup> | 1720 ( $^2J_{\text{PP}}$ 5.7)  |
|       |                                   |                  |                   |                               |                    | 12.8 <sup>k</sup> |                   |                   |                     | ( $^4J_{\text{HP}}$ 9.4)                       | 48.60 d <sup>m</sup> | 2351                           |
| 11    | 1552 s                            | 3297 m           | 2028 s            | -2.86 dd                      | 1152               | 164 <sup>j</sup>  |                   |                   | 8.32 d              | 74.7                                           | 59.88 d <sup>i</sup> | 1722 ( $^2J_{\text{PP}}$ 7.4)  |
|       |                                   |                  |                   |                               |                    | 13.2 <sup>k</sup> |                   |                   |                     | ( $^4J_{\text{HP}}$ 9.3)                       | 60.60 d <sup>m</sup> | 2236                           |

<sup>a</sup>Spectra were recorded as Nujol mulls.  $\nu$  is given in  $\text{cm}^{-1}$ . Abbreviations: s = strong; m = medium; w = weak. <sup>b</sup> $^1\text{H}$  NMR spectra were recorded in  $\text{CD}_2\text{Cl}_2$ . Proton chemical shifts are referenced to  $\text{Me}_4\text{Si}$  by taking the chemical shift of dichloromethane- $d_2$  as +5.32 ppm.  $J$  is given in Hz. Abbreviations: s = singlet; d = doublet; t = triplet; m = multiplet; q = quartet. <sup>c</sup>Spectra were recorded in  $\text{CD}_2\text{Cl}_2$  with  $\text{H}_3\text{PO}_4$  external reference. Abbreviations: s = singlet; d = doublet; q = quartet.  $J$  is given in Hz. <sup>d</sup>Not located. <sup>e</sup>5a. <sup>f</sup>5b. <sup>g</sup>5c. <sup>h</sup>Insufficiently intense to be observed. <sup>i</sup>Masked. <sup>j</sup> $^2J_{\text{HP(Trans)}}$ . <sup>k</sup> $^2J_{\text{HP(cis)}}$ . <sup>l</sup>Trans to H. <sup>m</sup>Trans to C.

Table II. Selected  $^{13}\text{C}\{^1\text{H}\}$  NMR Spectral Data for the Complexes<sup>a</sup>

| compd | $\delta(\text{C}_{\text{carbene}})$ | $^1J_{\text{CPt}}$ | $^2J_{\text{CP}}$ | $\delta(\text{R}_X)$                                                                         |
|-------|-------------------------------------|--------------------|-------------------|----------------------------------------------------------------------------------------------|
| 1     | 206.82 d                            | 759                | 28.0              | b                                                                                            |
| 2     | 204.94 d                            | c                  | 6.4               | b                                                                                            |
| 3     | 210.07 d                            | 753                | 49.6              | 7.69 dq <sup>d</sup> ( $^2J_{\text{CF}}$ 83, $^2J_{\text{CP}}$ 31.2, $^1J_{\text{CPt}}$ 619) |
| 4     | 206.03 m                            | 845                |                   | 141.19 dq <sup>e</sup> ( $^1J_{\text{CF}}$ 346, $^2J_{\text{CP}}$ 167)                       |
| 7     | 204.03 t                            | 823                | 8.0               |                                                                                              |
| 8     | 185.00 dd                           | 845                | 28.0 <sup>f</sup> |                                                                                              |
|       |                                     |                    | 97 <sup>g</sup>   |                                                                                              |
| 10    | 194.51 dd                           | 1134               | 8.0 <sup>f</sup>  |                                                                                              |
|       |                                     |                    | 115 <sup>g</sup>  |                                                                                              |

<sup>a</sup>Spectra were recorded in  $\text{CD}_2\text{Cl}_2$ . Chemical shifts are referenced to  $\text{Me}_4\text{Si}$  by taking the chemical shift of dichloromethane- $d_2$  as +53.80 ppm.  $J$  is given in Hz. Abbreviations: d = doublet; t = triplet; q = quartet; m = multiplet. <sup>b</sup>Insufficiently intense to be observed. <sup>c</sup> $^{195}\text{Pt}$  satellites insufficiently intense to be observed. <sup>d</sup> $\text{CH}_2\text{CF}_3$ . <sup>e</sup> $\text{CF}_3$ . <sup>f</sup> $^2J_{\text{CP(cis)}}$ . <sup>g</sup> $^2J_{\text{CP(trans)}}$ .

dithiocarbene ligand<sup>12</sup>) and comparable to those found for *trans*-PtH(R) $\text{L}_2$  (R = alkyl, aryl; L = phosphine) complexes.<sup>6</sup> Medium to strong absorptions in the range 1525–1549  $\text{cm}^{-1}$  (Nujol) are assigned to  $\nu(\text{C}=\text{N})$  and  $\nu(\text{C}-\text{N}-\text{H})$  vibrations of the carbene moiety. The  $\nu(\text{N}-\text{H})$  band appears in the range 3267–3374  $\text{cm}^{-1}$  in Nujol mull, as reported for other acyclic Pt(II) diaminocarbene complexes.<sup>21,22</sup> The stereochemistry of 1–4 can be deduced from their  $^1\text{H}$  NMR data. The hydrido resonance falls upfield in the range  $\delta$  -8.03 to -7.15, as found for several Pt(II) hydrides having a carbene<sup>12</sup> or an alkyl group<sup>6c</sup> as trans ligand. For 1 and 4 the hydride signal appears as a doublet of double quartets by coupling with the three equivalent fluorine atoms ( $^3J_{\text{HF}}$  = 15.0–15.1 Hz), the phosphorus atom ( $^2J_{\text{HP}}$  = 19.0–22.6 Hz), and the aminocarbene proton ( $^4J_{\text{HH}}$  = 2.7–3.6 Hz), as confirmed by H/D exchange with  $\text{D}_2\text{O}$ . For complexes 2 and 3 the hydride resonance shows up as a doublet of doublets by coupling with the cis phosphorus atom and the aminocarbene proton. The  $^2J_{\text{HP}}$  and  $^3J_{\text{HF}}$  values are comparable to those found for complexes having cis phosphorus and trifluoromethyl groups.<sup>6c,10</sup> The aminocarbene proton for 1–4 is trans to Pt, as indicated by  $^3J_{\text{HPt}}$  = 51.4–55.4 Hz.<sup>23</sup> The

$^1J_{\text{HPt}}$  values are 896 Hz (1), 796 Hz (2), 825 Hz (3), and 888 Hz (4), which are lower by ca. 100–200 Hz with respect to those found for the parent isocyanide precursors<sup>6c,10</sup> (see also Experimental Section). Thus, on the basis of  $^1\text{H}$  NMR data the trans influence of the diaminocarbene group is higher than that of isocyanides and also phosphine<sup>7</sup> ligands but lower than that of alkyl groups as in *trans*-PtH(R) $\text{L}_2$  complexes.<sup>6c</sup> Also  $^{19}\text{F}$  and  $^{31}\text{P}$  NMR data are consistent with the  $\text{PPh}_3$  ligand trans to the alkyl group  $\text{R}_X$ .<sup>6c</sup> The  $^{13}\text{C}$  NMR spectra of compounds 1–4 (Table II) show the signal assigned to the carbene carbon at low field in the range 204.94–210.07 ppm, as reported for other Pt(II) carbene complexes.<sup>21,24,25</sup> The signal appears as a doublet with  $^{195}\text{Pt}$  satellites ( $^1J_{\text{PtC}}$  = 753–845 Hz) due to coupling with the P atom. For the carbene ligands in 1–4 one  $\text{NCH}_2$  group is cis and the other trans to the platinum atom owing to restricted rotation about the C–N bond, as also found in related carbene systems.<sup>24a</sup> The lower field signal ( $\delta$  54.78 for 1, 54.74 for 2, 54.77 for 3, and 56.31 for 4) can be assigned to the  $\text{NCH}_2$  cis to platinum, having a  $^3J_{\text{PtCNC}}$  value larger (ca. 50 Hz) than that corresponding to  $\text{NCH}_2$  trans to platinum (14–34 Hz), which is displayed at higher field ( $\delta$  49.92 for 1, 50.62 for 2, 50.62 for 3, and 44.62 for 4). For the metal-coordinated  $\text{R}_X$  groups, the signals are in most cases insufficiently intense to be observed. However, they could be detected for  $\text{CF}_3$  in 4 ( $\delta$  141.19, Table II) and for the methylene carbon of  $\text{CH}_2\text{CF}_3$  in 3 ( $\delta$  7.69).

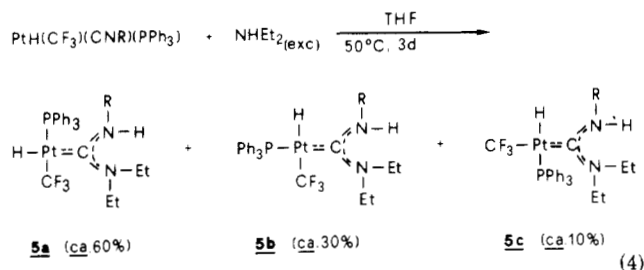
The reaction of  $\text{PtH}(\text{CF}_3)(\text{CNR})(\text{PPh}_3)$  with 1.2 equiv of  $\text{HNet}_2$  ( $\text{pK}_a$  = 10.99) does not proceed in THF at room temperature. However, when the complex is heated with an excess of  $\text{HNet}_2$  for 3 days at 50  $^\circ\text{C}$ , the mixture of hydrido carbene complexes 5a–c is formed (eq 4) in ca. 6:3:1 ratio, found by integration of the  $\text{CF}_3$  resonances in the  $^{19}\text{F}$  NMR spectrum. The species 5a–c could not be separated, but they could be identified by  $^1\text{H}$  and  $^{19}\text{F}$  NMR

(23) Crociani, B.; Richards, R. L. *J. Chem. Soc., Dalton Trans.* 1974, 693.

(24) (a) Chisholm, M. H.; Clark, H. C.; Ward, J. E. H.; Yasufuku, K. *Inorg. Chem.* 1975, 14, 893. (b) Cardin, D. J.; Cetinkaya, B.; Cetinkaya, E.; Lappert, M. F.; Randall, E. W.; Rosenberg, E. J. *J. Chem. Soc., Dalton Trans.* 1973, 1982. (c) Appleton, T. G.; Berry, R. D.; Hall, R. J.; Neale, D. W. *J. Organomet. Chem.* 1989, 364, 249.

(25) (a) Pregosin, P. S.; Kunz, R. W. In *NMR-16. Basic Principles and Progress*.  $^{31}\text{P}$  and  $^{13}\text{C}$  NMR of Transition Metal Phosphine Complexes; Springer-Verlag: New York, 1979. (b) Kalinowski, H. O.; Berger, S.; Braun, S. In *Carbon-13 NMR Spectroscopy*; Wiley: New York, 1984. (c) Chisholm, M. H.; Godleski, S. *Prog. Inorg. Chem.* 1976, 20, 341.

(22) Busetto, L.; Palazzi, A.; Crociani, B.; Belluco, U.; Badley, E. M.; Kilby, B. J. L.; Richards, R. L. *J. Chem. Soc., Dalton Trans.* 1972, 1800.



data (Experimental Section). Complex **5a** shows the Pt–H resonance as a doublet of double quartets at  $\delta$  –8.06 with  $^1J_{\text{PtH}} = 883$  Hz,  $^3J_{\text{HF}} = 15.7$  Hz, and  $^2J_{\text{HP}} = 22.9$  Hz, similar to those found for **1** and **4**. The Pt–H resonance of **5b** appears as a doublet of quartets at  $\delta$  –8.87 with  $^1J_{\text{PtH}} = 711$  Hz,  $^3J_{\text{HF}} = 25.6$  Hz, and  $^2J_{\text{HP}} = 25.8$  Hz. These latter values are consistent with a  $\text{CF}_3$  group trans to hydride.<sup>6c</sup> For **5c** the Pt–H signal appears as a doublet of quartets at  $\delta$  –5.12 with  $^1J_{\text{PtH}} = 1223$  Hz,  $^3J_{\text{HF}} = 16.6$  Hz, and  $^2J_{\text{HP}} = 184$  Hz, consistent with a phosphorus atom trans to hydride.<sup>6c</sup>

**Description of the Structure of  $\text{PtH}(\text{CH}_2\text{CN})[\text{C}(\text{NCH}_2\text{CH}_2\text{CH}_2\text{NH}(\text{C}_6\text{H}_4\text{-}p\text{-MeO}))(\text{PPh}_3)]$  (**2**).** An ORTEP view of the molecule is given in Figure 1. Crystal data for **2** are summarized in Table II together with some experimental details. The atomic coordinates are reported in Table IV and relevant bond distances and angles in Table V. The coordination geometry around Pt(II) is a distorted square plane with the diaminocarbene ligand trans to hydride: the coordination geometry is completed by one phosphorus atom of the triphenylphosphine and the carbon of the cyanomethyl group.

The least-squares best mean plane through P, C(1), C(5), and H indicates coplanarity of these donor atoms. The deviations ( $\text{\AA}$ ) from this plane are 0.03(5) (H), 0.000 (2) (P), 0.000 (4) (C(1)), and 0.000 (6) (C(5)), while Pt is 0.051 (1)  $\text{\AA}$  out of the plane. The Pt–H bond length of 1.61 (4)  $\text{\AA}$  is in the range of the observed Pt–H distances such as 1.72 (9)  $\text{\AA}$  in *trans*- $\text{PtH}(\text{CF}_3)(\text{PPh}_3)_2$ ,<sup>12a</sup> 1.66  $\text{\AA}$  in  $\text{PtH}(\text{SB}_9\text{H}_{10})(\text{PEt}_3)_2$ ,<sup>26</sup> and 1.78  $\text{\AA}$  in  $\text{PtH}(\mu\text{-SiMe}_2)[\text{P}(\text{C}_6\text{H}_{11})_3]_2$ .<sup>27</sup> The Pt–C(1)(carbene) bond length of 2.069 (4)  $\text{\AA}$  can be compared with the Pt–C(carbene) distance of *trans*- $\{(\text{Me}_2\text{PhP})_2\text{PtMe}[\text{C}(\text{NMe}_2)\text{Me}]\}\text{PF}_6$  (Pt–C(carbene) = 2.079 (13)  $\text{\AA}$ ), having a methyl group trans to the carbene, but it is longer than that reported for Pt–C(carbene) distances for carbene ligands trans to halides (Pt–C(carbene) = 1.92–2.00  $\text{\AA}$ ).<sup>29</sup> The geometry of the carbene ligand is rather planar. In fact, the phenyl ring is rotated with respect to the N(1)–C(1)–N(2) plane at 155.8 (4)° vs the value of 127.7 (5)° found for the same ligand in  $\{\text{Cl}(\text{PMe}_2\text{Ph})(\text{CH}_2\text{CH}_2\text{CH}_2\text{NH})\text{Pd}[\text{C}(\text{NCH}_2\text{CH}_2\text{CH}_2\text{NH}(\text{C}_6\text{H}_4\text{-}p\text{-MeO}))]\text{Cl}\}$ .<sup>21</sup> The plane of the carbene in **2** intersects the platinum square plane at an angle of 73.7 (2)°.

Other differences from the Pd derivative<sup>21</sup> are in the conformation of the azetidine moiety, which in the present compound shows a twisted molecular conformation (rather planar in the Pd derivative) with deviations from its best mean plane ranging from –0.046 (7) to +0.042 (7)  $\text{\AA}$ . The N(1)–C(1)–N(2) angle is here 113.6 (4)° vs 118.6 (5)° in

Table III. Crystal Data

|                                                       |                                                  |
|-------------------------------------------------------|--------------------------------------------------|
| formula                                               | $\text{C}_{31}\text{H}_{32}\text{N}_3\text{OPt}$ |
| mol wt                                                | 668.68                                           |
| cryst dimens, mm                                      | 0.12 $\times$ 0.20 $\times$ 0.22                 |
| cryst syst                                            | triclinic                                        |
| <i>a</i> , $\text{\AA}$                               | 12.998 (3)                                       |
| <i>b</i> , $\text{\AA}$                               | 11.833 (2)                                       |
| <i>c</i> , $\text{\AA}$                               | 10.257 (2)                                       |
| $\alpha$ , deg                                        | 100.83 (4)                                       |
| $\beta$ , deg                                         | 80.72 (3)                                        |
| $\gamma$ , deg                                        | 114.20 (4)                                       |
| <i>V</i> , $\text{\AA}^3$                             | 1406.0 (3)                                       |
| space group                                           | $P\bar{1}$                                       |
| <i>D</i> <sub>calc</sub> , g cm <sup>–3</sup>         | 1.63                                             |
| <i>z</i>                                              | 2                                                |
| <i>F</i> (000)                                        | 680                                              |
| radiation ( $\lambda$ , $\text{\AA}$ )                | Mo K $\alpha$ (0.710 69)                         |
| $\mu$ , cm <sup>–1</sup>                              | 48.11                                            |
| no. of rflns measd                                    | 5235                                             |
| scan method                                           | $\theta/2\theta$                                 |
| scan speed, deg min <sup>–1</sup>                     | 1.8                                              |
| scan width, deg                                       | 1.2                                              |
| bkgd counts, s                                        | 20                                               |
| $2\theta_{\text{max}}$ , deg                          | 50                                               |
| transmissn coeff                                      | 0.62–0.66                                        |
| $\sigma$ limit [ $I \geq n\sigma(I)$ ]                | 3                                                |
| no. of unique obsd data with $I \geq 3\sigma(I)$      | 4157                                             |
| weighting scheme <i>w</i>                             | $1.2154/[\sigma^2(F_o) + 0.000306(F_o^2)]^{-1}$  |
| $R = \sum[ F_o  -  F_c ]/\sum F_o $                   | 0.022                                            |
| $R_w = [\sum w( F_o  -  F_c )^2/\sum w F_o ^2]^{1/2}$ | 0.022                                            |
| <i>S</i>                                              | 1.15                                             |

Table IV. Atomic Coordinates ( $\times 10^4$ ) for Non-Hydrogen Atoms and *U*<sub>eq</sub> Values ( $\times 10^3$ ) with Esd's in Parentheses

| atom  | <i>x/a</i> | <i>y/b</i> | <i>z/c</i> | <i>U</i> <sub>eq</sub> , $\text{\AA}^2$ <sup>a</sup> |
|-------|------------|------------|------------|------------------------------------------------------|
| Pt    | 2011.3 (1) | 3438.3 (2) | 2037.3 (2) | 32.6 (1)                                             |
| P     | 2948 (1)   | 2371 (1)   | 2551 (1)   | 32.9 (4)                                             |
| N(1)  | 751 (3)    | 3268 (3)   | 4684 (4)   | 41 (2)                                               |
| N(2)  | 1981 (3)   | 5248 (3)   | 4635 (4)   | 41 (1)                                               |
| N(3)  | –885 (4)   | 3715 (5)   | 2604 (5)   | 64 (2)                                               |
| O     | 5251 (3)   | –380 (3)   | 2861 (4)   | 64 (2)                                               |
| C(13) | 5963 (6)   | –412 (6)   | 1662 (7)   | 87 (3)                                               |
| C(1)  | 1559 (3)   | 4069 (4)   | 3976 (4)   | 37 (2)                                               |
| C(2)  | 31 (4)     | 1941 (4)   | 4334 (5)   | 49 (2)                                               |
| C(3)  | –447 (5)   | 1909 (5)   | 5810 (6)   | 63 (3)                                               |
| C(4)  | 240 (5)    | 3322 (5)   | 6080 (5)   | 56 (2)                                               |
| C(5)  | 1104 (4)   | 4290 (5)   | 1320 (5)   | 45 (2)                                               |
| C(6)  | –12 (4)    | 3977 (4)   | 2013 (5)   | 46 (2)                                               |
| C(7)  | 2857 (3)   | 6314 (4)   | 4152 (4)   | 36 (2)                                               |
| C(8)  | 3693 (4)   | 6266 (4)   | 3150 (5)   | 45 (2)                                               |
| C(9)  | 4508 (4)   | 7346 (4)   | 2700 (5)   | 46 (2)                                               |
| C(10) | 4505 (4)   | 8494 (4)   | 3268 (4)   | 44 (2)                                               |
| C(11) | 3707 (5)   | 8568 (5)   | 4307 (5)   | 53 (2)                                               |
| C(12) | 2886 (4)   | 7497 (4)   | 4749 (5)   | 46 (2)                                               |
| C(14) | 4473 (3)   | 2938 (4)   | 2026 (4)   | 36 (2)                                               |
| C(15) | 5211 (4)   | 2671 (4)   | 2665 (5)   | 44 (2)                                               |
| C(16) | 6350 (4)   | 3075 (5)   | 2213 (5)   | 49 (2)                                               |
| C(17) | 6767 (4)   | 3764 (4)   | 1162 (5)   | 47 (2)                                               |
| C(18) | 6056 (4)   | 4041 (5)   | 551 (5)    | 47 (2)                                               |
| C(19) | 4911 (4)   | 3634 (4)   | 976 (4)    | 40 (2)                                               |
| C(20) | 2395 (4)   | 724 (4)    | 1832 (4)   | 38 (2)                                               |
| C(21) | 2947 (4)   | –69 (4)    | 1851 (5)   | 46 (2)                                               |
| C(22) | 2501 (5)   | –1302 (5)  | 1277 (5)   | 57 (2)                                               |
| C(23) | 1501 (5)   | –1778 (5)  | 700 (6)    | 65 (3)                                               |
| C(24) | 928 (5)    | –1038 (5)  | 706 (6)    | 68 (3)                                               |
| C(25) | 1378 (4)   | 223 (5)    | 1254 (5)   | 51 (2)                                               |
| C(26) | 2915 (3)   | 2356 (4)   | 4335 (4)   | 37 (2)                                               |
| C(27) | 3451 (4)   | 3496 (5)   | 5122 (5)   | 49 (2)                                               |
| C(28) | 3354 (5)   | 3574 (6)   | 6480 (5)   | 62 (3)                                               |
| C(29) | 2727 (6)   | 2555 (7)   | 7104 (6)   | 76 (3)                                               |
| C(30) | 2206 (6)   | 1418 (7)   | 6355 (6)   | 78 (3)                                               |
| C(31) | 2310 (5)   | 1316 (5)   | 4983 (5)   | 56 (2)                                               |

<sup>a</sup> *U*<sub>eq</sub> = one-third of the trace of the orthogonalized *U*<sub>ij</sub> tensor.

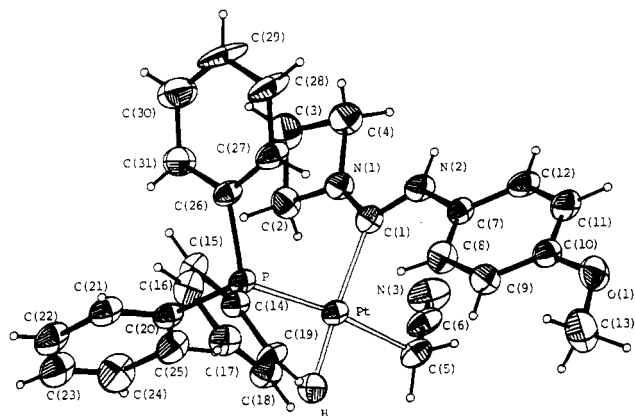
the Pd derivative. However, the higher degree of planarity of the overall ligand in **2** allows a better electron delo-

(26) Kane, A. R.; Guggenberger, L. J.; Muetterties, E. L. *J. Am. Chem. Soc.* 1970, 92, 2571.

(27) Auburn, M.; Ciriano, M.; Howard, J. A. K.; Murray, M.; Pugh, N. J.; Spencer, J. L.; Stone, F. G. A.; Woodward, P. *J. Chem. Soc., Dalton Trans.* 1980, 659.

(28) Stepaniak, R. F.; Payne, N. C. *Inorg. Chem.* 1974, 13, 797.

(29) Schubert, U. In *Transition Metal Carbene Complexes*; Verlag Chemie: Weinheim, FRG, 1983; p 73.

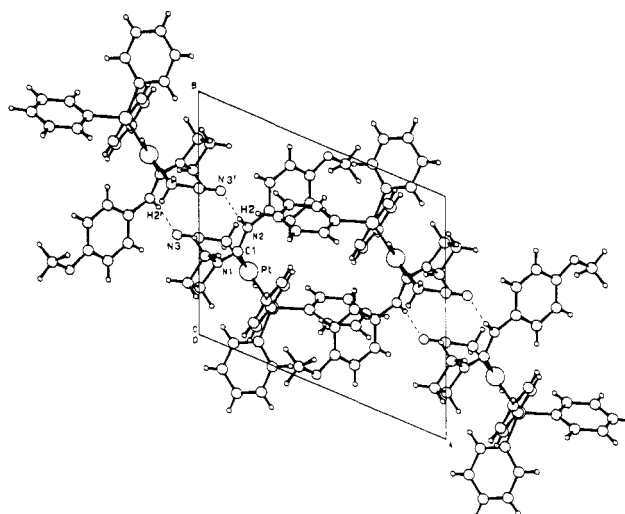


**Figure 1.** ORTEP plot of  $\text{PtH}(\text{CH}_2\text{CN})[\text{C}(\text{NCH}_2\text{CH}_2\text{CH}_2)\text{NH}-(\text{C}_6\text{H}_4\text{-}p\text{-OMe})](\text{PPh}_3)$  (**2**) showing the atom-numbering scheme. The thermal ellipsoids are drawn at the 40% probability level.

**Table V.** Selected Bond Lengths (Å) and Angles (deg)

| (a) Bond Lengths  |           |                   |            |
|-------------------|-----------|-------------------|------------|
| Pt-H              | 1.61 (4)  | Pt-P              | 2.252 (2)  |
| Pt-C(1)           | 2.069 (4) | Pt-C(5)           | 2.116 (7)  |
| P-C(14)           | 1.834 (4) | P-C(20)           | 1.828 (4)  |
| P-C(26)           | 1.827 (5) | N(1)-C(1)         | 1.313 (5)  |
| N(1)-C(2)         | 1.470 (5) | N(1)-C(4)         | 1.480 (6)  |
| N(2)-C(1)         | 1.357 (5) | N(2)-C(7)         | 1.417 (5)  |
| N(3)-C(6)         | 1.145 (6) | O-C(13)           | 1.419 (8)  |
| C(2)-C(3)         | 1.541 (8) | C(3)-C(4)         | 1.533 (7)  |
| C(5)-C(6)         | 1.439 (7) | C(7)-C(8)         | 1.381 (6)  |
| C(7)-C(12)        | 1.407 (7) | C(8)-C(9)         | 1.386 (6)  |
| C(9)-C(10)        | 1.375 (7) | C(10)-C(11)       | 1.378 (7)  |
| C(11)-C(12)       | 1.379 (6) | C(14)-C(15)       | 1.406 (8)  |
| C(14)-C(19)       | 1.383 (6) | C(15)-C(16)       | 1.383 (6)  |
| C(16)-C(17)       | 1.378 (8) | C(17)-C(18)       | 1.366 (9)  |
| C(18)-C(19)       | 1.385 (6) | C(20)-C(21)       | 1.399 (9)  |
| C(20)-C(25)       | 1.388 (7) | C(21)-C(22)       | 1.380 (7)  |
| C(22)-C(23)       | 1.371 (9) | C(23)-C(24)       | 1.361 (11) |
| C(24)-C(25)       | 1.400 (7) | C(26)-C(27)       | 1.399 (6)  |
| C(26)-C(31)       | 1.386 (7) | C(27)-C(28)       | 1.368 (7)  |
| C(28)-C(29)       | 1.368 (9) | C(29)-C(30)       | 1.375 (9)  |
| C(30)-C(31)       | 1.379 (8) |                   |            |
| (b) Bond Angles   |           |                   |            |
| C(1)-Pt-C(5)      | 90.0 (2)  | P-Pt-C(5)         | 172.7 (1)  |
| P-Pt-C(1)         | 96.7 (1)  | H-Pt-C(5)         | 85 (1)     |
| H-Pt-C(1)         | 174 (1)   | H-Pt-P            | 88 (1)     |
| Pt-P-C(26)        | 114.6 (2) | Pt-P-C(20)        | 113.0 (2)  |
| Pt-P-C(14)        | 116.4 (2) | C(20)-P-C(26)     | 105.0 (2)  |
| C(14)-P-C(26)     | 102.1 (2) | C(14)-P-C(20)     | 104.3 (2)  |
| C(2)-N(1)-C(4)    | 93.9 (4)  | C(1)-N(1)-C(4)    | 134.9 (4)  |
| C(1)-N(1)-C(2)    | 131.3 (4) | C(1)-N(2)-C(7)    | 127.2 (4)  |
| N(1)-C(1)-N(2)    | 113.6 (4) | Pt-C(1)-N(2)      | 128.0 (3)  |
| Pt-C(1)-N(1)      | 118.4 (3) | N(1)-C(2)-C(3)    | 88.4 (4)   |
| C(2)-C(3)-C(4)    | 89.0 (4)  | N(1)-C(4)-C(3)    | 88.3 (4)   |
| Pt-C(5)-C(6)      | 110.8 (4) | N(3)-C(6)-C(5)    | 177.2 (6)  |
| N(2)-C(7)-C(12)   | 117.7 (4) | N(2)-C(7)-C(8)    | 124.3 (4)  |
| C(8)-C(7)-C(12)   | 118.0 (4) | C(7)-C(8)-C(9)    | 121.2 (5)  |
| C(8)-C(9)-C(10)   | 120.0 (5) | C(9)-C(10)-C(11)  | 119.7 (4)  |
| C(10)-C(11)-C(12) | 120.5 (5) | C(7)-C(12)-C(11)  | 120.4 (5)  |
| P-C(14)-C(19)     | 119.8 (4) | P-C(14)-C(15)     | 121.2 (3)  |
| C(15)-C(14)-C(19) | 119.0 (5) | C(14)-C(15)-C(16) | 119.7 (5)  |
| C(15)-C(16)-C(17) | 120.3 (5) | C(16)-C(17)-C(18) | 120.2 (5)  |
| C(17)-C(18)-C(19) | 120.6 (5) | C(14)-C(19)-C(18) | 120.2 (5)  |
| P-C(20)-C(25)     | 119.2 (4) | P-C(20)-C(21)     | 122.8 (4)  |
| C(21)-C(20)-C(25) | 118.0 (4) | C(20)-C(21)-C(22) | 120.5 (5)  |
| C(21)-C(22)-C(23) | 120.7 (6) | C(22)-C(23)-C(24) | 120.0 (6)  |
| C(23)-C(24)-C(25) | 120.2 (6) | C(20)-C(25)-C(24) | 120.5 (5)  |
| P-C(26)-C(31)     | 124.5 (4) | P-C(26)-C(27)     | 117.7 (3)  |
| C(27)-C(26)-C(31) | 117.5 (4) | C(26)-C(27)-C(28) | 120.7 (5)  |
| C(27)-C(28)-C(29) | 121.1 (6) | C(28)-C(29)-C(30) | 119.5 (6)  |
| C(29)-C(30)-C(31) | 120.3 (6) | C(26)-C(31)-C(30) | 120.9 (5)  |

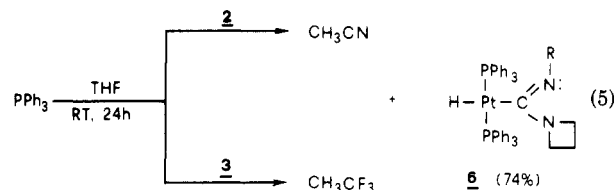
calization along the N(1)-C(1)-N(2) system, with C(1)-N(1) = 1.313 (5) Å and C(1)-N(2) = 1.357 (5) Å (the corresponding values in the Pd derivative are 1.298 (8) and 1.334 (8) Å, respectively).



**Figure 2.** Packing diagram of **2** down the *c* axis, showing the dimer formation.

The Pt-C(5) cyanomethyl bond distance of 2.116 (7) Å is shorter than the Pt-CH<sub>2</sub>CN bond length found in *trans*-PtH(CH<sub>2</sub>CN)(PPh<sub>3</sub>)<sub>2</sub> (2.15 (1) Å) but longer than that found in *trans*-PtCl(CH<sub>2</sub>CN)(PPh<sub>3</sub>)<sub>2</sub> (2.08 (1) Å).<sup>31</sup> The Pt-C(5)-C(6) angle is 110.8 (0)°, which is larger than the corresponding value found in *trans*-PtH(CH<sub>2</sub>CN)-(PPh<sub>3</sub>)<sub>2</sub> (106 (1)°). This opening of the angle could be related to the intermolecular interaction between the H(2) proton of the carbene ligand and N(3') of an adjacent molecule at  $-x, 1-y, 1-z$  (N(2)H...N(3') = 2.36 (5) Å, N(2)-H(2)...N(3') = 171 (4)°, and N(2)...N(3') = 3.222 (6) Å; see Figure 2). These intermolecular contacts could be responsible for the shrinking of the N(1)-C(1)-N(2) angle described before in order to achieve a more favorable orientation for the H-bond interactions.

**Reactivity: Metal-Alkyl and Metal-Carbene Bond Cleavage.** (a) **Reactions with PPh<sub>3</sub>.** Complexes **1-4** are quite stable in the solid state and in solution. No reductive elimination of HR<sub>x</sub> is observed in refluxing THF for several hours even in the presence of a 5-fold excess of diphenylacetylene. In contrast to the case for **3**, the parent complex *cis*-PtH(CH<sub>2</sub>CF<sub>3</sub>)(PPh<sub>3</sub>)<sub>2</sub> undergoes facile 1,1-reductive elimination of CH<sub>3</sub>CF<sub>3</sub> at room temperature with formation of Pt(0) species.<sup>7</sup> On the other hand, complexes **2** and **3** are found to react with 1 equivalent of PPh<sub>3</sub> at room temperature to give **6** and HR<sub>x</sub> as the only reaction products (eq 5). The hydrido carbene complexes **1** and

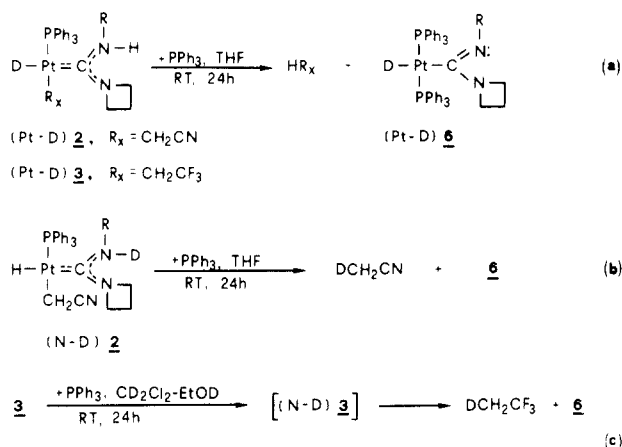


**4**, having CF<sub>3</sub> as the alkyl ligand, are unreactive toward PPh<sub>3</sub> under the same experimental conditions outlined in eq 5. Compound **6** has been characterized by analytical (Experimental Section) and IR and <sup>1</sup>H and <sup>31</sup>P NMR data (Table I). The *trans* geometry of **6** has been confirmed by its <sup>1</sup>H and <sup>31</sup>P NMR spectra. It was not possible to record the <sup>13</sup>C NMR spectrum of **6** because it slowly pro-

(30) Del Pra, A.; Forsellini, E.; Bombieri, G.; Michelin, R. A.; Ros, R. *J. Chem. Soc., Dalton Trans.* 1979, 1862.

(31) Ros, R.; Michelin, R. A.; Belluco, U.; Zanotti, G.; Del Pra, A.; Bombieri, G. *Inorg. Chim. Acta* 1978, 29, L187.

Scheme I



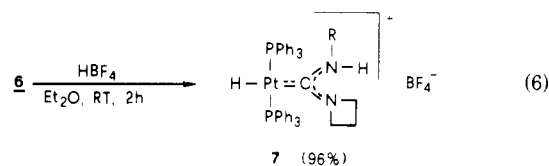
tonates in  $\text{CD}_2\text{Cl}_2$ , probably due to traces of  $\text{HCl}$ , to afford a compound with  $^1\text{H}$  and  $^{31}\text{P}$  NMR data similar to those reported for **7** (see below).

The formation of  $\text{HR}_X$  in reaction 5 is *not* due to a reductive-elimination process involving  $\text{Pt-H}$  and  $\text{Pt-R}_X$  bond ruptures. Isotopic experiments with  $\text{Pt-D}$  and  $\text{N-D}$  derivatives (Scheme I) indicate instead that what actually occurs is the protonolysis of the  $\text{Pt-R}_X$  bond by the  $\text{N-H}$  proton. The deuteride derivatives  $(\text{Pt-D})\mathbf{2}$  and  $(\text{Pt-D})\mathbf{3}$  (Scheme I) have been prepared and characterized as reported in the Experimental Section. The reaction (a) leads to the selective and quantitative formation of  $\text{HR}_X$  ( $R_X = \text{CH}_2\text{CN}$ ,  $\text{CH}_2\text{CF}_3$ ) and the corresponding  $\text{Pt(II)}$  deuteride  $(\text{Pt-D})\mathbf{6}$  with no cleavage of the  $\text{Pt-D}$  bond being observed. On the other hand, the deuterated aminocarbene complex  $(\text{N-D})\mathbf{2}$  reacts under analogous conditions with  $\text{PPh}_3$  to give **6** and  $\text{DCH}_2\text{CN}$  (reaction b) as confirmed by  $^1\text{H}$  NMR data (see Experimental Section). Analogously, the reaction of **3** in  $\text{CD}_2\text{Cl}_2\text{-EtOD}$  with  $\text{PPh}_3$  (eq c) affords quantitatively  $\text{DCH}_2\text{CF}_3$ , which has been identified by comparison of the  $^{19}\text{F}$  NMR data with those reported for the reductive elimination of *cis*- $\text{PtD}(\text{CH}_2\text{CF}_3)(\text{PPh}_3)_2$ .<sup>7</sup> It is likely that reaction c proceeds initially by  $\text{N-H}/\text{N-D}$  exchange due to the presence of  $\text{EtOD}$  to give the intermediate  $(\text{N-D})\mathbf{3}$ , which eventually converts to **6** by elimination of  $\text{DCH}_2\text{CF}_3$ .

Despite repeated attempts, we were unable to detect any reaction intermediate involved in reaction 5. However, we have observed that external attack of a proton acid ( $\text{HBF}_4$  and  $\text{HCl}$ ) on **2** always leads to the selective cleavage of the  $\text{Pt-H}$  bond. This experimental evidence agrees with similar reactivity shown by other *cis* hydrido alkyl complexes of  $\text{Pt(II)}$ <sup>9</sup> and provides evidence against a mechanism involving  $\text{N-H}$  dissociation promoted by  $\text{PPh}_3$  and subsequent proton attack on the  $\text{Pt-R}_X$  bond. Conversely, the observed selective cleavage of the  $\text{Pt-R}_X$  bond might suggest that a possible mechanistic pathway for reaction 5 is a concerted process promoted by  $\text{PPh}_3$  involving rupture of both the  $\text{Pt-R}_X$  and  $\text{N-H}$  bonds. Although we have no detailed kinetic data on reaction 5, qualitative observations of the reaction times obtained for **3** with different amounts of  $\text{PPh}_3$ , by monitoring of the integration ratios between the  $\text{CH}_2\text{CF}_3$  formed and the coordinated  $\text{CH}_2\text{CF}_3$  group in the  $^{19}\text{F}$  NMR spectra, indicate that the reaction rate increases with increasing  $\text{PPh}_3$  concentration. This would suggest that in the first step  $\text{PPh}_3$  coordinates to the metal and then  $\text{HR}_X$  is eliminated.

The electrophilicity of the  $\text{N-H}$  group in aminocarbene complexes of  $\text{Pt(II)}$  and  $\text{Pd(II)}$  has been recently demonstrated<sup>16</sup> by some deprotonation reactions with bases to

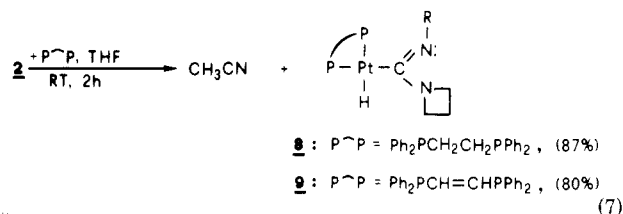
give imino intermediates, whose nitrogen reacts with electrophiles to regenerate carbene complexes. Similarly, the imino nitrogen of **6** is sufficiently basic to react with  $\text{HBF}_4$  to yield the diaminocarbene complex **7** (eq 6).



Compound **7** was characterized by its analytical and spectroscopic data (Experimental Section). The  $^{13}\text{C}$  NMR spectrum shows the signal assigned to the carbene carbon at 204.03 ppm as a triplet due to coupling with the two P atoms. By comparing the  $^{13}\text{C}$  NMR spectrum of **7** with that of the similar *trans*- $\{\text{Br}(\text{PPh}_3)_2\text{Pt}[\text{C}(\text{NCH}_2\text{CH}_2\text{CH}_2\text{NHR})]\text{BF}_4\}$ ,<sup>21</sup> we observed a shielding of the carbene carbon from the 204.03 ppm value of **7** to 174.90 ppm with an increase of  $^1J_{\text{PtC}}$  from 823 to 1534 Hz. This effect may be ascribed to the different  $\sigma$ -donor abilities of the *trans* ligand, as similarly observed for other  $\text{Pt(II)}$  carbene complexes,<sup>24</sup> and may be interpreted in terms of a higher *trans* influence of the hydride proton relative to that of bromide.<sup>24a</sup>

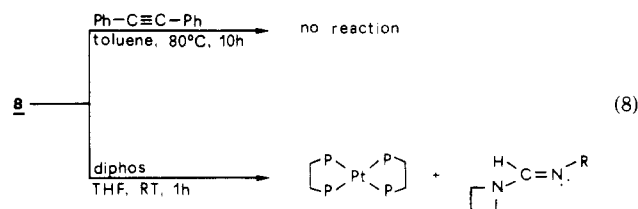
**(b) Reactions with Diphosphines.** Complexes **1**, **2**, and **4** react with equivalent amounts of  $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$  (diphos) or  $\text{Ph}_2\text{PCH}=\text{CHPPh}_2$  (diphoe) to yield different products according to the nature of the alkyl ligand  $R_X$  bound to the metal.

Again, when  $R_X = \text{CH}_2\text{CN}$ , reactions with diphos or diphoe lead to the selective cleavage of the  $\text{Pt-R}_X$  bond and formation of the *cis* hydrido imino derivative **8** or **9**, respectively (eq 7). Although isotopic experiments with



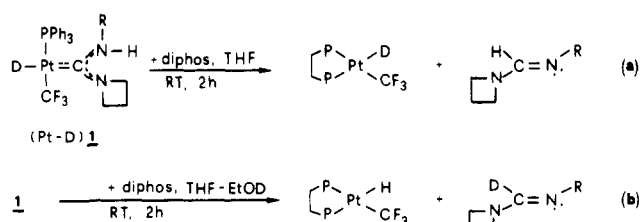
the corresponding  $\text{Pt-D}$  and  $\text{N-D}$  derivatives were not carried out, presumably reaction 7 proceeds through coordination of one phosphorus group of the diphosphine, as proposed for similar reactions with  $\text{PPh}_3$  (eq 5). Elimination of  $\text{HR}_X$  and metal chelation of the remaining P atom of the diphosphine lead to **8** and **9**.

Compounds **8** and **9** are stable in the solid state and in solution. No reductive elimination of the formamidine  $\text{HC}(\text{CH}_2\text{CH}_2\text{CH}_2\text{N})\text{C}=\text{N(R)}$  is observed upon heating **8** in toluene at  $80^\circ\text{C}$  for 10 h, even in the presence of a 3-fold excess of diphenylacetylene. However, reaction of **8** with 1 equiv of diphos leads to the formation of  $\text{Pt}(\text{diphos})_2$ <sup>32</sup> and liberation of the organic formamidine  $\text{HC}(\text{CH}_2\text{CH}_2\text{CH}_2\text{N})\text{C}=\text{N(R)}$  (eq 8). The stereochemistry of



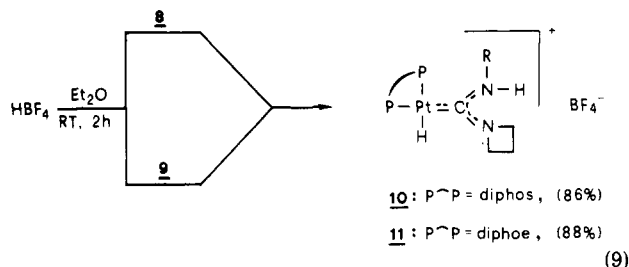


Scheme II



**8** and **9** has been deduced from IR and  $^1\text{H}$  and  $^{31}\text{P}$  NMR (Table I) and  $^{13}\text{C}$  NMR (Table II) data. Diagnostic features are the  $\nu(\text{C}=\text{N})$  and  $\nu(\text{PtH})$  bonds at 1499 and 1510  $\text{cm}^{-1}$  and 1982 and 2007  $\text{cm}^{-1}$ , respectively. The Pt-H resonances fall at  $\delta$  -2.39 and -2.28, respectively (doublet of doublets by coupling with trans and cis phosphorus atoms) with  $^1J_{\text{PtH}} = 1212$  and 1241 Hz. All these data compare well with the values reported for the similar  $\text{PtH}(\text{CH}_2\text{CN})(\text{P-P})$  derivatives.<sup>6a</sup>

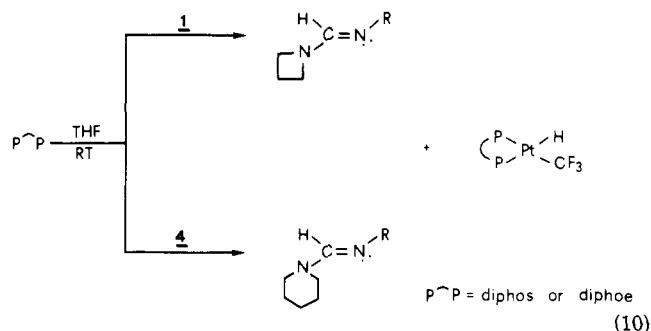
Compounds **8** and **9** react with ethereal  $\text{HBF}_4$  to give the cis hydrido carbene derivatives **10** and **11**, respectively (eq 9). Compounds **10** and **11** have been identified by



their IR and NMR spectra (Tables I and II). The IR spectra show  $\nu(\text{PtH})$ ,  $\nu(\text{NH})$ , and  $\nu(\text{C}=\text{N})$  bands at 1976 and 2028, 3302 and 3297, and 1552 and 1552  $\text{cm}^{-1}$ , respectively. The Pt-H resonances appear at  $\delta$  -1.53 and -2.86 as a doublet of doublets owing to coupling with trans and cis phosphorus atoms with  $^1J_{\text{PtH}} = 1134$  and 1152 Hz, respectively. The N-H resonances are located at  $\delta$  8.16 and 8.32 as a doublet with  $^{195}\text{Pt}$  satellites ( $^3J_{\text{PtH}} = 74.5$  and 74.7 Hz) by coupling with the trans phosphorus atom ( $^4J_{\text{HP}} = 9.4$  and 9.3 Hz). The  $^{13}\text{C}$  NMR spectrum of **10** shows the carbene carbon at  $\delta$  194.51 as a doublet of doublets with  $^{195}\text{Pt}$  satellites ( $^1J_{\text{PtC}} = 1134$  Hz)<sup>24</sup> by coupling with trans and cis phosphorus atoms ( $^2J_{\text{CP}} = 115$  and 8.0 Hz, respectively).<sup>25</sup>

Compounds **10** and **11** appear to be the first isolated cis hydrido carbene complexes of a transition metal. Such complexes are important in that they may be involved in some stoichiometric and catalytic processes.<sup>1b</sup> Previous examples of cis hydrido carbene complexes have been reported as reactive intermediates in metal to carbene 1,2-hydrogen migration, occurring in the protonation of low-valent Fischer-type carbene complexes of iron and molybdenum.<sup>33</sup>

In contrast to **2** (eq 7) compounds **1** and **4**, having  $\text{CF}_3$  as the alkyl ligand, react with diphos or diphoe, leading to the selective cleavage of the metal-carbene bond with formation of formamidines and cis hydrido trifluoromethyl complexes (eq 10).<sup>6c</sup> Isotopic experiments have been carried out for **1** and are summarized in Scheme II. Reactions a and b of Scheme II indicate that the Pt-D bond is not involved in the metal-carbene cleavage, which is conversely due to an intramolecular 1,2-hydrogen transfer



of the aminocarbene proton leading to the formamidine. A similar mechanism has been proposed for the displacement of the aminocarbene ligand in several metal complexes of Cr,<sup>34a,b</sup> Pd,<sup>34c</sup> and Au<sup>34d-f</sup> promoted by donor ligands. The reactions of **1** and **4** with the more flexible diphos occur faster than the corresponding reactions with the sterically rigid diphoe. For this latter ligand, coordination and subsequent ring closure are hampered by its stereochemical conformation. In the experimental conditions we used, the formamidines are present as a unique isomer presumably in the anti conformation, which is reported to be more stable.<sup>35</sup>

## Conclusions

(1) Hydrido alkyl Pt(II) species having cis Pt-H and Pt-R<sub>x</sub> (R<sub>x</sub> = cyanoalkyl, fluoroalkyl) bonds are stabilized toward thermal reductive elimination by the presence of a metal-coordinated diaminocarbene ligand. Furthermore, the complexes  $\text{PtH}(\text{R}_x)(\text{diaminocarbene})(\text{PPh}_3)$  (**1-4**) do not reductively eliminate by reaction with P-donors.

(2) The results of the reactions of **1-4** with  $\text{PPh}_3$  or diphosphines appear to be strongly dependent on the nature of the R<sub>x</sub> group. The metal-carbon  $\sigma$  bond in perfluoroalkyl complexes of transition metals is much more thermally stable and more resistant to chemical attack than that of other derivatives.<sup>6c</sup> Thus, P-donors react with **2** and **3**, affording the protolysis and elimination of  $\text{HR}_x$  (R<sub>x</sub> =  $\text{CH}_2\text{CN}$ ,  $\text{CH}_2\text{CF}_3$ ), but with **1** and **4** (R<sub>x</sub> =  $\text{CF}_3$ ) bidentate P-donors only promote the protolysis and elimination of the carbene ligand, yielding an organic formamidine. This latter process is unprecedented in Pt(II) carbene chemistry.

(3) The reactions of **2** with diphosphines and the subsequent reaction with  $\text{HBF}_4$  lead to quite new cis hydrido carbene derivatives, whose reaction chemistry is now being studied.

## Experimental Section

**General Information.** All manipulations were performed under nitrogen, with use of standard Schlenk techniques. Solvents were distilled over sodium-benzophenone ketyl (tetrahydrofuran, diethyl ether), sodium (*n*-heptane, toluene) or  $\text{CaH}_2$  (dichloromethane). All other solvents were of reagent grade purity and were used without further purification.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded at 400 MHz on a Bruker AM-400 spectrometer.  $^{31}\text{P}\{^1\text{H}\}$  and  $^{19}\text{F}$  NMR spectra were recorded at 32.203 and 74.844 MHz, respectively, on a Varian FT 80A instrument. All NMR spectra were recorded in  $\text{CD}_2\text{Cl}_2$  at 25 °C. The following ab-

(33) (a) Le Bozec, H.; Fillant, J. L.; Dixneuf, P. H. *J. Chem. Soc., Chem. Commun.* 1986, 1182. (b) Osborn, J. A.; Parker, C. A.; Winter, M. J. *J. Chem. Soc., Chem. Commun.* 1986, 1185.

(34) (a) Fischer, E. O.; Leupold, M. *Chem. Ber.* 1972, 105, 599. (b) Connor, J. A.; Rose, P. D. *J. Organomet. Chem.* 1972, 46, 329. (c) Ito, Y.; Hirao, T.; Saegusa, T. *J. Organomet. Chem.* 1977, 131, 121. (d) Parks, J. E.; Balch, A. L. *J. Organomet. Chem.* 1974, 71, 453. (e) Minghetti, G.; Baratto, L.; Bonati, F. *J. Organomet. Chem.* 1975, 102, 397. (f) Minghetti, G.; Bonati, F.; Banditelli, G. *Inorg. Chem.* 1976, 15, 1718.

(35) (a) Tennant, G. In *Comprehensive Organic Chemistry*; Sutherland, I. O., Ed.; Pergamon Press: Oxford, England, 1979; Vol. 2, Chapter 8, p 385. (b) Hegarty, A. E.; Chandler, A. *Tetrahedron Lett.* 1980, 21, 885.

breviations are used: s = singlet, d = doublet, t = triplet, q = quartet, Q = quintet, m = multiplet. IR spectra (abbreviations: s = strong, m = medium) were taken on a Perkin-Elmer 983 spectrophotometer. The FAB (fast atom bombardment) mass spectrum of **2** was obtained by bombarding a glycerol solution of the sample with 8 keV of Xe atoms. GC/MS determinations were obtained by a Carlo Erba QMD 1000 instrument operating under electron impact conditions (70 eV, 100  $\mu$ A). GC conditions were the following: OV1, 25 m  $\times$  0.25 mm i.d., column temperature 100–250 °C at 10 °C/min, flow rate 2 mL/min, He, 0.5- $\mu$ L samples of the reaction mixtures. Melting points (uncorrected) were determined in air on a hot-plate apparatus. Elemental analyses were performed by the Department of Chemistry of the University of Padua. Throughout this paper, unless otherwise noted, the R group of the isocyanide (RNC) and carbene ligands is *p*-MeOC<sub>6</sub>H<sub>4</sub>.

**Starting Complexes.** The complexes *trans*-PtH(R<sub>X</sub>)(PPh<sub>3</sub>)<sub>2</sub> (R<sub>X</sub> = CH<sub>2</sub>CN, <sup>6a</sup>CF<sub>3</sub><sup>6c</sup>), *cis*-PtX(CH<sub>2</sub>CF<sub>3</sub>)(PPh<sub>3</sub>)<sub>2</sub> (X = H, D),<sup>7</sup> and PtH(R<sub>X</sub>)(CNR)(PPh<sub>3</sub>) (R<sub>X</sub> = CH<sub>2</sub>CN,<sup>10</sup> CF<sub>3</sub><sup>6c</sup>) were prepared according to literature procedures. The following complexes are new.

***trans*-PtD(CH<sub>2</sub>CN)(PPh<sub>3</sub>)<sub>2</sub>.** A suspension of *trans*-PtCl-(CH<sub>2</sub>CN)(PPh<sub>3</sub>)<sub>2</sub> (795 mg, 1.00 mmol) in EtOD (100 mL) at 40 °C was added dropwise to NaBD<sub>4</sub> (63 mg, 1.50 mmol) in EtOD (50 mL) over a period of 30 min. After the addition was complete, a yellow solution was obtained, which was stirred at room temperature for an additional 1 h. Then the solution was reduced to half of the volume under reduced pressure. A cream solid precipitated. The mixture was stirred at 0 °C for 30 min; then the solid was filtered and recrystallized from benzene/*n*-hexane: yield 520 mg, 72%; mp 160–162 °C. Anal. Calcd for PtP<sub>2</sub>NC<sub>38</sub>DH<sub>32</sub>: C, 59.91; H, 4.50; N, 1.84. Found: C, 60.12; H, 4.45; N, 1.80. <sup>1</sup>H NMR (80 MHz):  $\delta$  0.58 (t, 2 H, CH<sub>2</sub>, <sup>3</sup>J<sub>HP</sub> = 6.2, <sup>2</sup>J<sub>HPt</sub> = 67 Hz). <sup>31</sup>P NMR:  $\delta$  31.5 (t, <sup>2</sup>J<sub>PD</sub> = 2.2, <sup>1</sup>J<sub>PtP</sub> = 3025 Hz). IR (KBr):  $\nu$ (CN) 2183 (s) cm<sup>-1</sup>;  $\nu$ (PtD) 1353 (m) cm<sup>-1</sup>.

***trans*-PtD(CF<sub>3</sub>)(PPh<sub>3</sub>)<sub>2</sub>.** A suspension of *trans*-(PPh<sub>3</sub>)<sub>2</sub>Pt-(CF<sub>3</sub>)Br (1736 mg, 2.00 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (50 mL) was treated with a 1.025 M AgBF<sub>4</sub> solution in acetone (2.0 mL, 2.05 mmol) and the mixture stirred at room temperature for 30 min. The solid AgBr was filtered off, and the pale yellow solution was concentrated under reduced pressure to ca. 10 mL. Dropwise addition of Et<sub>2</sub>O gave the solid *trans*-[(PPh<sub>3</sub>)<sub>2</sub>Pt(CF<sub>3</sub>)(solvent)]BF<sub>4</sub> (1560 mg, 81% yield for solv = CH<sub>2</sub>Cl<sub>2</sub>). All the cationic intermediate (1560 mg, 1.62 mmol) was suspended in EtOD (30 mL) at 0 °C and treated dropwise over ca. 30 min with a solution of NaBD<sub>4</sub> (80 mg, 1.91 mmol) in EtOD (20 mL). The grayish solid obtained was filtered off and recrystallized twice from benzene/*n*-hexane to give the deuteride derivative: yield 820 mg, 64%; mp 176–178 °C dec. Anal. Calcd for PtP<sub>2</sub>F<sub>3</sub>C<sub>37</sub>DH<sub>30</sub>: C, 56.20; H, 4.08. Found: C, 56.00; H, 4.10. <sup>31</sup>P NMR:  $\delta$  29.5 (dq, <sup>3</sup>J<sub>PF</sub> = 8.5, <sup>3</sup>J<sub>PD</sub> = 2.3, <sup>1</sup>J<sub>PtP</sub> = 3085 Hz). <sup>19</sup>F NMR:  $\delta$  -16.6 (tt, <sup>3</sup>J<sub>FD</sub> = 4.2, <sup>3</sup>J<sub>FP</sub> = 8.5, <sup>2</sup>J<sub>FPt</sub> = 443 Hz). The  $\nu$ (PtD) band in the IR spectrum could not be located in either Nujol mull of KBr.

**PtH(CH<sub>2</sub>CF<sub>3</sub>)(CNR)(PPh<sub>3</sub>)<sub>2</sub>.** A suspension of *cis*-PtH-(CH<sub>2</sub>CF<sub>3</sub>)(PPh<sub>3</sub>)<sub>2</sub> (1900 mg, 2.36 mmol) was treated in *n*-heptane (80 mL) with RNC (540 mg, 4.06 mmol). The reaction mixture was stirred at room temperature for 5 h, and the cream solid was filtered off, washed with *n*-hexane (3  $\times$  10 mL), and recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/*n*-hexane: yield 1416 mg, 89%; mp 125–128 °C dec. Anal. Calcd for PtPOF<sub>3</sub>NC<sub>28</sub>H<sub>25</sub>: C, 49.86; H, 3.73; N, 2.07. Found: C, 49.59; H, 3.81; N, 1.98. <sup>1</sup>H NMR:  $\delta$  -5.35 (d, 1 H, PtH, <sup>2</sup>J<sub>HP</sub> = 18.5, <sup>1</sup>J<sub>HPt</sub> = 999 Hz), 2.45 (dq, 2 H, CH<sub>2</sub>, <sup>3</sup>J<sub>HF</sub> = 16.7, <sup>3</sup>J<sub>HP</sub> = 7.8, <sup>2</sup>J<sub>HPt</sub> = 85 Hz), 3.77 (s, 3 H, OCH<sub>3</sub>). <sup>31</sup>P NMR:  $\delta$  25.3 (q, <sup>4</sup>J<sub>PF</sub> = 16.0, <sup>1</sup>J<sub>PtP</sub> = 2227 Hz). <sup>19</sup>F NMR:  $\delta$  -52.0 (ddt, <sup>3</sup>J<sub>FH</sub> = <sup>4</sup>J<sub>FP</sub> = 16.0, <sup>4</sup>J<sub>FPt</sub> = 1.5, <sup>3</sup>J<sub>FPt</sub> = 191 Hz). IR (Nujol):  $\nu$ (CN) 2181 (s) cm<sup>-1</sup>;  $\nu$ (PtH) 2073 (s) cm<sup>-1</sup>.

**PtD(R<sub>X</sub>)(CNR)(PPh<sub>3</sub>)<sub>2</sub> (R<sub>X</sub> = CH<sub>2</sub>CN, CH<sub>2</sub>CF<sub>3</sub>, CF<sub>3</sub>).** These compounds were prepared by treating the corresponding PtD-(R<sub>X</sub>)(PPh<sub>3</sub>)<sub>2</sub> complexes (1.0 mmol) in *n*-heptane (20 mL) at room temperature with solid RNC (1.5 mmol). After the mixtures were stirred for 5 h, the solids were filtered off and recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/*n*-hexane: yields ca. 90%.

**R<sub>X</sub> = CH<sub>2</sub>CN.** Mp: 131–133 °C dec. Anal. Calcd for PtPN<sub>2</sub>OC<sub>28</sub>DH<sub>24</sub>: C, 53.16; H, 4.14; N, 4.43. Found: C, 52.94; H, 3.96; N, 4.42. <sup>1</sup>H NMR:  $\delta$  2.17 (d, 2 H, CH<sub>2</sub>, <sup>3</sup>J<sub>HP</sub> = 9.4, <sup>2</sup>J<sub>HPt</sub> = 95 Hz), 3.78 (s, 3 H, OCH<sub>3</sub>). <sup>31</sup>P NMR:  $\delta$  24.38 (s, <sup>1</sup>J<sub>PtP</sub> = 2419

Hz). IR (KBr):  $\nu$ (CN) 2197 (s) cm<sup>-1</sup>;  $\nu$ (PtD) 1461 (m) cm<sup>-1</sup>.

**R<sub>X</sub> = CH<sub>2</sub>CF<sub>3</sub>.** Mp: 124–127 °C dec. Anal. Calcd for PtPONF<sub>3</sub>C<sub>28</sub>DH<sub>24</sub>: C, 49.78; H, 3.87; N, 2.07. Found: C, 49.39; H, 3.87; N, 1.92. <sup>1</sup>H NMR:  $\delta$  2.45 (dq, 2 H, CH<sub>2</sub>, <sup>3</sup>J<sub>HF</sub> = 16.6, <sup>3</sup>J<sub>HP</sub> = 8.5, <sup>2</sup>J<sub>HPt</sub> = 91 Hz), 3.78 (s, 3 H, OCH<sub>3</sub>). <sup>31</sup>P NMR:  $\delta$  25.36 (q, <sup>4</sup>J<sub>PF</sub> = 16.0, <sup>1</sup>J<sub>PtP</sub> = 2228 Hz). <sup>19</sup>F NMR:  $\delta$  -52.1 (dt, <sup>3</sup>J<sub>FP</sub> = <sup>3</sup>J<sub>FH</sub> = 16.6, <sup>3</sup>J<sub>FPt</sub> = 192 Hz). IR (KBr):  $\nu$ (CN) 2172 (s) cm<sup>-1</sup>;  $\nu$ (PtD) 1460 (m) cm<sup>-1</sup>.

**R<sub>X</sub> = CF<sub>3</sub>.** Mp: 130–132 °C dec. Anal. Calcd for PtPF<sub>3</sub>ONC<sub>27</sub>DH<sub>22</sub>: C, 49.02; H, 3.66; N, 2.12. Found: C, 48.52; H, 3.50; N, 2.03. <sup>1</sup>H NMR:  $\delta$  3.78 (s, 3 H, OCH<sub>3</sub>). <sup>31</sup>P NMR:  $\delta$  21.60 (dq, <sup>2</sup>J<sub>PD</sub> = 2.5, <sup>3</sup>J<sub>PF</sub> = 58, <sup>1</sup>J<sub>PtP</sub> = 2055 Hz). <sup>19</sup>F NMR:  $\delta$  -12.6 (d, <sup>2</sup>J<sub>FPt</sub> = 800, <sup>3</sup>J<sub>FP</sub> = 58 Hz). IR (KBr):  $\nu$ (CN) 2178 (s) cm<sup>-1</sup>;  $\nu$ (PtD) 1459 (m) cm<sup>-1</sup>.

**PtH(CF<sub>3</sub>)(PPh<sub>3</sub>)[C(NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>)NHR] (1).** To a solution of PtH(CF<sub>3</sub>)(CNR)(PPh<sub>3</sub>) (660 mg, 1.0 mmol) in THF (20 mL) was added azetidine (81  $\mu$ L, 1.2 mmol) and the reaction mixture stirred at 0 °C for 0.5 h to give a clear solution. The stirring was then continued while the temperature of the bath was allowed to rise slowly to room temperature. After 12 h an IR spectrum of the solution did not reveal any band at 2179 cm<sup>-1</sup> due to  $\nu$ (C $\equiv$ N) of the starting isocyanide complex but showed  $\nu$ (C $\equiv$ N) at 1545 cm<sup>-1</sup> of the carbene complex. The stirring was then continued for 5 h. The white precipitate formed during this time was filtered, washed with *n*-hexane (3  $\times$  5 mL), and dried under vacuum. The product was recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/*n*-hexane: yield 660 mg, 92%; mp 188–190 °C dec. Anal. Calcd for PtPF<sub>3</sub>ON<sub>2</sub>C<sub>30</sub>H<sub>30</sub>: C, 50.21; H, 4.21; N, 3.90. Found: C, 50.44; H, 4.22; N, 3.84. <sup>1</sup>H NMR:  $\delta$  -7.15 (ddq, 1 H, PtH, <sup>3</sup>J<sub>HF</sub> = 15.0, <sup>2</sup>J<sub>HP</sub> = 19.0, <sup>4</sup>J<sub>HH</sub> = 3.6, <sup>1</sup>J<sub>HPt</sub> = 896 Hz), 2.27 (m, 1 H, CH), 2.07 (m, 1 H, CH), 4.54 (m, 1 H, NCH), 4.00 (m, 1 H, NCH), 3.84 (m, 1 H, NCH), 3.42 (m, 1 H, NCH), 3.75 (s, 3 H, OCH<sub>3</sub>), 6.47 (d, 1 H, NH, <sup>3</sup>J<sub>HPt</sub> = 53.2, <sup>4</sup>J<sub>HH</sub> = 3.6 Hz). <sup>31</sup>P NMR:  $\delta$  22.10 (q, <sup>3</sup>J<sub>PF</sub> = 56.7, <sup>1</sup>J<sub>PtP</sub> = 2220 Hz). <sup>19</sup>F NMR:  $\delta$  -12.58 (dd, <sup>2</sup>J<sub>FPt</sub> = 797, <sup>3</sup>J<sub>FP</sub> = 56.7, <sup>3</sup>J<sub>FH</sub> = 15.0 Hz). <sup>13</sup>C NMR:  $\delta$  206.82 (dm, <sup>2</sup>J<sub>PC</sub> = 28.0, <sup>1</sup>J<sub>Cpt</sub> = 759 Hz), 157.25–113.89 (phenyl carbons), 55.73 (s, OCH<sub>3</sub>), 54.78 (s, NCH<sub>2</sub> cis to Pt, <sup>3</sup>J<sub>Cpt</sub> = 51.3), 49.92 (s, NCH<sub>2</sub> trans to Pt, <sup>3</sup>J<sub>Cpt</sub> = 24.2 Hz), 15.67 (s, CH<sub>2</sub>), CF<sub>3</sub> insufficiently intense to be observed. IR (Nujol):  $\nu$ (C $\equiv$ N) 1545 (s) cm<sup>-1</sup>;  $\nu$ (NH) 3346 (m) cm<sup>-1</sup>;  $\nu$ (PtH) 2042 (s) cm<sup>-1</sup>.

**PtH(CH<sub>2</sub>CN)(PPh<sub>3</sub>)[C(NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>)NHR] (2).** This compound was prepared as described for **1** by starting from PtH(CH<sub>2</sub>CN)(CNR)(PPh<sub>3</sub>) (1500 mg, 2.38 mmol) and azetidine (193  $\mu$ L, 2.85 mmol) in THF (50 mL). An IR spectrum of the solution recorded after 12 h did not show  $\nu$ (C $\equiv$ N) at 2177 cm<sup>-1</sup> for the starting isocyanide complex but the presence of  $\nu$ (C $\equiv$ N) at 1544 cm<sup>-1</sup> for the carbene derivative. The stirring was prolonged for 5 h. The white precipitate formed was filtered, washed with Et<sub>2</sub>O (3  $\times$  5 mL), and dried under vacuum: yield 1260 mg, 77%; mp 178–180 °C dec. Anal. Calcd for PtPON<sub>2</sub>C<sub>31</sub>H<sub>32</sub>: C, 54.06; H, 4.68; N, 6.10. Found: C, 54.16; H, 4.80; N, 5.99. <sup>1</sup>H NMR:  $\delta$  -7.34 (dd, 1 H, PtH, <sup>2</sup>J<sub>HP</sub> = 20.3, <sup>4</sup>J<sub>HH</sub> = 3.5, <sup>1</sup>J<sub>HPt</sub> = 796 Hz), 2.21 (m, 1 H, CH), 1.96 (m, 1 H, CH), 4.38 (m, 1 H, NCH), 3.88 (m, 2 H, NCH), 3.46 (m, 1 H, NCH), 3.73 (s, 3 H, OCH<sub>3</sub>), 6.64 (d, 1 H, NH, <sup>3</sup>J<sub>HPt</sub> = 55.4, <sup>4</sup>J<sub>HH</sub> = 3.5 Hz), 1.68 (dd, 1 H, CH, <sup>3</sup>J<sub>HP</sub> = 9.6, <sup>2</sup>J<sub>HH</sub> = 15.6, <sup>2</sup>J<sub>HPt</sub> = 91 Hz), 1.95 (dd, 1 H, CH, <sup>3</sup>J<sub>HP</sub> = 8.3, <sup>2</sup>J<sub>HH</sub> = 15.6, <sup>2</sup>J<sub>HPt</sub> = 97 Hz). <sup>31</sup>P NMR:  $\delta$  24.20 (s, <sup>1</sup>J<sub>PtP</sub> = 2682). <sup>13</sup>C NMR:  $\delta$  204.94 (d, satellites insufficiently intense to be observed, <sup>2</sup>J<sub>PC</sub> = 6.4 Hz), 156.9–113.8 (phenyl carbons), 55.72 (s, OCH<sub>3</sub>), 54.74 (s, NCH<sub>2</sub> cis to Pt, <sup>3</sup>J<sub>Cpt</sub> = 50.8 Hz), 50.62 (s, NCH<sub>2</sub> trans to Pt, <sup>3</sup>J<sub>Cpt</sub> = 29.2 Hz), 15.61 (s, CH<sub>2</sub>), CH<sub>2</sub>CN insufficiently intense to be observed. IR (Nujol):  $\nu$ (C $\equiv$ N) 1549 (s) cm<sup>-1</sup>;  $\nu$ (NH) 3267 (m) cm<sup>-1</sup>;  $\nu$ (PtH) 2005 (m) cm<sup>-1</sup>;  $\nu$ (CN) 2192 (s) cm<sup>-1</sup>; MS (FAB; *m/z* relative abundance, %): 688 ([M]<sup>+</sup>, 5), 647 ([M - CH<sub>3</sub>CN]<sup>+</sup>, 15), 386 ([PtON<sub>2</sub>C<sub>11</sub>H<sub>15</sub>]<sup>+</sup>, 20), 191 ([ON<sub>2</sub>C<sub>11</sub>H<sub>15</sub>]<sup>+</sup>, 100).

**PtH(CH<sub>2</sub>CF<sub>3</sub>)(PPh<sub>3</sub>)[C(NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>)NHR] (3).** This compound was prepared as described for **1** by starting from PtH(CH<sub>2</sub>CF<sub>3</sub>)(CNR)(PPh<sub>3</sub>) (703 mg, 1.04 mmol) and azetidine (84  $\mu$ L, 1.25 mmol) in THF (15 mL). An IR spectrum of the solution run after 12 h showed that almost all the starting complex had reacted and the carbene complex had formed, as indicated by the absence of  $\nu$ (C $\equiv$ N) at 2176 cm<sup>-1</sup> and the presence of  $\nu$ (C $\equiv$ N) at 1538 cm<sup>-1</sup>. The brownish solution was then reduced under low pressure to a small volume (5 mL) and a white product



precipitated by adding *n*-hexane (30 mL). The product was filtered, washed with *n*-hexane (3 × 5 mL), and dried under vacuum: yield 600 mg, 82%; mp 168–170 °C dec. Anal. Calcd for  $\text{PtPF}_3\text{ON}_2\text{C}_3\text{H}_3$ : C, 50.89; H, 4.40; N, 3.83. Found: C, 50.80; H, 4.40; N, 3.80.  $^1\text{H}$  NMR:  $\delta$  -7.23 (dd, 1 H, PtH,  $^2J_{\text{HPt}} = 20.7$ ,  $^4J_{\text{HH}} = 2.7$ ,  $^1J_{\text{HPt}} = 825$  Hz), 2.16 (m, 1 H, CH), 1.92 (m, 1 H, CH), 2.03 (dq, 1 H, CH,  $^3J_{\text{HPt}} = 8.5$ ,  $^3J_{\text{HF}} = 16.8$  Hz,  $^{195}\text{Pt}$  satellites masked), 2.07 (dq, 1 H, CH,  $^3J_{\text{HPt}} = 8.3$ ,  $^3J_{\text{HF}} = 16.6$  Hz,  $^{195}\text{Pt}$  satellites masked), 4.24 (m, 1 H, NCH), 3.82 (m, 2 H, NCH), 3.36 (m, 1 H, NCH), 3.73 (s, 3 H,  $\text{OCH}_3$ ), 6.51 (d, 1 H, NH,  $^3J_{\text{HPt}} = 51.4$ ,  $^4J_{\text{HH}} = 2.7$  Hz).  $^{31}\text{P}$  NMR:  $\delta$  25.49 (q,  $^4J_{\text{PF}} = 16.6$ ,  $^1J_{\text{PPt}} = 2506$  Hz).  $^{19}\text{F}$  NMR:  $\delta$  -51.54 (ddq,  $^4J_{\text{FH}} = 2.9$ ,  $^3J_{\text{FPt}} = 210$ ,  $^4J_{\text{FPt}} = 16.6$  Hz).  $^{13}\text{C}$  NMR:  $\delta$  210.07 (d,  $^2J_{\text{PC}} = 50.9$ ,  $^1J_{\text{PC}} = 753$  Hz), 156.6–113.6 (phenyl carbons), 55.72 (s,  $\text{OCH}_3$ ), 54.77 (s,  $\text{NCH}_2$  cis to Pt,  $^3J_{\text{PtC}} = 56.6$  Hz), 50.62 (s,  $\text{NCH}_2$  trans to Pt,  $^3J_{\text{PtC}} = 34.7$  Hz), 15.49 (s,  $\text{CH}_2$ ), 7.69 (dq,  $^2J_{\text{CF}} = 83$ ,  $^2J_{\text{CP}} = 31.2$ ,  $^1J_{\text{CPt}} = 619$  Hz),  $\text{CF}_3$  insufficiently intense to be observed. IR (Nujol):  $\nu(\text{C}=\text{N})$  1525 (s)  $\text{cm}^{-1}$ ;  $\nu(\text{NH})$  3332 (m)  $\text{cm}^{-1}$ ;  $\nu(\text{PtH})$  2004 (m)  $\text{cm}^{-1}$ .

**PtH(CF<sub>3</sub>)(PPh<sub>3</sub>)[C(NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>)NHR] (4).** This compound was prepared as described for 1 by starting from PtH(CF<sub>3</sub>)(CNR)(PPh<sub>3</sub>) (500 mg, 0.75 mmol) and piperidine (90  $\mu\text{L}$ , 0.91 mmol) in THF (15 mL). An IR spectrum of the solution after 12 h showed that almost all the starting complex had reacted and the carbene complex had formed, as indicated by the absence of  $\nu(\text{C}\equiv\text{N})$  at 2179  $\text{cm}^{-1}$  and the presence of  $\nu(\text{C}=\text{N})$  at 1537  $\text{cm}^{-1}$ . The stirring was prolonged for 5 h. The white precipitate formed during this time was filtered, washed with Et<sub>2</sub>O (3 × 5 mL), and dried under vacuum: yield 460 mg, 82%; mp 179–180 °C dec. Anal. Calcd for  $\text{PtPOF}_3\text{N}_2\text{C}_3\text{H}_{34}$ : C, 51.56; H, 4.59; N, 3.76. Found: C, 51.41; H, 4.31; N, 3.36.  $^1\text{H}$  NMR:  $\delta$  -8.03 (ddq, 1 H, PtH,  $^2J_{\text{HPt}} = 22.6$ ,  $^4J_{\text{HH}} = 3.3$ ,  $^3J_{\text{HF}} = 15.1$ ,  $^1J_{\text{HH}} = 888$  Hz), 1.70 (m, 1 H, CH), 1.54 (m, 1 H, CH), 2.93 (m, 1 H, CH), 4.72 (m, 1 H, NCH), 3.84 (m, 1 H, NCH), 3.32 (m, 1 H, NCH), 3.78 (s, 1 H,  $\text{OCH}_3$ ), NH not located.  $^{31}\text{P}$  NMR:  $\delta$  20.90 (q,  $^3J_{\text{PF}} = 56.4$ ,  $^1J_{\text{PPt}} = 2272$  Hz).  $^{19}\text{F}$  NMR:  $\delta$  -11.15 (dd,  $^2J_{\text{FPt}} = 788$ ,  $^3J_{\text{FPt}} = 56.4$  Hz).  $^{13}\text{C}$  NMR:  $\delta$  206.03 (m,  $^1J_{\text{CPt}} = 845$  Hz), 141.19 (dq,  $\text{CF}_3$ ,  $^1J_{\text{CF}} = 346$ ,  $^2J_{\text{CP}} = 167$  Hz,  $^{195}\text{Pt}$  satellites insufficiently intense to be observed), 157.9–102.3 (phenyl carbons), 55.70 (s,  $\text{OCH}_3$ ), 56.31 (s,  $\text{NCH}_2$  cis to Pt,  $^3J_{\text{CPt}} = 63$  Hz), 44.62 (s,  $\text{NCH}_2$  trans to Pt,  $^3J_{\text{CPt}} = 14.0$  Hz), 25.75 (s,  $\text{NCH}_2\text{CH}_2$ ), 24.45 (s,  $\text{CH}_2$ ). IR (Nujol):  $\nu(\text{C}=\text{N})$  1540 (s)  $\text{cm}^{-1}$ ;  $\nu(\text{NH})$  3374 (m)  $\text{cm}^{-1}$ ;  $\nu(\text{PtH})$  2044 (m)  $\text{cm}^{-1}$ .

**PtD(CF<sub>3</sub>)(PPh<sub>3</sub>)[C(NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>)NHR] ((Pt-D)1).** This compound was prepared as described for 1 by starting from PtD(CF<sub>3</sub>)(CNR)(PPh<sub>3</sub>) (500 mg, 0.75 mmol) and azetidine (60  $\mu\text{L}$ , 0.90 mmol) in THF (20 mL): yield 400 mg, 74%; mp 186–188 °C dec. Anal. Calcd for  $\text{PtPF}_3\text{ON}_2\text{C}_{30}\text{DH}_{29}$ : C, 50.14; H, 4.35; N, 3.90. Found: C, 50.34; H, 4.52; N, 3.80.  $^1\text{H}$  NMR:  $\delta$  2.08 (m, 1 H, CH), 2.27 (m, 1 H, CH), 3.42 (m, 1 H, NCH), 3.85 (m, 1 H, NCH), 4.00 (m, 1 H, NCH), 4.45 (m, 1 H, NCH), (s, 3 H,  $\text{OCH}_3$ ), 6.47 (s, 1 H, NH,  $^3J_{\text{HPt}} = 53.3$  Hz).  $^{31}\text{P}$  NMR:  $\delta$  22.5 (q,  $^3J_{\text{PF}} = 57.0$ ,  $^1J_{\text{PPt}} = 2220$  Hz).  $^{19}\text{F}$  NMR:  $\delta$  -12.7 (d,  $^3J_{\text{FPt}} = 57.0$ ,  $^3J_{\text{FPt}} = 798$  Hz). IR (KBr):  $\nu(\text{PtD})$  masked;  $\nu(\text{C}=\text{N})$  1523 (s)  $\text{cm}^{-1}$ ;  $\nu(\text{NH})$  3332 (m)  $\text{cm}^{-1}$ .

**PtD(CH<sub>2</sub>CN)(PPh<sub>3</sub>)[C(NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>)NHR] ((Pt-D)2).** This compound was prepared as described for 2 by starting from PtD(CH<sub>2</sub>CN)(CNR)(PPh<sub>3</sub>) (220 mg, 0.34 mmol) and azetidine (28  $\mu\text{L}$ , 0.42 mmol) in THF (10 mL): yield 180 mg, 73%; mp 176–178 °C dec. Anal. Calcd for  $\text{PtPON}_3\text{C}_{31}\text{DH}_{31}$ : C, 53.99; H, 4.82; N, 6.09. Found: C, 53.88; H, 4.86; N, 5.99.  $^1\text{H}$  NMR:  $\delta$  2.19 (m, 2 H, CH), 4.38 (m, 1 H, NCH), 3.88 (m, 2 H, NCH), 3.47 (m, 1 H, NCH), 1.96 (dd, 1 H, CH,  $^3J_{\text{HPt}} = 9.2$ ,  $^2J_{\text{HH}} = 15.0$ ,  $^2J_{\text{HPt}} = 97$  Hz), 1.69 (dd, 1 H, CH,  $^3J_{\text{HPt}} = 9.5$ ,  $^2J_{\text{HH}} = 15.0$ ,  $^2J_{\text{HPt}} = 99$  Hz), 3.74 (s, 3 H,  $\text{OCH}_3$ ), 6.74 (s, 1 H, NH,  $^3J_{\text{HPt}} = 52.2$  Hz).  $^{31}\text{P}$  NMR:  $\delta$  24.20 (s,  $^1J_{\text{PPt}} = 2687$  Hz). IR (KBr):  $\nu(\text{PtD})$  1462 (s)  $\text{cm}^{-1}$ . IR (Nujol):  $\nu(\text{C}=\text{N})$  1547 (s)  $\text{cm}^{-1}$ ;  $\nu(\text{NH})$  3263 (m)  $\text{cm}^{-1}$ .

**PtD(CH<sub>2</sub>CF<sub>3</sub>)(PPh<sub>3</sub>)[C(NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>)NHR] ((Pt-D)3).** This compound was prepared as described for 3 by starting from PtD(CH<sub>2</sub>CF<sub>3</sub>)(CNR)(PPh<sub>3</sub>) (675 mg, 1.0 mmol) and azetidine (81  $\mu\text{L}$ , 1.2 mmol) in THF (10 mL): yield 540 mg, 74%; mp 175–177 °C. Anal. Calcd for  $\text{PtPF}_3\text{ON}_2\text{C}_{31}\text{DH}_{33}$ : C, 50.82; H, 4.54; N, 3.82. Found: C, 49.98; H, 4.44; N, 3.83.  $^1\text{H}$  NMR:  $\delta$  2.17 (m, 1 H, CH), 1.92 (m, 1 H, CH), 4.25 (m, 1 H, NCH), 3.82 (m, 2 H, NCH), 3.36 (m, 1 H, NCH), 2.03 (dq, 1 H, CH,  $^3J_{\text{HPt}} = 8.6$ ,  $^3J_{\text{HF}} = 16.9$  Hz,  $^{195}\text{Pt}$  satellites masked), 2.06 (dq,  $^3J_{\text{HPt}} = 8.5$ ,  $^3J_{\text{HF}} =$

17 Hz,  $^{195}\text{Pt}$  satellites masked), 3.73 (s, 3 H,  $\text{OCH}_3$ ), 6.55 (s, 1 H, NH,  $^3J_{\text{HPt}}$  masked).  $^{31}\text{P}$  NMR:  $\delta$  25.51 (q,  $^4J_{\text{PF}} = 16.7$ ,  $^1J_{\text{PPt}} = 2507$  Hz).  $^{19}\text{F}$  NMR:  $\delta$  -51.55 (dt,  $^4J_{\text{PF}} = ^3J_{\text{HF}} = 16.7$ ,  $^3J_{\text{FPt}} = 209$  Hz). IR (KBr):  $\nu(\text{PtD})$  1461 (s)  $\text{cm}^{-1}$ ;  $\nu(\text{C}=\text{N})$  1523 (s)  $\text{cm}^{-1}$ ;  $\nu(\text{NH})$  3332 (m)  $\text{cm}^{-1}$ .

**PtH(CF<sub>3</sub>)(PPh<sub>3</sub>)[C(NEt<sub>2</sub>)NHR] (5).** This compound was prepared by starting from PtH(CF<sub>3</sub>)(CNR)(PPh<sub>3</sub>) (500 mg, 0.75 mmol) and diethylamine (1 mL, 9.7 mmol) in THF (20 mL). The reaction mixture was stirred at 50 °C for 3 days. The solution did not reveal any band at 2179  $\text{cm}^{-1}$  due to  $\nu(\text{C}\equiv\text{N})$  of the starting isocyanide complex but showed  $\nu(\text{C}=\text{N})$  at 1533  $\text{cm}^{-1}$  of the carbene derivative. The solution was reduced under reduced pressure to ca. 5 mL and a white product precipitated by adding *n*-hexane (50 mL). The product was filtered, washed with *n*-hexane (3 × 5 mL), and dried under vacuum: yield 500 mg, 92%; mp 158–165 °C dec. Anal. Calcd for  $\text{PtPF}_3\text{ON}_2\text{C}_{31}\text{H}_{32}$ : C, 50.75; H, 4.67; N, 3.82. Found: C, 50.59; H, 4.53; N, 3.79.  $^1\text{H}$  NMR:  $\delta$  1.12 (m, 4 H, CH), 1.32 (m, 2 H, CH), 3.23 (m, 2 H, NCH), 4.08 (m, 1 H, NCH), 4.41 (m, 1 H, NCH), NH not located. Data for **5a** are as follows.  $^1\text{H}$  NMR:  $\delta$  -8.06 (ddq,  $^1J_{\text{HPt}} = 883$ ,  $^2J_{\text{HPt}} = 22.9$ ,  $^3J_{\text{HF}} = 15.7$ ,  $^4J_{\text{HH}} = 3.4$  Hz), 3.78 (s,  $\text{OCH}_3$ ).  $^{31}\text{P}$  NMR:  $\delta$  20.27 (q,  $^3J_{\text{PF}} = 56.3$ ,  $^1J_{\text{PPt}} = 2272$  Hz).  $^{19}\text{F}$  NMR:  $\delta$  -11.67 (dd,  $^3J_{\text{HF}} = 15.7$ ,  $^3J_{\text{FPt}} = 56.3$ ,  $^2J_{\text{FPt}} = 790$  Hz). Data for **5b** are as follows.  $^1\text{H}$  NMR:  $\delta$  -8.87 (dq,  $^3J_{\text{HF}} = 25.6$ ,  $^2J_{\text{HPt}} = 25.8$ ,  $^1J_{\text{HPt}} = 711$  Hz).  $^{31}\text{P}$  NMR:  $\delta$  25.29 (q,  $^3J_{\text{PF}} = 7.3$ ,  $^1J_{\text{PPt}} = 2760$  Hz).  $^{19}\text{F}$  NMR:  $\delta$  -16.77 (dd,  $^3J_{\text{PF}} = 7.3$ ,  $^3J_{\text{HF}} = 25.6$ ,  $^2J_{\text{FPt}} = 476$  Hz). Data for **5c** are as follows.  $^1\text{H}$  NMR:  $\delta$  -5.12 (dq,  $^3J_{\text{HF}} = 16.6$ ,  $^2J_{\text{HPt}} = 184$ ,  $^1J_{\text{HPt}} = 1223$  Hz).  $^{19}\text{F}$  NMR:  $\delta$  -8.14 (dd,  $^2J_{\text{FPt}} = 684$ ,  $^3J_{\text{FPt}} = 12.9$ ,  $^3J_{\text{HF}} = 16.6$  Hz). IR (Nujol):  $\nu(\text{C}=\text{N})$  1532 (m)  $\text{cm}^{-1}$ ;  $\nu(\text{NH})$  3378 (m), 3351 (m)  $\text{cm}^{-1}$ ;  $\nu(\text{PtH})$  2046 (m), and 2020 (m)  $\text{cm}^{-1}$ .

**Reaction of 2 and (Pt-D)2 with PPh<sub>3</sub>.** To a suspension of 2 (689 mg, 1 mmol) was added PPh<sub>3</sub> (262 mg, 1 mmol) in THF (20 mL) at room temperature. The reaction was followed by IR and  $^1\text{H}$  NMR spectroscopies. The IR spectrum revealed the disappearance of the bands at 1544 and 2014  $\text{cm}^{-1}$  due to  $\nu(\text{C}=\text{N})$  and  $\nu(\text{PtH})$ , respectively, of the starting complex and formation of the corresponding bands at 1600 and 1952  $\text{cm}^{-1}$  of the final hydrido derivative. The formation of  $\text{CH}_3\text{CN}$  as the only organic product was confirmed by IR ( $\nu(\text{C}\equiv\text{N})$  2252  $\text{cm}^{-1}$ ), GC/MS, and  $^1\text{H}$  NMR spectroscopy ( $\delta$  1.97,  $\text{CH}_3$ ). After 24 h the yellow solution was reduced to ca. 5 mL, and when Et<sub>2</sub>O was added (30 mL), the yellow compound *trans*-(PPh<sub>3</sub>)<sub>2</sub>PtH[C(NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>)NR] (**6**) precipitated. It was filtered, washed with Et<sub>2</sub>O (3 × 5 mL), and recrystallized from C<sub>6</sub>H<sub>6</sub>/*n*-hexane: yield 670 mg, 74%; mp 169–171 °C dec. Anal. Calcd for  $\text{PtP}_2\text{ON}_2\text{C}_{47}\text{H}_{44}$ : C, 62.04; H, 4.87; N, 3.08. Found: C, 62.13; H, 4.92; N, 3.00.  $^1\text{H}$  NMR:  $\delta$  -6.16 (t, 1 H, PtH,  $^2J_{\text{HPt}} = 18.6$ ,  $^1J_{\text{HPt}} = 620$  Hz), 1.58 (Q, 2 H,  $\text{CH}_2$ ,  $^3J_{\text{HH}} = 15.3$  Hz), 3.51 (t, 4 H, NCH<sub>2</sub>,  $^3J_{\text{HH}} = 15.3$  Hz), 3.66 (s, 3 H,  $\text{OCH}_3$ ).  $^{31}\text{P}$  NMR:  $\delta$  24.80 (s,  $^1J_{\text{PPt}} = 3037$  Hz). IR (Nujol):  $\nu(\text{PtH})$  1971 (s)  $\text{cm}^{-1}$ ;  $\nu(\text{C}=\text{N})$  masked. The reaction of (Pt-D)2 with PPh<sub>3</sub> was performed similarly to that of 2. The compound (Pt-D)6 was recovered in 72% (660 mg) yield; mp 170–172 °C. Anal. Calcd for  $\text{PtP}_2\text{ON}_2\text{C}_{47}\text{DH}_{43}$ : C, 62.04; H, 4.87; N, 3.08. Found: C, 62.02; H, 4.90; N, 3.08.  $^1\text{H}$  NMR:  $\delta$  1.60 (Q, 2 H,  $\text{CH}_2$ ), 3.55 (t, 4 H, NCH<sub>2</sub>), 3.66 (s, 3 H,  $\text{OCH}_3$ ).  $^{31}\text{P}$  NMR:  $\delta$  26.00 (s,  $^1J_{\text{PPt}} = 2235$  Hz). IR (KBr):  $\nu(\text{PtD})$  and  $\nu(\text{C}=\text{N})$  masked.

**Reaction of 3 and (Pt-D)3 with PPh<sub>3</sub>.** These reactions were performed as described for 2, and they were followed by  $^{19}\text{F}$  NMR spectroscopy in order to observe the formation of  $\text{CH}_3\text{CF}_3$  ( $\delta$  -59.40, q,  $^3J_{\text{HF}} = 12.7$  Hz). Again, these reactions lead to the formation of **6** and (Pt-D)6, respectively.

**Reaction of 2 with PPh<sub>3</sub> in EtOD.** To a suspension of 2 (150 mg, 0.22 mmol) in THF (10 mL) and EtOD (1 mL) was added PPh<sub>3</sub> (57 mg, 0.22 mmol). The reaction was followed by  $^1\text{H}$  NMR spectroscopy to observe the formation of  $\text{DCH}_2\text{CN}$  ( $\delta$  1.94; 1:1:1 triplet,  $^2J_{\text{HD}} = 2.5$  Hz). The reaction was complete in 24 h.

In a separate experiment the (N-D)2 compound was isolated from the reaction of 2 with EtOD (3 mL) in Et<sub>2</sub>O (10 mL) for 12 h. The IR spectrum of this compound in a Nujol mull showed the partial H/D exchange as confirmed by the presence of the band at 2396  $\text{cm}^{-1}$  due to  $\nu(\text{ND})$  and the band at 3267  $\text{cm}^{-1}$  due to  $\nu(\text{NH})$  of the starting material. The reaction of (N-D)2 with PPh<sub>3</sub> was followed by  $^1\text{H}$  NMR spectroscopy, showing the formation of  $\text{DCH}_2\text{CN}$  together with  $\text{CH}_3\text{CN}$ .

**Reaction of 3 with  $\text{PPh}_3$  in EtOD.** This reaction was performed as described for 2 and leads to the formation of  $\text{CD}_2\text{HCF}_3$ , which was identified by  $^{19}\text{F}$  NMR spectroscopy ( $\delta$  -59.61, tt,  $^2J_{\text{HF}} = 1.8$ ,  $^3J_{\text{HF}} = 12.8$  Hz).

**Reaction of 6 with  $\text{HBF}_4$ .** To a suspension of 6 (100 mg, 0.11 mmol) in  $\text{Et}_2\text{O}$  (10 mL) was added an ethereal solution (ca. 6 M) of  $\text{HBF}_4$  (0.1 mL, 6.0 mmol) and the reaction mixture stirred for 2 h. The complex  $\text{trans}\{-[\text{PPh}_3]_2\text{Pt}[\text{C}(\text{NCH}_2\text{CH}_2\text{CH}_2)\text{NHR}]\}-\text{BF}_4$  (7) was filtered, washed with  $\text{Et}_2\text{O}$  ( $3 \times 5$  mL), and dried under vacuum: yield 106 mg (96%); mp 239–241 °C. Anal. Calcd for  $\text{PtP}_2\text{F}_4\text{ON}_2\text{C}_{47}\text{H}_{45}$ : C, 56.58; H, 4.55; N, 2.81. Found: C, 56.38; H, 4.62; N, 2.90.  $^1\text{H}$  NMR:  $\delta$  -6.97 (td, 1 H, PtH,  $^2J_{\text{PH}} = 14.5$ ,  $^4J_{\text{HH}} = 3.3$ ,  $^1J_{\text{HPt}} = 645$  Hz), 1.69 (m, 2 H,  $\text{CH}_2$ ), 3.51 (m, 4 H, NCH), 3.69 (s, 3 H,  $\text{OCH}_3$ ), NH not located.  $^{31}\text{P}$  NMR:  $\delta$  24.18 (s,  $^1J_{\text{PPt}} = 2902$  Hz).  $^{13}\text{C}$  NMR:  $\delta$  204.03 (t, PtC,  $^2J_{\text{PC}} = 8.0$ ,  $^1J_{\text{CPt}} = 823$  Hz), 157.55–113.80 (phenyl carbons), 55.67 (s,  $\text{OCH}_3$ ), 54.38 (s, NCH<sub>2</sub> cis to Pt,  $^3J_{\text{PtC}} = 47.8$  Hz), 51.33 (s, NCH<sub>2</sub> trans to Pt,  $^3J_{\text{PtC}} = 28.2$  Hz), 15.31 (s,  $\text{CH}_2$ ). IR (Nujol):  $\nu(\text{C}=\text{N})$  1553 (s)  $\text{cm}^{-1}$ ;  $\nu(\text{NH})$  3305 (m)  $\text{cm}^{-1}$ ;  $\nu(\text{PtH})$  2038 (m)  $\text{cm}^{-1}$ .

**Reaction of 1 and (Pt-D)1 with Diphosphines.** A suspension of 1 (415 mg, 0.58 mmol) in THF (20 mL) was treated with  $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$  (230 mg, 0.58 mmol) to give a clear solution. The IR spectrum of the reaction mixture showed the disappearance of the band at 1545  $\text{cm}^{-1}$  of 1 and the formation of a band at 1628  $\text{cm}^{-1}$  due to the organic formamidine  $\text{HC}(\text{NCH}_2\text{CH}_2\text{CH}_2)=\text{N(R)}$ . The solution was analyzed by GC/MS (retention time of the formamidine 5 min;  $m/z$  190  $[\text{M}]^{+}$ ). After 2 h the solution mixture was reduced to 5 mL and *n*-hexane (39 mL) was added. A white product precipitated, which was identified as  $\text{PtH}(\text{CF}_3)(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)^{6c}$ . The mother liquors were reduced to a small volume and cooled at -10 °C. After 24 h, white

crystals of  $\text{HC}(\text{NCH}_2\text{CH}_2\text{CH}_2)=\text{N(R)}$  were formed, which were filtered and dried under vacuum; yield 100 mg (91%). Anal. Calcd for  $\text{ON}_2\text{C}_{11}\text{H}_{14}$ : C, 69.45; H, 7.42; N, 14.73. Found: C, 70.42; H, 7.28; N, 14.68.  $^1\text{H}$  NMR:  $\delta$  2.38 (q, 2 H,  $\text{CH}_2$ ,  $^3J_{\text{HH}} = 7.7$  Hz), 4.05 (t, 4 H, NCH<sub>2</sub>), 3.74 (s, 3 H,  $\text{OCH}_3$ ), 7.43 (s, 1 H, CH).  $^{13}\text{C}$  NMR:  $\delta$  151.80 (CH), 155.98, 145.61, 121.72, 114.57 ( $\text{C}_6\text{H}_4$ ), 55.76 ( $\text{OCH}_3$ ), 50.16 (NCH<sub>2</sub>), 17.65 ( $\text{CH}_2$ ). MS:  $m/z$  190 ( $[\text{M}]^{+}$ , relative abundance 100%), 175 ( $[\text{M} - \text{CH}_3]^+$ , 42%), 143 ( $[\text{ON}_2\text{C}_{10}\text{H}_{11}]^{+}$ , 75%), 108 ( $[\text{C}_6\text{H}_5\text{OCH}_3]^+$ , 26%), 77 ( $[\text{C}_6\text{H}_5]^+$ , 34%). IR (Nujol):  $\nu(\text{C}=\text{N})$  1618  $\text{cm}^{-1}$ . The same reaction was performed by treating 1 with an equimolar amount of  $\text{Ph}_2\text{PCH}=\text{CHPPh}_2$ . Again, the IR spectrum of the reaction mixture showed the appearance of the band at 1628  $\text{cm}^{-1}$  due to the free formamidine. The reaction is completed in 10 days. After this time the solution was worked up as described above for the dipos reaction to give  $\text{PtH}(\text{CF}_3)(\text{Ph}_2\text{PCH}=\text{CHPPh}_2)^{6c}$  and the formamidine. In a separate experiment 1 was treated with  $\text{Ph}_2\text{PCH}=\text{CHPPh}_2$  in THF/EtOD (10 mL/2 mL). As described above, the D-C formamidine  $\text{DC}(\text{NCH}_2\text{CH}_2\text{CH}_2)=\text{N(R)}$  was recovered. MS:  $m/z$  191 ( $[\text{M}]^{+}$ , 100%), 176 ( $[\text{M} - \text{CH}_3]^+$ , 42%), 135 ( $[\text{ON}_2\text{C}_{10}\text{DH}_9]^+$ , 75%). To a suspension of (Pt-D)1 (250 mg, 0.35 mmol) in THF (20 mL) was added  $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$  (150 mg, 0.37 mmol). The reaction mixture was stirred for 3 h to give a clear solution. Then it was taken to dryness, *n*-hexane (5 mL) was added, and the white solid was filtered off, dried under vacuum, and identified as  $\text{PtD}(\text{CF}_3)(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)$ : yield 180 mg, 77%; mp 196–198 °C dec. Anal. Calcd for  $\text{PtP}_2\text{F}_3\text{C}_{27}\text{DH}_{24}$ : C, 48.80; H, 3.94. Found: C, 48.91; H, 3.88.  $^{31}\text{P}$  NMR:  $\delta$  P trans to  $\text{CF}_3$  48.2 (dq,  $^3J_{\text{PF}} = 58$ ,  $^2J_{\text{PD}} = 1.8$ ,  $^1J_{\text{PPt}} = 1958$  Hz), P trans to D 49.2 (dq,  $^3J_{\text{PF}} = 14.6$ ,  $^2J_{\text{PD}} = 28.0$ ,  $^1J_{\text{PPt}} = 1803$  Hz).  $^{19}\text{F}$  NMR:  $\delta$  -10.7 (ddd,  $^3J_{\text{FD}} = 1.5$ ,  $^3J_{\text{PF}} = 58$ ,  $^2J_{\text{PF}} = 14.6$ ,  $^2J_{\text{FPt}} = 759$  Hz). IR (KBr):  $\nu(\text{PtD})$  1456 (m)  $\text{cm}^{-1}$ .

**Reaction of 4 with Diphosphines.** A suspension of 4 (375 mg, 0.5 mmol) in THF (20 mL) was treated with  $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$  (200 mg, 0.5 mmol) at room temperature for 2 h. This resulted in a colorless solution. The IR spectrum of the reaction mixture showed the appearance of the band at 1629  $\text{cm}^{-1}$  due to the free formamidine  $\text{HC}(\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_2)=\text{N(R)}$ . The solution mixture was analyzed by GC/MS (retention time of the formamidine 19 min;  $m/z$  218,  $[\text{M}]^{+}$ ). A white precipitate was recovered by addition of *n*-hexane (30 mL) and identified as  $\text{PtH}(\text{CF}_3)(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)^{6c}$ . Organic form-

amidine was isolated as white crystals from concentrated mother liquors kept at -10 °C for 24 h; yield 95 mg (87%). Anal. Calcd for  $\text{ON}_2\text{C}_{13}\text{H}_{16}$ : C, 71.53; H, 8.31; N, 12.83. Found: C, 70.80; H, 8.29; N, 12.90.  $^1\text{H}$  NMR:  $\delta$  1.62 (m, 4 H,  $\text{CH}_2$ ), 1.26 (m, 2 H,  $\text{CH}_2$ ), 3.39 (m, 4 H, NCH<sub>2</sub>), 3.74 (s, 3 H,  $\text{OCH}_3$ ), 7.46 (s, 1 H, CH).  $^{13}\text{C}$  NMR:  $\delta$  152.44 (s, CH), 155.70, 146.17, 121.69, 114.57 ( $\text{C}_6\text{H}_4$ ), 55.72 (s,  $\text{OCH}_3$ ), 53.22 (s, NCH<sub>2</sub>), 25.16 (s,  $\text{CH}_2$ ). IR (Nujol):  $\nu(\text{C}=\text{N})$  1628 (s)  $\text{cm}^{-1}$ . MS:  $m/z$  218 ( $[\text{M}]^{+}$ , relative abundance 100%), 190 ( $[\text{M} - \text{C}_2\text{H}_4]^+$ , 55%), 84 ( $[\text{C}_5\text{H}_{10}\text{N}]^+$ , 75%). The same reaction carried out between 4 and an equimolar amount of  $\text{Ph}_2\text{PCH}=\text{CHPPh}_2$  under the same experimental conditions reported above for diphos leads to the formation of the free formamidine  $\text{HC}(\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_2)=\text{N(R)}$  and  $\text{PtH}(\text{CF}_3)(\text{Ph}_2\text{PCH}=\text{CHPPh}_2)^{6c}$  in a period of 10 days.

**Reactions of 2 with Diphosphines.** To a suspension of 2 (257 mg, 0.37 mmol) in THF (20 mL) was added  $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$  (151 mg, 0.38 mmol). After 2 h a pale yellow solution was obtained, which did not show the  $\nu(\text{C}=\text{N})$  band of the  $\text{Pt}-\text{CH}_2\text{CN}$  group at 2193  $\text{cm}^{-1}$ , while it showed the absorption of free  $\text{CH}_3\text{CN}$  at 2252  $\text{cm}^{-1}$ . It was concentrated under reduced pressure to ca. 10 mL and *n*-heptane (30 mL) added. The pale yellow solid that formed was filtered and dried under vacuum.

It was identified as  $(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)\text{PtH}[\text{C}(\text{NCH}_2\text{CH}_2\text{CH}_2)\text{NR}]$  (8): yield 490 mg (87%); mp 168–170 °C dec. Anal. Calcd for  $\text{PtP}_2\text{ON}_2\text{C}_{37}\text{H}_{36}$ : C, 56.70; H, 4.89; N, 3.57. Found: C, 56.62; H, 4.93; N, 3.48.  $^1\text{H}$  NMR:  $\delta$  -2.39 (dd, 1 H, PtH,  $^2J_{\text{HPt(trans)}} = 179$ ,  $^2J_{\text{HPt(cis)}} = 14.8$ ,  $^1J_{\text{HPt}} = 1212$  Hz), 1.70 (m, 2 H, CH), 2.17 (m, 2 H, PCH), 2.55 (m, 2 H, PCH), 3.85 (m, 4 H, NCH<sub>2</sub>), 3.75 (s, 3 H,  $\text{OCH}_3$ ).  $^{31}\text{P}$  NMR:  $\delta$  47.95 (d,  $^1J_{\text{PPt}} = 1720$ , P trans to H,  $^2J_{\text{PP}} = 5.0$  Hz), 48.76 (d,  $^1J_{\text{PPt}} = 2354$ , P trans to carbene group,  $^2J_{\text{HH}} = 5.0$  Hz).  $^{13}\text{C}$  NMR:  $\delta$  185.00 (d, PtC,  $^1J_{\text{PtC}} = 845$ ,  $^2J_{\text{CP(cis)}} = 28.8$ ,  $^2J_{\text{CP(trans)}} = 97$  Hz), 154.6–113.49 (phenyl carbons), 55.61 (s,  $\text{OCH}_3$ ), 51.78 (s, NCH<sub>2</sub>,  $^3J_{\text{PtC}} = 65.3$  Hz), 17.05 ( $\text{CH}_2$ ), 26.12 and 26.91 ( $\text{PCH}_2$ ). IR (Nujol):  $\nu(\text{PtH})$  1982 (m)  $\text{cm}^{-1}$ ;  $\nu(\text{C}=\text{N})$  1499 (s)  $\text{cm}^{-1}$ . The complex  $(\text{Ph}_2\text{PCH}=\text{CHPPh}_2)\text{PtH}[\text{C}(\text{NCH}_2\text{CH}_2\text{CH}_2)\text{NR}]$  (9) was obtained as described for 8 by starting from 2 (257 mg, 0.37 mmol) and  $\text{Ph}_2\text{PCH}=\text{CHPPh}_2$  (150 mg, 0.38 mmol): yield 231 mg (80%); mp 189–190 °C dec. Anal. Calcd for  $\text{PtP}_2\text{ON}_2\text{C}_{37}\text{H}_{36}$ : C, 56.77; H, 4.76; N, 3.54. Found: C, 56.70; H, 4.78; N, 3.50.  $^1\text{H}$  NMR:  $\delta$  -2.28 (dd,  $^2J_{\text{HPt(trans)}} = 185$ ,  $^2J_{\text{HPt(cis)}} = 15.8$ ,  $^1J_{\text{HPt}} = 1241$  Hz), 1.82 (m, 2 H, CH), 3.70 (m, 4 H, NCH<sub>2</sub>), 3.71 (s, 3 H,  $\text{OCH}_3$ ), 6.42 (m, 1 H, PCH), 6.44 (m, 1 H, PCH).  $^{31}\text{P}$  NMR:  $\delta$  58.04 (d,  $^2J_{\text{PP}} = 11.4$ ,  $^1J_{\text{PPt}} = 1810$ ,  $^2J_{\text{PP}} = 11.4$  Hz, P trans to H), 60.31 (d,  $^1J_{\text{PPt}} = 1955$  Hz, P trans to carbene group). IR (Nujol):  $\nu(\text{PtH})$  2007 (m)  $\text{cm}^{-1}$ ;  $\nu(\text{C}=\text{N})$  1510 (s)  $\text{cm}^{-1}$ .

**Reaction of 8 and 9 with  $\text{HBF}_4$ .** These reactions were carried out by analogous procedures, which we describe for 8. Compound 8 (190 mg, 0.24 mmol) was suspended in dry  $\text{Et}_2\text{O}$  (20 mL) and treated with an ethereal solution (ca. 6 M) of  $\text{HBF}_4$  (0.2 mL, 12 mmol). After the mixture was stirred for 2 h, the complex  $\{(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)\text{PtH}[\text{C}(\text{NCH}_2\text{CH}_2\text{CH}_2)\text{NHR}]\text{BF}_4\}$  (10) was isolated as a white solid, which was filtered off and washed with  $\text{Et}_2\text{O}$  ( $3 \times 5$  mL): yield 180 mg (86%); mp 180–181 °C dec. Anal. Calcd for  $\text{PtP}_2\text{F}_4\text{ON}_2\text{C}_{37}\text{BH}_{36}$ : C, 50.99; H, 4.51; N, 3.21. Found: C, 49.99; H, 4.50; N, 3.23.  $^1\text{H}$  NMR:  $\delta$  -1.53 (dd,  $^2J_{\text{HPt(trans)}} = 172$ ,  $^2J_{\text{HPt(cis)}} = 12.8$ ,  $^1J_{\text{HPt}} = 1134$  Hz), 1 H, PtH), 1.58 (m, 2 H,  $\text{CH}_2$ ), 2.80 (m, 2 H, PCH), 2.19 (m, 2 H, PCH), 3.78 (s, 3 H,  $\text{OCH}_3$ ), 3.44 (m, 1 H, NCH), 3.97 (m, 1 H, NCH), 4.12 (m, 2 H, NCH), 8.16 (d, 1 H, NH,  $^4J_{\text{HP}} = 9.4$ ,  $^3J_{\text{HPt}} = 74.5$  Hz).  $^{31}\text{P}$  NMR:  $\delta$  47.92 (P trans to H, d,  $^2J_{\text{PP}} = 5.7$ ,  $^1J_{\text{PPt}} = 1720$  Hz),  $\delta$  49.60 (P trans to carbene group, d,  $^1J_{\text{PPt}} = 2351$ ,  $^2J_{\text{PP}} = 5.7$  Hz).  $^{13}\text{C}$  NMR:  $\delta$  15.90 ( $\text{CH}_2$ ), 26.58 and 28.43 ( $\text{PCH}_2$ ), 52.32 and 55.09 (NCH<sub>2</sub>), 55.79 ( $\text{OCH}_3$ ), 114.12–158.00 (phenyl carbons), 194.51 (dd, PtC,  $^2J_{\text{CP(cis)}} = 8.0$ ,  $^2J_{\text{CP(trans)}} = 115$ ,  $^1J_{\text{PtC}} = 1134$  Hz). IR (Nujol):  $\nu(\text{PtH})$  1976 (s)  $\text{cm}^{-1}$ ;  $\nu(\text{C}=\text{N})$  1552 (s)  $\text{cm}^{-1}$ ;  $\nu(\text{NH})$  3302 (m)  $\text{cm}^{-1}$ . The

complex  $\{(\text{Ph}_2\text{PCH}=\text{CHPPh}_2)\text{PtH}[\text{C}(\text{NCH}_2\text{CH}_2\text{CH}_2)\text{NHR}]\text{BF}_4\}$  (11) was isolated in 88% yield (182 mg); mp 155–156 °C dec. Anal. Calcd for  $\text{PtP}_2\text{F}_4\text{ON}_2\text{C}_{37}\text{BH}_{37}$ : C, 51.09; H, 4.25; N, 3.22. Found: C, 50.99; H, 4.30; N, 3.21.  $^1\text{H}$  NMR:  $\delta$  -2.86 (dd, 1 H, PtH,  $^2J_{\text{HPt(cis)}} = 13.2$ ,  $^2J_{\text{HPt(trans)}} = 164$ ,  $^1J_{\text{HPt}} = 1152$  Hz), 1.84 (m, 1 H, CH), 2.12 (m, 1 H, CH), 3.74 (s, 3 H,  $\text{OCH}_3$ ), 4.16 (m, 4 H, NCH<sub>2</sub>), 6.84 (m, 1 H, PCH), 7.10 (m, 1 H, PCH), 8.32 (d, 1 H, NH,  $^4J_{\text{HP}} = 9.3$ ,  $^3J_{\text{HPt}}$

= 74.7 Hz).  $^{31}\text{P}$  NMR:  $\delta$  59.88 (d, P trans to H,  $^2J_{\text{PP}} = 7.4$ ,  $^1J_{\text{PPt}} = 1722$  Hz), 60.60 (d, P trans to carbene,  $^2J_{\text{PP}} = 7.4$ ,  $^1J_{\text{PPt}} = 2236$  Hz). IR (Nujol):  $\nu(\text{PtH})$  2028 (s)  $\text{cm}^{-1}$ ;  $\nu(\text{C}=\text{N})$  1552 (s)  $\text{cm}^{-1}$ ;  $\nu(\text{NH})$  3297 (m)  $\text{cm}^{-1}$ .

**X-ray Structure Analysis of  $\text{C}_{31}\text{H}_{32}\text{N}_3\text{OPPt}$ .** Colorless transparent crystals were grown by slow diffusion of  $\text{CH}_2\text{Cl}_2$  into an *n*-hexane solution at 0 °C. A crystal suitable for X-ray analysis was mounted on a Lindemann capillary in air and then transferred to a Philips PW1100 diffractometer. A summary of the data collection is given in Table III. The  $\pm h, \pm k, \pm l$  reflections were collected. The intensity data were corrected for Lorentz-polarization effects and for absorption on the basis of  $\psi$  scans of four Bragg reflections by following the method of North et al.<sup>36</sup> The 4157 observed reflections with  $I \geq 3\sigma(I)$  were used for the structure solution (Patterson and Fourier methods) and refinement. The hydrogen atom positions were derived from difference maps, except those of the  $\text{CH}_3$  group, which were introduced at calculated positions and were allowed to ride on associated carbon atoms during the least-squares refinement ( $d_{\text{C-H}} = 1.08$  Å and  $U_{\text{iso}} = 0.07$  Å<sup>2</sup>). The non-hydrogen atoms were refined anisotropically, while the hydrogen atoms were refined isotropically. Final  $R$  values were  $R = 0.022$  and  $R_w = 0.022$ . The largest peak in the final difference map ( $0.5 \text{ e}/\text{\AA}^3$ ) was located near the Pt atom position. All calculations were done by using the SHELX 76<sup>37</sup> program package with the atomic scattering factors taken from ref 38.

(36) North, A. C. T.; Phillips, D. C.; Matheus, F. S. *Acta Crystallogr.* 1968, A24, 351.

(37) Sheldrick, C. M. SHELX 76, Program for Crystal Structure Determination; University of Cambridge, Cambridge, England, 1976.

(38) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1975; Vol. 4.

**Acknowledgment.** R.A.M. thanks the Ministero Pubblica Istruzione for financial support.

**Registry No.** 1, 126018-84-6; (Pt-D)1, 126019-00-9; 2, 126018-85-7; (Pt-D)2, 126019-01-0; (N-D)2, 126019-04-3; 3, 126018-86-8; (Pt-D)3, 126019-02-1; 4, 126018-87-9; 5a, 126018-88-0; 5b, 126106-96-5; 5c, 126107-91-3; 6, 125956-34-5; (Pt-D)6, 126019-03-2; 7, 126018-90-4; 8, 126018-91-5; 9, 126018-92-6; 10, 126018-94-8; 11, 126035-25-4; *trans*-PtCl(CH<sub>2</sub>CN)(PPh<sub>3</sub>)<sub>2</sub>, 42481-62-9; *trans*-PtD(CH<sub>2</sub>CN)(PPh<sub>3</sub>)<sub>2</sub>, 126018-95-9; *p*-MeOC<sub>6</sub>H<sub>4</sub>NC, 10349-38-9; *trans*-(PPh<sub>3</sub>)<sub>2</sub>Pt(CF<sub>3</sub>)Br, 64933-32-0; *trans*-PtD(CF<sub>3</sub>)(PPh<sub>3</sub>)<sub>2</sub>, 126018-96-0; *trans*-[(PPh<sub>3</sub>)<sub>2</sub>Pt(CF<sub>3</sub>)-(CH<sub>2</sub>Cl)]BF<sub>4</sub>, 87249-59-0; *cis*-PtH(CH<sub>2</sub>CF<sub>3</sub>)(PPh<sub>3</sub>)<sub>2</sub>, 85319-86-4; PtH(CF<sub>3</sub>)(CNC<sub>6</sub>H<sub>4</sub>-*p*-OMe)(PPh<sub>3</sub>), 125949-93-1; PtH(CH<sub>2</sub>CN)-(CNC<sub>6</sub>H<sub>4</sub>-*p*-OMe)(PPh<sub>3</sub>), 63637-41-2; PtH(CH<sub>2</sub>CF<sub>3</sub>)(CNC<sub>6</sub>H<sub>4</sub>-*p*-OMe)(PPh<sub>3</sub>), 126106-97-6; PtD(CH<sub>2</sub>CN)(CNC<sub>6</sub>H<sub>4</sub>-*p*-OMe)(PPh<sub>3</sub>), 126018-97-1; PtD(CH<sub>2</sub>CF<sub>3</sub>)(CNC<sub>6</sub>H<sub>4</sub>-*p*-OMe)(PPh<sub>3</sub>), 126018-98-2; PtD(CF<sub>3</sub>)(CNC<sub>6</sub>H<sub>4</sub>-*p*-OMe)(PPh<sub>3</sub>), 126018-99-3; *trans*-PtD-(CH<sub>2</sub>CF<sub>3</sub>)(PPh<sub>3</sub>)<sub>2</sub>, 126106-98-7; PtH(CF<sub>3</sub>)(Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>), 125892-79-7; PtH(CF<sub>3</sub>)(Ph<sub>2</sub>PCH=CHPPh<sub>2</sub>), 64933-31-9; PtD-(CF<sub>3</sub>)(Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>), 126019-05-4; NHEt<sub>2</sub>, 109-89-7; CD<sub>2</sub>H-CF<sub>3</sub>, 558-53-2; HC(NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>)=N(C<sub>6</sub>H<sub>4</sub>-*p*-OMe), 126018-82-4; DC(NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>)=N(C<sub>6</sub>H<sub>4</sub>-*p*-OMe), 126018-83-5; HC-(NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>)=N(C<sub>6</sub>H<sub>4</sub>-*p*-OMe), 74530-23-7; azetidine, 503-29-7; piperidine, 110-89-4.

**Supplementary Material Available:** Listings of hydrogen atom coordinates, bond distances and angles, and thermal parameters (4 pages); a list of observed and calculated structure factors (15 pages). Ordering information is given on any current masthead page.

## Syntheses and X-ray Crystal Structures of the Compounds [ArPAs]<sub>2</sub> and [ArPSb]<sub>2</sub> (Ar = 2,4,6-(*t*-Bu)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>). P<sub>2</sub>As<sub>2</sub>- and P<sub>2</sub>Sb<sub>2</sub>-Substituted Analogues of Bicyclo[1.1.0]butane

Peter Jutzi,\*† Udo Meyer,† Sylvia Opiela,† Marilyn M. Olmstead,‡ and Philip P. Power‡

Faculty of Chemistry, University of Bielefeld, Universitätsstrasse, 4800 Bielefeld, FRG, and Department of Chemistry, University of California, Davis, California 95616

Received August 29, 1989

The syntheses and X-ray crystal structures of the new bicyclo compounds [ArPAs]<sub>2</sub>, 1, and [ArPSb]<sub>2</sub>, 2 (Ar = 2,4,6-(*t*-Bu)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>) are reported. Both 1 and 2 represent the first well-characterized examples of their type to be described. They are analogues of the bicyclotetraphosphanes [P<sub>4</sub>N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>, 3, and [P<sub>4</sub>Ar]<sub>2</sub>, 4, which were recently reported. The P<sub>2</sub>As<sub>2</sub> compound 1 adopts a structure similar to those of 3 and 4 with the aryl groups in the exo-exo orientation. In addition the bridgehead As-As bond is somewhat short averaging 2.383 (1) Å. In sharp contrast the P<sub>2</sub>Sb<sub>2</sub> compound 2 adopts the exo,endo configuration with a significantly larger fold angle of 103.2° than those in 1, 3, and 4, which average near 95°. The bridgehead Sb-Sb bond length is 2.723 (1) Å and is also significantly shorter than the sum of the covalent radii for antimony. Crystal data with Mo K $\alpha$  ( $\lambda = 0.71069$  Å) radiation at 130 K are as follows: 1,  $a = 20.777$  (5) Å,  $b = 16.024$  (2) Å,  $c = 25.958$  (4) Å,  $\beta = 100.20$  (1)°,  $Z = 8$ , monoclinic, space group  $P2_1/n$ ,  $R_w = 0.063$ ; 2,  $a = 10.126$  (3) Å,  $b = 13.770$  (3) Å,  $c = 15.250$  (4) Å,  $\alpha = 66.09$  (2)°,  $\beta = 85.97$  (2)°,  $\gamma = 77.71$  (2)°,  $Z = 2$ , triclinic, space group  $P\bar{1}$ ,  $R_w = 0.041$ .

### Introduction

The first heavier main group 5 analogue of bicyclo[1.1.0]butane was reported in 1982 by Niecke and co-workers.<sup>1</sup> This compound, [P<sub>4</sub>N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>, 3, involved the N(SiMe<sub>3</sub>)<sub>2</sub> substituents in a symmetric exo,exo con-

figuration and a folded P<sub>4</sub> arrangement. Perhaps the most interesting feature of the structure was the short P-P bond, 2.129 Å, involving the bridgehead phosphorus atoms. These structural features were later confirmed in the compound [P<sub>4</sub>Ar]<sub>2</sub>,<sup>2</sup> which also had a short P-P bond of

\* University of Bielefeld.

† University of California.

(1) Niecke, E.; Rüger, R.; Krebs, B. *Angew. Chem.* 1982, 94, 553; *Angew. Chem., Int. Ed. Engl.* 1982, 21, 544.