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del CNR, Istituto di Chimica Industriale, Facoltà di Ingegneria, Università di Padova, 35100 Padova, Italy,
Dipartimento Chimico "G. Ciamician", Università di Bologna, 40126 Bologna, Italy,
and Department of Chemistry, Iowa State University, Ames, Iowa 50011

Transition-Metal-Promoted Cyclization Reactions of Isocyanide Ligands. Synthesis of Cyclic Diaminocarbenes from Isocyanide Complexes of Palladium(II) and Platinum(II) and X-ray Structure of *cis*-$Br_2Pt[CN(C_6H_4$-*p*-$Me)CH_2CH_2N(H)](PPh_3)$

Rino A. Michelin,*[1a] Livio Zanotto,[1a] Dario Braga,*[1b] Piera Sabatino,[1b] and Robert J. Angelici*[1c]

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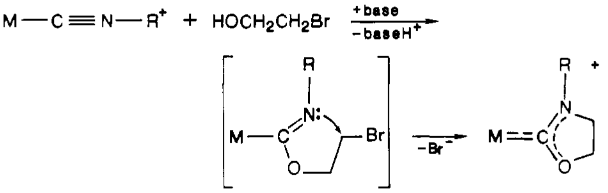
Electrophilic isocyanide ligands in cationic Pt(II) and Pd(II) complexes of the type *trans*-$[L_2M(CNR)X]BF_4$ (I) (L = phosphine; R = alkyl, aryl; X = halide, Me) are converted to the five-membered cyclic diaminocarbene derivatives *trans*-$\{L_2M[CN(R)CH_2CH_2N(H)]X\}BF_4$ (II) by reaction with 2-bromoethylamine hydrobromide in the presence of *n*-BuLi. 2-Bromoethylamine reacts also with one or even two RNC ligands in neutral complexes of the type *cis*-$Cl_2Pt(CNC_6H_4$-*p*-$Me)(PPh_3)$ and *cis*-$Cl_2Pd(CNC_6H_4$-*p*-$Me)_2$ to form the corresponding mono- and bis(diaminocarbene) derivatives *cis*-$Br_2Pt[CN(C_6H_4$-*p*-$Me)CH_2CH_2N(H)](PPh_3)$ and *cis*-$Br_2Pd[CN(C_6H_4$-*p*-$Me)CH_2CH_2N(H)]_2$, respectively. It is suggested that such reactions proceed by nucleophilic attack of 2-bromoethylamine on the metal-bound isocyanide carbon atom to form an imido intermediate which cyclizes intramolecularly to give the carbene products II. The Pt(II)– and Pd(II)–cyclic diaminocarbene complexes were characterized by their elemental analysis and IR and ^1H and ^{31}P NMR spectra. The structure of *cis*-$Br_2Pt[CN(C_6H_4$-*p*-$Me)CH_2CH_2N(H)](PPh_3)$ was established by an X-ray diffraction study. The structural model was refined to $R = 0.029$ ($R_w = 0.030$) for 2930 independent reflections. Crystal data: triclinic, space group $P\bar{1}$, $a = 11.255$ (3) Å, $b = 13.393$ (2) Å, $c = 10.020$ (2) Å, $\alpha = 106.55$ (1)°, $\beta = 112.00$ (4)°, $\gamma = 76.99$ (3)°, $Z = 2$. The angle formed between the platinum square plane and the carbene ligand is 102.1°. The cyclic diaminocarbene ligand is strictly planar with C(sp^2)–N(1) and C(sp^2)–N(2) bond lengths of 1.34 (1) and 1.36 (1) Å, indicating extensive π-bonding between the nitrogen atoms and the carbene carbon. The N–H group in II can be deprotonated by *n*-BuLi to give the imino intermediate *trans*-$\{L_2M[CN(R)CH_2CH_2N:]X\}BF_4$, which rapidly reacts with electrophiles such as allyl bromide and propargyl bromide to give the new functionalized carbenes *trans*-$\{L_2M[CN(R)CH_2CH_2N{-}CH_2CH{=}CH_2]X\}BF_4$ (M = Pd, Pt) and *trans*-$\{L_2M[CN(R)CH_2CH_2N{-}CH_2C{\equiv}CH]X\}BF_4$ (M = Pt).

Introduction

We have recently shown[2] that one or even two RNC ligands in Pt(II) complexes of the type *trans*-$[L_2Pt(CNR)Cl]BF_4$ (L = PPh_3, PMe_2Ph; R = alkyl, aryl) and *cis*-$Cl_2Pt(CNC_6H_4$-*p*-$OMe)_2$ can be converted in high yield to the corresponding five-membered cyclic aminooxycarbene derivatives *trans*-$\{L_2Pt[CN(R)CH_2CH_2O]X\}BF_4$ (X = Cl, Br) and $Br_2Pt[C(C_6H_4$-*p*-$OMe)CH_2CH_2O]_2$, respectively, by reaction with 2-bromoethanol in the presence of *n*-BuLi (eq 1). Carbon monoxide ligands in certain



(1)

metal carbonyl complexes react similarly[3] with 2-bromoethanol to give cyclic dioxycarbene complexes. The CO in these complexes also reacts with 2-bromoethylamine to give products with cyclic aminooxycarbene ligands.[3] The occurrence of this latter reaction and the well-known ability[4,5] of Pd(II)- and Pt(II)-isocyanide complexes to react with amines to give metal–carbene complexes led us to investigate reactions of $H_2NCH_2CH_2Br$ with Pd and Pt isocyanide complexes, the results of which are reported herein.

Experimental Section

Starting Materials. $[BrCH_2CH_2NH_3]Br$, $BrCH_2CH{=}CH_2$, and $BrCH_2C{\equiv}CH$ were Fluka products and used as received. *n*-BuLi (Fluka) was standardized by titration before use.[6] The complexes *trans*-$[(PPh_3)_2M(CNR)Cl]BF_4$ (M = Pd, Pt; R = *p*-$MeOC_6H_4$, *p*-MeC_6H_4, Me), *trans*-$[(PMePh_2)_2Pt(CNC_6H_4$-*p*-$OMe)Me]BF_4$, and *cis*-$Cl_2Pd(CNC_6H_4$-*p*-$Me)_2$ were prepared as previously reported.[2] The complex *cis*-$Cl_2Pt(CNC_6H_4$-*p*-$Me)(PPh_3)$ was obtained in 90% yield by reaction of $[(PPh_3)PtCl_2]_2$[7] (830 mg, 1.58 mmol) with *p*-MeC_6H_4NC (190 mg, 1.62 mmol) in C_6H_6 as previously described for similar complexes.[8] Spectroscopic features are as follows. IR (cm^{-1}): ν(NC) 2208 s (CH_2Cl_2); ν(PtCl) 338 m, 301 m (Nujol mull). ^1H NMR (CD_2Cl_2): δ(Me) 2.31 s. $^{31}P\{^1H\}$ NMR (CD_2Cl_2; internal reference 85% H_3PO_4): δ(P) 8.47 s, ^1J(PPt) 3351 Hz.

General Procedures. Solvents were dried and purified by standard procedures. Reactions were carried out under an N_2 or Ar atmosphere. Products were characterized by elemental analysis and IR and NMR spectra as previously described.[2] Infrared spectra were obtained in Nujol mulls.

Reaction with 2-Bromoethylamine. Synthesis of the Cyclic Diaminocarbene Complexes *trans*-$\{(PPh_3)_2Pt[CN(R)CH_2CH_2N(H)]Br\}BF_4$ (R = *p*-$MeOC_6H_4$ (1), *p*-MeC_6H_4 (2), Me (3)). These diaminocarbene complexes were prepared similarly. A typical procedure is given for **1**. A stirred suspension of $Br[NH_3CH_2CH_2Br]$ (84 mg, 0.40 mmol) in THF (15 mL) at 0 °C was treated with a 1.5 M *n*-hexane solution of *n*-BuLi (0.3 mL, 0.45 mmol). To the colorless solution so obtained was added in one portion solid *trans*-$[(PPh_3)_2Pt(CNC_6H_4$-*p*-$OMe)Cl]BF_4$ (200 mg, 0.20 mmol). The yellow reaction mixture was allowed to reach room temperature, and after ca. 30 min a pale yellow solution was obtained. Stirring was continued for an additional 45 min, during which time a white solid started to precipitate. A solution IR spectrum revealed no ν(N≡C) absorption for the starting complex. The reaction mixture was then taken to dryness; the residue was dissolved in acetone (20 mL) and treated with $NaBF_4$ (220 mg, 2.00 mmol). After it was stirred at room temperature for ca. 3 h, the reaction mixture was taken to dryness and

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[1] (a) CNR, Università di Padova. (b) Università di Bologna. (c) Iowa State University.
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Table I. IR and ^1H and $^{31}P\{^1H\}$ NMR Data for Cyclic Diaminocarbene Complexes of Pt(II) and Pd(II)

	IR[a]		^1H NMR[b]		$^{31}P\{^1H\}$ NMR[b]	
compd	ν(CN)	ν(NH)	δ(NCH_2)	δ(other)	δ(P)	^1J(PPt)
trans-$\{(PPh_3)_2Pt[\overline{CN(C_6H_4\text{-}p\text{-}OMe)CH_2CH_2N}(H)\}Br\}BF_4$ (**1**)	1511 s	3345 w	2.70 m	3.83 s,[c] 9.36 s[d,e]	15.79 s	2582
trans-$\{(PPh_3)_2Pt[\overline{CN(C_6H_4\text{-}p\text{-}Me)CH_2CH_2N}(H)]Br\}BF_4$ (**2**)	1513 s, 1539 m	3336 w	2.54 m, 2.86 m	2.37 s,[f] 9.71 s[d,g]	15.69 s	2585
trans-$\{(PPh_3)_2Pt[\overline{CN(Me)CH_2CH_2N}(H)]Br\}BF_4$ (**3**)	1520 m, 1539 m	3355 w	2.38 s, br	2.81 s,[h,i] 8.81 br[d,j]	17.13 s	2558
trans-$\{(PMePh_2)_2Pt[\overline{CN(C_6H_4\text{-}p\text{-}OMe)CH_2CH_2N}(H)]Me\}BF_4$ (**4**)	1510 s	3387 w	2.80 m	0.01 t,[k] 2.26 t,[l] 3.82 s,[c] 9.61 br[d,m]	7.38 s	2843
trans-$\{(PPh_3)_2Pd[\overline{CN(C_6H_4\text{-}p\text{-}OMe)CH_2CH_2N}(H)]Br\}BF_4$ (**5**)	1510 s	3345 m-w	2.77 m	3.85 s,[c] 8.22 br[d]	19.77 s	
trans-$\{(PPh_3)_2Pd[\overline{CN(C_6H_4\text{-}p\text{-}Me)CH_2CH_2N}(H)]Br\}BF_4$ (**6**)	1513 s	3349 w	2.75 m	2.39 s,[f] 8.84 br[d]	19.86 s	
trans-$\{(PPh_3)_2Pd[\overline{CN(Me)CH_2CH_2N}(H)]Br\}BF_4$ (**7**)	1519 m, 1531 m	3349 w	2.45 m	2.86 s,[h] 8.87 br[d]	20.83 s	
cis-$Br_2Pt[\overline{CN(C_6H_4\text{-}p\text{-}Me)CH_2CH_2N}(H)](PPh_3)$ (**8**)	1511 s	3334 m	3.59 t, 3.26 t	2.38[f,n]	8.18 s	3954
$Br_2Pd[\overline{CN(C_6H_4\text{-}p\text{-}Me)CH_2CH_2N}(H)]_2$ (**9**)	1517 s	3317 m-s	3.68 m	2.35 s[f,n]		
trans-$\{(PPh_3)_2Pt[\overline{CN(C_6H_4\text{-}p\text{-}Me)CH_2CH_2N}(CH_2CH{=}CH_2)]Br\}BF_4$[o] (**10**)	1510 s		3.53 t, 3.08 t	2.36 s,[f] 4.15 d,[p] 4.91–5.17 m[q]	14.65 s	2544
trans-$\{(PPh_3)_2Pd[\overline{CN(C_6H_4\text{-}p\text{-}OMe)CH_2CH_2N}(CH_2CH{=}CH_2)]Br\}BF_4$[r] (**11**)	1509 s		3.49 t, 3.00 t	3.82 s,[c] 3.98 d,[p] 4.92–5.07 m[q]	20.10 s	
trans-$\{(PPh_3)_2Pt[\overline{CN(C_6H_4\text{-}p\text{-}Me)CH_2CH_2N}(CH_2C{\equiv}CH)]Br\}BF_4$[s] (**12**)	1508 s		3.42 t, 3.12 t	2.30 s,[f] 2.31 t,[t] 4.35 d[u]	14.89 s	2510

[a] Nujol mull, cm^{-1}. Abbreviations: s = strong; m = medium; w = weak. [b] The ^1H and ^{31}P NMR spectra were recorded in CD_2Cl_2. Proton chemical shifts are reported from Me_4Si by taking the chemical shift of dichloromethane-d_2 as +5.32 ppm. Phosphorus chemical shifts are from external H_3PO_4 85%. Positive chemical shifts are downfield from the reference; J in Hz. Abbreviations: s = singlet; d = doublet; t = triplet; m = multiplet; br = broad. [c] OMe. [d] NH. [e] ^3J(HPt) = 20.4 Hz. [f] Me. [g] ^3J(HPt) = 20.0 Hz. [h] *N*-Me. [i] ^4J(HPt) = 5.7 Hz. [j] ^3J(HPt) = ca. 15 Hz. [k] Pt–Me; ^2J(HPt) = 53.8 Hz, ^3J(HP) = 7.5 Hz. [l] *P*-Me; ^2J(HP) + ^4J(HP) = 7.1 Hz, ^3J(HPt) = 35.8 Hz. [m] No Pt–N–H coupling was detected. [n] The NH signal could not be located. [o] ν(C=C) = 1612 (vw) cm^{-1}. [p] $NCH_2CH{=}CH_2$, J(HH) = 6.1 Hz. For complex 10 $^4J(^{195}PtNCH_2CH{=}CH_2)$ = 7 Hz. [q] $NCH_2CH{=}CH_2$. [r] ν(C=C) = 1611 (w) cm^{-1}. [s] ν(C≡C) = 2114 (w) cm^{-1}. [t] $NCH_2C{\equiv}CH$, J(HH) = 2.6 Hz. [u] $NCH_2C{\equiv}CH$, J(HH) = 2.6 Hz, $^4J(^{195}PtNCH_2C{\equiv}CH)$ = 7.2 Hz.

the residue taken up with CH_2Cl_2 (10 mL). To the filtered solution was added dropwise *n*-pentane (50 mL), causing precipitation of the white product: yield 180 mg, 85%; mp 178–182 °C dec. Anal. Calcd for $C_{46}H_{42}N_2OBrP_2PtBF_4{\cdot}1.5CH_2Cl_2$: C, 47.94; H, 3.81; N, 2.35. Found: C, 48.37; H, 3.64; N, 2.47. **2**: yield 78%; mp >270 °C. Anal. Calcd for $C_{46}H_{42}N_2BrP_2PtBF_4$: C, 52.79; H, 4.04; N, 2.67. Found: C, 52.47; H, 4.13; N, 2.76. **3**: yield 66%; mp >280 °C dec. Anal. Calcd for $C_{40}H_{38}N_2BrP_2PtBF_4{\cdot}CH_2Cl_2$: C, 46.65; H, 3.82; N, 2.65. Found: C, 46.17; H, 3.59; N, 2.79.

In a separate experiment, stirring of the reaction mixture leading to **2** was continued for 24 h at room temperature. After this time, it was taken to dryness; the residue was dissolved in the minimum amount of CH_2Cl_2 (ca. 10 mL), and *n*-pentane (40 mL) was added. The white solid obtained (ca. 70% yield) showed no ν(BF_4) in the IR spectrum, while all the other spectral features were identical with those of the tetrafluoroborate salt **2** (Table I). Anal. Calcd for $C_{46}H_{42}N_2Br_2P_2Pt{\cdot}CH_2Cl_2$: C, 50.19; H, 3.94; N, 2.49; Cl + Br, 20.51. Found: C, 49.78; H, 3.91; N, 2.70; Cl + Br, 20.17. On the basis of spectral and analytical data, the compound was formulated as the bromide salt *trans*-$\{(PPh_3)_2[\overline{CN(C_6H_4\text{-}p\text{-}Me)CH_2CH_2N}(H)]Br\}Br$. This same compound (together with a small amount of **8**; see text) was also obtained by reacting a pure sample of **2** with fivefold excess of LiBr in MeOH for 24 h at room temperature following the procedure in the previous paragraph.

***trans*-$\{(PMePh_2)_2Pt[\overline{CN(C_6H_4\text{-}p\text{-}OMe)CH_2CH_2N}(H)]Me\}BF_4$ (4).** This compound was prepared as described above for **1** by starting with $Br[NH_3CH_2CH_2Br]$ (205 mg, 1.00 mmol), 1.5 M *n*-BuLi in *n*-hexane (0.7 mL, 1.05 mmol) in THF (15 mL) at 0 °C, and *trans*-$[(PMePh_2)_2Pt(CNC_6H_4\text{-}p\text{-}OMe)Me]BF_4$ (208 mg, 0.25 mmol). The reaction mixture was warmed to room temperature and stirred for 24 h. At this time, an IR spectrum showed no ν(N≡C) absorption. The solution was worked up as for **1** to yield 150 mg (68%) of the product: mp 153–155 °C dec. Anal. Calcd for $C_{37}H_{41}N_2OP_2PtBF_4$: C, 50.87; H, 4.73; N, 3.20. Found: C, 50.48; H, 4.54; N, 3.02.

***trans*-$\{(PPh_3)_2Pd[\overline{CN(R)CH_2CH_2N}(H)]Br\}BF_4$ (R = *p*-$MeOC_6H_4$ (5), *p*-MeC_6H_4 (6), Me (7)).** These Pd(II)–carbene complexes were prepared under the same reaction conditions used for the analogous Pt(II) complexes (see **1**) by using a [Pd–isocyanide]:[$Br(NH_3CH_2CH_2Br)$] ratio of 1:2 starting from *trans*-$[(PPh_3)_2Pd(CNR)Cl]BF_4$ (R = *p*-$MeOC_6H_4$, *p*-MeC_6H_4, Me). The reaction times were on the order of 1–2 h for **5** and **6** and ca. 15 h for the *N*-methyl derivative **7**. **5**: yield 37%; mp 255–260 °C. Anal. Calcd for $C_{46}H_{42}N_2OBrP_2PdBF_4{\cdot}0.5CH_2Cl_2$: C, 54.95; H, 4.26; N, 2.75. Found: C, 54.97; H, 4.32; N, 2.70. **6**: yield 52%; mp 260–265 °C. Anal. Calcd for $C_{46}H_{42}N_2BrP_2PdBF_4{\cdot}0.5CH_2Cl_2$: C, 55.82; H, 4.33; N, 2.80. Found: C, 56.08; H, 4.38; N, 2.91. **7**: yield 40%; mp 278–283 °C dec. Anal. Calcd for $C_{40}H_{38}N_2BrP_2PdBF_4{\cdot}0.5CH_2Cl_2$: C, 56.28; H, 4.48; N, 2.65. Found: C, 56.42; H, 4.28; N, 2.98.

***cis*-$Br_2Pt[\overline{CN(C_6H_4\text{-}p\text{-}Me)CH_2CH_2N}(H)](PPh_3)$ (8).** To a suspension of $Br[NH_3CH_2CH_2Br]$ (210 mg, 1.00 mmol) in THF (10 mL) at 0 °C was added 1.5 M *n*-BuLi (0.66 mL, 1.00 mmol). To the colorless solution so obtained was added *cis*-$Cl_2Pt(CNC_6H_4\text{-}p\text{-}Me)(PPh_3)$ (325 mg, 0.50 mmol) and the reaction mixture stirred at room temperature for 30 min, after which time no ν(N≡C) absorption was present. The reaction mixture was evaporated to dryness, and the residue was taken up with CH_2Cl_2 (80 mL). This solution was filtered and concentrated under reduced pressure to 10 mL, and *n*-pentane (40 mL) was added. The resulting white solid was filtered off and dried under vacuum: yield 240 mg, 62%; mp >280 °C. Anal. Calcd for $C_{28}H_{27}N_2Br_2PPt{\cdot}CH_2Cl_2$: C, 38.95; H, 3.38; N, 3.24; Br + Cl, 26.71. Found: C, 39.41; H, 3.42; N, 3.73; Br + Cl, 26.25.

$Br_2Pd[\overline{CN(C_6H_4\text{-}p\text{-}Me)CH_2CH_2N}(H)]_2$ (9). To a suspension of $Br[NH_3CH_2CH_2Br]$ (200 mg, 0.97 mmol) in THF (15 mL) at 0 °C was added 1.5 M *n*-BuLi (0.7 mL, 1.05 mmol). To the colorless solution was added immediately in one portion solid *cis*-$Cl_2Pd(CNC_6H_4\text{-}p\text{-}Me)_2$ (200 mg, 0.48 mmol), and the reaction mixture was allowed to reach room temperature. After 15 min, an IR spectrum of the solution showed the presence of only one ν(N≡C) absorption at 2197 cm^{-1} together with a band at 1515 cm^{-1} corresponding to ν(N=C). The course of the reaction was followed by IR for 3 h, during which time no substantial decrease of the 2197-cm^{-1} absorption was observed. However, during this time a white precipitate formed, which was filtered off, washed with *n*-pentane (3 × 10 mL), and dried under vacuum: yield 60 mg, 25%; mp 265–268 °C. Anal. Calcd for $C_{20}H_{24}N_4Br_2Pd{\cdot}2CH_2Cl_2$: C, 34.93; H, 3.73; N, 7.41. Found: C, 35.21; H, 3.38; N, 8.03. **9** is insoluble in most common organic solvents. Attempts to isolate the monoisocyanide–carbene complex $Br_2Pd[\overline{CN(C_6H_4\text{-}p\text{-}Me)CH_2CH_2N}(H)](CNC_6H_4\text{-}p\text{-}Me)$ from the mother liquor were unsuccessful.

Reactions of the Deprotonated Diaminocarbene Complexes. Synthesis of *trans*-$\{(PPh_3)_2Pt[\overline{CN(C_6H_4\text{-}p\text{-}Me)CH_2CH_2N}(CH_2CH{=}CH_2)]Br\}BF_4$ (10). A suspension of **2** (300 mg, 0.29 mmol) in THF (20 mL) at –8 °C (ice–water–NH_4Cl bath) was treated with 1.6 M *n*-BuLi in *n*-hexane (0.19 mL, 0.3 mmol) and subsequently an excess of allyl bromide (0.25 mL, 2.95 mmol). The reaction mixture was allowed to reach room temperature. After 30 min, a clear solution was obtained. It was taken

Table II. Crystal Data and Intensity Collection Parameters for **8**

formula	$C_{28}H_{27}Br_2N_2PPt$
M_r	777.4
cryst syst	triclinic
space group	$P\bar{1}$
a, Å	11.255 (3)
b, Å	13.393 (2)
c, Å	10.020 (2)
α, deg	106.55 (1)
β, deg	112.00 (4)
γ, deg	76.99 (3)
U, Å^3	1330.4
Z	2
D(calcd), g cm^{-3}	1.94
μ(Mo Kα), cm^{-1}	83.8
cryst dimens, mm	0.25 × 0.35 × 0.3
scan mode	$\omega/2\vartheta$
ϑ range, deg	2.5–25
octants of rec space explored	$\pm h,k,\pm l$
measd reflcns	3127
obsd unique reflcns with $I > 2.5\sigma(I)$	2930
final R and R_w indices	0.029, 0.030
ω-scan width, deg	$1 + 0.35 \tan \vartheta$
prescan speed, deg min^{-1}	8
prescan acceptance $\sigma(I)/I$	0.5
max scan time, s	140
requested $\sigma(I)/I$	0.01
params refined	312

Table III. Fractional Atomic Coordinates and Thermal Parameters (Å) for **8**

atom	x	y	z	U_{iso} or U_{eq}, Å^2
Pt	0.45698 (3)	0.19278 (3)	0.00684 (4)	0.0278 (2)
Br(1)	0.54573 (10)	0.21265 (8)	0.18867 (11)	0.0550 (6)
Br(2)	0.67971 (9)	0.14465 (8)	0.15789 (11)	0.0469 (6)
P(1)	0.2594 (2)	0.2363 (2)	0.1591 (2)	0.031 (1)
N(1)	0.3548 (7)	0.2404 (5)	0.2442 (7)	0.040 (4)
N(2)	0.3905 (7)	0.0742 (5)	0.1497 (8)	0.048 (5)
C(1)	0.3964 (7)	0.1720 (6)	0.1387 (9)	0.031 (5)
C(2)	0.3135 (11)	0.1890 (7)	0.3335 (11)	0.061 (7)
C(3)	0.3424 (11)	0.0731 (8)	0.2646 (13)	0.071 (7)
C(4)	0.3459 (8)	0.3504 (6)	0.2750 (9)	0.037 (5)
C(5)	0.4419 (9)	0.4021 (7)	0.2863 (10)	0.046 (6)
C(6)	0.4294 (10)	0.5119 (8)	0.3202 (11)	0.054 (6)
C(7)	0.3216 (11)	0.5703 (7)	0.3454 (10)	0.055 (6)
C(8)	0.2226 (12)	0.5198 (8)	0.3300 (14)	0.077 (8)
C(9)	0.2322 (10)	0.4105 (8)	0.2951 (13)	0.066 (7)
C(10)	0.3115 (13)	0.6907 (7)	0.3888 (13)	0.071 (8)
C(11)	0.1269 (7)	0.2455 (6)	−0.0927 (8)	0.031 (4)
C(12)	0.1025 (9)	0.1557 (7)	−0.0699 (11)	0.045 (5)
C(13)	0.0048 (10)	0.1590 (8)	−0.0168 (12)	0.057 (6)
C(14)	−0.0742 (10)	0.2514 (9)	0.0081 (12)	0.067 (7)
C(15)	−0.0519 (12)	0.3412 (9)	−0.0138 (16)	0.093 (9)
C(16)	0.0476 (9)	0.3392 (7)	−0.0634 (12)	0.059 (6)
C(17)	0.2492 (8)	0.3640 (6)	−0.1968 (10)	0.038 (5)
C(18)	0.3180 (9)	0.4372 (7)	−0.0889 (12)	0.050 (6)
C(19)	0.3138 (10)	0.5369 (8)	−0.1094 (16)	0.065 (8)
C(20)	0.2425 (12)	0.5594 (8)	−0.2426 (16)	0.077 (8)
C(21)	0.1754 (16)	0.4889 (10)	−0.3514 (14)	0.098 (11)
C(22)	0.1756 (12)	0.3888 (8)	−0.3320 (12)	0.072 (8)
C(23)	0.2090 (8)	0.1427 (7)	−0.3353 (9)	0.040 (5)
C(24)	0.0834 (9)	0.1545 (9)	−0.4344 (11)	0.057 (7)
C(25)	0.0465 (12)	0.0839 (11)	−0.5678 (12)	0.074 (8)
C(26)	0.1315 (14)	−0.0012 (10)	−0.6007 (13)	0.081 (9)
C(27)	0.2556 (12)	−0.0156 (8)	−0.5043 (12)	0.068 (8)
C(28)	0.2935 (10)	0.0561 (7)	−0.3704 (10)	0.050 (6)

to dryness; the residue was extracted with CH_2Cl_2 (30 mL) and the solution filtered. The CH_2Cl_2 solution was evaporated to dryness. Addition of acetone (20 mL) and Et_2O (30 mL) gave a white precipitate of the product: yield 200 mg, 64%; mp 151–154 °C. Anal. Calcd for $C_{49}H_{46}N_2BrP_2PtBF_4\cdot 0.5CH_2Cl_2$: C, 52.75; H, 4.02; N, 2.48. Found: C, 52.11; H, 3.98; N, 2.60.

***trans*-$\{(PPh_3)_2Pd[\overline{CN(C_6H_4\text{-}p\text{-}OMe)CH_2CH_2N}(CH_2CH{=}CH_2)]Br\}BF_4$ (11).** To a suspension of **5** (1.20 mg, 1.23 mmol) in THF (50 mL) at −8 °C (ice–water–NH_4Cl bath) was added 1.5 M *n*-BuLi in *n*-hexane (0.93 mL, 1.40 mmol). The resulting brownish solution was treated with allyl bromide (ca. 0.5 mL, 5.91 mmol) in one portion. The reaction mixture was warmed to room temperature and stirred for an additional 30 min. It was then taken to dryness, and the residue was dissolved in CH_2Cl_2 (50 mL). After filtration, the solution was concentrated until a pale yellow solid started to precipitate. Addition of Et_2O (30 mL) and acetone (5 mL) gave a pale yellow solid, which was filtered and dried under vacuum: yield 350 mg, 28%; mp 194–197 °C dec. Anal. Calcd for $C_{49}H_{46}N_2OBrP_2PdBF_4\cdot 0.5CH_2Cl_2$: C, 56.28; H, 4.48; N, 2.65. Found: C, 56.74; H, 4.69; N, 2.70.

Table IV. Relevant Bond Distances (Å) and Angles (deg) for **8**

Bond Distances			
Pt–Br(1)	2.479 (1)	C(8)–C(9)	1.39 (1)
Pt–Br(2)	2.491 (1)	C(11)–C(12)	1.39 (1)
Pt–P(1)	2.235 (2)	C(11)–C(16)	1.39 (1)
Pt–C(1)	1.93 (1)	C(12)–C(13)	1.38 (1)
P(1)–C(11)	1.82 (1)	C(13)–C(14)	1.37 (1)
P(1)–C(17)	1.82 (1)	C(14)–C(15)	1.37 (1)
P(1)–C(23)	1.82 (1)	C(15)–C(16)	1.38 (1)
N(1)–C(1)	1.34 (1)	C(17)–C(18)	1.36 (1)
N(1)–C(2)	1.52 (1)	C(17)–C(22)	1.39 (1)
N(1)–C(4)	1.40 (1)	C(18)–C(19)	1.40 (1)
N(2)–C(1)	1.36 (1)	C(19)–C(20)	1.35 (1)
N(2)–C(3)	1.45 (1)	C(20)–C(21)	1.33 (1)
C(2)–C(3)	1.52 (1)	C(21)–C(22)	1.41 (1)
C(4)–C(5)	1.36 (1)	C(23)–C(24)	1.40 (1)
C(4)–C(9)	1.40 (1)	C(23)–C(28)	1.38 (1)
C(5)–C(6)	1.40 (1)	C(24)–C(25)	1.38 (1)
C(6)–C(7)	1.36 (1)	C(25)–C(26)	1.36 (1)
C(7)–C(8)	1.37 (1)	C(26)–C(27)	1.38 (1)
C(7)–C(10)	1.53 (1)	C(27)–C(28)	1.39 (1)
Bond Angles			
Br(1)–Pt–Br(2)	90.3 (1)	C(11)–P(1)–C(17)	106.5 (4)
Br(1)–Pt–P(1)	88.1 (1)	C(11)–P(1)–C(23)	100.9 (4)
Br(1)–Pt–C(1)	176.8 (2)	C(17)–P(1)–C(23)	108.1 (4)
Br(2)–Pt–P(1)	178.4 (1)	N(1)–C(1)–N(2)	107 (1)
Br(2)–Pt–C(1)	86.8 (2)	Pt–C(1)–N(1)	132 (1)
P(1)–Pt–C(1)	94.8 (2)	N(1)–C(2)–C(3)	101 (1)
Pt–P(1)–C(11)	115.7 (3)	N(2)–C(3)–C(2)	104 (1)
Pt–P(1)–C(17)	109.9 (3)	N(1)–C(4)–C(5)	124 (1)
Pt–P(1)–C(23)	115.2 (3)	N(1)–C(4)–C(9)	118 (1)
C(1)–N(1)–C(2)	114 (1)	C(5)–C(4)–C(9)	118 (1)
C(1)–N(1)–C(4)	126 (1)	C(4)–C(5)–C(6)	121 (1)
C(2)–N(1)–C(4)	120 (1)	C(5)–C(6)–C(7)	120 (1)
C(1)–N(2)–C(3)	115 (1)	C(6)–C(7)–C(10)	120 (1)
C(7)–C(8)–C(9)	122 (1)	C(8)–C(7)–C(10)	121 (1)
C(4)–C(9)–C(8)	119 (1)	C(6)–C(7)–C(8)	119 (1)
Pt–C(1)–N(2)	122 (1)		

***trans*-$\{(PPh_3)_2Pt[\overline{CN(C_6H_4\text{-}p\text{-}Me)CH_2CH_2N}(CH_2C{\equiv}CH)]Br\}BF_4$ (12).** This compound was obtained as described for **10** by starting from **2** (300 mg, 0.29 mmol), 1.6 M *n*-BuLi in *n*-hexane (0.19 mL, 0.30 mmol), and propargyl bromide (0.25 mL, 3.31 mmol): yield 220 mg, 71%; mp 194–197 °C. Anal. Calcd for $C_{49}H_{44}N_2BrP_2PtBF_4$: C, 54.16; H, 4.27; N, 2.58. Found: C, 53.58; H, 4.62; N, 2.54.

X-ray Structural Determination. Crystal data for **8** are summarized in Table II together with some experimental details. Crystallization of **2** (see also text) from CH_2Cl_2/Et_2O gave a few crystals suitable for X-ray structural characterization together with some nondiffracting material. The latter was identified by IR and ^1H and ^{31}P NMR as an amorphous residue of **2**, only **8** being present as single crystals.

Diffraction intensities were collected at room temperature on an Enraf-Nonius CAD-4 diffractometer with Mo Kα radiation (λ = 0.71069 Å) and reduced to F_o values. Absorption correction was applied by using the Walker and Stuart method,[9] after a complete structural model was obtained and all atoms were refined isotropically. The relative correction factors varied from 1.0 to 0.93. The structure was solved by direct methods[10] and Fourier methods and refined by full-matrix least squares, the minimized function being $\sum w(|F_o| - |F_c|)^2$. The weighting scheme employed was $w = k/[\sigma^2(F_o) + |g|F_o^2]$, where k and g were refined (1.393 and 0.0004, respectively).

The SHELX76[11] package of crystallographic programs was used for

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[9] Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A: Found Crystallogr.* **1983**, *A39*, 158.

[10] Sheldrick, G. M. "SHELX86", University of Göttingen: Göttingen, FRG, 1986.

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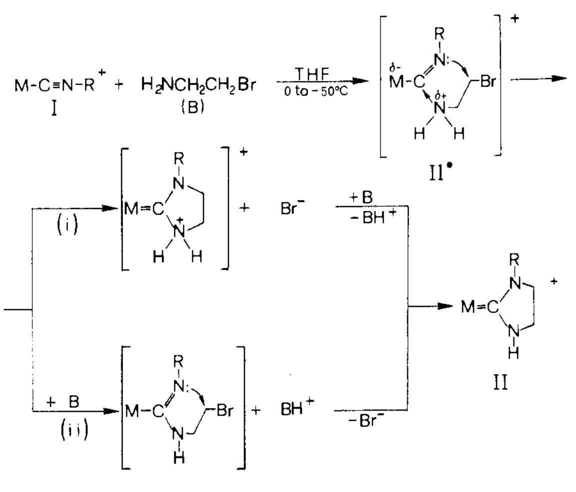
Scheme I

$$2\,Br^{-}\,{}^{+}H_3NCH_2CH_2Br + 2\,n\text{-}BuLi \xrightarrow[0\text{ to }-50\,^{\circ}C]{THF} 2\,H_2NCH_2CH_2Br + 2\,LiBr + 2\,n\text{-}BuH$$



M=Pd, Pt; R=aryl, alkyl

most of the computations, with the analytical scattering factors, corrected for the real and imaginary parts of anomalous dispersions, taken from ref 11b. Thermal vibrations were treated anisotropically for all non-hydrogen atoms. H atoms were added in calculated positions (C–H = 1.08 Å) and refined "riding" on the corresponding C or N atoms. A final difference Fourier map showed residual peaks lower than 1.5 e Å^{-3} in the proximity of the Pt atom. The atomic coordinates are reported in Table III and relevant bond distances and angles in Table IV.

Results and Discussion

Synthesis of Pt(II) and Pd(II) Diaminocarbene Complexes. 2-Bromoethylamine, generated by reaction of [$BrCH_2CH_2NH_3$]Br and *n*-BuLi in THF at 0 °C, reacts with the isocyanide ligand in the cationic Pt(II) complexes *trans*-[$L_2Pt(CNR)X$]BF_4 (L = PPh_3, R = *p*-$MeOC_6H_4$, *p*-MeC_6H_4, Me, X = Cl; L = $PMePh_2$, R = *p*-$MeOC_6H_4$, X = Me) and Pd(II) complexes *trans*-[$(PPh_3)_2Pd(CNR)Cl$]BF_4 (R = *p*-$MeOC_6H_4$, *p*-MeC_6H_4, Me) to form the corresponding air-stable five-membered cyclic diaminocarbene complexes of type II (Scheme I). The proposed mechanism involves nucleophilic attack of 2-bromoethylamine on the carbon of the coordinated isocyanide to give the intermediate imino–metal(II) species II*. Subsequent steps to give the final carbene complex II may involve either (route i) intramolecular cyclization of the imino intermediate II* and subsequent deprotonation of the cyclic carbene by an additional 2-bromoethylamine molecule or (route ii) initial deprotonation of II* by 2-bromoethylamine to give the imido intermediate, which subsequently undergoes ring closure to the final product II. As noted for the corresponding reactions (eq 1) with 2-bromoethanol,[2] none of the suggested intermediates in Scheme I could be detected. A similar mechanism has been proposed[5] for the reaction of Pd(II)-coordinated isocyanides with various amines and for the cyclization reactions of CO groups in metal carbonyl complexes with 2-bromoethylamine or aziridine in the presence of a halide.[3,12]

The Pt(II)–cyclic diaminocarbene complexes of the type *trans*-{$(PPh_3)_2Pt[CN(R)CH_2CH_2N(H)]Br$}$BF_4$ (R = *p*-$MeOC_6H_4$ (**1**), *p*-MeC_6H_4 (**2**), Me (**3**)) were isolated in 66–85% yield from the reaction of the precursor isocyanide derivatives with 2 mol of 2-bromoethylamine for ca. 1 h. The Me complex *trans*-{$(PMePh_2)_2Pt[CN(C_6H_4$-*p*-$OMe)CH_2CH_2N]Me$}BF_4 (**4**) was produced in 68% yield, but the reaction required prolonged stirring of the isocyanide complex (24 h) with excess 2-bromoethylamine (4 mol) to go to completion. The slowness of this reaction is explained by the less electrophilic character of the isocyanide carbon in *trans*-{$(PMePh_2)_2Pt(CNC_6H_4$-*p*-OMe)-Me}BF_4 being trans to a methyl group, i.e., a stronger σ-donor ligand, compared to chloride in *trans*-{$(PMePh_2)_2Pt(CNC_6H_4$-*p*-OMe)Cl}BF_4. The Pd(II)–carbene derivatives *trans*-{$(PPh_3)_2Pd[CN(R)CH_2CH_2N(H)]Br$}$BF_4$ (R = *p*-$MeOC_6H_4$ (**5**), *p*-MeC_6H_4 (**6**), Me (**7**)) were obtained similarly but in lower yields (37–52%) compared to the corresponding Pt(II) analogues.

The cyclization process shown in Scheme I may involve one or even two isocyanide ligands in neutral Pt(II) and Pd(II) complexes. Thus, the *p*-tolyl isocyanide ligand in *cis*-$Cl_2Pt(CNC_6H_4$-*p*-Me)(PPh_3) is converted to the corresponding cyclic diaminocarbene derivative *cis*-$Br_2Pt[CN(C_6H_4$-*p*-Me)-$CH_2CH_2N(H)](PPh_3)$ (**8**) in 62% yield by reaction in THF with 2 mol of 2-bromoethylamine for ca. 30 min at room temperature. The *p*-tolyl isocyanide ligands in *cis*-$Cl_2Pd(CNC_6H_4$-*p*-$Me)_2$ give the bis(diaminocarbene) complex *cis*-$Br_2Pd[CN(C_6H_4$-*p*-Me)-$CH_2CH_2N(H)]_2$ (**9**) in 25% yield by reaction with 4 mol of 2-bromoethylamine. The reaction proceeds stepwise through the rapid formation of a carbene–isocyanide complex, which slowly converts to the final dicarbene product **9**. The intermediate mixed carbene–isocyanide complex was not isolated from the reaction mixture but was detected by IR spectroscopy in solution (see Experimental Section).

The five-membered cyclic diaminocarbene complexes **1**–**9** were characterized by their elemental analyses (Experimental Section) and IR and ^1H and ^{31}P NMR spectra (Table I). The IR spectra show medium to strong ν(C–H) peaks in the range 1510–1539 cm^{-1} and medium to weak ν(N–H) absorptions in the range 3317–3355 cm^{-1}, as are also found in Pt(II) and Pd(II) complexes of noncyclic diaminocarbenes.[13] The cationic carbene complexes **1**–**7** and **10**–**12** show $\nu(BF_4)$ as a strong absorption at ca. 1050 cm^{-1} as observed for the aminooxycarbene derivatives.[2] Compounds **2**, **3**, and **7** also show a high-frequency band of medium intensity in the region 1531–1539 cm^{-1}, which can be assigned to the NH deformation.[12b,c] The absence of ν(Pt–Cl) absorptions in the IR spectra of complexes **1**–**3** and **5**–**9** coupled with the presence of only one phosphorus resonance for the two trans phosphine ligands in the ^{31}P NMR spectra suggests that complete replacement of the chloride ligand in the *trans*-[$L_2Pt(CNR)Cl$]BF_4 starting complexes by bromide occurred in the cyclization reactions, in contrast to that found in the aminooxy system, where only partial Cl^- substitution was observed.[2] This is reasonable since excess bromide is present in the reacting 2-bromoethyl ammonium bromide salt (Scheme I). Analytical and spectroscopic results also indicate that complete BF_4^- for Br^- exchange occurs under prolonged stirring of the reaction mixtures leading to complexes II (Scheme I). This has been experimentally checked in the case of **2**, which afforded after ca. 24 h of stirring at room temperature a white solid showing no $\nu(BF_4)$ bands in the IR spectrum but having all the other spectroscopic features identical with those of the tetrafluoroborate salt **2**. This complex has been formulated as the bromo cationic derivative *trans*-{$(PPh_3)_2Pt[CN(C_6H_4$-*p*-$Me)CH_2CH_2N(H)]Br$}Br on the basis of analytical data. Pure samples of the tetrafluoroborate complexes II can be obtained by stirring II in acetone with an excess of $NaBF_4$ for ca. 3 h at room temperature (see Experimental Section).

Exchanges of chloride and tetrafluoroborate ions in the cationic complexes II (Scheme I) are not the only side reactions occurring during cyclizations of coordinated isocyanide ligands in I by 2-bromoethylamine. In the preparation of **2**, the neutral complex *cis*-$Br_2Pt[CN(C_6H_4$-*p*-$Me)CH_2CH_2N(H)](PPh_3)$ (**8**) has been obtained in small amounts as a crystalline product and structurally

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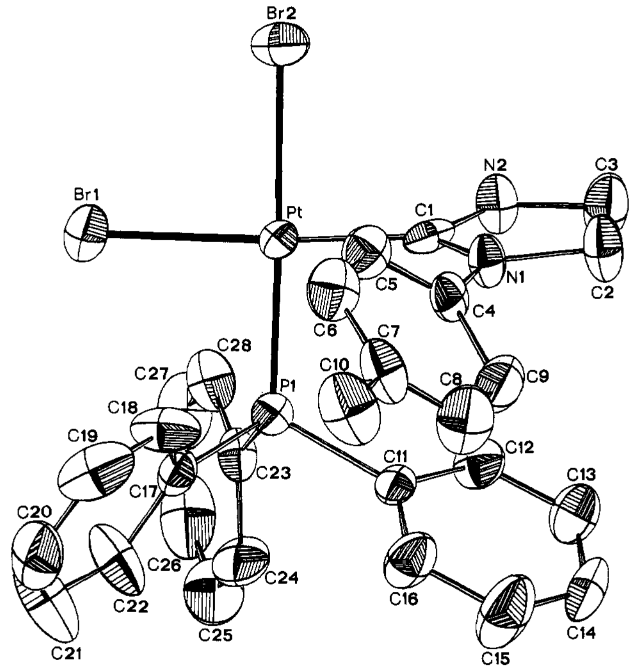

Figure 1. ORTEP drawing of the molecule *cis*-$Br_2Pt[CN(C_6H_4$-*p*-Me)$CH_2CH_2N(H)](PPh_3)$ (**8**) showing the atom labeling.

characterized (see below and Experimental Section). The ^{31}P NMR spectrum of **2** showed an additional signal (<5% by integration of the ^{31}P signals) at δ 8.18, identical with that found for **8** which has been independently prepared (see Experimental Section). A plausible explanation for the formation of **8** and **2** would entail displacement of a PPh_3 ligand by Br^- present in the reaction mixture (Scheme I). This has been confirmed in a separate experiment by reacting **2** with a fivefold excess of LiBr in MeOH at room temperature for 12 h (eq 2 and Experimental Section). The white solid obtained after workup showed the IR

$$trans\text{-}\{(PPh_3)_2Pt[CN(C_6H_4\text{-}p\text{-}Me)CH_2CH_2N(H)]Br\}BF_4 + \text{LiBr (excess)} \xrightarrow[\text{12 h, room temp}]{\text{MeOH}}$$

$$trans\text{-}\{(PPh_3)_2Pt[CN(C_6H_4\text{-}p\text{-}Me)CH_2CH_2N(H)]Br\}Br + \underset{\text{major product}}{}$$

$$LiBF_4 + \underset{\textbf{8}\text{, minor product}}{cis\text{-}Br_2Pt[CN(C_6H_4\text{-}p\text{-}Me)CH_2CH_2N(H)](PPh_3)} + PPh_3 \quad (2)$$

spectrum of **2** except that no $\nu(BF_4)$ absorption was present. The ^{31}P NMR spectrum (CD_2Cl_2) showed peaks at δ 15.69 (90% by integration, $^1J_{PPt}$ = 2585 Hz) and δ 8.18 ($^1J_{PPt}$ = 3954 Hz). From comparison with spectral data of authentic samples (see Experimental Section and Table I), it is concluded that the reaction of **2** with excess bromide leads mainly to exchange of BF_4^- by Br^-. The formation of the neutral complex **8** does occur but is rather limited. This observation is also in agreement with the elemental analysis data for complexes **1**–**7**, which are always correct for the proposed formulas.

The ^1H NMR spectra of **1**–**7** and **9** show the $-NCH_2$ signals of the carbene ring in the range δ 2.38–3.68 as broad AA'BB' multiplets in CD_2Cl_2 at 80 MHz, but as triplets for **8** (δ 3.59, 3.26). The ^1H NMR spectra of **10**–**12** were taken at 300 MHz ($CDCl_3$), and the $-NCH_2$ signals are triplets (see also below). The N–H resonance of complexes **1**–**7** shows up as a broad signal in the range δ 8.22–9.71. For the Pt(II) complexes **1**–**3**, the N–H resonance is further split by coupling with ^{195}Pt ($^3J_{HPt} \simeq$ 15–20 Hz) as found in other Pt(II) aminocarbene complexes.[14]

Description of the Structure of *cis*-$Br_2Pt[CN(C_6H_4$-*p*-Me)$CH_2CH_2N(H)](PPh_3)$ (8). The molecular structure of **8** is shown in Figure 1 together with the atom labeling. The Pt(II) atom adopts the expected square-planar coordination; the maximum deviation from the mean plane defined by the atoms Br(1), Br(2), P(1), C(1), and Pt is 0.17 Å (C(1)).

The two Br atoms are cis with a Br(1)–Pt–Br(2) angle of 90.3 (1)°; the Br(2)–Pt–C(1) and P(1)–Pt–C(1) angles (86.8 (2) and 94.8 (2)°, respectively) show that the whole carbenoid system is pushed toward Br(2) by the bulkier PPh_3 ligand. Part of the deformation is also accommodated by the Br(1)–Pt–P(1) angle (88.1 (1)°). Despite the angular deformations at the Pt center, the Br(1)–Pt–C(1) angle approaches linearity (176.8 (2)°).

The whole set of bond distances from the Pt-atom center in **8** shows significant differences from the values observed in the closely related aminooxycarbene complex *trans*-$\{(PPh_3)_2Pt[CN(C_6H_4$-*p*-Me)$CH_2CH_2O]Br\}BF_4$[1] (hereafter A). For instance, the slight lengthening of the Pt–Br(1) distance trans to the C(carbene) atom in **8** with respect to the corresponding distance in A (2.479 (1) and 2.469 (1) Å, respectively) is accompanied by an appreciable shortening of the Pt–C(carbene) bond length (1.93 (1) and 1.98 (1) Å, respectively). Also, the Pt–P bond length trans to Br(2) (2.235 (2) Å) appears considerably shorter than that found for mutually trans PPh_3 ligands in A (mean value 2.327 (1) Å)[2] but compares well with the value of 2.220 (2) Å found in *cis*-$Cl_2Pt[CHN(Me)_2](PPh_3)$,[15] where the phosphine ligand is trans to a Cl atom. Moreover, the two Pt–Br distances in **8** (2.479 (1) and 2.491 (1) Å, respectively) clearly show a higher trans influence of the carbene ligand compared to that of PPh_3.

As observed in the related aminooxycarbene A,[2] the cyclic carbene ligand is strictly planar (maximum deviation 0.01 Å for N(1)). Both C(1)–N(1) and C(1)–N(2) bond lengths (1.34 (1), 1.36 (1) Å) suggest extensive π-bonding within the N(1)–C(carbene)–N(2) system. Although the C(1)–N(1) value appears to be longer than the corresponding value in A (1.30 (1) Å), both C–N bond distances are comparable to the values quoted by Stepaniak and Payne (1.30–1.37 Å)[16] for Pt(II)–aminocarbene derivatives.

The angle formed between the platinum square plane and the carbene ring (102.1°) differs from that observed in A (93.4°), thus reflecting the dissymmetry of the steric pressure exerted by the two different cis ligands on the carbenoid system.

The related effect on the tilting of the *p*-tolyl group with respect to the carbene ring is even more remarkable. The dihedral angle between these two planes is 45.9°, close to the values found for the similar 1,3-diphenylimidazolidin-2-ylidene complexes *cis*- and *trans*-$Cl_2Pt[C(PhNCH_2)_2](PEt_3)$[17] (cis, 53.1°; trans, 48.4 and 49.3°)[18] but larger than that previously found in A (20.7°).[2] In this latter complex the tilting was recognized as a result of a compromise between repulsive Pt–O and Pt–H (*p*-tolyl) interactions, deformation of the sp^2 angles, and torsion of the N–C bond joining the two cyclic moieties. The same cooperative interactions are at work in **8**. Therefore, considering the close similarity of the two carbenoid systems in the aminooxy and diamino species, the dramatic variation in the plane tilting must be ascribed only or mainly to the replacement of one PPh_3 ligand in A with the smaller Br ligand in **8**, thus allowing the *p*-tolyl ligand to move away from the "Pt side". Thus, the values of the contacts Pt–H5 (bonded to C(5), see Figure 1) and H9–H2B (bonded to C(9) and C(2), respectively) are longer than in A (2.95, 2.20 Å in 8 and 2.51, 2.10 Å in A). In other words, repulsive interactions with the Pt atom are alleviated by further tilting of the *p*-tolyl ligand. However, the dihedral angle formed between the imidazole and phenyl rings in metal-free systems shows a great

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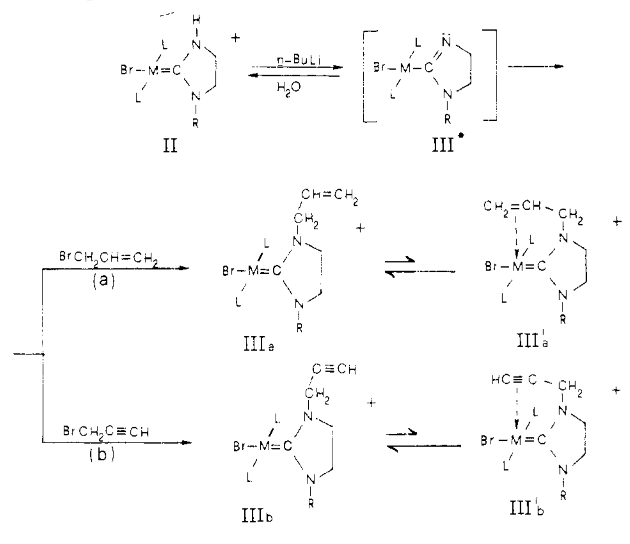
Scheme II



L = PPh₃ ; (a) M = Pt , R = p-MeC₆H₄ ; M = Pd , R = p-MeOC₆H₄
(b) M = Pt , R = p-MeC₆H₄

variability ranging from 60–80°[19-21] to values much closer to coplanarity.[22-24]

Finally, it is noteworthy that deformations of the sp² angles in both the carbenoid and *p*-tolyl moiety are substantially the same as those in A, thus showing larger inner (side facing Pt(II)) than outer values (Pt–C(1)–N(1) = 132 (1)°, C(1)–N(1)–C(4) = 126 (1)°, C(2)–N(1)–C(4) = 120 (1)°, N(1)–C(4)–C(5) = 124 (1)°, and N(1)–C(4)–C(9) = 118 (1)°). The deformations of these bond angles also contribute to minimizing the steric interactions in the molecule. A comparison of the Pt–C(1)–N(2) angle in **8** (122 (1)°) with the values observed in A (115 (1)°) suggests that a similar contraction of this angle is prevented in **8** probably because of the presence of the H(1) atom bonded to N(2).

Reactions of Deprotonated Diaminocarbene Complexes. The aminooxycarbene $Cp(CO)_2Fe(=\overline{COCH_2CH_2NH})^+$[3,25] reacts with bases such as NaH or K_2CO_3 to give the neutral imino complex $Cp(CO)_2Fe(=\overline{COCH_2CH_2N}{:})$. The nucleophilicity of the imino nitrogen has been demonstrated by its reactions with electrophiles.[3,25] This reactivity suggests that the Pt(II) and Pd(II) diaminocarbenes described in this paper could be deprotonated and reacted with electrophiles to give functionalized diaminocarbenes. Such reactions are shown in Scheme II; the N–H group in the Pt(II)- and Pd(II)-cyclic diaminocarbene complexes **2** and **5** is deprotonated at −8 °C by *n*-BuLi to give the intermediate imino complex III*, which rapidly reacts with allyl bromide or propargyl bromide to afford the corresponding N-substituted products IIIa and IIIb, respectively (compounds **10**–**12**, Table I). The imino intermediate III* could not be isolated, being rapidly hydrolyzed by traces of H_2O to give the starting aminocarbene II. Complexes **10**–**12** have been characterized by elemental analyses (see Experimental Section) and IR and ¹H and ³¹P NMR spectra (Table I).

With the carbene ring likely to be oriented perpendicular to the Pt square plane, the olefinic group in complexes of type IIIa (i.e., **10** and **11**) and the acetylenic group in the complex of type IIIb (i.e., **12**) could be in a favorable position to interact with the metal center (structures III'a and III'b of Scheme II). Complexes of type III'a with cis carbene and olefin ligands are of particular interest since such species have been proposed as key intermediates in catalytic processes such as olefin metathesis, cyclopropanation of alkenes, and the Ziegler–Natta polymerization of alkenes. Considerable effort has been spent in the isolation, characterization, and reactivity of such complexes.[26] It has been suggested on the basis of IR and ¹H NMR data that, in the allyl-substituted aminothiocarbene complex *trans*-$\{(PPh_3)_2Pt[C(SCH_2CH{=}CH_2)NMe_2]Br\}BF_4$,[27] Pt(II) coordination of the olefin double bond occurs. More recently,[25] it has been observed that UV photolysis of the *N*-allyl carbene $Cp(CO)_2Fe(\overline{COCH_2CH_2N}CH_2CH{=}CH_2)^+$ results in the loss of one CO ligand and coordination of the olefinic bond of the allyl group to the Fe to give $Cp(CO)\overline{Fe(COCH_2CH_2NCH_2CH{=}CH_2)}^+$.

The ¹H NMR spectra of **10**–**12** in $CDCl_3$ at 300 MHz show the $-NCH_2$ protons of the carbene ring as triplets at δ 3.53 and 3.08 (**10**), δ 3.49 and 3.00 (**11**), and δ 3.42 and 3.12 (**12**). The $-NCH_2$ protons of the allyl group (structure IIIa of Scheme II) in **10** and **11** are observed as a doublet at δ 4.15 (J_{HH} = 6.1 Hz, M = Pt) and δ 3.98 (J_{HH} = 6.1 Hz, M = Pd). Broad $^{195}Pt-NCH_2$ coupling of ca. 7 Hz is observed, which is comparable to that found for the *N*-methyl derivative **3**, in which $^4J_{HPt}$ = 5.7 Hz. The CH and CH_2 olefinic protons give rise to complex multiplets in the range δ 4.91–5.17 for **10** (M = Pt) and δ 4.92–5.07 for **11** (M = Pd). The corresponding olefinic protons for the uncoordinated allyl group in $Cp(CO)_2Fe(\overline{COCH_2CH_2N}CH_2CH{=}CH_2)^+$ appear as multiplets in the range δ 5.39–5.90 but move upfield to δ 5.48 (CH) and δ 3.04 ($=CH_2$) upon coordination to the Fe in $Cp(CO)\overline{Fe(COCH_2CH_2NCH_2CH{=}CH_2)}$.[25] In the *N*-allylaminothiocarbene complex *trans*-$\{(PPh_3)_2Pt[C(SCH_2CH{=}CH_2)NMe_2]\}BF_4$,[27] the olefinic protons are observed at δ 5.1 as a complex multiplet. The complexity of the signal has been suggested to arise in part from ¹⁹⁵Pt coupling to these protons. The complexity of the olefinic signals in **10** (M = Pt) could mask coupling to ¹⁹⁵Pt, but it is also possible that no pentacoordination takes place or that the interconversion between four- and five-coordinate forms is fast on the NMR time scale. On the other hand, the four-coordinate structure IIIa appears to be preferred in the solid state. This conclusion is based on IR spectra of **10** and **11** in Nujol, which show weak bands at 1612 and 1611 cm⁻¹, respectively; these bands may be assigned to ν(C=C) of an uncoordinated olefin (the *N*-alkyl-substituted aminothiocarbene shows ν(C=C) at 1637 cm⁻¹ in CH_2Cl_2). Finally, the ³¹P NMR spectra of **10** and **11** show a sharp singlet flanked by ¹⁹⁵Pt satellites for the phosphine ligands, indicating that phosphine is not displaced by the olefin at the probe temperature (28 °C).

The IR spectrum of the *N*-propargyl carbene **12** in Nujol shows ν(C≡C) at 2114 cm⁻¹ as a weak absorption. The ν(C≡C) absorption could not be detected in IR spectra of several coordinated monosubstituted[28] and disubstituted[29] cationic acetylene compounds of the type *trans*-$[L_2Pt(RC{\equiv}CR')Me]^+$ (L = phosphine, arsine; R = alkyl, aryl; R' = H, alkyl, aryl). However, Raman spectra of the disubstituted acetylene complexes[29] all showed ν(C≡C) in the range 2000–2125 cm⁻¹ as an intense polarizable absorption.

In the ¹H NMR spectrum of **12**, the $-NCH_2C{\equiv}CH$ methylene signal occurs as a doublet (4.35) due to coupling with the acetylene proton (J_{HH} = 2.6 Hz); there is also coupling to ¹⁹⁵Pt ($^4J_{HPt}$ = 7.2 Hz). The acetylene proton is observed as the expected triplet at δ 2.31. The ¹H NMR spectrum of free $BrCH_2C{\equiv}CH$ shows a doublet for the CH_2 protons at δ 3.89 with $^4J_{HH}$ = 2.6 Hz; the CH proton occurs as a triplet at δ 2.56 with the same coupling

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constant. No ^{195}Pt–acetylenic proton coupling is observed for **12**. This would imply that no triple-bond coordination to the metal takes place (structure IIIb of Scheme II), unless there is rapid interconversion on the NMR time scale between the coordinated (III′b) and uncoordinated (IIIb) triple-bond forms (Scheme II). Also, there is no evidence for acetylene displacement of the phosphine from the ^{31}P NMR spectrum, which shows a sharp singlet flanked by ^{195}Pt satellites for the two trans phosphines. Thus, there is no unequivocal evidence for allyl or propargyl group coordination to the Pt(II), but it also cannot be ruled out.

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Registry No. **1**, 111139-87-8; **2**, 111159-37-6; **3**, 111139-89-0; **4**, 111139-91-4; **5**, 111139-93-6; **6**, 111139-95-8; **7**, 111139-97-0; **8**, 111139-99-2; **9**, 111159-38-7; **10**, 111159-40-1; **11**, 111140-01-3; **12**, 111140-03-5; *trans*-$[(PPh_3)_2Pt(CNC_6H_4\text{-}p\text{-}OMe)Cl]BF_4$, 110313-73-0; *trans*-$[(PMePh_2)_2Pt(CNC_6H_4\text{-}p\text{-}OMe)Me]BF_4$, 110330-07-9; *trans*-$[(PPh_3)_2Pd(CN\text{-}p\text{-}C_6H_4OMe)Cl]BF_4$, 110313-86-5; *trans*-$[(PPh_3)_2Pd(CN\text{-}p\text{-}C_6H_4Me)Cl]BF_4$, 110313-88-7; *trans*-$[(PPh_3)_2Pd(CNMe)Cl]BF_4$, 110313-90-1; *cis*-$Cl_2Pt(CNC_6H_4\text{-}p\text{-}Me)(PPh_3)$, 111140-04-6; *cis*-$Cl_2Pd(CNC_6H_4\text{-}p\text{-}Me)_2$, 40927-16-0; $Br[NH_3CH_2CH_2Br]$, 2576-47-8; allyl bromide, 106-95-6; propargyl bromide, 106-96-7.

Supplementary Material Available: Hydrogen atom coordinates (Table S-I), anisotropic thermal parameters (Table S-II), and bond distances and angles (Table S-IV) (13 pages); observed and calculated structural factors (Table S-III) (17 pages). Ordering information is given on any current masthead page.

Contribution from the Laboratorium voor Anorganische Chemie, Rijksuniversiteit Groningen, Nijenborgh 16,
9747 AG Groningen, The Netherlands, and Istituto di Strutturistica Chimica,
Centro di Studio per la Strutturistica Diffrattometrica del CNR, Università di Parma, 43100 Parma, Italy

Synthesis, Reactivity, and Crystal Structure of $CpV(CO)_3tht$ (tht = Tetrahydrothiophene). A Mild-Condition Synthetic Pathway to Substitution Derivatives of $CpV(CO)_4$ and Preparation and X-ray Characterization of *cis*-$CpV(CO)_2bpy$ (bpy = 2,2′-Bipyridine)

Sandro Gambarotta,*[†] Angiola Chiesi-Villa,[‡] and Carlo Guastini[‡]

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Irradiation of $CpV(CO)_4$ in the presence of tht (tht = tetrahydrothiophene) affords the complex $CpV(CO)_3tht$ (**1**), in which one carbonyl group has been replaced by the thioether ligand. **1** reacts readily with several ligands including 2,2′-bipyridine (bpy) and pyrrolidine (pyrr), providing a mild-condition pathway to the new derivatives *cis*-$CpV(CO)_2bpy$ (**2**) and $CpV(CO)_3pyrr$ (**3**). The structures of **1** and **2** have been determined by X-ray analysis. Both complexes are orthorhombic: **1** has a *Pbca* space group with $a = 14.171$ (4) Å, $b = 14.184$ (5) Å, $c = 13.035$ (4) Å, $V = 2620$ (1) Å^3, $Z = 8$, and $D_{calcd} = 1.461$ g cm^{-3}, and the final R factor for 1937 reflections was 0.054; **2** has a *Pnma* space group with $a = 7.687$ (4) Å, $b = 15.073$ (6) Å, $c = 12.593$ (5) Å, $V = 1459$ (1) Å^3, $Z = 4$, and $D_{calcd} = 1.494$ g cm^{-3}, and the final R value for 1423 reflections was 0.035. The structure of **3** has been assigned on the basis of its ^{13}C and ^{1}H NMR, IR, and analytical data.

Introduction

The monocyclopentadienyl carbonyl complexes of transition metals have received much attention as versatile compounds in coordination chemistry, oxidative-addition reactions, and metal-promoted organic synthesis.[1] Attractive results have been obtained also in the field of dinitrogen fixation by using the manganese derivative $CpMn(CO)_3$.[2]

The chemistry of the vanadium analogue, $CpV(CO)_4$, is currently limited to the photosubstitution of one or two carbonyls by ligands such as phosphines, arsines, stibines, bismuthines,[3] aromatic alkynes,[4] and nitric oxide,[5] which are able to resist the harsh photochemical conditions.

The elusive $CpV(CO)_3thf$ (thf = tetrahydrofuran), analogous to the well-known $CpMn(CO)_2thf$, has been recently obtained by low-temperature irradiation of dilute solutions of $CpV(CO)_4$, any attempt to isolate this species affording $Cp_2V_2(CO)_5$ in quite low yield.[6] The acetonitrile derivative, $CpV(CO)_3CH_3CN$, has been detected in solution as a complex too reactive to be isolated.[7] The utilization of tetrahydrothiophene (tht) instead of the isostructural tetrahydrofuran allowed the preparation of crystalline $CpMn(CO)_2tht$, in which the labile thioether ligand permits easy manipulation of the complex, while keeping intact the reactivity of the $CpMn(CO)_2$ moiety.[8]

We wish to report here the large-scale preparation of $CpV(CO)_3tht$ (**1**) together with a brief investigation of its utilization for the synthesis of new $CpV(CO)_nL$ derivatives.

Experimental Section

All operations were performed under dry nitrogen with use of standard Schlenk techniques or in a nitrogen-filled drybox (Braun MB 200). $CpV(CO)_4$ was prepared according to published procedures.[9] Solvents were dried and distilled by following standard procedures. Cyclohexyl isocyanide (Aldrich) was distilled before use, pyrrolidine (Aldrich) was dried over potassium pyrrolidide and distilled with the use of 15-in. Vigreux column, tetrahydrothiophene (Aldrich) was dried over potassium and distilled twice with the use of a 15-in. Vigreux column, and 2,2′-bipyridine (Pro Labo) was used without further purification. NMR solvents (benzene-d_6, thf-d_8) were vacuum-transferred from Na-K alloy. ^{1}H and ^{13}C NMR spectra were recorded on a Varian VXR 300 spectrometer. Chemical shifts are reported in units of δ, referenced to tet-

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[†] Rijksuniversiteit Groningen.
[‡] Università di Parma.

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