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

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Hydrido alkyl carbene complexes of the type $PtH(R_X)[C(\overline{N(CH_2)_nCH_2})NHR](PPh_3)$ ($n = 2$, $R_X = CF_3$ (**1**), CH_2CN (**2**), CH_2CF_3 (**3**); $n = 4$, $R_X = CF_3$ (**4**); R = *p*-$MeOC_6H_4$) have been prepared by reaction of the parent isocyanide precursors $PtH(R_X)(CNR)(PPh_3)$ with azetidine or piperidine. Complexes **1–4** have cis Pt–H and Pt–R_x bonds with the carbene ligand trans to hydride. They have been characterized by analytical data and their IR and ^1H, ^{19}F, ^{31}P, and ^{13}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 CH_2CN 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–CH_2CN = 2.116 (7) Å, and Pt–P = 2.252 (2) Å. The isocyanide complex $PtH(CF_3)(CNR)(PPh_3)$ reacts with excess $HNEt_2$ in refluxing THF for 3 days to give a mixture of isomers with the carbene ligand trans to hydride (**5a**), PPh_3 (**5b**), or trifluoromethyl (**5c**). Complexes **1–5** are stable in the solid state and in solution, and no reductive elimination of 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 PPh_3 to give *trans*-$(PPh_3)_2PtH[C(\overline{NCH_2CH_2CH_2})NR]$ (**6**) and formation of CH_3CN and CH_3CF_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 PPh_3. Complex **6** reacts with HBF_4 to give the hydrido carbene derivative *trans*-$\{(PPh_3)_2PtH[C(\overline{NCH_2CH_2CH_2})NHR]\}BF_4$ (**7**). Similarly the reactions of **2** with equimolar amounts of diphosphines yield (P-P)$PtH[C(\overline{NCH_2CH_2CH_2})NR]$ (P-P = $Ph_2PCH_2CH_2PPh_2$ (**8**), $Ph_2PCH{=}CHPPh_2$ (**9**)) and CH_3CN. Complexes **8** and **9** react with HBF_4 to produce the cis hydrido carbene derivatives $\{$(P-P)$PtH[C(\overline{NCH_2CH_2CH_2})NHR]\}BF_4$ (**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)$PtH(CF_3)$ and the formamidines $HC(\overline{NCH_2CH_2CH_2}){=}N(R)$ and $HC[\overline{N(CH_2)_4CH_2}]{=}N(R)$, respectively.

Introduction

Hydrido alkyl[1] and carbene[2] complexes of transition metals are important reagents or intermediates in many stoichiometric and catalytic processes. The stabilities and reactivities of Pt(II) hydrido alkyls $PtH(R_H)L_2$ (R_H = alkyl, aryl; L = tertiary phosphine or $^1/_2$ diphosphine) depend markedly on the metal complex geometry and the natures of the R_H and L ligands.[3-5] The increased thermal stability found for $PtH(R_X)L_2$ complexes (R_X = cyanoalkyl, fluoroalkyl; L = monophosphine or $^1/_2$ diphosphine) has been explained by the enhanced Pt–R_X bond strength due to the presence of the electron-withdrawing cyano or fluoro groups in the alkyl chain.[6] The reaction chemistry for

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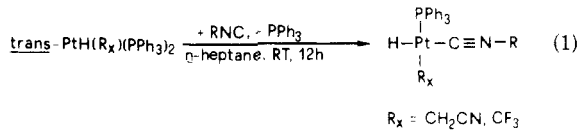
such complexes has been thoroughly investigated and includes (i) insertion of olefins into the Pt–H bond,[6b] (ii) thermal[7] and photolytic[8] reductive eliminations, (iii) reductive elimination by reaction with neutral ligands such as CO, PR_3, diphosphine, diphenylacetylene, and RNC,[9,10] and (iv) reactions with electrophiles such as proton acids,[11,12] halogens,[9] and alkyl halides.[9]

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.[2a,13] 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[14] and neutral[15] 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[14] are also inert toward neutral ligands (PR_3, CO, RNC, pyridine) and $EtO_2CCH{=}CHCO_2Et$, $MeO_2CC{\equiv}CCO_2Me$, and $MeC{\equiv}CMe$ (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[16] and reactions of phosphonium-substituted carbene complexes[17] to give platina heterocycles.[18] 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 $PtH(R_X)(carbene)(PPh_3)$ (R_X = CH_2CN, CH_2CF_3, CF_3; carbene = diaminocarbene ligand) having adjacent Pt–H and Pt–R_X 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_X or Pt–carbene bonds.

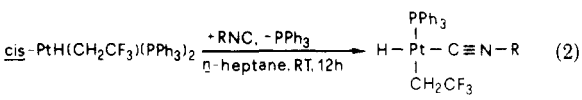
Results and Discussion

Synthesis. The preparation of hydrido alkyl diaminocarbene complexes of platinum(II) reported in this work takes advantage of the reactivity of *trans*-$PtH(R_X)(PPh_3)_2$ (R_X = CH_2CN,[6a] CF_3[6c]) derivatives with isocyanides to afford complexes of the type $PtH(R_X)(CNR)(PPh_3)$,[6c,10] having cis Pt–H and Pt–R_X bonds with the CNR ligand trans to hydride (eq 1) (hereafter R =



(1)

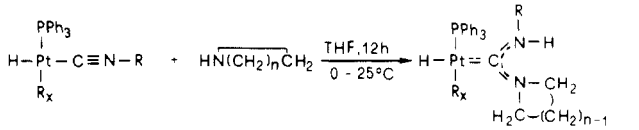
p-$MeOC_6H_4$). Also the reaction of the cis hydrido alkyl complex *cis*-$PtH(CH_2CF_3)(PPh_3)_2$[7] with *p*-$MeOC_6H_4NC$ in *n*-heptane gives an analogous isocyanide derivative (eq 2). For this latter reaction, no reductive elimination of



(2)

CH_3CF_3 is observed, although *cis*-$PtH(CH_2CF_3)(PPh_3)_2$ is known to slowly decompose at room temperature to Pt(0) species in THF and benzene solvents.[7]

The RNC ligand in $PtH(R_X)(CNR)(PPh_3)$ species displays $\nu(C{\equiv}N)$ values in the range 2176–2179 cm^{-1} in THF. The corresponding $\Delta\nu = \nu(C{\equiv}N)_{coord} - \nu(C{\equiv}N)_{free}$ values are in the range 48–51 cm^{-1}, indicating that the isocyanide is less electrophilic than that having chloride as a trans ligand.[19] However, a positive value of $\Delta\nu > 40$ cm^{-1} was previously observed to indicate CNR ligand susceptibility to nucleophilic attack.[20] Thus, the RNC ligand in these hydrido alkyl complexes does not react with aziridine (pK_a = 8.4) to form five-membered cyclic diaminocarbene derivatives[19b] but with stronger nucleophiles such as azetidine (pK_a = 11.29) and piperidine (pK_a = 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.[21]



1: $R_X = CF_3$, n = 2, (92%)
2: $R_X = CH_2CN$, n = 2, (77%)
3: $R_X = CH_2CF_3$, n = 2, (82%)
4: $R_X = CF_3$, n = 4, (82%)

(3)

Compounds **1–4** were characterized by their IR and ^1H and ^{31}P NMR spectra (Table I) and their ^{13}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^{-1} in Nujol mull and 2006–2040 cm^{-1} in THF solvent, which is lower by ca. 40–50 cm^{-1} than those found for cationic hydrido carbene complexes *trans*-$[PtH(carbene)(PPh_3)_2]BF_4$ (carbene = dioxo- or

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

	IR, cm^{-1} [a]			^1H NMR[b]							$^{31}P\{^1H\}$ NMR[c]	
compd	ν(CN)	ν(NH)	ν(PtH)	δ(PtH)	$^1J_{HPt}$	$^2J_{HP}$	$^3J_{HF}$	$^4J_{HH}$	δ(NH)	$^3J_{HPt}$	δ	$^1J_{PPt}$
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 ($^3J_{PF}$ 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 ($^4J_{PF}$ 16.6)
4	1540 s	3374 m	2044 m	−8.03 ddq	888	22.6	15.1	3.3	*d*		20.90 q	2272 ($^3J_{PF}$ 56.4)
5	1532 s	3378 m	2046 m	−8.06 ddq[e]	883	22.9	15.7	3.4	*d*		20.27 q[e]	2272 ($^3J_{PF}$ 56.3)
		3351 m	2020 m	−8.87 dq[f]	711	25.8	25.6		*d*		25.29 q[f]	2760 ($^3J_{PF}$ 7.3)
				−5.12 dq[g]	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[j]					47.95 d[l]	1720 ($^2J_{PP}$ 5.0)
						14.8[k]					48.76 d[m]	2354
9	1510 s		2007 m	−2.28 dd	1241	185[j]					58.04 d[l]	1810 ($^2J_{PP}$ 11.4)
						15.8[k]					60.31 d[m]	1955
10	1552 s	3302 m	1976 s	−1.53 dd	1134	172[j]			8.16 d	74.5	47.92 d[l]	1720 ($^2J_{PP}$ 5.7)
						12.8[k]				($^4J_{HP}$ 9.4)	48.60 d[m]	2351
11	1552 s	3297 m	2028 s	−2.86 dd	1152	164[j]			8.32 d	74.7	59.88 d[l]	1722 ($^2J_{PP}$ 7.4)
						13.2[k]				($^4J_{HP}$ 9.3)	60.60 d[m]	2236

[a] Spectra were recorded as Nujol mulls. ν is given in cm^{-1}. Abbreviations: s = strong; m = medium; w = weak. [b] ^1H NMR spectra were recorded in CD_2Cl_2. Proton chemical shifts are referenced to Me_4Si 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. [c] Spectra were recorded in CD_2Cl_2 with H_3PO_4 external reference. Abbreviations: s = singlet; d = doublet; q = quartet. J is given in Hz. [d] Not located. [e] **5a**. [f] **5b**. [g] **5c**. [h] Insufficiently intense to be observed. [i] Masked. [j] $^2J_{HP(trans)}$. [k] $^2J_{HP(cis)}$. [l] Trans to H. [m] Trans to C.

Table II. Selected $^{13}C\{^1H\}$ NMR Spectral Data for the Complexes[a]

compd	$\delta(C_{carbene})$	$^1J_{CPt}$	$^2J_{CP}$	$\delta(R_X)$
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[d] ($^2J_{CF}$ 83, $^2J_{CP}$ 31.2, $^1J_{CPt}$ 619)
4	206.03 m	845		141.19 dq[e,e] ($^1J_{CF}$ 346, $^2J_{CP}$ 167)
7	204.03 t	823	8.0	
8	185.00 dd	845	28.0[f]	
			97[g]	
10	194.51 dd	1134	8.0[f]	
			115[g]	

[a] Spectra were recorded in CD_2Cl_2. Chemical shifts are referenced to Me_4Si 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. [b] Insufficiently intense to be observed. [c] ^{195}Pt satellites insufficiently intense to be observed. [d] CH_2CF_3. [e] CF_3. [f] $^2J_{CP(cis)}$. [g] $^2J_{CP(trans)}$.

dithiocarbene ligand[12]) and comparable to those found for *trans*-PtH(R)L_2 (R = alkyl, aryl; L = phosphine) complexes.[6] Medium to strong absorptions in the range 1525–1549 cm^{-1} (Nujol) are assigned to ν(C=N) and ν(C—N—H) vibrations of the carbene moiety. The ν(N—H) band appears in the range 3267–3374 cm^{-1} in Nujol mull, as reported for other acyclic Pt(II) diaminocarbenes.[21,22] The stereogeometry of **1–4** can be deduced from their ^1H NMR data. The hydrido resonance falls upfield in the range δ −8.03 to −7.15, as found for several Pt(II) hydrides having a carbene[12] or an alkyl group[6c] 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 ($^3J_{HF}$ = 15.0–15.1 Hz), the phosphorus atom ($^2J_{HP}$ = 19.0–22.6 Hz), and the aminocarbene proton ($^4J_{HH}$ = 2.7–3.6 Hz), as confirmed by H/D exchange with D_2O. 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 $^2J_{HP}$ and $^3J_{HF}$ values are comparable to those found for complexes having cis phosphorus and trifluoromethyl groups.[6c,10] The aminocarbene proton for **1–4** is trans to Pt, as indicated by $^3J_{HPt}$ = 51.4–55.4 Hz.[23] The $^1J_{HPt}$ 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[6c,10] (see also Experimental Section). Thus, on the basis of ^1H NMR data the trans influence of the diaminocarbene group is higher than that of isocyanides and also phosphine[7] ligands but lower than that of alkyl groups as in *trans*-PtH(R)L_2 complexes.[6c] Also ^{19}F and ^{31}P NMR data are consistent with the PPh_3 ligand trans to the alkyl group R_X.[6c] The ^{13}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.[21,24,25] The signal appears as a doublet with ^{195}Pt satellites ($^1J_{PtC}$ = 753–845 Hz) due to coupling with the P atom. For the carbene ligands in **1–4** one 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.[24a] The lower field signal (δ 54.78 for **1**, 54.74 for **2**, 54.77 for **3**, and 56.31 for **4**) can be assigned to the NCH_2 cis to platinum, having a $^3J_{PtCNC}$ value larger (ca. 50 Hz) than that corresponding to NCH_2 trans to platinum (14–34 Hz), which is displayed at higher field (δ 49.92 for **1**, 50.62 for **2**, 50.62 for **3**, and 44.62 for **4**). For the metal-coordinated R_X groups, the signals are in most cases insufficiently intense to be observed. However, they could be detected for CF_3 in **4** (δ 141.19, Table II) and for the methylene carbon of CH_2CF_3 in **3** (δ 7.69).

The reaction of $PtH(CF_3)(CNR)(PPh_3)$ with 1.2 equiv of $HNEt_2$ (pK_a = 10.99) does not proceed in THF at room temperature. However, when the complex is heated with an excess of $HNEt_2$ for 3 days at 50 °C, the mixture of hydrido carbene complexes **5a–c** is formed (eq 4) in ca. 6:3:1 ratio, found by integration of the CF_3 resonances in the ^{19}F NMR spectrum. The species **5a–c** could not be separated, but they could be identified by ^1H and ^{19}F NMR

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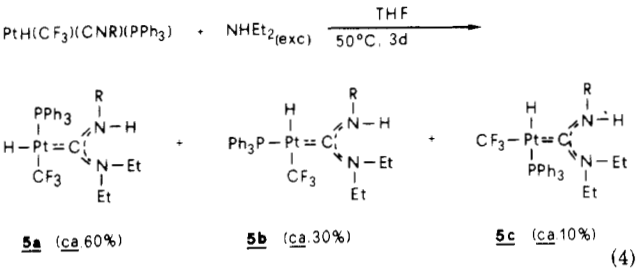


(4)

data (Experimental Section). Complex **5a** shows the Pt–H resonance as a doublet of double quartets at δ −8.06 with $^1J_{PtH}$ = 883 Hz, $^3J_{HF}$ = 15.7 Hz, and $^2J_{HP}$ = 22.9 Hz, similar to those found for **1** and **4**. The Pt–H resonance of **5b** appears as a doublet of quartets at δ −8.87 with $^1J_{PtH}$ = 711 Hz, $^3J_{HF}$ = 25.6 Hz, and $^2J_{HP}$ = 25.8 Hz. These latter values are consistent with a CF_3 group trans to hydride.[6c] For **5c** the Pt–H signal appears as a doublet of quartets at δ −5.12 with $^1J_{PtH}$ = 1223 Hz, $^3J_{HF}$ = 16.6 Hz, and $^2J_{HP}$ = 184 Hz, consistent with a phosphorus atom trans to hydride.[6c]

Description of the Structure of PtH(CH_2CN)[C($\overline{NCH_2CH_2CH_2}$)NH(C_6H_4-*p*-MeO)](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 (Å) 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) Å out of the plane. The Pt–H bond length of 1.61 (4) Å is in the range of the observed Pt–H distances such as 1.72 (9) Å in *trans*-$PtH(CF_3)(PPh_3)_2$,[12a] 1.66 Å in $PtH(SB_9H_{10})(PEt_3)_2$,[26] and 1.78 Å in $PtH(\mu\text{-}SiMe_2)[P(C_6H_{11})_3]_2$.[27] The Pt–C(1)(carbene) bond length of 2.069 (4) Å can be compared with the Pt–C(carbene) distance of *trans*-$\{(Me_2PhP)_2PtMe[C(NMe_2)Me]\}PF_6$[28] (Pt–C(carbene) = 2.079 (13) Å), 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 Å).[29] 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 $\{Cl(PMe_2Ph)(\overline{CH_2CH_2CH_2NH})Pd[C(\overline{NCH_2CH_2CH_2})NH(C_6H_4\text{-}p\text{-}MeO)]\}Cl$.[21] 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[21] 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) Å. The N(1)–C(1)–N(2) angle is here 113.6 (4)° vs 118.6 (5)° in the Pd derivative. However, the higher degree of planarity of the overall ligand in **2** allows a better electron delo-

Table III. Crystal Data

formula	$C_{31}H_{32}N_3OPPt$
mol wt	668.68
cryst dimens, mm	0.12 × 0.20 × 0.22
cryst syst	triclinic
a, Å	12.998 (3)
b, Å	11.833 (2)
c, Å	10.257 (2)
α, deg	100.83 (4)
β, deg	80.72 (3)
γ, deg	114.20 (4)
V, Å^3	1406.0 (3)
space group	$P\bar{1}$
D_{calcd}, g cm^{-3}	1.63
z	2
F(000)	680
radiation (λ, Å)	Mo Kα (0.71069)
μ, cm^{-1}	48.11
no. of rflns measd	5235
scan method	$\theta/2\theta$
scan speed, deg min^{-1}	1.8
scan width, deg	1.2
bkgd counts, s	20
$2\theta_{max}$, deg	50
transmissn coeff	0.62–0.66
σ limit [$I \geq n\sigma(I)$]	3
no. of unique obsd data with $I \geq 3\sigma(I)$	4157
weighting scheme *w*	$1.2154/[\sigma^2(F_o) + 0.000306(F_o^2)]^{-1}$
$R = \sum[\|F_o\| - \|F_c\|]/\sum\|F_o\|$	0.022
$R_w = [\sum w(\|F_o\| - \|F_c\|)^2/\sum w\|F_o\|^2]^{1/2}$	0.022
S	1.15

Table IV. Atomic Coordinates (×10^4) for Non-Hydrogen Atoms and U_{eq} Values (×10^3) with Esd's in Parentheses

atom	*x/a*	*y/b*	*z/c*	U_{eq}, Å^2[a]
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)

[a] U_{eq} = one-third of the trace of the orthogonalized U_{ij} tensor.

(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*; Verlg Chemie: Weinheim, FRG, 1983; p 73.

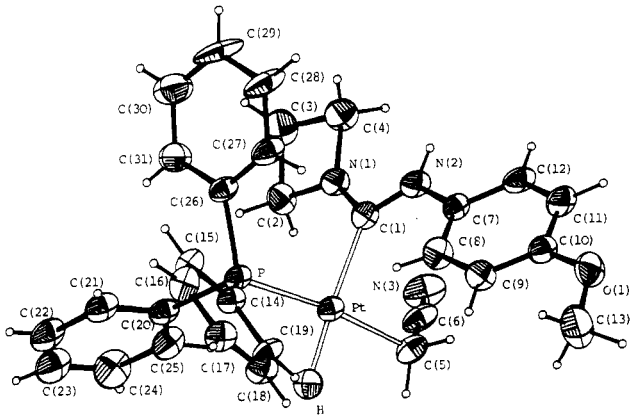


Figure 1. ORTEP plot of $PtH(CH_2CN)[C(\overline{NCH_2CH_2CH_2})NH(C_6H_4\text{-}p\text{-}OMe)](PPh_3)$ (**2**) showing the atom-numbering scheme. The thermal ellipsoids are drawn at the 40% probability level.

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).

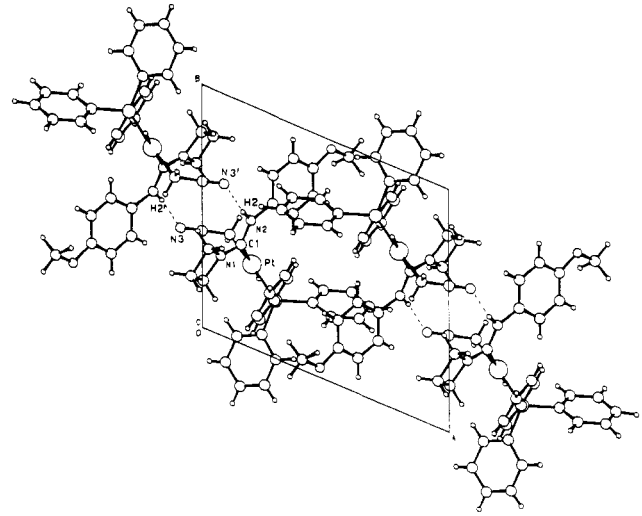
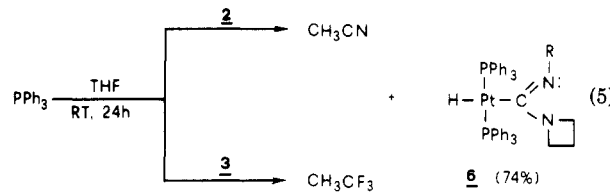


Figure 2. Packing diagram of **2** down the *c* axis, showing the dimer formation.

The Pt-C(5) cyanomethyl bond distance of 2.116 (7) Å is shorter than the Pt-CH_2CN bond length found in *trans*-$PtH(CH_2CN)(PPh_3)_2$[30] (2.15 (1) Å) but longer than that found in *trans*-$PtCl(CH_2CN)(PPh_3)_2$ (2.08 (1) Å).[31] The Pt-C(5)-C(6) angle is 110.8 (0)°, which is larger than the corresponding value found in *trans*-$PtH(CH_2CN)(PPh_3)_2$ (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)′(CH_2CN) 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_3. Complexes **1**-**4** are quite stable in the solid state and in solution. No reductive elimination of HR_X 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*-$PtH(CH_2CF_3)(PPh_3)_2$ undergoes facile 1,1-reductive elimination of CH_3CF_3 at room temperature with formation of Pt(0) species.[7] On the other hand, complexes **2** and **3** are found to react with 1 equivalent of PPh_3 at room temperature to give **6** and HR_X as the only reaction products (eq 5). The hydrido carbene complexes **1** and

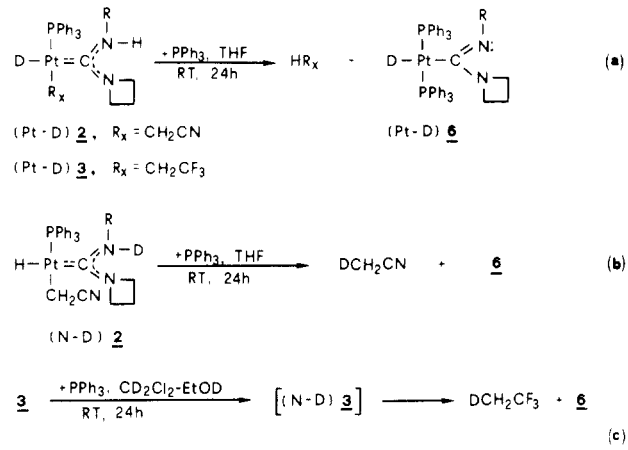


4, having CF_3 as the alkyl ligand, are unreactive toward PPh_3 under the same experimental conditions outlined in eq 5. Compound **6** has been characterized by analytical (Experimental Section) and IR and ^1H and ^{31}P NMR data (Table I). The trans geometry of **6** has been confirmed by its ^1H and ^{31}P NMR spectra. It was not possible to record the ^{13}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

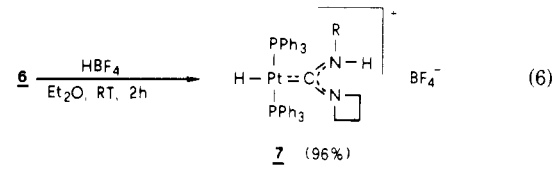


tonates in CD_2Cl_2, probably due to traces of HCl, to afford a compound with ^1H and ^{31}P NMR data similar to those reported for **7** (see below).

The formation of HR_X in reaction 5 is *not* due to a reductive-elimination process involving Pt–H and Pt–R_X bond ruptures. Isotopic experiments with Pt–D and N–D derivatives (Scheme I) indicate instead that what actually occurs is the protonolysis of the Pt–R_X bond by the N–H proton. The deuteride derivatives (Pt-D)**2** and Pt-D)**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 HR_X (R_X = CH_2CN, CH_2CF_3) and the corresponding Pt(II) deuteride (Pt-D)**6** with no cleavage of the Pt–D bond being observed. On the other hand, the deuterated aminocarbene complex (N-D)**2** reacts under analogous conditions with PPh_3 to give **6** and DCH_2CN (reaction b) as confirmed by ^1H NMR data (see Experimental Section). Analogously, the reaction of **3** in CD_2Cl_2–EtOD with PPh_3 (eq c) affords quantitatively DCH_2CF_3, which has been identified by comparison of the ^{19}F NMR data with those reported for the reductive elimination of *cis*-$PtD(CH_2CF_3)(PPh_3)_2$.[7] It is likely that reaction c proceeds initially by N–H/N–D exchange due to the presence of EtOD to give the intermediate (N-D)**3**, which eventually converts to **6** by elimination of DCH_2CF_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 (HBF_4 and HCl) on **2** always leads to the selective cleavage of the Pt–H bond. This experimental evidence agrees with similar reactivity shown by other cis hydrido alkyl complexes of Pt(II)[9] and provides evidence against a mechanism involving N–H dissociation promoted by PPh_3 and subsequent proton attack on the Pt–R_X bond. Conversely, the observed selective cleavage of the Pt–R_X bond might suggest that a possible mechanistic pathway for reaction 5 is a concerted process promoted by PPh_3 involving rupture of both the Pt–R_X and 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 PPh_3, by monitoring of the integration ratios between the CH_3CF_3 formed and the coordinated CH_2CF_3 group in the ^{19}F NMR spectra, indicate that the reaction rate increases with increasing PPh_3 concentration. This would suggest that in the first step PPh_3 coordinates to the metal and then HR_X is eliminated.

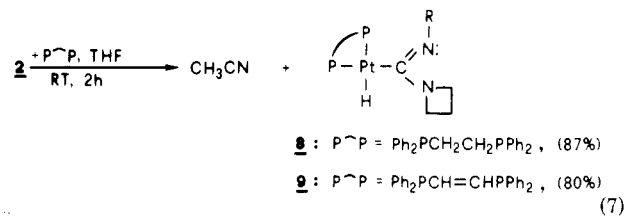
The electrophilicity of the N–H group in aminocarbene complexes of Pt(II) and Pd(II) has been recently demonstrated[16] by some deprotonation reactions with bases to give imino intermediates, whose nitrogen reacts with electrophiles to regenerate carbene complexes. Similarly, the imino nitrogen of **6** is sufficiently basic to react with HBF_4 to yield the diaminocarbene complex **7** (eq 6).



Compound **7** was characterized by its analytical and spectroscopic data (Experimental Section). The ^{13}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}C NMR spectrum of **7** with that of the similar *trans*-{$Br(PPh_3)_2Pt[C(\overline{NCH_2CH_2CH_2})NHR]$}$BF_4$,[21] we observed a shielding of the carbene carbon from the 204.03 ppm value of **7** to 174.90 ppm with an increase of $^1J_{PtC}$ from 823 to 1534 Hz. This effect may be ascribed to the different σ-donor abilities of the trans ligand, as similarly observed for other Pt(II) carbene complexes,[24] and may be interpreted in terms of a higher trans influence of the hydride proton relative to that of bromide.[24a]

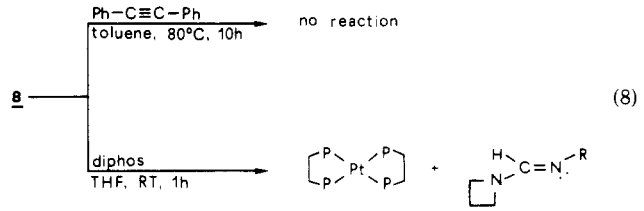
(b) Reactions with Diphosphines. Complexes **1**, **2**, and **4** react with equivalent amounts of $Ph_2PCH_2CH_2PPh_2$ (diphos) or $Ph_2PCH{=}CHPPh_2$ (diphoe) to yield different products according to the nature of the alkyl ligand R_X bound to the metal.

Again, when R_X = CH_2CN, reactions with diphos or diphoe lead to the selective cleavage of the Pt–R_X bond and formation of the cis hydrido imino derivative **8** or **9**, respectively (eq 7). Although isotopic experiments with



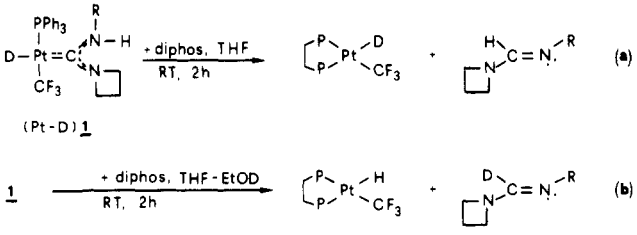
the corresponding Pt–D and N–D derivatives were not carried out, presumably reaction 7 proceeds through coordination of one phosphorus group of the diphosphine, as proposed for similar reactions with PPh_3 (eq 5). Elimination of HR_X and metal chelation of the remaining P atom of the diphosphine lead to **8** and **9**.

Compounds **8** and **9** are stable in the solid state and in solution. No reductive elimination of the formamidine $HC(\overline{CH_2CH_2CH_2N})C{=}N(R)$ is observed upon heating **8** in toluene at 80 °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 $Pt(diphos)_2$[32] and liberation of the organic formamidine $HC(\overline{CH_2CH_2CH_2N})C{=}N(R)$ (eq 8). The stereogeometry of



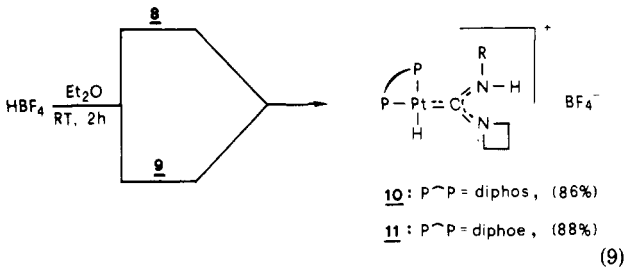
(32) King, R. B.; Kapoor, P. N. *Inorg. Chem.* **1972**, *11*, 1524.

Scheme II



8 and 9 has been deduced from IR and ^1H and ^{31}P NMR (Table I) and ^{13}C NMR (Table II) data. Diagnostic features are the ν(C=N) and ν(PtH) bonds at 1499 and 1510 cm^{-1} and 1982 and 2007 cm^{-1}, respectively. The Pt—H resonances fall at δ −2.39 and −2.28, respectively (doublet of doublets by coupling with trans and cis phosphorus atoms) with $^1J_{PtH}$ = 1212 and 1241 Hz. All these data compare well with the values reported for the similar PtH(CH_2CN)(P-P) derivatives.[6a]

Compounds 8 and 9 react with ethereal HBF_4 to give the cis hydrido carbene derivatives 10 and 11, respectively (eq 9). Compounds 10 and 11 have been identified by

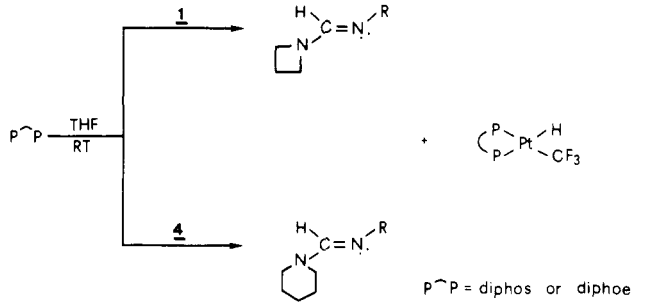


(9)

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

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.[1b] 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.[33]

In contrast to 2 (eq 7) compounds 1 and 4, having 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).[6c] 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



(10)

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,[34a,b] Pd,[34c] and Au[34d-f] 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.[35]

Conclusions

(1) Hydrido alkyl Pt(II) species having cis Pt–H and Pt–R_X (R_X = cyanoalkyl, fluoroalkyl) bonds are stabilized toward thermal reductive elimination by the presence of a metal-coordinated diaminocarbene ligand. Furthermore, the complexes PtH(R_X)(diaminocarbene)(PPh_3) (1–4) do not reductively eliminate by reaction with P-donors.

(2) The results of the reactions of 1–4 with PPh_3 or diphosphines appear to be strongly dependent on the nature of the R_X group. The metal–carbon σ bond in perfluoroalkyl complexes of transition metals is much more thermally stable and more resistant to chemical attack than that of other derivatives.[6c] Thus, P-donors react with 2 and 3, affording the protolysis and elimination of HR_X (R_X = CH_2CN, CH_2CF_3), but with 1 and 4 (R_X = 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 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 CaH_2 (dichloromethane). All other solvents were of reagent grade purity and were used without further purification. ^1H and ^{13}C NMR spectra were recorded at 400 MHz on a Bruker AM-400 spectrometer. $^{31}P\{^1H\}$ and ^{19}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 CD_2Cl_2 at 25 °C. The following ab-

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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 μA). GC conditions were the following: OV1, 25 m × 0.25 mm i.d., column temperature 100–250 °C at 10 °C/min, flow rate 2 mL/min, He, 0.5-μL samples of the reaction mixtures. Melting points (uncorrected) were determinated 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*-$MeOC_6H_4$.

Starting Complexes. The complexes *trans*-$PtH(R_X)(PPh_3)_2$ (R_X = CH_2CN,[6a] CF_3[6c]), *cis*-$PtX(CH_2CF_3)(PPh_3)_2$ (X = H, D),[7] and $PtH(R_X)(CNR)(PPh_3)$ (R_X = CH_2CN,[10] CF_3[6c]) were prepared according to literature procedures. The following complexes are new.

***trans*-PtD(CH_2CN)(PPh_3)$_2$.** A suspension of *trans*-$PtCl(CH_2CN)(PPh_3)_2$ (795 mg, 1.00 mmol) in EtOD (100 mL) at 40 °C was added dropwise to $NaBD_4$ (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 $PtP_2NC_{38}DH_{32}$: C, 59.91; H, 4.50; N, 1.84. Found: C, 60.12; H, 4.45; N, 1.80. ^{1}H NMR (80 MHz): δ 0.58 (t, 2 H, CH_2, $^3J_{HP}$ = 6.2, $^2J_{HPt}$ = 67 Hz). ^{31}P NMR: δ 31.5 (t, $^2J_{PD}$ = 2.2, $^1J_{PPt}$ = 3025 Hz). IR (KBr): ν(CN) 2183 (s) cm^{-1}; ν(PtD) 1353 (m) cm^{-1}.

***trans*-PtD(CF_3)(PPh_3)$_2$.** A suspension of *trans*-$(PPh_3)_2Pt(CF_3)Br$ (1736 mg, 2.00 mmol) in CH_2Cl_2 (50 mL) was treated with a 1.025 M $AgBF_4$ 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_2O gave the solid *trans*-$[(PPh_3)_2Pt(CF_3)(solv)]BF_4$ (1560 mg, 81% yield for solv = CH_2Cl_2). 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 $NaBD_4$ (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 $PtP_2F_3C_{37}DH_{30}$: C, 56.20; H, 4.08. Found: C, 56.00; H, 4.10. ^{31}P NMR: δ 29.5 (dq, $^3J_{PF}$ = 8.5, $^3J_{PD}$ = 2.3, $^1J_{PPt}$ = 3085 Hz). ^{19}F NMR: δ −16.6 (tt, $^3J_{FD}$ = 4.2, $^3J_{FP}$ = 8.5, $^2J_{FPt}$ = 443 Hz). The ν(PtD) band in the IR spectrum could not be located in either Nujol mull of KBr.

PtH(CH_2CF_3)(CNR)(PPh_3). A suspension of *cis*-$PtH(CH_2CF_3)(PPh_3)_2$ (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 × 10 mL), and recrystallized from CH_2Cl_2/*n*-hexane: yield 1416 mg, 89%; mp 125–128 °C dec. Anal. Calcd for $PtPOF_3NC_{28}H_{25}$: C, 49.86; H, 3.73; N, 2.07. Found: C, 49.59; H, 3.81; N, 1.98. ^{1}H NMR: δ −5.35 (d, 1 H, PtH, $^2J_{HP}$ = 18.5, $^1J_{HPt}$ = 999 Hz), 2.45 (dq, 2 H, CH_2, $^3J_{HF}$ = 16.7, $^3J_{HP}$ = 7.8, $^2J_{HPt}$ = 85 Hz), 3.77 (s, 3 H, OCH_3). ^{31}P NMR: δ 25.3 (q, $^4J_{PF}$ = 16.0, $^1J_{PPt}$ = 2227 Hz). ^{19}F NMR: δ −52.0 (ddt, $^3J_{FH}$ = $^4J_{FP}$ = 16.0, $^4J_{FH}$ = 1.5, $^3J_{FPt}$ = 191 Hz). IR (Nujol): ν(CN) 2181 (s) cm^{-1}; ν(PtH) 2073 (s) cm^{-1}.

PtD(R_X)(CNR)(PPh_3) (R_X = CH_2CN, CH_2CF_3, CF_3). These compounds were prepared by treating the corresponding $PtD(R_X)(PPh_3)_2$ 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_2Cl_2/*n*-hexane; yields ca. 90%.

R_X = CH_2CN. Mp: 131–133 °C dec. Anal. Calcd for $PtPN_2OC_{28}DH_{24}$: C, 53.16; H, 4.14; N, 4.43. Found: C, 52.94; H, 3.96; N, 4.42. ^{1}H NMR: δ 2.17 (d, 2 H, CH_2, $^3J_{HP}$ = 9.4, $^2J_{HPt}$ = 95 Hz), 3.78 (s, 3 H, OCH_3). ^{31}P NMR: δ 24.38 (s, $^1J_{PPt}$ = 2419 Hz). IR (KBr): ν(CN) 2197 (s) cm^{-1}; ν(PtD) 1461 (m) cm^{-1}.

R_X = CH_2CF_3. Mp: 124–127 °C dec. Anal. Calcd for $PtPONF_3C_{28}DH_{24}$: C, 49.78; H, 3.87; N, 2.07. Found: C, 49.39; H, 3.87; N, 1.92. ^{1}H NMR: δ 2.45 (dq, 2 H, CH_2, $^3J_{HF}$ = 16.6, $^3J_{HP}$ = 8.5, $^2J_{HPt}$ = 91 Hz), 3.78 (s, 3 H, OCH_3). ^{31}P NMR: δ 25.36 (q, $^4J_{PF}$ = 16.0, $^1J_{PPt}$ = 2228 Hz). ^{19}F NMR: δ −52.1 (dt, $^3J_{FP}$ = $^3J_{FH}$ = 16.6, $^3J_{FPt}$ = 192 Hz). IR (KBr): ν(CN) 2172 (s) cm^{-1}; ν(PtD) 1460 (m) cm^{-1}.

R_X = CF_3. Mp: 130–132 °C dec. Anal. Calcd for $PtPF_3ONC_{27}DH_{22}$: C, 49.02; H, 3.66; N, 2.12. Found: C, 48.52; H, 3.50; N, 2.03. ^{1}H NMR: δ 3.78 (s, 3 H, OCH_3). ^{31}P NMR: δ 21.60 (dq, $^2J_{PD}$ = 2.5, $^3J_{PF}$ = 58, $^1J_{PPt}$ = 2055 Hz). ^{19}F NMR: δ −12.6 (d, $^2J_{FPt}$ = 800, $^3J_{FP}$ = 58 Hz). IR (KBr): ν(CN) 2178 (s) cm^{-1}; ν(PtD) 1459 (m) cm^{-1}.

PtH(CF_3)(PPh_3)[C(NCH$_2$CH$_2$CH$_2$)NHR] (1). To a solution of $PtH(CF_3)(CNR)(PPh_3)$ (660 mg, 1.0 mmol) in THF (20 mL) was added azetidine (81 μL, 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^{-1} due to ν(C≡N) of the starting isocyanide complex but showed ν(C=N) at 1545 cm^{-1} 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 × 5 mL), and dried under vacuum. The product was recrystallized from CH_2Cl_2/*n*-hexane: yield 660 mg, 92%; mp 188–190 °C dec. Anal. Calcd for $PtPF_3ON_2C_{30}H_{30}$: C, 50.21; H, 4.21; N, 3.90. Found: C, 50.44; H, 4.22; N, 3.84. ^{1}H NMR: δ −7.15 (ddq, 1 H, PtH, $^3J_{HF}$ = 15.0, $^2J_{HP}$ = 19.0, $^4J_{HH}$ = 3.6, $^1J_{HPt}$ = 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_3), 6.47 (d, 1 H, NH, $^3J_{HPt}$ = 53.2, $^4J_{HH}$ = 3.6 Hz). ^{31}P NMR: δ 22.10 (q, $^3J_{PF}$ = 56.7, $^1J_{PPt}$ = 2220 Hz). ^{19}F NMR: δ −12.58 (dd, $^2J_{FPt}$ = 797, $^3J_{FP}$ = 56.7, $^3J_{FH}$ = 15.0 Hz). ^{13}C NMR: δ 206.82 (dm, $^2J_{PC}$ = 28.0, $^1J_{CPt}$ = 759 Hz), 157.25–113.89 (phenyl carbons), 55.73 (s, OCH_3), 54.78 (s, NCH_2 cis to Pt, $^3J_{CPt}$ = 51.3), 49.92 (s, NCH_2 trans to Pt, $^3J_{CPt}$ = 24.2 Hz), 15.67 (s, CH_2), CF_3 insufficiently intense to be observed. IR (Nujol): ν(C=N) 1545 (s) cm^{-1}; ν(NH) 3346 (m) cm^{-1}; ν(PtH) 2042 (s) cm^{-1}.

PtH(CH_2CN)(PPh_3)[C(NCH$_2$CH$_2$CH$_2$)NHR] (2). This compound was prepared as described for **1** by starting from $PtH(CH_2CN)(CNR)(PPh_3)$ (1500 mg, 2.38 mmol) and azetidine (193 μL, 2.85 mmol) in THF (50 mL). An IR spectrum of the solution recorded after 12 h did not show ν(C≡N) at 2177 cm^{-1} for the starting isocyanide complex but the presence of ν(C=N) at 1544 cm^{-1} for the carbene derivative. The stirring was prolonged for 5 h. The white precipitate formed was filtered, washed with Et_2O (3 × 5 mL), and dried under vacuum: yield 1260 mg, 77%; mp 178–180 °C dec. Anal. Calcd for $PtPON_3C_{31}H_{32}$: C, 54.06; H, 4.68; N, 6.10. Found: C, 54.16; H, 4.80; N, 5.99. ^{1}H NMR: δ −7.34 (dd, 1 H, PtH, $^2J_{HP}$ = 20.3, $^4J_{HH}$ = 3.5, $^1J_{HPt}$ = 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_3), 6.64 (d, 1 H, NH, $^3J_{HPt}$ = 55.4, $^4J_{HH}$ = 3.5 Hz), 1.68 (dd, 1 H, CH, $^3J_{HP}$ = 9.6, $^2J_{HH}$ = 15.6, $^2J_{HPt}$ = 91 Hz), 1.95 (dd, 1 H, CH, $^3J_{HP}$ = 8.3, $^2J_{HH}$ = 15.6, $^2J_{HPt}$ = 97 Hz). ^{31}P NMR: δ 24.20 (s, $^1J_{PPt}$ = 2682). ^{13}C NMR: δ 204.94 (d, satellites insufficiently intense to be observed, $^2J_{PC}$ = 6.4 Hz), 156.9–113.8 (phenyl carbons), 55.72 (s, OCH_3), 54.74 (s, NCH_2 cis to Pt, $^3J_{CPt}$ = 50.8 Hz), 50.62 (s, NCH_2 trans to Pt, $^3J_{PtC}$ = 29.2 Hz), 15.61 (s, CH_2), CH_2CN insufficiently intense to be observed. IR (Nujol): ν(C=N) 1549 (s) cm^{-1}; ν(NH) 3267 (m) cm^{-1}; ν(PtH) 2005 (m) cm^{-1}; ν(CN) 2192 (s) cm^{-1}; MS (FAB; *m/z* relative abundance, %): 688 ([M]$^+$, 5), 647 ([M − CH_3CN]$^+$, 15), 386 ([$PtON_2C_{11}H_{15}$]$^+$, 20), 191 ([$ON_2C_{11}H_{15}$]$^+$, 100).

PtH(CH_2CF_3)(PPh_3)[C(NCH$_2$CH$_2$CH$_2$)NHR] (3). This compound was prepared as described for **1** by starting from $PtH(CH_2CF_3)(CNR)(PPh_3)$ (703 mg, 1.04 mmol) and azetidine 84 μL, 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 ν(C≡N) at 2176 cm^{-1} and the presence of ν(C=N) at 1538 cm^{-1}. 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 $PtPF_3ON_2C_{31}H_{32}$: C, 50.89; H, 4.40; N, 3.83. Found: C, 50.80; H, 4.40; N, 3.80. ^1H NMR: δ −7.23 (dd, 1 H, PtH, $^2J_{HP}$ = 20.7, $^4J_{HH}$ = 2.7, $^1J_{HPt}$ = 825 Hz), 2.16 (m, 1 H, CH), 1.92 (m, 1 H, CH), 2.03 (dq, 1 H, CH, $^3J_{HP}$ = 8.5, $^3J_{HF}$ = 16.8 Hz, ^{195}Pt satellites masked), 2.07 (dq, 1 H, CH, $^3J_{HP}$ = 8.3, $^3J_{HF}$ = 16.6 Hz, ^{195}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, OCH_3), 6.51 (d, 1 H, NH, $^3J_{HPt}$ = 51.4, $^4J_{HH}$ = 2.7 Hz). ^{31}P NMR: δ 25.49 (q, $^4J_{PF}$ = 16.6, $^1J_{PPt}$ = 2506 Hz). ^{19}F NMR: δ −51.54 (ddq, $^4J_{FH}$ = 2.9, $^3J_{FPt}$ = 210, $^4J_{FP}$ = 16.6 Hz). ^{13}C NMR: δ 210.07 (d, $^2J_{PC}$ = 50.9, $^1J_{PtC}$ = 753 Hz), 156.6–113.6 (phenyl carbons, 55.72 (s, OCH_3), 54.77 (s, NCH_2 cis to Pt, $^3J_{PtC}$ = 56.6 Hz), 50.62 (s, NCH_2 trans to Pt, $^3J_{PtC}$ = 34.7 Hz), 15.49 (s, CH_2), 7.69 (dq, $^2J_{CF}$ = 83, $^2J_{CP}$ = 31.2, $^1J_{CPt}$ = 619 Hz), CF_3 insufficiently intense to be observed. IR (Nujol): ν(C≡N) 1525 (s) cm^{-1}; ν(NH) 3332 (m) cm^{-1}; ν(PtH) 2004 (m) cm^{-1}.

PtH(CF_3)(PPh_3)[C(NCH$_2$CH$_2$CH$_2$CH$_2$)NHR] (4). This compound was prepared as described for **1** by starting from PtH(CF_3)(CNR)(PPh_3) (500 mg, 0.75 mmol) and piperidine (90 μL, 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 ν(C≡N) at 2179 cm^{-1} and the presence of ν(C=N) at 1537 cm^{-1}. The stirring was prolonged for 5 h. The white precipitate formed during this time was filtered, washed with Et_2O (3 × 5 mL), and dried under vacuum: yield 460 mg, 82%; mp 179–180 °C dec. Anal. Calcd for $PtPOF_3N_2C_{32}H_{34}$: C, 51.56; H, 4.59; N, 3.76. Found: C, 51.41; H, 4.31; N, 3.36. ^1H NMR: δ −8.03 (ddq, 1 H, PtH, $^2J_{HP}$ = 22.6, $^4J_{HH}$ = 3.3, $^3J_{HF}$ = 15.1, $^1J_{HH}$ = 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, OCH_3), NH not located. ^{31}P NMR: δ 20.90 (q, $^3J_{PF}$ = 56.4, $^1J_{PPt}$ = 2272 Hz). ^{19}F NMR: δ −11.15 (dd, $^2J_{FPt}$ = 788, $^3J_{FP}$ = 56.4 Hz). ^{13}C NMR: δ 206.03 (m, $^1J_{CPt}$ = 845 Hz), 141.19 (dq, CF_3, $^1J_{CF}$ = 346, $^2J_{CP}$ = 167 Hz, ^{195}Pt satellites insufficiently intense to be observed), 157.9–102.3 (phenyl carbons), 55.70 (s, OCH_3), 56.31 (s, NCH_2 cis to Pt, $^3J_{CPt}$ = 63 Hz), 44.62 (s, NCH_2 trans to Pt, $^3J_{CPt}$ = 14.0 Hz), 25.75 (s, NCH_2CH_2), 24.45 (s, CH_2). IR (Nujol): ν(C=N) 1540 (s) cm^{-1}; ν(NH) 3374 (m) cm^{-1}; ν(PtH) 2044 (m) cm^{-1}.

PtD(CF_3)(PPh_3)[C(NCH$_2$CH$_2$CH$_2$)NHR] ((Pt-D)1). This compound was prepared as described for **1** by starting from PtD(CF_3)(CNR)(PPh_3) (500 mg, 0.75 mmol) and azetidine (60 μL, 0.90 mmol) in THF (20 mL): yield 400 mg, 74%; mp 186–188 °C dec. Anal. Calcd for $PtPF_3ON_2C_{30}DH_{29}$: C, 50.14; H, 4.35; N, 3.90. Found: C, 50.34; H, 4.52; N, 3.80. ^1H NMR: δ 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, OCH_3), 6.47 (s, 1 H, NH, $^3J_{HPt}$ = 53.3 Hz). ^{31}P NMR: δ 22.5 (q, $^3J_{PF}$ = 57.0, $^1J_{PPt}$ = 2220 Hz). ^{19}F NMR: δ −12.7 (d, $^3J_{FP}$ = 57.0, $^3J_{FPt}$ = 798 Hz). IR (KBr): ν(PtD) masked; ν(C=N) 1523 (s) cm^{-1}; ν(NH) 3332 (m) cm^{-1}.

PtD(CH_2CN)(PPh_3)[C(NCH$_2$CH$_2$CH$_2$)NHR] ((Pt-D)2). This compound was prepared as described for **2** by starting from PtD(CH_2CN)(CNR)(PPh_3) (220 mg, 0.34 mmol) and azetidine (28 μL, 0.42 mmol) in THF (10 mL): yield 180 mg, 73%: mp 176–178 °C dec. Anal. Calcd for $PtPON_3C_{31}DH_{31}$: C, 53.99; H, 4.82; N, 6.09. Found: C, 53.88; H, 4.86; N, 5.99. ^1H NMR: δ 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, $^3J_{HP}$ = 9.2, $^2J_{HH}$ = 15.0, $^2J_{HPt}$ = 97 Hz), 1.69 (dd, 1 H, CH, $^3J_{HP}$ = 9.5, $^2J_{HH}$ = 15.0, $^2J_{HPt}$ = 99 Hz), 3.74 (s, 3 H, OCH_3), 6.74 (s, 1 H, NH, $^3J_{HPt}$ = 52.2 Hz). ^{31}P NMR: δ 24.20 (s, $^1J_{PPt}$ = 2687 Hz). IR (KBr): ν(PtD) 1462 (s) cm^{-1}. IR (Nujol): ν(C=N) 1547 (s) cm^{-1}; ν(NH) 3263 (m) cm^{-1}.

PtD(CH_2CF_3)(PPh_3)[C(NCH$_2$CH$_2$CH$_2$)NHR] ((Pt-D)3). This compound was prepared as described for **3** by starting from PtD(CH_2CF_3)(CNR)(PPh_3) (675 mg, 1.0 mmol) and azetidine (81 μL, 1.2 mmol) in THF (10 mL): yield 540 mg, 74%; mp 175–177 °C. Anal. Calcd for $PtPF_3ON_2C_{31}DH_{33}$: C, 50.82; H, 4.54; N, 3.82. Found: C, 49.98; H, 4.44; N, 3.83. ^1H NMR: δ 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, $^3J_{HP}$ = 8.6, $^3J_{HF}$ = 16.9 Hz, ^{195}Pt satellites masked), 2.06 (dq, $^3J_{HP}$ = 8.5, $^3J_{HF}$ = 17 Hz, ^{195}Pt satellites masked), 3.73 (s, 3 H, OCH_3), 6.55 (s, 1 H, NH, $^3J_{HPt}$ masked). ^{31}P NMR: δ 25.51 (q, $^4J_{PF}$ = 16.7, $^1J_{PPt}$ = 2507 Hz). ^{19}F NMR: δ −51.55 (dt, $^4J_{PF}$ = $^3J_{HF}$ = 16.7, $^3J_{FPt}$ = 209 Hz). IR (KBr): ν(PtD) 1461 (s) cm^{-1}; ν(C=N) 1523 (s) cm^{-1}; ν(NH) 3332 (m) cm^{-1}.

PtH(CF_3)(PPh_3)[C(NEt_2)NHR] (5). This compound was prepared by starting from PtH(CF_3)(CNR)(PPh_3) (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 cm^{-1} due to ν(C≡N) of the starting isocyanide complex but showed ν(C=N) at 1533 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 $PtPF_3ON_2C_{31}H_{32}$: C, 50.75; H, 4.67; N, 3.82. Found: C, 50.59; H, 4.53; N, 3.79. ^1H NMR: δ 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. ^1H NMR: δ −8.06 (ddq, $^1J_{HPt}$ = 883, $^2J_{HP}$ = 22.9, $^3J_{HF}$ = 15.7, $^4J_{HH}$ = 3.4 Hz), 3.78 (s, OCH_3). ^{31}P NMR δ 20.27 (q, $^3J_{PF}$ = 56.3, $^1J_{PPt}$ = 2272 Hz). ^{19}F NMR: δ −11.67 (dd, $^3J_{HF}$ = 15.7, $^3J_{PF}$ = 56.3, $^2J_{FPt}$ = 790 Hz). Data for **5b** are as follows. ^1H NMR: δ −8.87 (dq, $^3J_{HF}$ = 25.6, $^2J_{HP}$ = 25.8, $^1J_{HPt}$ = 711 Hz). ^{31}P NMR: δ 25.29 (q, $^3J_{PF}$ = 7.3, $^1J_{PPt}$ = 2760 Hz). ^{19}F NMR: δ −16.77 (dd, $^3J_{PF}$ = 7.3, $^3J_{HF}$ = 25.6, $^2J_{FPt}$ = 476 Hz). Data for **5c** are as follows. ^1H NMR: δ −5.12 (dq, $^3J_{HF}$ = 16.6, $^2J_{HP}$ = 184, $^1J_{HPt}$ = 1223 Hz). ^{19}F NMR: δ −8.14 (dd, $^2J_{FPt}$ = 684, $^3J_{FP}$ = 12.9, $^3J_{FH}$ = 16.6 Hz). IR (Nujol): ν(C=N) 1532 (m) cm^{-1}; ν(NH) 3378 (m), 3351 (m) cm^{-1}; ν(PtH) 2046 (m), and 2020 (m) cm^{-1}.

Reaction of 2 and (Pt-D)2 with PPh_3. To a suspension of **2** (689 mg, 1 mmol) was added PPh_3 (262 mg, 1 mmol) in THF (20 mL) at room temperature. The reaction was followed by IR and ^1H NMR spectroscopies. The IR spectrum revealed the disappearance of the bands at 1544 and 2014 cm^{-1} due to ν(C=N) and ν(PtH), respectively, of the starting complex and formation of the corresponding bands at 1600 and 1952 cm^{-1} of the final hydrido derivative. The formation of CH_3CN as the only organic product was confirmed by IR (ν(C≡N) 2252 cm^{-1}), GC/MS, and ^1H NMR spectroscopy (δ 1.97, CH_3). After 24 h the yellow solution was reduced to ca. 5 mL, and when Et_2O was added (30 mL), the yellow compound *trans*-(PPh_3)$_2$PtH[C(NCH$_2$CH$_2$CH$_2$)NR] (**6**) precipitated. It was filtered, washed with Et_2O (3 × 5 mL), and recrystallized from C_6H_6/*n*-hexane: yield 670 mg, 74%; mp 169–171 °C dec. Anal. Calcd for $PtP_2ON_2C_{47}H_{44}$: C, 62.04; H, 4.87; N, 3.08. Found: C, 62.13; H, 4.92; N, 3.00. ^1H NMR: δ −6.16 (t, 1 H, PtH, $^2J_{HP}$ = 18.6, $^1J_{HPt}$ = 620 Hz), 1.58 (Q, 2 H, CH_2, $^3J_{HH}$ = 15.3 Hz), 3.51 (t, 4 H, NCH_2, $^3J_{HH}$ = 15.3 Hz), 3.66 (s, 3 H, OCH_3). ^{31}P NMR: δ 24.80 (s, $^1J_{PPt}$ = 3037 Hz). IR (Nujol): ν(PtH) 1971 (s) cm^{-1}; ν(C=N) masked. The reaction of (Pt-D)**2** with PPh_3 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 $PtP_2ON_2C_{47}DH_{43}$: C, 62.04; H, 4.87; N, 3.08. Found: C, 62.02; H, 4.90; N, 3.08. ^1H NMR: δ 1.60 (Q, 2 H, CH_2), 3.55 (t, 4 H, NCH_2), 3.66 (s, 3 H, OCH_3). ^{31}P NMR: δ 26.00 (s, $^1J_{PtP}$ = 2235 Hz). IR (KBr): ν(PtD) and ν(C=N) masked.

Reaction of 3 and (Pt-D)3 with PPh_3. These reactions were performed as described for **2**, and they were followed by ^{19}F NMR spectroscopy in order to observe the formation of CH_3CF_3 (δ −59.40, q, $^3J_{HF}$ = 12.7 Hz). Again, these reactions lead to the formation of **6** and (Pt-D)**6**, respectively.

Reaction of 2 with PPh_3 in EtOD. To a suspension of **2** (150 mg, 0.22 mmol) in THF (10 mL) and EtOD (1 mL) was added PPh_3 (57 mg, 0.22 mmol). The reaction was followed by ^1H NMR spectroscopy to observe the formation of DCH_2CN (δ 1.94; 1:1:1 triplet, $^2J_{HD}$ = 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_2O (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 cm^{-1} due to ν(ND) and the band at 3267 cm^{-1} due to ν(NH) of the starting material. The reaction of (N-D)**2** with PPh_3 was followed by ^1H NMR spectroscopy, showing the formation of DCH_2CN together with CH_3CN.

Reaction of 3 with PPh_3 in EtOD. This reaction was performed as described for **2** and leads to the formation of CD_2HCF_3, which was identified by ^{19}F NMR spectroscopy (δ −59.61, tt, $^2J_{HD}$ = 1.8, $^3J_{HF}$ = 12.8 Hz).

Reaction of 6 with HBF_4. To a suspension of **6** (100 mg, 0.11 mmol) in Et_2O (10 mL) was added an ethereal solution (ca. 6 M) of HBF_4 (0.1 mL, 6.0 mmol) and the reaction mixture stirred for 2 h. The complex *trans*-{$(PPh_3)_2PtH[C(\overline{NCH_2CH_2CH_2})NHR]$}$BF_4$ (**7**) was filtered, washed with Et_2O (3 × 5 mL), and dried under vacuum: yield 106 mg (96%); mp 239–241 °C. Anal. Calcd for $PtP_2F_4ON_2C_{47}BH_{45}$: C, 56.58; H, 4.55; N, 2.81. Found: C, 56.38; H, 4.62; N, 2.90. ^1H NMR: δ −6.97 (td, 1 H, PtH, $^2J_{PH}$ = 14.5, $^4J_{HH}$ = 3.3, $^1J_{HPt}$ = 645 Hz), 1.69 (m, 2 H, CH_2), 3.51 (m, 4 H, NCH), 3.69 (s, 3 H, OCH_3), NH not located. ^{31}P NMR: δ 24.18 (s, $^1J_{PPt}$ = 2902 Hz). ^{13}C NMR: δ 204.03 (t, PtC, $^2J_{PC}$ = 8.0, $^1J_{CPt}$ = 823 Hz), 157.55–113.80 (phenyl carbons), 55.67 (s, OCH_3), 54.38 (s, NCH_2 cis to Pt, $^3J_{PtC}$ = 47.8 Hz), 51.33 (s, NCH_2 trans to Pt, $^3J_{PtC}$ = 28.2 Hz), 15.31 (s, CH_2). IR (Nujol): ν(C=N) 1553 (s) cm^{-1}; ν(NH) 3305 (m) cm^{-1}; ν(PtH) 2038 (m) 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 $Ph_2PCH_2CH_2PPh_2$ (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 cm^{-1} of **1** and the formation of a band at 1628 cm^{-1} due to the organic formamidine $HC(\overline{NCH_2CH_2CH_2})$=N(R). The solution was analyzed by GC/MS (retention time of the formamidine 5 min; m/z 190 $[M]^+$). After 2 h the solution miture was reduced to 5 mL and *n*-hexane (39 mL) was added. A white product precipitated, which was identified as $PtH(CF_3)(Ph_2PCH_2CH_2PPh_2)$.[6c] The mother liquors were reduced to a small volume and cooled at −10 °C. After 24 h, white crystals of $HC(\overline{NCH_2CH_2CH_2})$=N(R) were formed, which were filtered and dried under vacuum; yield 100 mg (91%). Anal. Calcd for $ON_2C_{11}H_{14}$: C, 69.45; H, 7.42, N, 14.73. Found: C, 70.42; H, 7.28; N, 14.68. ^1H NMR: δ 2.38 (Q, 2 H, CH_2, $^3J_{HH}$ = 7.7 Hz), 4.05 (t, 4 H, NCH_2), 3.74 (s, 3 H, OCH_3), 7.43 (s, 1 H, CH). ^{13}C NMR: δ 151.80 (CH), 155.98, 145.61, 121.72, 114.57 (C_6H_4), 55.76 (OCH_3), 50.16 (NCH_2), 17.65 (CH_2). MS: m/z 190 ($M^{\bullet+}$, relative abundance 100%), 175 ($[M - CH_3]^+$, 42%), 143 ($[ON_2C_{10}H_{11}]^{\bullet+}$, 75%), 108 ($[C_6H_5OCH_3]^+$, 26%), 77 ($[C_6H_5]^{\bullet+}$, 34%). IR (Nujol): ν(C=N) 1618 cm^{-1}. The same reaction was performed by treating **1** with an equimolar amount of Ph_2PCH=$CHPPh_2$. Again, the IR spectrum of the reaction mixture showed the appearance of the band at 1628 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 diphos reaction to give $PtH(CF_3)(Ph_2PCH$=$CHPPh_2)$[6c] and the formamidine. In a separate experiment **1** was treated with Ph_2PCH=$CHPPh_2$ in THF/EtOD (10 mL/2 mL). As described above, the D-C formamidine $DC(\overline{NCH_2CH_2CH_2})$=N(R) was recovered. MS: m/z 191 ($[M]^{\bullet+}$, 100%), 176 ($[M - CH_3]^+$, 42%), 135 ($[ON_2C_{10}DH_9]^+$, 75%). To a suspension of (Pt-D)**1** (250 mg, 0.35 mmol) in THF (20 mL) was added $Ph_2PCH_2CH_2PPh_2$ (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 $PtD(CF_3)(Ph_2PCH_2CH_2PPh_2)$: yield 180 mg, 77%; mp 196–198 °C dec. Anal. Calcd for $PtP_2F_3C_{27}DH_{24}$: C, 48.80; H, 3.94. Found: C, 48.91; H, 3.88. ^{31}P NMR: δ P trans to CF_3 48.2 (dq, $^3J_{PF}$ = 58, $^2J_{PD}$ = 1.8, $^1J_{PPt}$ = 1958 Hz), P trans to D 49.2 (dq, $^3J_{PF}$ = 14.6, $^2J_{PD}$ = 28.0, $^1J_{PPt}$ = 1803 Hz). ^{19}F NMR: δ −10.7 (ddd, $^3J_{FD}$ = 1.5, $^3J_{PF}$ = 58, $^3J_{PF}$ = 14.6, $^2J_{FPt}$ = 759 Hz). IR (KBr): ν(PtD) 1456 (m) cm^{-1}.

Reaction of 4 with Diphosphines. A suspension of **4** (375 mg, 0.5 mmol) in THF (20 mL) was treated with $Ph_2PCH_2CH_2PPh_2$ (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 cm^{-1} due to the free formamidine $HC(\overline{NCH_2CH_2CH_2CH_2CH_2})$=N(R). The solution mixture was analyzed by GC/MS (retention time of the formamidine 19 min; m/z 218, $[M]^{\bullet+}$). A white precipitate was recovered by addition of *n*-hexane (30 mL) and identified as $PtH(CF_3)(Ph_2PCH_2CH_2PPh_2)$.[6c] Organic formamidine was isolated as white crystals from concentrated mother liquors kept at −10 °C for 24 h; yield 95 mg (87%). Anal. Calcd for $ON_2C_{13}H_{18}$: C, 71.53; H, 8.31; N, 12.83. Found: C, 70.80; H, 8.29; N, 12.90. ^1H NMR: δ 1.62 (m, 4 H, CH_2), 1.26 (m, 2 H, CH_2), 3.39 (m, 4 H, NCH_2), 3.74 (s, 3 H, OCH_3), 7.46 (s, 1 H, CH). ^{13}C NMR: δ 152.44 (s, CH), 155.70, 146.17, 121.69, 114.57 (C_6H_4), 55.72 (s, OCH_3), 53.22 (s, NCH_2), 25.16 (s, CH_2). IR (Nujol): ν(C=N) 1628 (s) cm^{-1}. MS: m/z 218 ($[M]^{\bullet+}$, relative abundance 100%), 190 ($[M - C_2H_4]^{\bullet+}$, 55%), 84 ($[C_5H_{10}N]^+$, 75%). The same reaction carried out between **4** and an equimolar amount of Ph_2PCH=$CHPPh_2$ under the same experimental conditions reported above for diphos leads to the formation of the free formamidine $HC(\overline{NCH_2CH_2CH_2CH_2CH_2})$=N(R) and $PtH(CF_3)(Ph_2PCH$=$CHPPh_2)$[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 $Ph_2PCH_2CH_2PPh_2$ (151 mg, 0.38 mmol). After 2 h a pale yellow solution was obtained, which did not show the ν(C≡N) band of the Pt–CH_2CN group at 2193 cm^{-1}, while it showed the absorption of free CH_3CN at 2252 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 $(Ph_2PCH_2CH_2PPh_2)PtH[C(\overline{NCH_2CH_2CH_2})NR]$ (**8**): yield 490 mg (87%); mp 168–170 °C dec. Anal. Calcd for $PtP_2ON_2C_{37}H_{38}$: C, 56.70; H, 4.89; N, 3.57. Found: C, 56.62; H, 4.93; N, 3.48. ^1H NMR: δ −2.39 (dd, 1 H, PtH, $^2J_{HP(trans)}$ = 179, $^2J_{HP(cis)}$ = 14.8, $^1J_{HPt}$ = 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_2), 3.75 (s, 3 H, OCH_3). ^{31}P NMR: δ 47.95 (d, $^1J_{PtP}$ = 1720, P trans to H, $^2J_{PP}$ = 5.0 Hz), 48.76 (d, $^1J_{PPt}$ = 2354, P trans to carbene group, $^2J_{HH}$ = 5.0 Hz). ^{13}C NMR: δ 185.00 (d, PtC, $^1J_{PtC}$ = 845, $^2J_{CP(cis)}$ = 28.8, $^2J_{CP(trans)}$ = 97 Hz), 154.6–113.49 (phenyl carbons), 55.61 (s, OCH_3), 51.78 (s, NCH_2, $^3J_{PtC}$ = 65.3 Hz), 17.05 (CH_2), 26.12 and 26.91 (PCH_2). IR (Nujol): ν(PtH) 1982 (m) cm^{-1}; ν(C=N) 1499 (s) cm^{-1}. The complex $(Ph_2PCH$=$CHPPh_2)PtH[C(\overline{NCH_2CH_2CH_2})NR]$ (**9**) was obtained as described for **8** by starting from **2** (257 mg, 0.37 mmol) and Ph_2PCH=$CHPPh_2$ (150 mg, 0.38 mmol): yield 231 mg (80%); mp 189–190 °C dec. Anal. Calcd for $PtP_2ON_2C_{37}H_{36}$: C, 56.77; H, 4.76; N, 3.54. Found: C, 56.70; H, 4.78; N, 3.50. ^1H NMR: δ −2.28 (dd, $^2J_{HP(trans)}$ = 185, $^2J_{HP(cis)}$ = 15.8, $^1J_{HPt}$ = 1241 Hz), 1.82 (m, 2 H, CH), 3.70 (m, 4 H, NCH_2), 3.71 (s, 3 H, OCH_3), 6.42 (m, 1 H, PCH), 6.44 (m, 1 H, PCH). ^{31}P NMR: δ 58.04 (d, $^2J_{PP}$ = 11.4, $^1J_{PPt}$ = 1810, $^2J_{PP}$ = 11.4 Hz, P trans to H), 60.31 (d, $^1J_{PPt}$ = 1955 Hz, P trans to carbene group). IR (Nujol): ν(PtH) 2007 (m) cm^{-1}; ν(C=N) 1510 (s) cm^{-1}.

Reaction of 8 and 9 with 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 Et_2O (20 mL) and treated with an ethereal solution (ca. 6 M) of HBF_4 (0.2 mL, 12 mmol). After the mixture was stirred for 2 h, the complex {$(Ph_2PCH_2CH_2PPh_2)PtH[C(\overline{NCH_2CH_2CH_2})NHR]BF_4$} (**10**) was isolated as a white solid, which was filtered off and washed with Et_2O (3 × 5 mL): yield 180 mg (86%); mp 180–181 °C dec. Anal. Calcd for $PtP_2F_4ON_2C_{37}BH_{39}$: C, 50.99; H, 4.51; N, 3.21. Found: C, 49.99; H, 4.50; N, 3.23. ^1H NMR: δ −1.53 (dd, $^2J_{HP(trans)}$ = 172, $^2J_{HP(cis)}$ = 12.8, $^1J_{HPt}$ = 1134 Hz, 1 H, PtH), 1.58 (m, 2 H, CH_2), 2.80 (m, 2 H, PCH), 2.19 (m, 2 H, PCH), 3.78 (s, 3 H, 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, $^4J_{HP}$ = 9.4, $^3J_{HPt}$ = 74.5 Hz). ^{31}P NMR: δ 47.92 (P trans to H, d, $^2J_{PP}$ = 5.7, $^1J_{PPt}$ = 1720 Hz), δ 49.60 (P trans to carbene group, d, $^1J_{PPt}$ = 2351, $^2J_{PP}$ = 5.7 Hz). ^{13}C NMR: δ 15.90 (CH_2), 26.58 and 28.43 (PCH_2), 52.32 and 55.09 (NCH_2), 55.79 (OCH_3), 114.12–158.00 (phenyl carbons), 194.51 (dd, PtC, $^2J_{CP(cis)}$ = 8.0, $^2J_{CP(trans)}$ = 115, $^1J_{PtC}$ = 1134 Hz). IR (Nujol): ν(PtH) 1976 (s) cm^{-1}; ν(C=N) 1552 (s) cm^{-1}; ν(NH) 3302 (m) cm^{-1}. The complex {$(Ph_2PCH$=$CHPPh_2)PtH[C(\overline{NCH_2CH_2CH_2})NHR]BF_4$} (**11**) was isolated in 88% yield (182 mg); mp 155–156 °C dec. Anal. Calcd for $PtP_2F_4ON_2C_{37}BH_{37}$: C, 51.09; H, 4.25; N, 3.22. Found: C, 50.99; H, 4.30; N, 3.21. ^1H NMR: δ −2.86 (dd, 1 H, PtH, $^2J_{HP(cis)}$ = 13.2, $^2J_{HP(trans)}$ = 164, $^1J_{HPt}$ = 1152 Hz), 1.84 (m, 1 H, CH), 2.12 (m, 1 H, CH), 3.74 (s, 3 H, OCH_3), 4.16 (m, 4 H, NCH_2), 6.84 (m, 1 H, PCH), 7.10 (m, 1 H, PCH), 8.32 (d, 1 H, NH, $^4J_{HP}$ = 9.3, $^3J_{HPt}$

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

X-ray Structure Analysis of $C_{31}H_{32}N_3OPPt$. Colorless transparent crystals were grown by slow diffusion of CH_2Cl_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 $\pm h,\pm k,+l$ reflections were collected. The intensity data were corrected for Lorentz–polarization effects and for absorption on the basis of ψ scans of four Bragg reflections by following the method of North et al.[36] 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 CH_3 group, which were introduced at calculated positions and were allowed to ride on associated carbon atoms during the least-squares refinement (d_{C-H} = 1.08 Å and U_{iso} = 0.07 Å^2). 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 e/Å^3) was located near the Pt atom position. All calculations were done by using the SHELX 76[37] program package with the atomic scattering factors taken from ref 38.

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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_2CN)(PPh_3)$_2$, 42481-62-9; *trans*-PtD(CH_2CN)(PPh_3)$_2$, 126018-95-9; *p*-$MeOC_6H_4NC$, 10349-38-9; *trans*-(PPh_3)$_2$Pt(CF_3)Br, 64933-32-0; *trans*-PtD(CF_3)(PPh_3)$_2$, 126018-96-0; *trans*-[(PPh_3)$_2$Pt(CF_3)(CH_2Cl_2)]BF_4, 87249-59-0; *cis*-PtH(CH_2CF_3)(PPh_3)$_2$, 85319-86-4; PtH(CF_3)(CNC_6H_4-*p*-OMe)(PPh_3), 125949-93-1; PtH(CH_2CN)(CNC_6H_4-*p*-OMe)(PPh_3), 63637-41-2; PtH(CH_2CF_3)(CNC_6H_4-*p*-OMe)(PPh_3), 126106-97-6; PtD(CH_2CN)(CNC_6H_4-*p*-OMe)(PPh_3), 126018-97-1; PtD(CH_2CF_3)(CNC_6H_4-*p*-OMe)(PPh_3), 126018-98-2; PtD(CF_3)(CNC_6H_4-*p*-OMe)(PPh_3), 126018-99-3; *trans*-PtD(CH_2CF_3)(PPh_3)$_2$, 126106-98-7; PtH(CF_3)($Ph_2PCH_2CH_2PPh_2$), 125892-79-7; PtH(CF_3)(Ph_2PCH=$CHPPh_2$), 64933-31-9; PtD(CF_3)($Ph_2PCH_2CH_2PPh_2$), 126019-05-4; $NHEt_2$, 109-89-7; CD_2H-CF_3, 558-53-2; HC($\overline{NCH_2CH_2CH_2}$)=N(C_6H_4-*p*-OMe), 126018-82-4; DC($\overline{NCH_2CH_2CH_2}$)=N(C_6H_4-*p*-OMe), 126018-83-5; HC($\overline{NCH_2CH_2CH_2CH_2CH_2}$)=N($C_6H_4$-*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 $[ArPAs]_2$ and $[ArPSb]_2$ (Ar = 2,4,6-(t-Bu)$_3C_6H_2$). P_2As_2- and P_2Sb_2-Substituted Analogues of Bicyclo[1.1.0]butane

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The syntheses and X-ray crystal structures of the new bicyclo compounds $[ArPAs]_2$, **1**, and $[ArPSb]_2$, **2** (Ar = 2,4,6-(t-Bu)$_3C_6H_2$) are reported. Both **1** and **2** represent the first well-characterized examples of their type to be described. They are analogues of the bicyclotetraphosphanes $[P_4\{N(SiMe_3)_2\}_2]$, **3**, and $[P_4Ar_2]$, **4**, which were recently reported. The P_2As_2 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_2Sb_2 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 Kα (λ = 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, β = 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, α = 66.09 (2)°, β = 85.97 (2)°, γ = 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 coworkers.[1] This compound, $[P_4\{N(SiMe_3)_2\}_2]$, **3**, involved the $N(SiMe_3)_2$ substituents in a symmetric exo,exo configuration and a folded P_4 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 $[P_4Ar_2]$,[2] which also had a short P–P bond of

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