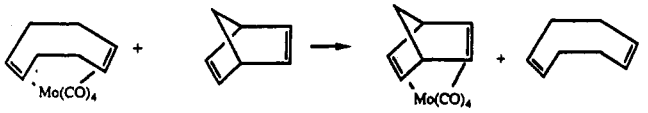
of dimethylphenanthroline is 1.2 kcal/mol less stable than the unsubstituted phenanthroline ligand, presumably due to steric repulsion between the methyl groups and coordinated carbon monoxide ligands.

Cyclooctadiene versus Norbornadiene. As discussed in this section, substitution of norbornadiene for cyclooctadiene as shown in eq 15 is exothermic by about 2 kcal/mol. This is opposite to



(15)

the heat of binding to Pd(II), where cyclooctadiene was 0.3 kcal/mol more stable.[17] The reasons for these relatively small differences are not clear.

Conclusion

Data for monodentate and bidentate ligands are combined in Table V, which also includes IR spectral data. In general, the stabilities of $L_2Mo(CO)_4$ complexes are similar to those in our earlier work on $L_3Mo(CO)_3$. The importance of steric factors is reduced, as expected. The changing electronic nature of the metal center may also play a role in influencing complex stability. For bidentate ligands forming metallacycles, four-membered rings are less stable than five-membered rings by 8 kcal/mol. Six- and seven-membered rings are slightly less stable than four-membered rings (1-2 kcal/mol). In the absence of ring strain, or special steric effects, heats of reaction can be estimated to fair accuracy on the basis of data for related complexes. Additional work in progress is aimed at extending those data in order to generate a complete picture of the factors controlling stability in these and other organomolybdenum systems.

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Registry No. dppe, 1663-45-2; COD, 111-78-4; NBD, 121-46-0; bpy, 366-18-7; dpae, 4431-24-7; tmeda, 110-18-9; Mephen, 484-11-7; dppm, 2071-20-7; phen, 66-71-7; arphos, 23582-06-1; dppb, 7688-25-7; dppp, 6737-42-4; dmpm, 64065-08-3; dppbz, 13991-08-7; dmpe, 23936-60-9; py, 110-86-1; $(PCl_3)_2Mo(CO)_4$, 16244-51-2; $(Ph_3As)_2Mo(CO)_4$, 16742-97-5; $[P(OMe)_3]_2Mo(CO)_4$, 15631-22-8; $(py)_2Mo(CO)_4$, 16742-99-7; $(Ph_3P)_2Mo(CO)_4$, 16742-93-1; $(Et_3As)_2Mo(CO)_4$, 111265-67-9; $[P(OPh)_3]_2Mo(CO)_4$, 59599-01-8; $(PPh_2Me)_2Mo(CO)_4$, 37438-49-6; $(PPhMe_2)_2Mo(CO)_4$, 24554-47-0; $(P\text{-}n\text{-}Bu_3)_2Mo(CO)_4$, 16244-54-5; $(CyNC)_2Mo(CO)_4$, 15227-72-2; $(PEt_3)_2Mo(CO)_4$, 19217-80-2; $(PMe_3)_2Mo(CO)_4$, 16027-45-5; (COD)$Mo(CO)_4$, 12109-74-9; (bpy)$Mo(CO)_4$, 15668-64-1; (dpae)$Mo(CO)_4$, 38536-63-9; (dppe)$Mo(CO)_4$, 14971-45-0; (tmeda)$Mo(CO)_4$, 23301-98-6; (dppm)$Mo(CO)_4$, 26743-81-7; (phen)$Mo(CO)_4$, 15740-78-0; (arphos)$Mo(CO)_4$, 53557-42-9; (dppb)$Mo(CO)_4$, 15553-69-2; (dppp)$Mo(CO)_4$, 15553-68-1; (dppe)$Mo(CO)_4$, 15444-66-3; (dmpm)$Mo(CO)_4$, 90624-09-2; (dppbz)$Mo(CO)_4$, 111189-30-1; (dmpe)$Mo(CO)_4$, 40544-97-6; (NBD)$Mo(CO)_4$, 12146-37-1; $Mo(CO)_6$, 13939-06-5; Ph_3As, 603-32-7; Ph_3P, 603-35-0; Et_3As, 617-75-4; $P(OPh)_3$, 101-02-0; PPh_2Me, 1486-28-8; CO, 630-08-0; $PPhMe_2$, 672-66-2; $P(OMe)_3$, 594-09-2; $P\text{-}n\text{-}Bu_3$, 998-40-3; CyNC, 931-53-3; PEt_3, 554-70-1; PMe_3, 594-09-2; PCl_3, 7719-12-2; P, 7723-14-0; Mo, 7439-98-7.

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Contribution from the Centro di Chimica e Tecnologia dei Composti Metallorganici degli Elementi di Transizione del CNR, Istituto di Chimica Industriale, Facoltà di Ingegneria, Università di Padova, 35100 Padova, Italy, Dipartimento di Chimica "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 Aminooxycarbene Complexes of Platinum(II) and X-ray Structure of *trans*-$\{(PPh_3)_2Pt[\overline{CN(C_6H_4\text{-}p\text{-}Me)CH_2CH_2O}]Br\}BF_4$

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Electrophilic isocyanide CNR ligands in cationic Pt(II) complexes of the type *trans*-$[(PR'_3)_2Pt(CNR)Cl]BF_4$ (I) ($PR'_3 = PPh_3$, PMe_2Ph; R = *p*-$MeOC_6H_4$, *p*-MeC_6H_4, *p*-$NO_2C_6H_4$, Me, C_6H_{11}) are converted to the corresponding 5-membered cyclic aminooxycarbene derivatives *trans*-$\{(PR'_3)_2Pt[\overline{CN(R)CH_2CH_2O}]X\}BF_4$ (II) (X = Cl, Br) by reaction in THF with 2-bromoethanol in the presence of *n*-BuLi. These reactions are likely to proceed by nucleophilic attack of the alkoxide on the isocyanide carbon atom to give an imidoyl intermediate, which cyclizes intramolecularly to yield the carbene products. The less sterically hindered CNMe and aryl isocyanide ligands in I are converted in a few minutes to the final products II in ca. 70-90% yield; the more bulky CNC_6H_{11} derivative gives only a 25% yield. The *t*-BuNC ligand in the complex *trans*-$[(PPh_3)_2Pt(CN\text{-}t\text{-}Bu)Cl]BF_4$ does not react at all, nor does *p*-$MeOC_6H_4NC$ in *trans*-$[(PCy_3)_2Pt(CNC_6H_4\text{-}p\text{-}OMe)Cl]BF_4$ with bulky PCy_3 ligands. Treatment of *cis*-$Cl_2Pt(CNC_6H_4\text{-}p\text{-}OMe)_2$ with 2 equiv of 2-bromoethoxide gave the bis(aminooxycarbene) $Br_2Pt[\overline{CN(C_6H_4\text{-}p\text{-}OMe)CH_2CH_2O}]_2$. The Pt(II)-cyclic aminooxycarbenes II were characterized by their elemental analysis and IR, ^1H NMR, and ^{31}P NMR spectra.

An X-ray-determined structure of *trans*-$\{(PPh_3)_2Pt[\overline{CN(C_6H_4\text{-}p\text{-}Me)CH_2CH_2O}]Br\}BF_4$, space group $P2_1/a$, a = 12.175 (2) Å, b = 26.137 (3) Å, c = 13.274 (4) Å, β = 91.61 (2)°, and Z = 4, was refined to R = 0.039 (R_w = 0.044) for 5325 independent reflections. The coordination geometry around the Pt(II) atom is square planar with the carbene ligand perpendicular to the plane. The cyclic aminooxycarbene ligand is planar with $C(sp^2)$-N and $C(sp^2)$-O bond distances of 1.30 (1) and 1.33 (1) Å, indicating significant π-bonding between the nitrogen, oxygen, and carbene carbon.

Introduction

Cyclization reactions of electrophilic metal-coordinated isocyanide ligands leading to heterocyclic carbene complexes have been accomplished by different synthetic strategies (Scheme I).[2-6] For instance, paths a and b of Scheme I take advantage of the reactivity of suitably functionalized isocyanides which undergo

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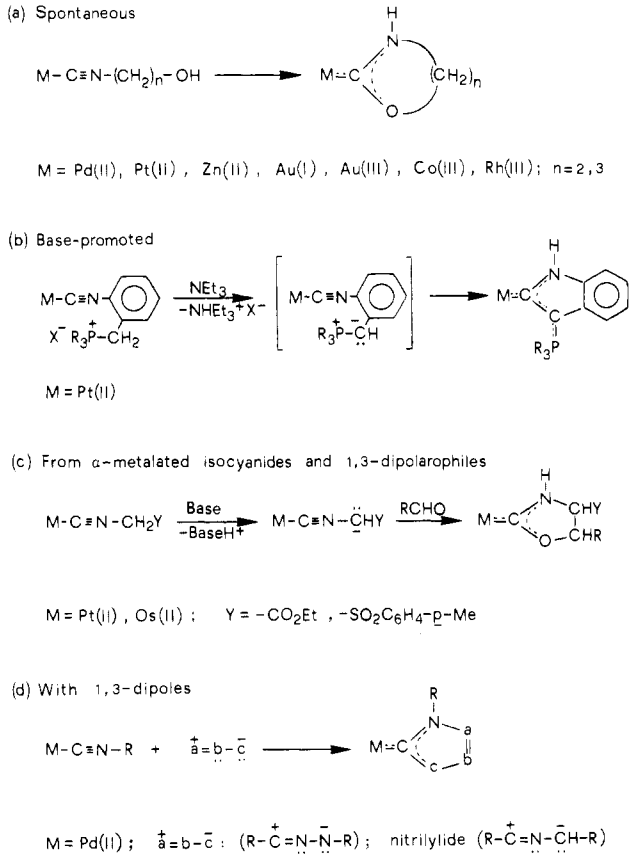
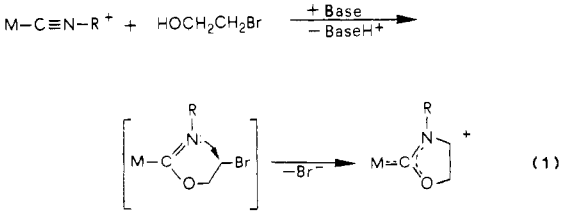
Scheme I. Cyclization Processes of Metal-Coordinated Isocyanide Ligands



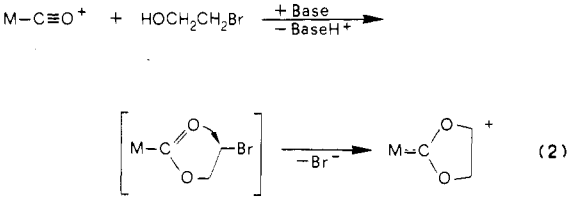
spontaneous[2] (path a) or base-promoted[3] (path b) intramolecular ring closure. Isocyanides with acidic C–H bonds in the α-position can be anionized with an appropriate base. The resulting α-metalated compounds can add to polar double bonds to form heterocycles[4,5] (path c). Finally, cyclic carbene complexes have been produced by reactions of RNC ligands with 1,3-dipoles such as nitrilimines and nitrilylides[6] (path d).

The well-known ability[7] of metal-activated isocyanide ligands to react with protic nucleophiles such as alcohols to give metal–carbene complexes led us to investigate their reactions with 2-bromoethanol, which has an easily displaced Br^- at the β-carbon atom. The reaction is likely to proceed, in the presence of an appropriate base, by nucleophilic attack of 2-bromoethoxide on the metal-bound isocyanide carbon atom to give an imidoyl intermediate, which cyclizes intramolecularly to give the carbene product (eq 1).



(1)

The isocyanide–cyclic carbene conversion described in eq 1 appears to be unprecedented in isocyanide–metal reaction chemistry. However, similar reactions have been shown[8] to occur with sufficiently electropositive CO ligands in several metal carbonyl complexes of iron and manganese, where one or even two CO groups could be converted to carbene ligands (eq 2). The electronic and steric properties of RNC ligands in contrast to CO can be modified by changing the R group. Different isocyanide



(2)

ligands as well as different metal complexes were examined to establish the range of complexes that participate in reaction 1; the results are reported herein.

Experimental Section

The reagents 2-bromoethanol, 2-chloroethanol, cyclohexyl isocyanide, and *tert*-butyl isocyanide were of the highest quality commercially available and used as supplied. *n*-Butyllithium (ca. 1.6 M in hexane, Fluka) was titrated before use according to the reported procedure.[9] The isocyanides *p*-$MeOC_6H_4NC$,[10] *p*-MeC_6H_4NC,[11] *p*-$NO_2C_6H_4NC$,[11] and MeNC[12] were prepared according to literature methods. Tetrahydrofuran (THF) was distilled from sodium/benzophenone before use. All other solvents were of reagent grade and used without further purification. All reactions were performed under an N_2 or Ar atmosphere. Product isolations were carried out in air. Infrared spectra were taken on a Perkin-Elmer 983 spectrophotometer calibrated against polystyrene film and are accurate within ± 2 cm^{-1}. ^1H and $^{31}P\{^1H\}$ NMR spectra were obtained on a Varian FT-80A spectrometer. Melting points were determined on a hot plate apparatus and are uncorrected. Elemental analyses were performed by the Department of Analytical Chemistry of the University of Padua.

Starting Complexes. *cis*-$(PPh_3)_2PtCl_2$,[13] *trans*-$(PPh_3)_2PtCl_2$,[14] *cis*-$(PMe_2Ph)_2PtCl_2$,[15] *trans*-$(PMePh_2)_2Pt(Me)Cl$,[16] $(COD)PtCl_2$[17] (COD = 1,5-cyclooctadiene), *trans*-$(PCy_3)_2PtCl_2$,[18] and $(MeCN)_2PdCl_2$[19] were obtained as described in the literature. *trans*-$(PPh_3)_2PdCl_2$ was obtained in quantitative yield by adding dropwise 2 mol of PPh_3 dissolved in acetone to an acetone suspension of $(MeCN)_2PdCl_2$ at room temperature. After the addition was complete (ca. 20 min), the solution obtained was reduced to a small volume under reduced pressure and treated with Et_2O to give a yellow precipitate of the complex. Spectral data are as reported in the literature.[20]

Method A. *trans*-[$(PPh_3)_2Pt(CNR)Cl$]BF_4 (R = *p*-$MeOC_6H_4$ (1), *p*-$NO_2C_6H_4$ (3), Me (6)). These complexes were prepared by the same general procedure that is described here for **1**. A suspension of *cis*-$(PPh_3)_2PtCl_2$ (650 mg, 0.77 mmol) in CH_2Cl_2 (30 mL) was treated with a solution of 0.82 M $AgBF_4$ (0.94 mL, 0.77 mmol) in acetone at room temperature, and the reaction mixture was stirred for 1 h. It was then filtered to remove solid AgCl and treated dropwise at 0 °C with a solution of *p*-$MeOC_6H_4NC$ (103 mg, 0.77 mmol) in CH_2Cl_2 (10 mL). After the addition was complete, the reaction mixture was allowed to reach room temperature. It was then concentrated under reduced pressure to 10 mL, and Et_2O (50 mL) was added. The resulting white precipitate was filtered off and recrystallized from CH_2Cl_2/Et_2O: yield 600 mg (80%); mp 238–241 °C. Anal. Calcd for $C_{44}H_{37}NOClP_2PtBF_4 \cdot 0.5CH_2Cl_2$: C, 52.52; H, 3.76; N, 1.37. Found: C, 52.25; H, 3.63; N, 1.33. For **3**: yield 75%; mp 213–215 °C. Anal. Calcd for $C_{43}H_{34}N_2O_2P_2ClPtBF_4$: C, 52.16; H, 3.46; N, 2.83. Found: C, 51.96; H, 3.50; N, 2.88. For **6**: yield 82%; mp 220–223 °C. Anal. Calcd for $C_{38}H_{33}NClP_2PtBF_4 \cdot 0.5\ CH_2Cl_2$: C, 49.96; H, 3.70; N, 1.51. Found: C, 49.98; H, 3.60; N, 1.49.

Method B. *trans*-[$(PPh_3)_2Pt(CNR)Cl$]BF_4 (R = *p*-MeC_6H_4 (2), C_6H_{11} (7), *t*-Bu (8)). These compounds were obtained by a procedure that is outlined here for **2**. To a suspension of *trans*-$(PPh_3)_2PtCl_2$ (1581 mg, 2.00 mmol) in acetone (80 mL) in the presence of $NaBF_4$ (1100 mg, 10.00 mmol) was added dropwise over a period of 20 min *p*-MeC_6H_4NC (246 mg, 2.10 mmol) in acetone (20 mL) at room temperature. The reaction mixture was vigorously stirred for 1 h and then taken to dryness. After the residue was dissolved in CH_2Cl_2 (80 mL), the solution was

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Table I. Selected IR and ^{31}P NMR Data for Pt(II)- and Pd(II)-Isocyanide Complexes

no.	compd[a]	IR, cm^{-1} $\nu(N{\equiv}C)_{coord}$[b]	$\nu(N{\equiv}C)_{free}$[b]	$\Delta\nu$[c]	$\nu(M-Cl)$[d]	$^{31}P\{^1H\}$ NMR[e] $\delta(P)$	$^1J(PPt)$, Hz
1	*trans*-$[(PPh_3)_2Pt(CNC_6H_4$-*p*-$OMe)Cl]BF_4$[f]	2207 s	2128 s	79	352 w	18.38 s	2189
2	*trans*-$[(PPh_3)_2Pt(CNC_6H_4$-*p*-$Me)Cl]BF_4$[g]	2208 s	2129 s	79	346 w	18.52 s	2184
3	*trans*-$[(PPh_3)_2Pt(CNC_6H_4$-*p*-$NO_2)Cl]BF_4$	2202 s	2128 s	74	338 w	18.57 s	2158
4	*trans*-$[(PMe_2Ph)_2Pt(CNC_6H_4$-*p*-$OMe)Cl]BF_4$[h]	2205 s	2129 s	76	338 m	−3.64 s	2032
5	*trans*-$[(PMePh_2)_2Pt(CNC_6H_4$-*p*-$OMe)Me]BF_4$[i]	2183 s	2129 s	54		7.13 s	2618
6	*trans*-$[(PPh_3)_2Pt(CNMe)Cl]BF_4$[j]	2259 s	2168 s	91	333 w	18.02 s	2203
7	*trans*-$[(PPh_3)_2Pt(CNC_6H_{11})Cl]BF_4$[k]	2227 s	2145 s	82	338 w	18.51 s	2198
8	*trans*-$[(PPh_3)_2Pt(CNBu$-*t*$)Cl]BF_4$[l]	2220 s	2139 s	81	352 w	19.18 s	2221
9	*trans*-$[(PCy_3)_2Pt(CNC_6H_4$-*p*-$OMe)Cl]BF_4$[m]	2212 s[n]			336 w	*m*	*m*
10	*trans*-$[(PPh_3)_2Pd(CNC_6H_4$-*p*-$OMe)Cl]BF_4$[o]	2210 s	2128 s	82	339 m, w	23.64 s	
11	*trans*-$[(PPh_3)_2Pd(CNC_6H_4$-*p*-$Me)Cl]BF_4$[p]	2208 s	2129 s	79	347 w	23.76 s	
12	*trans*-$[(PPh_3)_2Pd(CNMe)Cl]BF_4$[q]	2261 s	2168 s	93	311 m, w	22.90 s	
13	*trans*-$[(PPh_3)_2Pd(CNC_6H_{11})Cl]BF_4$[r]	2231 s	2145 s	86	345 w	23.76 s	
14	*cis*-$Cl_2Pt(CNC_6H_4$-*p*-$OMe)_2$[s]	2236 s, 2207 s	2128	108, 79	345 m, 324 m		
15	*cis*-$Cl_2Pd(CNC_6H_4$-*p*-$Me)_2$[t]	2237 s, 2215 s	2129	108, 89	333 m, 313 m		

[a] The ^1H NMR spectra are given in the footnotes and are recorded on solutions 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; J in Hz; s = singlet, t = triplet, and m = multiplet. [b] In CH_2Cl_2; s = strong, m = medium, and w = weak. [c] $\Delta\nu = \nu(N{\equiv}C)_{coord} - \nu(N{\equiv}C)_{free}$. [d] Nujol mull. [e] CD_2Cl_2, H_3PO_4 85% external reference; s = singlet. [f] $\delta(OMe) = 3.77$ s. [g] $\delta(Me) = 2.29$ s. [h] $\delta(P$-*Me*$) = 2.06$ t, $^2J(HP) + {}^4J(HP) = 8.10$, $^3J(HPt) = 29.6$; $\delta(OMe) = 3.78$ s. [i] $\delta(Me) = 0.34$ t, $^2J(HPt) = 61.2$, $^3J(HP) = 7.9$; $\delta(P$-*Me*$) = 2.25$ t, $^2J(HP) + {}^4J(HP) = 7.1$, $^3J(HPt) = 34.3$; $\delta(OMe) = 3.71$ s. [j] $\delta(Me) = 2.36$ t, $^4J(HPt) = 20.2$, $^5J(HP) = 1.1$. [k] $\delta(C_6H_{11}) = 1.10$ m. [l] $\delta(Bu$-*t*$) = 0.63$ s. [m] Too insoluble for ^1H and ^{31}P NMR spectra. [n] Nujol mull. [o] $\delta(OMe) = 3.77$ s. [p] $\delta(Me) = 2.31$ s. [q] $\delta(Me) = 2.55$ s. [r] $\delta(C_6H_{11}) = 1.08$ m. [s] $\delta(OMe) = 3.83$ s. [t] $\delta(Me) = 2.40$ s.

filtered and concentrated to a small volume (ca. 20 mL). Addition of Et_2O gave **2** as a white solid: yield 1600 mg, 84%; mp 220–223 °C. Anal. Calcd for $C_{44}H_{37}NCl_2P_2PtBF_4{\cdot}0.5CH_2Cl_2$: C, 53.09; H, 3.83; N, 1.30. Found: C, 53.37; H, 3.82; N, 1.40. For **7**: yield 92%; mp 203–205 °C. Anal. Calcd for $C_{43}H_{41}NP_2ClPtBF_4$: C, 54.30; H, 4.35; N, 1.47. Found: C, 54.10; H, 4.62; N, 1.74. For **8**: yield 75%; mp >280 °C. Anal. Calcd for $C_{41}H_{39}NCl_2P_2PtBF_4{\cdot}0.5CH_2Cl_2$: C, 52.27; H, 4.04; N, 1.44. Found: C, 51.92; H, 4.17; N, 1.45. Spectroscopic data for these and the other isocyanide complexes are listed in Table I.

***trans*-[$(PMe_2Ph)_2Pt(CNC_6H_4$-*p*-$OMe)Cl]BF_4$ (4).** This complex was prepared by method B starting from *cis*-$(PMe_2Ph)_2PtCl_2$ (542 mg, 1.00 mmol), $NaBF_4$ (550 mg, 5.00 mmol), and *p*-$MeOC_6H_4NC$ (133 mg, 1.00 mmol) in acetone: yield 625 mg, 86%; mp 157–160 °C. Anal. Calcd for $C_{24}H_{29}NOClP_2PtBF_4$: C, 39.66; H, 4.02; N, 1.93. Found: C, 39.31; H, 3.95; N, 1.73.

***trans*-[$(PMePh_2)_2Pt(CNC_6H_4$-*p*-$OMe)Me]BF_4$ (5).** This compound was prepared by method B starting from *trans*-$(PMePh_2)_2Pt(Me)Cl$ (646 mg, 1.00 mmol), $NaBF_4$ (550 mg, 5.00 mmol), and *p*-$MeOC_6H_4NC$ (150 mg, 1.12 mmol) in acetone: yield 670 mg, 80%; mp 170–173 °C. Anal. Calcd for $C_{35}H_{36}NOP_2PtBF_4{\cdot}0.5CH_2Cl_2$: C, 49.30; H, 4.25; N, 1.61. Found: C, 48.84; H, 4.27; N, 1.60.

***trans*-[$(PCy_3)_2Pt(CNC_6H_4$-*p*-$OMe)Cl]BF_4$ (9).** This complex was prepared by method B starting with *trans*-$(PCy_3)_2PtCl_2$ (560 mg, 0.68 mmol), $NaBF_4$ (*ca.* 5.00 mmol) in acetone, and *p*-$MeOC_6H_4NC$ (90.5 mg, 0.68 mmol) in acetone: yield 400 mg, 58%; mp >280 °C. Anal. Calcd for $C_{44}H_{73}NOClP_2PtBF_4$: C, 52.25; H, 7.27; N, 1.38. Found: C, 51.88; H, 7.19; N, 1.31.

***trans*-[$(PPh_3)_2Pd(CNR)Cl]BF_4$ (R = *p*-$MeOC_6H_4$ (10), *p*-MeC_6H_4 (11), Me (12), C_6H_{11} (13)).** All these complexes were prepared by method B starting from *trans*-$(PPh_3)_2PdCl_2$ (1050 mg, 1.50 mmol), the required RNC ligand (1.50 mmol), and $NaBF_4$ (ca. 8.00 mmol) in acetone. The compounds are pale-yellow. For **10**: yield 93%; mp 222–226 °C. Anal. Calcd for $C_{44}H_{37}NOClP_2PdBF_4$: C, 59.61; H, 4.20; N, 1.58. Found: C, 59.39; H, 4.32; N, 1.58. For **11**: yield 86%; mp 218–221 °C. Anal. Calcd for $C_{44}H_{37}NClP_2PdBF_4$: C, 60.71; H, 4.28; N, 1.61. Found: C, 60.59; H, 4.42; N, 1.54. For **12**: yield 83%, mp 216–218 °C. Anal. Calcd for $C_{38}H_{33}NClP_2PdBF_4$: C, 57.46; H, 4.19; N, 1.76. Found: C, 56.97; H, 4.05; N, 1.84. For **13**: yield 85%; mp 198–200 °C. Anal. Calcd for $C_{43}H_{41}NClP_2PdBF_4$: C, 59.88; H, 4.79; N, 1.62. Found: C, 59.72; H, 4.93; N, 1.82.

***cis*-$Cl_2Pt(CNC_6H_4$-*p*-$OMe)_2$ (14).** To a solution of $(COD)PtCl_2$ (374 mg, 1.00 mmol) in CH_2Cl_2 (50 mL) was added dropwise over a period of 5 min a solution of *p*-$MeOC_6H_4NC$ (266 mg, 2.00 mmol) in CH_2Cl_2 (10 mL), and the reaction mixture was stirred at room temperature for 1 h. Addition of MeOH (20 mL) and concentration under reduced pressure gave the white solid product, which was filtered off and dried under vacuum: yield 450 mg, 84%; mp 167–171 °C. Anal. Calcd for $C_{16}H_{14}N_2O_2Cl_2Pt$: C, 36.10; H, 2.65; N, 5.26. Found: C, 36.23; H, 2.44; N, 5.13.

***cis*-$Cl_2Pd(CNC_6H_4$-*p*-$Me)_2$ (15).** This compound was prepared by the method used for **14** starting from $Pd(MeCN)_2Cl_2$ (259 mg, 1.00 mmol) and *p*-MeC_6H_4NC (234 mg, 2.00 mmol): yield 340 mg, 82%; mp 188–192 °C. Anal. Calcd for $C_{16}H_{14}N_2Cl_2Pd$: C, 46.69; H, 3.43; N, 6.80. Found: C, 46.38; H, 3.24; N, 6.55.

Reactions with 2-Bromoethanol. Synthesis of the Cyclic Aminooxycarbene Complexes *trans*-$\{(PR'_3)_2Pt[\overline{CN(R)CH_2CH_2O}]X\}BF_4$ (PR'_3 = PPh_3, R = *p*-$MeOC_6H_4$ (16), *p*-MeC_6H_4 (17), *p*-$NO_2C_6H_4$ (18), Me (20); $PR'_3 = PMe_2Ph$, R = *p*-$MeOC_6H_4$ (19); X = Br, Cl). All these complexes were prepared by an identical procedure, which is outlined for complex **16**. To a solution of $BrCH_2CH_2OH$ (0.05 mL, 0.7 mmol) in THF (15 mL) at 0 °C were added in one portion a 1.5 M solution of *n*-BuLi in *n*-hexane (0.22 mL, 0.33 mmol) and subsequently solid **1** (250 mg, 0.26 mmol). The reaction mixture was allowed to reach room temperature. The course of the reaction was followed by IR by monitoring the decrease of the $\nu(N{\equiv}C)$ absorption. After 15 min, no $\nu(N{\equiv}C)$ band of the starting material was present. The reaction mixture was taken to dryness, the residue was dissolved in CH_2Cl_2 (20 mL), and the solution was filtered and treated with *n*-pentane. The resulting white precipitate was filtered and dried under vacuum: yield 240 mg, 92%; mp 245–248 °C dec. Anal. Calcd for $C_{46}H_{41}NO_2BrP_2PtBF_4{\cdot}CH_2Cl_2$: C, 49.15; H, 3.77; N, 1.22. Found: C, 48.98; H, 3.53; N, 1.17. For **17**: yield 84%, mp 243–247 °C. Anal. Calcd for $C_{46}H_{41}NOBrP_2PtBF_4$: C, 52.74; H, 3.95; N, 1.34. Found: C, 52.46; H, 3.94; N, 1.28. For **18**: yield 78%; mp 238–240 °C dec. Anal. Calcd for $C_{45}H_{38}N_2O_3BrP_2PtBF_4$: C, 50.11; H, 3.55; N, 2.59. Found: C, 50.31; H, 3.38; N, 2.67. For **19**: yield 150 mg, 67%; mp 139–142 °C. Anal. Calcd for $C_{26}H_{33}NO_2BrP_2PtBF_4$: C, 38.30; H, 4.08; N, 1.72. Found: C, 38.00; H, 4.10; N, 1.65. For **20**: yield 82%; mp 220 °C dec. Anal. Calcd for $C_{40}H_{37}NOBrP_2PtBF_4{\cdot}1.5CH_2Cl_2$: C, 45.36; H, 3.61; N, 1.27. Found: C, 45.67; H, 3.57; N, 1.27. The spectroscopic data for these and the other carbene complexes are reported in Tables II and III.

***trans*-$\{(PPh_3)_2Pt[\overline{CN(C_6H_{11})CH_2CH_2O}]X\}BF_4$ (21).** To a solution of $BrCH_2CH_2OH$ (0.08 mL, 1.00 mmol) in THF (10 mL) at 0 °C were added in one portion 0.6 mL (0.9 mmol) of a 1.5 M *n*-hexane solution of *n*-LiBu and subsequently complex **7** (350 mg, 0.37 mmol). The clear solution so obtained was stirred for ca. 45 min at room temperature. After this time a white precipitate formed. An IR solution spectrum did not show residual $\nu(N{\equiv}C)$ bands. the reaction mixture was taken to dryness, and the residue was dissolved in CH_2Cl_2 (10 mL); the solution was filtered and *n*-pentane (20 mL) added to it. The resulting white precipitate was filtered and dried under vacuum: yield 90 mg, 24%; mp 217–220 °C dec. Anal. Calcd for $C_{45}H_{45}NOBrP_2PtBF_4{\cdot}CH_2Cl_2$: C, 49.12; H, 4.21; N, 1.24. Found: C, 48.98; H, 4.47; N, 1.17.

$Br_2Pt[\overline{CN(C_6H_4$-*p*-$OMe)CH_2CH_2O}]_2$ (22). To a solution of $BrCH_2CH_2OH$ (1 mL) in THF (15 mL) at 0 °C were added 1.5 M *n*-BuLi in *n*-hexane (1.7 mL, 1.1 mmol) and subsequently solid **14** (260 mg, 0.50 mmol). Immediately a white precipitate formed. An IR spectrum of the solution did not show any residual $\nu(N{\equiv}C)$ absorption. The reaction mixture was taken to dryness; the residue was taken up in CH_2Cl_2, and the solution was filtered and evaporated again to dryness. Addition of acetone (10 mL) and Et_2O (20 mL) gave the product as a white solid: yield 250 mg, 70%; mp 164–168 °C. Anal. Calcd for

Table II. IR and ^{1}H NMR Data for Cyclic Aminooxycarbene Complexes of Pt(II)

no.	compd	IR[a] ν(C≡N), cm^{-1}	^{1}H NMR[b] δ(OCH$_2$)	δ(NCH$_2$)	δ(other)
16	*trans*-{(PPh$_3$)$_2$Pt[CN(C$_6$H$_4$-*p*-OMe)CH$_2$CH$_2$O]X}BF$_4$	1510 s	3.73 m	3.39 m	3.90 s,[c] 3.88 s[c]
17	*trans*-{(PPh$_3$)$_2$Pt[CN(C$_6$H$_4$-*p*-Me)CH$_2$CH$_2$O]X}BF$_4$	1512 s	3.71 t	3.37 t	2.46[d]
18	*trans*-{(PPh$_3$)$_2$Pt[CN(C$_6$H$_4$-*p*-NO$_2$)CH$_2$CH$_2$O]X}BF$_4$	1522 s	3.73 m	3.49 m	
19	*trans*-{(PMe$_2$Ph)$_2$Pt[CN(C$_6$H$_4$-*p*-OMe)CH$_2$CH$_2$O]Br}BF$_4$	1511 s	4.38 t	3.58 t	3.82 s,[c] 1.96 t,[e,f] 1.80[e,g]
20	*trans*-{(PPh$_3$)$_2$Pt[CN(Me)CH$_2$CH$_2$O]X}BF$_4$	1571 s	3.63 t	2.68 t	2.97 s[h,i]
21	*trans*-{(PPh$_3$)$_2$Pt[CN(C$_6$H$_{11}$)CH$_2$CH$_2$O]X}BF$_4$	1530 m	3.67 t	3.59 t	1.08 m[j]
22	Br$_2$Pt[CN(C$_6$H$_4$-*p*-OMe)CH$_2$CH$_2$O]$_2$	1512 vs	4.52 t	4.05 t	3.85 s[c]

[a] Nujol mull; s = strong, m = medium. [b] Spectra were recorded on solutions in CD_2Cl_2; chemical shifts are reported from Me_4Si by taking the chemical shift of dichloromethane-d_2 as +5.32 ppm; s = singlet, t = triplet, and m = multiplet. [c] OMe. [d] Me. [e] P-Me. [f] ^2J(HP) + ^4J(HP) = 7.9 Hz, ^3J(HPt) = 28.8 Hz. [g] ^2J(HP) + ^4J(HP) = 7.8 Hz, ^3J(HPt) = 27.6 Hz. [h] Me. [i] ^4J(HPt) = 8.5 Hz. [j] C_6H_{11}.

Table III. ^{31}P{^{1}H} NMR Data for the Carbene Complexes

compd[a]	X (% X[b])	^{31}P{^{1}H} NMR[c] δ(P)	^1J(PPt), Hz
16	Br (60)	15.24 s	2512
	Cl (40)	17.33 s	2541
17	Br (90)	15.14 s	2512
	Cl (10)	17.29 s	2540
18	Br (65)	14.54 s	2423
	Cl (35)	16.66 s	2486
19		−10.47 s	2302
20	Br (80)	16.03 s	2473
	Cl (20)	17.68 s	2500
21	Br (88)	16.92 s	2510
	Cl (12)	18.99 s	2536

[a] See Table II. [b] Percentage of halide X derived from integration ratios of the ^{31}P resonances. [c] See footnotes *e* of Table I.

$C_{20}H_{22}N_2O_4Br_2Pt\cdot0.5CH_3COCH_3$: C, 34.97; H, 3.41; N, 3.79. Found: C, 34.98; H, 3.45; N, 3.54.

Reaction with 2-Chloroethanol. Synthesis of *trans*-{(PPh$_3$)$_2$Pt[CN(C$_6$H$_4$-*p*-Me)CH$_2$CH$_2$O]Cl}BF$_4$. The procedure is identical with that described for the synthesis of **16**, starting from $ClCH_2CH_2OH$ (0.02 mL, 0.3 mmol), 1.5 M n-BuLi in *n*-hexane (0.17 mL, 0.25 mmol), and complex **2** (200 mg, 0.21 mmol) in THF (10 mL) at 0 °C. The reaction mixture was stirred for 4 h at room temperature, after which time no ν(N≡C) band of the starting isocyanide complex was present. Workup as for **16** gave 170 mg of the product (81%). The IR spectrum (Nujol) showed a strong ν(C=N) absorption at 1510 cm^{-1}. ^{1}H and ^{31}P NMR data are reported in Tables II and III, respectively. Anal. Calcd for $C_{46}H_{41}NOClP_2PtBF_4\cdot CH_2Cl_2$: C, 51.88; H, 3.98; N, 1.29. Found: C, 52.33; H, 3.87; N, 1.20.

X-ray Structural Determination. Crystal data for **17** are summarized in Table IV together with some experimental details. Crystals suitable for X-ray analysis were obtained from CH_2Cl_2/Et_2O. Diffraction intensities were collected at room temperature on an Enraf-Nonius CAD-4 diffractometer with Mo Kα radiation (λ = 0.710 69 Å), reduced to F_o values and corrected for crystal decay. An empirical absorption correction was applied by measuring scans at intervals of 10° around the diffraction vectors of 12 selected reflections near χ = 90° (transmission range: 92–100%). The structure was solved by conventional Patterson and Fourier methods and refined by full-matrix least square, 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 (4.1 and 0.0002, respectively). The SHELX76 package of crystallographic programs[21] was used for all computations with the analytical scattering factors, corrected for the real and imaginary parts of anomalous dispersions, taken from ref 21b. Thermal vibrations were treated anisotropically for all nonhydrogen atoms of the cation except for the phenyl rings bonded to the P atoms. H atoms were added in calculated positions (C–H = 1.08 Å) and not refined although their contributions to the structure factors were taken into account. The F atoms of the BF_4^- anion showed extensive mean square displacements, which were taken as indicative of a slight librational disorder around the B atom; despite all attempts, different positions for the F atoms could not be distinguished. A final difference Fourier map showed residual peaks lower than 1.5 e Å^{-3} in the vicinity of the Pt atom. The atomic coordinates are reported in Table V, relevant bond distances and angles in Table VI.

Table IV. Crystal Data and Intensity Collection Parameters for **17**

formula	$C_{46}H_{41}BBrF_4NOP_2Pt$
M_r	1047.6
cryst syst	monoclinic
space group	$P2_1/a$
a, Å	12.175 (2)
b, Å	26.137 (3)
c, Å	13.274 (4)
β, deg	91.61 (2)
V, Å^3	4222.4
Z	4
D(calcd), g cm^{-3}	1.65
μ(Mo Kα), cm^{-1}	44.2
min transmissn factor	0.92
cryst dimens, mm	0.25 × 0.3 × 0.2
scan mode	$\omega/2\theta$
θ range, deg	2.5–25
octants of rec space explored	$\pm h,k,l$
no. of measd reflcns	7945
no. of obsd unique reflcns with $I > 2.5\sigma(I)$	5325
final R and R_w indices	0.039, 0.044
ω scan width, deg	0.8 + 0.35 tan θ
prescan speed, deg min^{-1}	8
prescan acceptance $\sigma(I)/I$	0.5
max scan time, s	140
requested $\sigma(I)/I$	0.01
no. of params refined	382

Results and Discussion

Isocyanide Complexes of Pt(II) and Pd(II). In order to explore the feasibility of reaction 1, we focused our attention on metals such as Pt(II) and Pd(II) for which synthetic and mechanistic details of the nucleophilic addition of alcohols and amines to coordinated isocyanides to form stable metal–carbene derivatives have been reported.[22] Thus, the homologous series of Pt(II) and Pd(II) cationic complexes of the general formula *trans*-[(PR′$_3$)$_2$M(CNR)X]BF$_4$ (I) (i.e., **1–13**, Table I), in which both the R group of the isocyanide ligand as well as the other metal substituents were varied over a wide range, were investigated. Such complexes are commonly prepared by two routes (see also ref 23–26). The first (eq 3 and method A of the Experimental

$$cis\text{-}(PPh_3)_2PtCl_2 \xrightarrow{+AgBF_4,\ -AgCl} cis\text{-}[(PPh_3)_2PtCl]_2(BF_4)_2 \xrightarrow{2RNC} 2trans\text{-}[(PPh_3)_2Pt(CNR)Cl]BF_4 \quad (3)$$

R = *p*-MeOC$_6$H$_4$ (**1**), *p*-NO$_2$C$_6$H$_4$ (**3**), Me (**6**)

(21) (a) Sheldrick, G. M. "SHELX76", University of Cambridge, 1976. (b) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1975; Vol. IV, pp 99, 149.

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Table V. Fractional Atomic Coordinates and Thermal Parameters (Å) for **17**

atom	x	y	z	U_{iso} or U_{eq}
Pt	0.65501 (2)	0.09477 (1)	0.16952 (2)	0.0342 (2)
Br	0.66582 (8)	0.04091 (3)	0.01732 (7)	0.0564 (5)
P_1	0.59648 (16)	0.16110 (7)	0.06472 (15)	0.0395 (11)
P_2	0.73168 (16)	0.02813 (8)	0.26474 (15)	0.0393 (11)
C_1	0.6513 (6)	0.1401 (3)	0.2891 (6)	0.041 (4)
O	0.7441 (4)	0.1652 (2)	0.3107 (4)	0.055 (3)
C_2	0.7293 (8)	0.1983 (4)	0.4004 (7)	0.072 (6)
C_3	0.6121 (7)	0.1895 (4)	0.4271 (7)	0.064 (6)
N	0.5747 (5)	0.1515 (2)	0.3511 (4)	0.043 (4)
C_4	0.4645 (6)	0.1306 (3)	0.3534 (6)	0.044 (4)
C_5	0.4351 (7)	0.0849 (3)	0.3095 (7)	0.061 (6)
C_6	0.3312 (7)	0.0652 (4)	0.3172 (7)	0.063 (6)
C_7	0.2528 (6)	0.0916 (4)	0.3744 (6)	0.057 (5)
C_8	0.2820 (7)	0.1380 (4)	0.4141 (7)	0.063 (6)
C_9	0.3859 (7)	0.1576 (4)	0.4055 (6)	0.055 (5)
C_{10}	0.1424 (7)	0.0678 (5)	0.3918 (8)	0.078 (7)
C_{11}	0.6962 (6)	0.1706 (3)	−0.0313 (6)	0.049 (2)
C_{12}	0.8064 (8)	0.1637 (4)	−0.0025 (8)	0.074 (3)
C_{13}	0.8918 (10)	0.1702 (4)	−0.0741 (9)	0.085 (3)
C_{14}	0.8578 (10)	0.1812 (5)	−0.1674 (9)	0.095 (4)
C_{15}	0.7564 (10)	0.1901 (4)	−0.2006 (10)	0.098 (4)
C_{16}	0.6715 (8)	0.1851 (3)	−0.1267 (7)	0.068 (3)
C_{17}	0.5846 (6)	0.2236 (3)	0.1263 (6)	0.043 (2)
C_{18}	0.6685 (7)	0.2592 (3)	0.1252 (7)	0.060 (2)
C_{19}	0.6593 (8)	0.3048 (4)	0.1751 (7)	0.077 (3)
C_{20}	0.5642 (9)	0.3144 (4)	0.2302 (8)	0.080 (3)
C_{21}	0.4835 (8)	0.2799 (4)	0.2318 (8)	0.072 (3)
C_{22}	0.4922 (7)	0.2345 (3)	0.1803 (6)	0.056 (2)
C_{23}	0.4607 (6)	0.1520 (3)	0.0065 (6)	0.045 (2)
C_{24}	0.4131 (8)	0.1911 (4)	−0.0486 (7)	0.064 (2)
C_{25}	0.3082 (9)	0.1838 (4)	−0.0946 (8)	0.074 (3)
C_{26}	0.2545 (8)	0.1382 (4)	−0.0799 (7)	0.070 (3)
C_{27}	0.3005 (8)	0.1007 (3)	−0.0252 (7)	0.062 (2)
C_{28}	0.4045 (7)	0.1060 (3)	0.0203 (6)	0.049 (2)
C_{29}	0.7527 (6)	0.0446 (3)	0.3958 (6)	0.047 (2)
C_{30}	0.8496 (8)	0.0656 (4)	0.4328 (7)	0.065 (2)
C_{31}	0.8588 (9)	0.0823 (4)	0.5355 (9)	0.083 (3)
C_{32}	0.7704 (10)	0.0790 (4)	0.5943 (9)	0.086 (3)
C_{33}	0.6743 (9)	0.0583 (4)	0.5606 (8)	0.079 (3)
C_{34}	0.6633 (7)	0.0404 (3)	0.4602 (7)	0.060 (2)
C_{35}	0.8660 (7)	0.0129 (3)	0.2168 (6)	0.051 (2)
C_{36}	0.9137 (9)	−0.0356 (4)	0.2261 (8)	0.084 (3)
C_{37}	1.0156 (11)	−0.0441 (5)	0.1828 (10)	0.105 (4)
C_{38}	1.0646 (11)	−0.0078 (5)	0.1356 (10)	0.103 (4)
C_{39}	1.0266 (10)	0.0417 (5)	0.1280 (9)	0.101 (4)
C_{40}	0.9215 (8)	0.0507 (4)	0.1701 (8)	0.071 (3)
C_{41}	0.6520 (6)	−0.0301 (3)	0.2690 (6)	0.045 (2)
C_{42}	0.5564 (6)	−0.0360 (3)	0.2117 (6)	0.045 (2)
C_{43}	0.4963 (7)	−0.0812 (3)	0.2185 (6)	0.054 (2)
C_{44}	0.5336 (8)	−0.1203 (4)	0.2827 (7)	0.071 (3)
C_{45}	0.6266 (9)	−0.1160 (4)	0.3381 (8)	0.081 (3)
C_{46}	0.6847 (8)	−0.0696 (4)	0.3349 (8)	0.072 (3)
B	0.0710 (13)	0.2062 (5)	0.6018 (12)	0.114 (8)
F_1	0.0782 (6)	0.1639 (3)	0.6496 (6)	0.126 (6)
F_2	0.1667 (8)	0.2244 (3)	0.5717 (7)	0.155 (8)
F_3	0.0275 (14)	0.2435 (5)	0.6512 (14)	0.357 (19)
F_4	0.0124 (13)	0.2002 (5)	0.5167 (12)	0.266 (15)

Section) used when starting from *cis*-$(PPh_3)_2PtCl_2$, involves initial chloride abstraction with an equivalent amount of $AgBF_4$ in CH_2Cl_2–acetone and subsequent treatment of the resulting cationic intermediate $[(PPh_3)_2PtCl]_2(BF_4)_2$ with an equivalent amount of the required RNC ligand. The dimeric $[(PPh_3)_2MCl]_2(BF_4)_2$ (M = Pd, Pt) intermediates have been reported previously as products of reactions between *cis*-$(PPh_3)_2MCl_2$ and $AgBF_4$[27a] or other reagents.[27b,c] They have been assigned a chloro-bridged dimeric structure on the basis of IR and molar conductance data.[28] In our case, $[(PPh_3)_2PtCl]_2(BF_4)_2$ can be isolated as a white solid in 90% yield after filtration of AgCl and addition of Et_2O to the filtrate.

Table VI. Relevant Bond Distances (Å) and Angles (deg) for *trans*-{$(PPh_3)_2Pt[CN(C_6H_4$-*p*-$Me)CH_2CH_2O]Br$}BF_4 (**17**)

Bond Distances			
Pt–Br	2.469 (1)	C_2–O	1.49 (1)
Pt–P_1	2.322 (2)	C_2–C_3	1.50 (1)
Pt–P_2	2.332 (2)	C_3–N	1.48 (1)
Pt–C_1	1.98 (1)	N–C_4	1.45 (1)
P_1–C_{11}	1.80 (1)	C_4–C_5	1.37 (1)
P_1–C_{17}	1.83 (1)	C_4–C_9	1.39 (1)
P_1–C_{23}	1.82 (1)	C_5–C_6	1.37 (1)
P_2–C_{29}	1.80 (1)	C_6–C_7	1.42 (1)
P_2–C_{35}	1.81 (1)	C_7–C_8	1.37 (1)
P_2–C_{41}	1.81 (1)	C_7–C_{10}	1.51 (1)
C_1–O	1.33 (1)	C_8–C_9	1.37 (1)
C_1–N	1.30 (1)		
Bond Angles			
P_2–Pt–C_1	91.7 (2)	C_3–N–C_4	120 (1)
P_1–Pt–C_1	91.2 (2)	C_1–N–C_4	127 (1)
P_1–Pt–P_2	173.7 (1)	N–C_4–C_9	118 (1)
Br–Pt–C_1	177.4 (2)	N–C_4–C_5	123 (1)
Br–Pt–P_2	89.3 (1)	C_5–C_4–C_9	118 (1)
Br–Pt–P_1	87.6 (1)	C_4–C_5–C_6	121 (1)
Pt–C_1–N	133 (1)	C_5–C_6–C_7	119 (1)
Pt–C_1–O	115 (1)	C_6–C_7–C_{10}	120 (1)
O–C_1–N	111 (1)	C_6–C_7–C_8	117 (1)
C_1–O–C_2	109 (1)	C_8–C_7–C_{10}	122 (1)
O–C_2–C_3	103 (1)	C_7–C_8–C_9	122 (1)
C_2–C_3–N	102 (1)	C_4–C_9–C_8	120 (1)
C_1–N–C_3	112 (1)		

The second method (eq 4 and method B of the Experimental Section) involves the reaction in acetone of equivalent amounts of complexes of the type *trans*- or *cis*-$(PR'_3)_2M(X)Cl$ and the required isocyanide ligand in the presence of a 5-fold excess of $NaBF_4$.

trans- or *cis*-$(PR'_3)_2M(X)Cl + NaBF_4 + RNC \xrightarrow[\text{room temperature}]{\text{acetone}} trans\text{-}[(PR'_3)_2M(CNR)X]BF_4 + NaCl$ (4)

M = Pt; PR'_3 = PPh_3; X = Cl;
R = *p*-MeC_6H_4 (**2**), C_6H_{11} (**7**), *t*-Bu (**8**)

M = Pt; PR'_3 = PMe_2Ph; X = Cl; R = *p*-$MeOC_6H_4$ (**4**)

M = Pt; PR'_3 = $PMePh_2$; X = Me; R = *p*-$MeOC_6H_4$ (**5**)

M = Pt; PR'_3 = PCy_3; X = Cl; R = *p*-$MeOC_6H_4$ (**9**)

M = Pd; PR'_3 = PPh_3; X = Cl; R =
p-$MeOC_6H_4$ (**10**), *p*-MeC_6H_4 (**11**), Me (**12**), C_6H_{11} (**13**)

Method B was generally employed when starting from complexes of trans geometry. Method B was particularly useful for the Pd(II) complex *trans*-$(PPh_3)_2PdCl_2$, which showed poor reactivity toward $AgBF_4$, giving low yields (ca. 20%) of the intermediate *cis*-$[(PPh_3)_2PdCl]_2(BF_4)_2$, which has been isolated previously.[27b] The Pt(II)–isocyanide complexes **1**, **3**, and **6**, prepared by method A, were isolated in 75–82% yield; complexes **2**, **4**, **5**, and **7**–**13**, obtained by method B, were isolated in 75–93% yield, except for **9**, in which the two bulky PCy_3 ligands apparently hinder the coordination of the isocyanide and give a 58% yield.

In addition to the cationic complexes, a few bis(isocyanide) complexes, *cis*-$Cl_2Pt(CNC_6H_4$-*p*-$OMe)_2$ (**14**) and *cis*-$Cl_2Pd(CNC_6H_4$-*p*-$Me)_2$ (**15**), were also prepared as reported for similar compounds[19,29] in ca. 90% yield according to eq 5.

$$cis\text{-}Cl_2ML_2 + 2RNC \rightarrow cis\text{-}Cl_2M(CNR)_2 + L_2 \quad (5)$$

M = Pt; L_2 = 1,5-cyclooctadiene; R = *p*-$MeOC_6H_4$ (**14**)

M = Pd; L_2 = 2MeCN; R = *p*-MeC_6H_4 (**15**)

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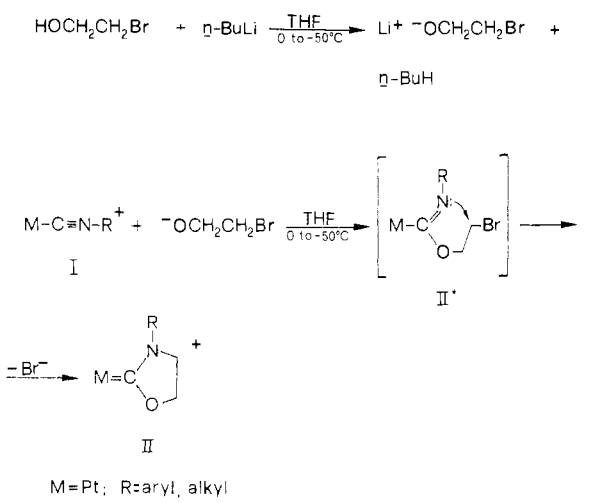
Scheme II



All the isocyanide complexes reported herein gave satisfactory C, H, and N elemental analyses (see Experimental Section), and they have been characterized by their IR, ^{1}H NMR, and ^{31}P NMR spectra (Table I). A notable feature of this series of complexes is the increase of ν(N≡C) on passing from the unbound isonitrile to the isonitrile coordinated in different environments; this is seen in the values of $\Delta\nu = \nu(N{\equiv}C)_{coord} - \nu(N{\equiv}C)_{free}$,[30] which reflect the electrophilic character[29] of the isocyanide carbon and therefore its ability to react with nucleophiles to form carbene complexes.[22] The correlation of $\Delta\nu$ vs. the susceptibility to nucleophilic attack of the CNR groups appears to parallel that of C–O stretching force constants (k_{CO}) with the electrophilicities of CO ligands in metal carbonyl complexes.[31] A positive value of $\Delta\nu \geq 40$ cm^{-1} was previously observed to indicate CNR ligand susceptibility to nucleophilic attack.[30] All the complexes **1–15** display positive $\Delta\nu$ values (Table I) in the range 54–108 cm^{-1} for M = Pt and 79–108 cm^{-1} for M = Pd, thus indicating that the isocyanide carbon is a potentially reactive electrophilic center. As expected, the lowest $\Delta\nu$ value is observed for complex **5**, where the strongly σ-electron-donating Me group is trans to the isocyanide ligand.[3b,32]

Cyclization Reactions. Aminooxycarbene Complexes of Pt(II). When the cationic Pt(II) complexes **1–4**, **6**, and **7** are added to a THF solution containing an excess of 2-bromoethoxide at 0 °C, the isocyanide groups are converted to the corresponding 5-membered cyclic aminooxycarbene derivatives **16–21** (Table II) in 24–92% yield. A reasonable mechanism for the transformation I → II (Scheme II) entails initial 2-bromoethanol deprotonation by *n*-BuLi, followed by nucleophilic attack on the isocyanide carbon atom of I to give the imidoyl intermediate II*, which undergoes intramolecular cyclization by imino nitrogen displacement of Br$^-$ to give the final carbene product II. (The representation of bonding in II in Scheme II is approximate since the carbene carbon also π-bonds to the nitrogen and oxygen atoms of the carbene ligand.[33])

Stable imidoyl complexes M—C(OR)=NR (M = Pt(II), Au(I), Ag(I)) are known to be formed by nucleophilic attack of alkoxide ions RO$^-$ on coordinated isocyanides.[34] In our case, no evidence was observed for the generation of the intermediate imidoyl species II*, even when R is an efficient electron-withdrawing group such as *p*-nitrophenyl, which would make the imino N atom less nucleophilic for Br$^-$ displacement. A similar imidoyl intermediate formed by alkyl migration to molybdenum-coordinated methyl isocyanide[35] has been proposed in the synthesis of the cyclic carbene *cis*-(η^5-C_5H_5)MoI[CN(Me)-$CH_2CH_2CH_2$](CO)$_2$.

The present isocyanide cyclization reaction is closely related to the conversion of CO ligands in several metal carbonyl complexes to cyclic carbene derivatives by $BrCH_2CH_2O^-$[8] or oxirane in the presence of a halide.[36] These latter reactions are also presumed to proceed via an alkoxycarbonyl intermediate, which was not detected but cyclizes rapidly to the carbene ligand.

The conversion I → II in Scheme II also occurs when 2-chloroethanol is used instead of the bromo reagent or when NaH is used as the base. In the latter case, however, the reaction proceeds in lower yields and with longer reaction times compared to those observed when *n*-BuLi is employed. The bromide ion that is liberated upon ring closure of II* displaces the chloride ion from complexes **1–4**, **6**, and **7** to various extents (ca. 60–100%) depending on reaction times (see below).

Treatment of *cis*-$Cl_2Pt(CNC_6H_4$-*p*-$OMe)_2$ (**14**) with 2 equiv of 2-bromoethoxide under reaction conditions analogous to those used for the cationic derivatives rapidly gives the bis(aminooxocarbene) **22** in 70% yield (eq 6). There is no IR evidence for the presumed (Scheme II) imidoyl intermediate. Also in this case, chloride–bromide exchange takes place.

$$cis\text{-}Cl_2Pt(CNC_6H_4\text{-}p\text{-}OMe)_2 + 2^-OCH_2CH_2Br \xrightarrow[0\ °C]{THF} Br_2Pt[CN(C_6H_4\text{-}p\text{-}OMe)CH_2CH_2O]_2 + 2Cl^- \quad (6)$$

The *p*-$MeOC_6H_4NC$ ligand in complex **5**, which shows the lowest $\Delta\nu$ (54 cm^{-1}, Table I) among those observed in this work, does not react with $^-OCH_2CH_2Br$. It is likely that the 2-bromoethoxide undergoes intramolecular cyclization to oxirane[36] faster than it attacks the weakly-activated isocyanide ligand.

No Pd(II)–carbene complexes were isolated from the analogous reactions of Pd(II)–isocyanide complexes **10–13** and **15** with 2-bromoethoxide, even at −50 °C and with an equivalent amount of the alkoxide. In all cases, red solutions were obtained in which no ν(C≡N) absorptions of the starting isocyanide or ν(C=N) of the carbene product were present, thereby suggesting the formation of Pd(0) species. This is not surprising since it has been reported[37] that the reaction of *trans*-$(PPh_3)_2Pd(R)Cl$ (R = Ph, CH=CCl_2) with NaOMe in toluene at 35 °C gives $[Pd(PPh_3)_2]_n$, whose formation has been accounted for by β-hydrogen elimination from the methoxo ligand in *trans*-$PdR(OMe)(PPh_3)_2$ to give HCHO and $PdR(H)(PPh_3)_2$, which subsequently undergoes reductive elimination of RH.

The aminooxycarbene complexes **16–22** have been characterized by their elemental analyses (see Experimental Section) and IR, ^{1}H NMR (Table II), and ^{31}P NMR (Table III) spectra. The ^{31}P NMR spectra of **16–21** show two singlets (flanked by ^{195}Pt satellites) of different intensities corresponding to the presence of both Cl$^-$ and Br$^-$ complexes. The lowest field resonance is assigned to the less abundant chloro derivative by comparison with the spectrum of a pure sample of of *trans*-{$(PPh_3)_2Pt$[CN(C_6H_4-*p*-Me)CH_2CH_2O]Cl}BF_4 obtained by reaction with 2-chloroethanol and *n*-BuLi (see Experimental Section). The X-ray structure of **17** reveals the presence of bromide as the ligand trans to the carbene (see below). The ^{1}H NMR spectra at 80 MHz of the aminooxycarbenes **16–22** display –OCH_2 and –NCH_2 resonances in the range δ 3.63–4.52 and 2.38–4.05, respectively. The methylene protons adjacent to the oxygen are assigned to the lower field resonances by comparison with values reported for related aminooxycarbenes in metal carbonyl systems.[8,36] Supporting this

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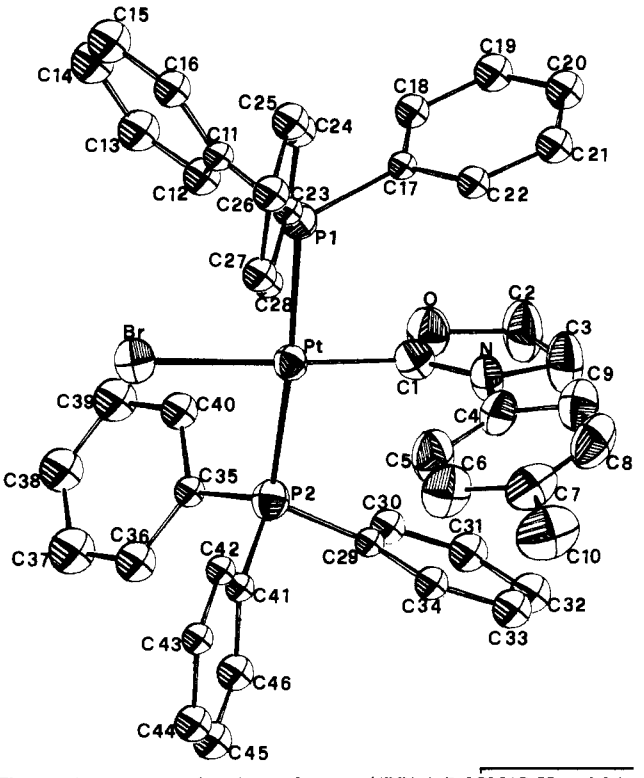

Figure 1. ORTEP drawing of *trans*-{$(PPh_3)_2Pt[\overline{CN(C_6H_4\text{-}p\text{-}Me)CH_2CH_2O}]Br$}$^+$ in **17**.

conclusion is the spectrum of the *N*-methyl-substituted carbene **20**, which shows the N–Me resonance at δ 2.97, close to the $-NCH_2$ signal (δ 2.68). The $-OCH_2$ and $-NCH_2$ resonances appear as broad triplets (AA'BB' type) in compounds **17** and **19–22** but as multiplets in **16** and **18**, probably owing to the presence of a mixture of chloro and bromo derivatives.

The IR spectra of compounds **16–22** show a medium to strong ν(C=N) absorption in the range 1510–1570 cm^{-1}. The related aminooxycarbenes in carbonyl systems display medium-intensity ν(C=N) absorptions in the range 1530–1570 cm^{-1}.[36b,c] Compounds **16–22** show ν(C—O) bands of medium intensity in the range 1250–1280 cm^{-1}. These latter assignments were made by comparison with ν(C—O) absorptions of several Pt(II)–alkoxycarbenes, which were reported to occur around 1300 cm^{-1}.[38]

Description of the Structure of *trans*-{$(PPh_3)_2Pt[\overline{CN(C_6H_4\text{-}p\text{-}Me)CH_2CH_2O}]Br$}$BF_4$ (17). The crystal contains *trans*-{$(PPh_3)_2Pt[\overline{CN(C_6H_4\text{-}p\text{-}Me)CH_2CH_2O}]Br$}$^+$ cations (Figure 1) and partially disordered BF_4^- anions. The coordination geometry around the Pt(II) atom is almost square planar with a maximum deviation from the Br–P_1–P_2–Pt–C_1 mean plane of 0.06 Å for the Pt atom. The Br–Pt–C_1 system approaches linearity (177.4 (2)°), while the P_1–Pt–P_2 angle shows a slight bending (173.7 (1)°) due to steric interactions between the bulky PPh_3 ligands and the carbenoid system. The Pt–P average distance of 2.327 (2) Å is within the expected values for these interactions and agrees well with that reported for *trans*-{$(PPh_3)_2Pt[\overline{CN(H)\text{-}o\text{-}C_6H_4C(PMe_3)}]Cl$}$BF_4$ (2.329 (1) Å).[3b] Although there appear to be no structural reports of Pt–Br bond distances trans to a carbene ligand and cis to two triphenylphosphines,[33] the observed value of 2.469 (1) Å in **17** is of a magnitude comparable to that found in *trans*-$(PEt_3)_2PtBr_2$ (2.428 (2) Å).[39]

The cyclic carbene ligand is strictly planar (maximum deviation 0.004 Å). The plane of the carbene intersects the platinum square plane at an angle of 93.4°, which is similar to values observed in several other Pt(II)–carbene complexes.[33] The Pt–carbene bond length of 1.98 (1) Å is in good agreement with other Pt–C(carbene) distances of square-planar Pt(II) systems, which generally occur in the range 1.82–2.01 Å when chloride is trans to the carbene ligand.[33]

Bond lengths within the 5-membered ring indicate significant π-bonding between the nitrogen and carbene carbon. The C_1–N value of 1.30 (1) Å is short and of comparable magnitude to that found in the complexes *cis*-$Cl_2(PPh_3)PtC(NMe_2)H$ (1.25 (1) Å),[40] *trans*-{$(PMe_2Ph)_2Pt[C(NMe_2)CH_2CH_2OH]Cl$}$PF_6$ (1.29 (2) Å),[41] *trans*-{$(PMe_2Ph)_2Pt[C(NMe_2)Me]Me$}$PF_6$ (1.266 (15) Å)[42] and *cis*-$CpMoI[\overline{CN(Me)CH_2CH_2CH_2}](CO)_2$ (1.284 Å),[35] in which the C(sp^2) atom is stabilized only by the adjacent nitrogen atom. The above structural data are thus consistent with substantial multiple bond character for the C–N bond, which is also supported by the ν(C=N) absorptions in the range 1510–1571 cm^{-1} characteristic of other aminooxycarbene complexes.[36]

The C_1–O distance of 1.33 (1) Å is shorter than the C_2–O distance (1.49 (1) Å) and is comparable to those found in the oxycarbene complexes *cis*-$Cl_2Pt[C(OEt)NHPh](PEt_3)$ (1.33 (2) Å)[43] and *trans*-{$(PMe_2Ph)_2Pt[C(OMe)Me]Me$}$PF_6$ (1.33 Å),[44] thus suggesting that the carbene carbon π-bonding also involves the O atom. The C_2–O bond length may be compared with analogous bond distances found in *trans*-{$(PMe_2Ph)_2Pt[\overline{COCH_2CH_2CH_2}]Me$}$^+$ (1.50 (2) Å)[45] and *cis*-{$MnCl[\overline{COCH_2CH_2O}](CO)_4$} (1.51 (4) Å).[46] The N–C_3 bond length of 1.48 (1) Å compares well with that found in the 1,3-diphenylimidazolidin-2-ylidene complex *cis*-$Cl_2Pt[\overline{CN(Ph)CH_2CH_2N(Ph)}](PEt_3)$ (1.482 (14) Å).[47] Finally, the C_2–C_3 distance of 1.50 (1) Å is slightly shorter than those found in the above mentioned 2-oxacyclopentylidene complex[45] (1.56 (1) Å) and the Mn–dioxycarbene derivative[46] (1.53 (4) Å).

A significant feature of the stereogeometry of the *trans*-{$(PPh_3)_2Pt[\overline{CN(C_6H_4\text{-}p\text{-}Me)CH_2CH_2O}]Br$}$^+$ cation is the tilting of the *p*-tolyl ligand with respect to the pentaatomic cycle that constitutes the carbenoid system. The angle between the two planes is 20.7°. This effect may be accounted for in terms of steric repulsion between the Pt(II) atoms and the *p*-tolyl H atom ortho to the carbon atom bonded to the pentaatomic cycle. In fact, the Pt–H_5 contact of 2.51 (1) Å is the shortest Pt–H contact in the molecule. A planar system comprising the hexa- and pentaatomic rings would give a further shortening of this interaction (to 2.34 Å after 20.7° rotation to coplanarity). The whole ligand system appears to be "pushed away" from the "Pt–H" side by tilting around the carbene C atom as can be seen by looking at the bond angles in the carbenoid plane (Pt–C_1–O = 115 (1)°, Pt–C_1–N = 133 (1)°), which indicate appreciable deformation of the carbene sp^2 bonding system. Part of the deformation is also shared with the other two neighboring sp^2 atoms (N, C_4) which show wider inner ("Pt-side") than outer angles (C_1–N–C_4 = 127 (1)°, C_3–N–C_4 = 120 (1)°; N–C_4–C_5 = 123 (1)°, N–C_4–C_9 = 118 (1)°). Altogether the stereogeometry of the Pt–ligand system is a compromise between Pt···O (2.82 (1) Å) and Pt···H_5 repulsive interactions, deformation of the sp^2 angles, and torsion around

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the N-C_4 bond. As a consequence, extensive delocalization through the C_1, N, and tolyl π-system is prevented as shown by the different C_1–N and N–C_4 bond lengths (1.30 (1) and 1.45 (1) Å, respectively).

Concluding Remarks

One or even two electrophilic RNC ligands in Pt(II) complexes are converted to cyclic aminooxycarbene complexes by reaction with 2-bromoethanol in the presence of *n*-BuLi, thus paralleling the reactivity of electrophilic CO ligands in metal carbonyl complexes.[8] Isocyanides coordinated to Pd(II) could not be converted to cyclic aminooxycarbenes, since reductive elimination to Pd(0) species occurs when Pd–CNR complexes are reacted with $^-OCH_2CH_2Br$.

In contrast to the reactions of CO ligands[8,36] where k_{CO} is useful for predicting the reactivity of CO ligands with 2-bromoethanol or oxirane in the presence of a halide, a high $\Delta\nu$ value (>60 cm^{-1}) appears to be a necessary but not sufficient condition for facilitating reactions of isocyanide ligands with this nucleophile. Steric factors also influence this reaction. Thus, the aryl isocyanides in the chloro complexes **1–4** ($\Delta\nu$ = 76–79 cm^{-1}) and the methyl isocyanide in complex **6** ($\Delta\nu$ = 91 cm^{-1}) are rapidly converted (in a few minutes) to the final carbenes with recrystallized product yields of ca. 70–90%. However, the more bulky $C_6H_{11}NC$ in complex **7** ($\Delta\nu$ = 82 cm^{-1}) is only partially transformed to the carbene product **21** after 1 h of reaction and gives after 24 h only a 24% yield of the isolated product. The bulky *t*-BuNC ligand in **8** ($\Delta\nu$ = 81 cm^{-1}) is not reactive at all under the same reaction conditions. It thus appears that the isocyanide cyclization reactions shown in Scheme II parallel those with alcohols and amines in which aryl isocyanides (higher electron-withdrawing properties of the substituent R) react faster than alkyl analogues.[22] As an example, in the reaction of *cis*-$Cl_2Pd(CNC_6H_4$-*p*-$Me)(CNC_6H_{11})$ with *p*-toluidine only the *p*-tolyl isocyanide group is attacked by the amine.[48] The importance of steric factors is further supported by reactions of *cis*-$Cl_2Pd(CNR)(PPh_3)$ (R=*p*-$C_6H_4NO_2$, *p*-C_6H_4Cl, *o*-C_6H_4Me, *o,o'*-$C_6H_3Me_2$) with anilines, where ortho substituents were introduced into the phenyl ring of the isocyanide ligand.[49] Such substitutions caused a marked decrease in the overall reaction rates relative to those of analogous para-substituted reactants.

Steric effects of the phosphine ligands cis to the electrophilic isocyanide carbon are also apparent. Nucleophilic attack is favored by decreasing the steric hindrance and increasing the π-accepting capability of the ancillary ligands L as noted for the series *cis*-$Cl_2Pd(CNC_6H_4$-*p*-$Me)(L)$ (L = $P(OMe)_3$, $P(OMe)_2Ph$, PPh_3, $PMePh_2$, PMe_2Ph, PEt_3, PCy_3).[50] When L = PCy_3 (complex **9**), the conditions are so unfavorable that no reaction occurs. On the contrary, when L = *p*-$MeOC_6H_4NC$ (complex **14**) or *p*-MeC_6H_4NC (**15**), i.e., with ligands less sterically demanding and better π-accepting than phosphines, the reaction of one isocyanide ligand with $^-OCH_2CH_2Br$ is very fast.

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Registry No. **1**, 110313-73-0; **2**, 110313-75-2; **3**, 110313-77-4; **4**, 110313-78-5; **5**, 110330-07-9; **6**, 110351-89-8; **7**, 110313-80-9; **8**, 110313-82-1; **9**, 110313-84-3; **10**, 110313-86-5; **11**, 110313-88-7; **12**, 110313-90-1; **13**, 110330-09-1; **14**, 27902-71-2; **15**, 40927-16-0; **16** (X = Br), 110313-92-3; **17** (X = Br), 110313-94-5; **17** (X = Cl), 110330-11-5; **18** (X = Br), 110313-96-7; **19**, 110313-98-9; **20**, 110314-00-6; **21** (X = Br), 110314-02-8; **22**, 110314-03-9; *cis*-$(PPh_3)_2PtCl_2$, 15604-36-1; *trans*-$(PPh_3)_2PtCl_2$, 14056-88-3; *cis*-$(PMe_2Ph)PtCl_2$, 15393-14-3; *trans*-$(PMePh_2)_2Pt(Me)Cl$, 24833-61-2; $(COD)PtCl_2$, 12080-32-9; *trans*-$(PCy_3)_2PtCl_2$, 60158-99-8; $(MeCN)_2PdCl_2$, 14592-56-4; *trans*-$(PPh_3)_2PdCl_2$, 28966-81-6; *p*-$MeOC_6H_4NC$, 10349-38-9; *p*-$O_2NC_6H_4NC$, 1984-23-2; MeNC, 593-75-9; *p*-MeC_6H_4NC, 7175-47-5; $C_6H_{11}NC$, 931-53-3; *t*-BuNC, 7188-38-7; $BrCH_2CH_2OH$, 540-51-2; $ClCH_2CH_2OH$, 107-07-3.

Supplementary Material Available: Listings of hydrogen atom coordinates (Table S-I), anisotropic thermal parameters (Table S-II), and bond distances and angles (Table S-IV) (21 pages); a listing of observed and calculated structure factors (Table S-III) (30 pages). Ordering information is given on any current masthead page.

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