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Reactions of Aziridine, Thiirane, and Oxirane with Isocyanide Ligands in Complexes of Palladium(II) and Platinum(II): Syntheses of Neutral Five-Membered Cyclic Diamino-, Aminothio-, and Aminooxycarbene Compounds

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Received January 5, 1988

Aziridine is observed to react spontaneously in THF at room temperature or below with the coordinated RNC ligand in each of the neutral isocyanide complexes *cis*-$Cl_2(L)M(CNR)$ (M = Pd, R = *t*-Bu, *p*-$MeOC_6H_4$, L = PPh_3, PMe_2Ph; M = Pt, R = *p*-$MeOC_6H_4$, *p*-MeC_6H_4, L = PPh_3) to form the corresponding five-membered cyclic diaminocarbene complexes *cis*-$Cl_2(L)M[\overline{CN(R)CH_2CH_2NH}]$. Aziridine reacts also with the bis(isocyanide) complexes *cis*-$Cl_2Pd(CNR)_2$ (R = *t*-Bu, *p*-$MeOC_6H_4$), converting one (R = *t*-Bu) or two (R = *p*-$MeOC_6H_4$) isocyanide ligands to cyclic carbenes. Reactions between thiirane and Pd(II)–isocyanide complexes such as *cis*-$Cl_2(L)Pd(CNC_6H_4$-*p*-OMe) (L = PPh_3, PMe_2Ph) in THF at room temperature yield the corresponding cyclic aminothiocarbene derivatives *cis*-$Cl_2(L)Pd[\overline{CN(R)CH_2CH_2S}]$. Thiirane reacts with *cis*-$Cl_2Pd(CNC_6H_{11})_2$ to give the mixed isocyanide–aminothiocarbene derivative *cis*-$Cl_2(C_6H_{11}NC)Pd[\overline{CN(C_6H_{11})CH_2CH_2S}]$. Oxirane alone is not reactive toward Pd(II)- and Pt(II)–isocyanide complexes. However, in the presence of NaCl, oxirane is observed to react in 2-chloroethanol with Pt(II)–isocyanide complexes such as *cis*-$Cl_2(Ph_3P)Pt(CNC_6H_4$-*p*-OMe) and *trans*-$[(PPh_3)_2Pt(CNC_6H_4$-*p*-OMe)Cl]BF_4 to form the corresponding five-membered cyclic $M{=}\overline{CN(R)CH_2CH_2O}$ aminooxycarbene complexes. Reaction of *cis*-$Cl_2Pt(CNC_6H_4$-*p*-OMe)$_2$ with oxirane in the presence of Cl^- ions produces the mixed isocyanide–aminooxycarbene complex *cis*-Cl_2(*p*-$MeOC_6H_4NC)Pt[\overline{CN(C_6H_4}$-*p*-$OMeCH_2CH_2O}]$. Similar reactions with Pd(II)–CNR derivatives fail to give any aminooxycarbene compound. The proposed reaction mechanisms for the cyclization reactions of coordinated RNC ligands by the heterocycles $\overline{YCH_2CH_2}$ (Y = NH, S, O) as well as the IR and ^1H and ^{31}P NMR spectra of the cyclic carbene products are discussed.

Introduction

Recently we reported[2,3] that metal-stabilized cyclic aminooxy- and diaminocarbene ligands can be prepared by reaction of 2-bromoethanol and 2-bromoethylamine hydrobromide in the presence of *n*-BuLi with isocyanide ligands in cationic complexes of Pd(II) and Pt(II). By this method also a few neutral bis(carbene) complexes of the type *cis*-$Br_2M[\overline{CN(R)CH_2CH_2Y}]_2$ (M = Pt, R = *p*-$MeOC_6H_4$, Y = O; M = Pd, Pt, R = *p*-MeC_6H_4, Y = NH) have been prepared.

Carbon monoxide ligands in certain metal carbonyl complexes react similarly with 2-bromoethoxide and 2-bromoethylamine to give cyclic dioxy- and aminooxycarbene complexes.[4] By taking advantage of the tendency of highly strained 3-membered heterocycles $\overline{YCH_2CH_2}$, where Y = NH (aziridine), S (thiirane), and O (oxirane), to undergo ring-opening reactions, Angelici and Singh reported[5] that sufficiently electropositive CO and CS ligands in cationic and/or neutral metal carbonyl and thiocarbonyl complexes react in the presence of a halide ion as catalyst with the heterocycles to afford cyclic carbene complexes.

Since the chemical behavior of isocyanide ligands bears strong similarities to that of carbonyl ligands, it would be expected that also RNC ligands in certain metal isocyanide complexes will react with the three-membered heterocycles $\overline{YCH_2CH_2}$ (Y = NH, S, O) to yield five-membered cyclic carbene compounds. However, it has been shown that the reactivity of RNC ligands in contrast to that of CO's is markedly influenced by steric and electronic properties of the R group.[2,3,6] Furthermore, the nature of the metal and the metal–ligand framework are important factors in determining the reactivity of isocyanides.[2,6]

In order to explore the chemistry of complexes containing the isocyanide ligands also in comparison with the reactivity of CO groups, we have studied the reactions of neutral Pd(II)- and Pt(II)–isocyanide complexes of the general formula *cis*-$Cl_2M(CNR)(L)$ (L = tertiary phosphine, isocyanide) with aziridine, thiirane, and oxirane. In this paper we describe the results of these studies and discuss the spectroscopic characterization of the new cyclic carbene compounds formed.

Results

The transformations undertaken in this study are given in Schemes I–III.

Spectroscopic Characterization of the Starting Materials. The isocyanide ligands and their Pd(II) and Pt(II) complexes that have been investigated in this work are listed in Table I together with their spectroscopic properties. The reactions of RNC ligands in complexes of analogous structure with various amines to give acyclic diaminocarbene derivatives have been described in the past. Mechanistic studies of these reactions have also been reported.[6]

The mono(isocyanide) complexes *cis*-$Cl_2(L)M(CNR)$ (M = Pd, Pt; **1–6**; Table I) display values of $\Delta\nu = \nu(N{\equiv}C)_{coord} - \nu(N{\equiv}C)_{free}$[7] in the range 78–90 cm^{-1}. For the bis(isocyanide) complexes *cis*-$Cl_2M(CNR)_2$ (M = Pd, Pt; **7–12**; Table I) the $\Delta\nu$ shifts are in the range 81–109 cm^{-1}. The positive $\Delta\nu$ values shown by **1–12** indicate that the isocyanide carbon is a potentially reactive electrophilic center[8] toward nucleophiles to give carbene complexes.[6] However, it has been noticed[2] that a positive value of $\Delta\nu$ (>60 cm^{-1}) appears to be a necessary but not sufficient condition for facilitating reactions of isocyanide ligands with nucleophiles. In order to test the influence of electronic and steric properties in the reactions of aziridine, thiirane, and oxirane with coordinated RNC ligands, we have examined as typical cases the behavior of aryl isocyanides such as *p*-$MeOC_6H_4NC$ and *p*-MeC_6H_4NC (higher electron-withdrawing properties of the substituent R) and alkyl isocyanides such as *t*-BuNC and $C_6H_{11}NC$ (higher sterically demanding properties of the R group).

Reactions of Aziridine. Synthesis of Five-Membered Cyclic Diaminocarbene Complexes. Aziridine (1.2–1.5 equiv) reacts

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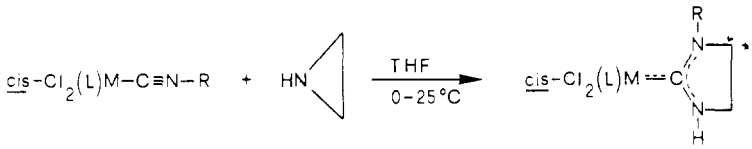
0020-1669/88/1327-2809$01.50/0

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

compd[a]	IR				$^{31}P\{^1H\}$ NMR[e]	
	$\nu(N\equiv C)_{coord}$[b]	$\nu(N\equiv C)_{free}$[b]	$\Delta\nu$[c]	$\nu(M-Cl)$[d]	$\delta(P)$	$^1J(PPt)$
cis-$Cl_2(Ph_3P)Pd(CN\text{-}t\text{-}Bu)$[f] (**1**)	2229 s	2139 s	90	295 m, 329 w	27.50 s	
cis-$Cl_2(Ph_3P)Pd(CNC_6H_4\text{-}p\text{-}OMe)$[g] (**2**)	2215 s	2128 s	87	295 m, 333 w	27.47 s	
cis-$Cl_2(PhMe_2P)Pd(CN\text{-}t\text{-}Bu)$[h] (**3**)	2225 s	2139 s	86	282 m, 327 w	8.05 s	
cis-$Cl_2(PhMe_2P)Pd(CNC_6H_4\text{-}p\text{-}OMe)$[i] (**4**)	2213 s	2128 s	85	279 m, 337 m	9.09 s	
cis-$Cl_2(Ph_3P)Pt(CNC_6H_4\text{-}p\text{-}OMe)$[j] (**5**)	2206 s	2128 s	78	302 m, 336 m	8.30 s	3359
cis-$Cl_2(Ph_3P)Pt(CNC_6H_4\text{-}p\text{-}Me)$[k] (**6**)	2208 s	2129 s	79	301 w, 338 w	8.47 s	3351
cis-$Cl_2Pd(CN\text{-}t\text{-}Bu)_2$[l] (**7**)	2230 s, 2247 s	2139 s	108, 91	317 m, 338 m		
cis-$Cl_2Pd(CNC_6H_{11})_2$[m] (**8**)	2237 s, 2254 s	2145 s	109, 92	319 m, 338 m		
cis-$Cl_2Pd(CNC_6H_4\text{-}p\text{-}OMe)_2$[n] (**9**)	2218 s, 2232 s	2128 s	104, 90	318 m, 339 m		
cis-$Cl_2Pd(CNC_6H_4\text{-}p\text{-}Me)_2$[o] (**10**)	2219 s, 2237 s	2129 s	108, 90	313 m, 334 m		
cis-$Cl_2Pt(CN\text{-}t\text{-}Bu)_2$[p] (**11**)	2220 s, 2248 s	2139 s	109, 81	323 m, 343 m		
cis-$Cl_2Pt(CNC_6H_4\text{-}p\text{-}OMe)_2$[q] (**12**)	2209 s, 2236 s	2128 s	108, 81	324 w, 346 m		

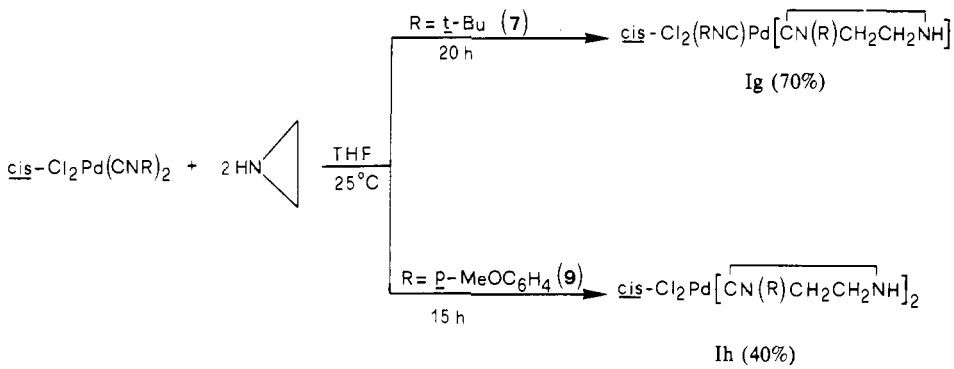
[a] The ^1H NMR spectra are given in the footnotes and are recorded in CD_2Cl_2. Proton chemical shifts are referenced to Me_4Si by taking the chemical shift of dichloromethane-d_2 as +5.32 ppm. J is given in Hz. Abbreviations: s = singlet; d = doublet; m = multiplet. [b] Spectra were recorded in CH_2Cl_2; ν is given in cm^{-1}. Abbreviations: s = strong; m = medium; w = weak. For $\nu(N\equiv C)_{free}$ data see also ref 2. [c] $\Delta\nu = \nu(N\equiv C)_{coord} - \nu(N\equiv C)_{free}$. [d] Nujol mull. [e] Spectra were recorded in CD_2Cl_2, with H_3PO_4 external reference; s = singlet. [f] $\delta(t\text{-Bu})$ 1.14 s. [g] $\delta(OMe)$ 3.80 s. [h] $\delta(t\text{-Bu})$ 1.24 s; $\delta(P\text{-Me})$ 1.98 d ($^2J(HP)$ = 12.6). [i] $\delta(OMe)$ 3.79 s; $\delta(PMe)$ 2.08 d ($^2J(HP)$ = 12.7). [j] $\delta(OMe)$ 3.77 s. [k] Spectroscopic data taken from ref 3. [l] $\delta(t\text{-Bu})$ 1.54 s. [m] $\delta(C_6H_{11})$ 1.10 m. [n] $\delta(OMe)$ 3.83 s. [o] $\delta(Me)$ 2.39 s. [p] $\delta(t\text{-Bu})$ 1.54 s. [q] $\delta(OMe)$ 3.83 s.

Scheme I. Reactions of Aziridine with Isocyanide Complexes of Pd(II) and Pt(II)



(1)

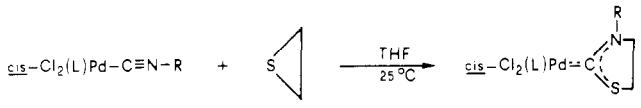
1: M = Pd, L = PPh_3, R = *t*-Bu — Ia (70%)
2: M = Pd, L = PPh_3, R = *p*-$MeOC_6H_4$ — Ib (55%)
3: M = Pd, L = PMe_2Ph, R = *t*-Bu — Ic (69%)
4: M = Pd, L = PMe_2Ph, R = *p*-$MeOC_6H_4$ — Id (58%)
5: M = Pt, L = PPh_3, R = *p*-$MeOC_6H_4$ — Ie (53%)
6: M = Pt, L = PPh_3, R = *p*-MeC_6H_4 — If (78%)



(2a)

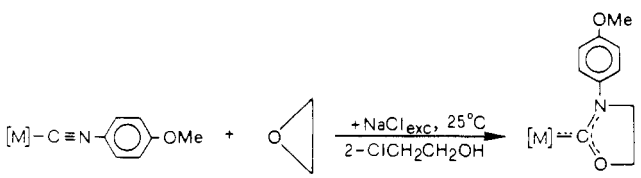
(2b)

Scheme II. Reactions of Thiirane with Isocyanide Complexes of Pd(II)



2: L = PPh_3, R = *p*-$MeOC_6H_4$ — IIa (38%)
4: L = PMe_2Ph, R = *p*-$MeOC_6H_4$ — IIb (75%)
8: L = $C_6H_{11}NC$, R = C_6H_{11} — IIc (21%)

Scheme III. Reactions of Oxirane with Isocyanide Complexes of Pt(II)



5: [M] = *cis*-$Cl_2(Ph_3P)Pt$ — IIIa (66%)
[M] = *trans*-$[(PPh_3)_2PtCl]BF_4$ — IIIb (47%)
12: [M] = *cis*-$Cl_2Pt(CNC_6H_4\text{-}p\text{-}OMe)$ — IIIc (23%)

spontaneously with the RNC ligand in each of the neutral isocyanide complexes *cis*-$Cl_2(L)M(CNR)$ (M = Pd, **1–4**; M = Pt, **5**, **6**; Table I) in THF solvent, affording five-membered cyclic diaminocarbene complexes according to eq 1 in Scheme I. Complexes Ia–f are isolated from the reaction mixtures as white, air-stable solids, slightly soluble in CH_2Cl_2 and acetone and insoluble in Et_2O and *n*-hexane.

The ligands *p*-$MeOC_6H_4NC$ in complexes **2**, **4**, and **5** and *p*-MeC_6H_4NC in complex **6** react faster than the bulky *t*-BuNC ligand in complexes **1** and **3**. The observed trend in reactivity parallels that found for reactions of coordinated RNC ligands with $^-OCH_2CH_2Br$[2] and $H_2NCH_2CH_2Br$.[3] It is also in order with the generally observed higher reactivity of aryl isocyanides with respect to alkyl analogues.[2,3,6]

The bis(isocyanide) complexes *cis*-$Cl_2Pd(CN\text{-}t\text{-}Bu)_2$ (**7**) and *cis*-$Cl_2Pd(CNC_6H_4\text{-}p\text{-}OMe)_2$ (**9**) react with 2 equiv of aziridine under experimental conditions analogous to those used for the mono(isocyanide) derivatives (Scheme II, eq 2a and 2b); the reactions proceed differently depending on the nature of the RNC ligand. When R = *t*-Bu, only one isocyanide ligand is converted to a carbene group by reaction with aziridine (Scheme I, eq 2a). On the other hand, when R = *p*-$MeOC_6H_4$, the reaction proceeds

Table II. IR and ^{1}H NMR Data for the Carbene Complexes

compd	IR[a] ν(CN)	IR[a] ν(NH)	IR[a] ν(MCl)	^{1}H NMR[b] δ(NCH$_2$)	δ(SCH$_2$)	δ(OCH$_2$)	δ(NH) and/or other
cis-Cl$_2$(Ph$_3$P)Pd[$\overline{CN(t\text{-Bu})CH_2CH_2NH}$] (Ia)	1506 s	3252 m	283 w, 311 w	3.55 m, 3.48 m, 3.03 m, 2.75 m			6.81 br,[c] 1.60 s[d]
cis-Cl$_2$(Ph$_3$P)Pd[$\overline{CN(C_6H_4\text{-}p\text{-OMe})CH_2CH_2NH}$] (Ib)	1510 s	3223 m	284 w, 311 w	3.86 m, 3.56 m, 3.27 m			8.73 br,[c] 3.89 s[e]
cis-Cl$_2$(PhMe$_2$P)Pd[$\overline{CN(t\text{-Bu})CH_2CH_2NH}$] (Ic)	1510 s	3291 s	271 m, 296 w	3.71 m, 3.43 m, 3.05 m			7.88 br,[c] 1.60 s,[d] 1.99 d,[f] 1.91 d[g]
cis-Cl$_2$(PhMe$_2$P)Pd[$\overline{CN(C_6H_4\text{-}p\text{-OMe})CH_2CH_2NH}$] (Id)	1510 s	3315 s	282 m, 296 sh	3.76 m, 3.52 m, 3.38 m, 3.18 m			8.77 b,[c] 3.85 s,[e] 1.84 d,[h] 1.48 d[i]
cis-Cl$_2$(Ph$_3$P)Pt[$\overline{CN(C_6H_4\text{-}p\text{-OMe})CH_2CH_2NH}$] (Ie)	1510 s	3273 s	283 m, 314 m	3.76 m, 3.60 m, 3.31 m			8.06 br,[c] 3.87 s[e]
cis-Cl$_2$(Ph$_3$P)Pt[$\overline{CN(C_6H_4\text{-}p\text{-Me})CH_2CH_2NH}$] (If)	1510 s	3319 s	282 w, 317 m	3.77 m, 3.61 m, 3.31 m			7.12 br,[c] 2.40 s[j]
cis-Cl$_2$(*t*-BuNC)Pd[$\overline{CN(t\text{-Bu})CH_2CH_2NH}$][k] (Ig)	1511 s	3265 s	295 m, 324 m	3.69 br			7.92 br,[c] 1.69 s,[d] 1.48[d]
cis-Cl$_2$Pd[$\overline{CN(C_6H_4\text{-}p\text{-OMe})CH_2CH_2NH}$]$_2$ (Ih)	1512 s	3285 s	293 w, 311 w	*l*			*l*
cis-Cl$_2$(Ph$_3$P)Pd[$\overline{CN(C_6H_4\text{-}p\text{-OMe})CH_2CH_2S}$] (IIa)	1506 s		281 m, 309 m	3.40 m, 2.99 m	4.05 m, 3.76 m		3.92 s[e]
cis-Cl$_2$(PhMe$_2$P)Pd[$\overline{CN(C_6H_4\text{-}p\text{-OMe})CH_2CH_2S}$] (IIb)	1510 s		280 m, 312 w	3.40 m, 3.03 m	4.14 m, 3.87[m]		3.87 s,[e] 1.70 d,[n] 1.46 d[o]
cis-Cl$_2$(C$_6$H$_{11}$NC)Pd[$\overline{CN(C_6H_{11})CH_2CH_2S}$][p] (IIc)	1530 s		302 w, 316 w	3.40 m, 3.30 m	4.08 m, 3.97 m		1.45–1.88 m[q]
cis-Cl$_2$(Ph$_3$P)Pt[$\overline{CN(C_6H_4\text{-}p\text{-OMe})CH_2CH_2O}$] (IIIa)	1517 s		294 m, 319 m	3.74 m, 3.36 m		4.74 m, 4.39 m	3.90 s[e]
trans-[(PPh$_3$)$_2$Pt[$\overline{CN(C_6H_4\text{-}p\text{-OMe})CH_2CH_2O}$]Cl]BF$_4$ (IIIb)	1510 s		318 w	3.30 t		3.75 t	3.90 s[e]
cis-Cl$_2$(*p*-MeOC$_6$H$_4$NC)Pt[$\overline{CN(C_6H_4\text{-}p\text{-OMe})CH_2CH_2O}$][r] (IIIc)	1539 s		296 w, 334 w	4.21 m		4.97 m	3.82 s,[e] 3.81 s[e]

[a] Spectra were recorded as Nujol mulls; ν is given in cm^{-1}. Abbreviations: s = strong; m = medium; w = weak, sh = shoulder. [b] ^{1}H NMR spectra were recorded in CD_2Cl_2. Proton chemical shifts are referenced to Me_4Si by taking the chemical shift of dichloromethane-d_2 as +5.32 ppm. J is given in Hz. Abbreviations: s = singlet; d = doublet; t = triplet; m = multiplet; br = broad. [c] NH signal. [d] δ(*t*-Bu). [e] δ(OMe). [f] δ(PMe) (^2J(HP) = 11.9). [g] δ(PMe) (^2J(HP) = 11.8). [h] δ(PMe) (^2J(HP) = 12.3). [i] δ(PMe) (^2J(HP) = 12.3). [j] δ(Me). [k] ν(N≡C) 2210 s. [l] Too insoluble for ^{1}H NMR measurement. [m] Signal covered by OMe resonance. [n] δ(PMe) (^2J(HP) = 11.9). [o] δ(PMe) (^2J(HP) = 12.1). [p] ν(N≡C) 2228 s. [q] δ(C$_6$H$_{11}$). [r] ν(N≡C) 2203 s.

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

compd[b]	δ(P)	^1J(PPt), Hz	compd[b]	δ(P)	^1J(PPt), Hz
Ia[c]	24.35 s		If[c]	7.19 s	4059
Ib	26.52 s		IIa	26.82 s	
Ic	1.63 s		IIb	4.02 s	
Id	4.40 s		IIIa	8.05 s	3908
Ie	8.18 s	4044	IIIb	17.33 s	2539

[a] In CD_2Cl_2 unless otherwise stated; 85% H_3PO_4 external reference. [b] See Table II. [c] In DMSO-d_6.

stepwise through the rapid formation of a carbene–isocyanide complex, which slowly converts to the final bis(carbene) product Ih (Scheme I, eq 2b). The intermediate mixed carbene–isocyanide complex was not isolated from the reaction mixture but was detected in solution (see Experimental Section). However, in analogous reactions of *cis*-Cl$_2$Pt(CNR)$_2$ (R = *t*-Bu, *p*-MeOC$_6$H$_4$) with aziridine no such products were obtained. The much higher reactivity of RNC ligands in *cis*-Cl$_2$Pd(CNR)(L) complexes (L = tertiary phosphine, isocyanide) as compared with that in the corresponding Pt(II) analogues has been previously observed.[6]

The cyclic diaminocarbene complexes Ia–h gave satisfactory C, H, and N elemental analyses (Experimental Section) and they were characterized by IR and ^{1}H NMR (Table II) and ^{31}P NMR (Table III) spectroscopies. The IR spectra show strong ν(C≡N) peaks in the range 1506–1512 cm^{-1} and medium to strong ν(NH) absorptions in the range 3223–3319 cm^{-1}, as are also found in Pd(II) and Pt(II) complexes of cyclic[3] and acyclic[8] diaminocarbenes. The presence of two medium to weak ν(M–Cl) bands in the range 271–324 cm^{-1} is indicative of a cis stereogeometry for the complexes Ia–h.[8]

The carbene ring protons of the diaminocarbene complexes Ia–g display ABCD-type ^{1}H NMR spectra at 400 MHz. Compounds Ia and Id show four separate multiplets in the ranges δ 2.75–3.55 and 3.18–3.76, respectively, one for each proton of the ring. Complexes Ib, Ic, Ie, and If give rise to only three resonances for the diaminocarbene protons. For these last four complexes it is observed that the two protons of a –NCH$_2$– group fall at about the same chemical shift, which always appears as the upfield resonance, i.e. δ 3.27 (Ib), 3.05 (Ic), and 3.31 (Ie and If). The –NCH$_2$– resonances of Ia–f have additional fine structure due to coupling with the NH proton and the phosphorus atom of the coordinated phosphine ligand. This has been proven by spin-decoupling the NH proton on the diaminocarbene complexes *cis*-Cl$_2$(L)Pd[$\overline{CN(C_6H_4\text{-}p\text{-OMe})CH_2CH_2NH}$] (L = PPh$_3$, PMe$_2$Ph). A similar coupling was also observed for aminooxycarbene complexes of the type CpM(CO)$_2$($\overline{COCH_2CH_2NH}$)$^+$ (M = Fe, Ru)[5b] and *cis*-M(CO)$_4$X($\overline{COCH_2CH_2NH}$) (M = Mn, Re; X = Cl, Br, I).[5c] Coupling of the aminocarbene protons with the phosphine ligand has been confirmed by spectral simulation analysis carried out for *cis*-Cl$_2$(PhMe$_2$P)Pd[$\overline{CN(C_6H_4\text{-}p\text{-OMe})CH_2CH_2NH}$] (Id). The mixed isocyanide–diaminocarbene complex *cis*-Cl$_2$(*t*-BuNC)Pd[$\overline{CN(t\text{-Bu})CH_2CH_2NH}$] (Ig) displays only one resonance for the –NCH$_2$CH$_2$N– protons, which appears as a broad signal at δ 3.69. The –CH$_2$CH$_2$– singlet in the ^{1}H NMR spectrum does not change even at –70 °C, thus suggesting that the equivalence of the NCH$_2$ groups is not due to rapid rotation around the Pd–C(carbene) bond. Such a process should also be disfavored by the presence of the two bulky *t*-BuNC ligands. The bis(diaminocarbene) complex Ih was too insoluble for ^{1}H NMR measurements. Finally, the NH resonances of Ia–g appear as broad signals in the range δ 6.81–8.77.

Reactions of Thiirane. Synthesis of Five-Membered Cyclic Aminothiocarbene Complexes. Thiirane is observed to react spontaneously with some RNC ligands in Pd(II) complexes in THF solvent at room temperature to yield five-membered cyclic aminothiocarbene derivatives. Thus, *p*-MeOC$_6$H$_4$NC in complexes

2 and **4** (Table I) reacts with 1.5 equiv of thiirane, affording after 10–12 h of stirring at room temperature the aminothiocarbene complexes IIa and IIb in 38 and 75% yield, respectively (Scheme II).

Thiirane does not react in THF solvent with the bulky *t*-BuNC ligand in *cis*-$Cl_2(Ph_3P)Pd(CN\text{-}t\text{-}Bu)$ to form the cyclic aminothiocarbene $Pd{=}\overline{CN(t\text{-}Bu)CH_2CH_2S}$ complex, the starting isocyanide complex being recovered unchanged after 24-h reaction at room temperature. Similarly, the reactions between the *p*-$MeOC_6H_4NC$ ligand in the Pt(II) complexes *cis*-$Cl_2(Ph_3P)Pt(CNC_6H_4\text{-}p\text{-}OMe)$ and *trans*-$[(PPh_3)_2Pt(CNC_6H_4\text{-}p\text{-}OMe)Cl]BF_4$ and a 3-fold excess of thiirane, under experimental conditions identical with those described above for the Pd–CN-*t*-Bu reaction, fail to give any aminothiocarbene derivative.

The reaction of the bis(isocyanide) complex *cis*-$Cl_2Pd(CNC_6H_{11})_2$ (**8**) with a 3-fold excess of thiirane leads to the conversion of only one cyclohexyl isocyanide ligand to the corresponding cyclic aminothiocarbene as in compound IIc after a 2-day reaction time (Scheme II). Since free $C_6H_{11}NC$ is detected in solution (see Experimental Section), it is possible that the reaction of **8** and thiirane proceeds through the rapid displacement of one isocyanide ligand, followed by coordination of one thiirane molecule and formation of a metal–isocyanide–thiirane intermediate. This latter species evolves then to the final complex IIc by reaction of the coordinated isocyanide with an additional molecule of thiirane and displacement of the coordinated thiirane by free $C_6H_{11}NC$. Attempts to isolate the intermediate species were unsuccessful. However, initial displacement of one RNC ligand by thiirane is not surprising since it is known that $X_2Pd(CNR)_2$ (X = halide) systems undergo substitution of one isocyanide group by ligands L such as PPh_3 and $AsPh_3$ to give the corresponding substitution products $X_2Pd(CNR)(L)$.[8] Although such a reactivity pattern was not observed in the reactions with aziridine and oxirane (see below), most previously described reactions of the heterocycles $\overline{YCH_2CH_2}$ (Y = NH, S, O) with transition-metal complexes are known to occur at the metal centers.[9-15]

The aminothiocarbene compounds IIa–c gave satisfactory elemental analyses for the proposed formulas (see Experimental Section). The IR and ^1H NMR data are reported in Table II. The ^{31}P NMR data are listed in Table III. Complexes IIa–c are stable in the solid state and in solution. They are slightly soluble in CH_2Cl_2 and insoluble in Et_2O, acetone, and *n*-hexane. Complexes IIa–c show $\nu(C{=}N)$ absorptions in the range 1506–1530 cm^{-1}. The $\nu(C{=}N)$ vibrations for acyclic aminothiocarbene complexes of Pt(II) of the type $\{PtCl[C(SR)NMe_2]L_2\}^+$ (R = Me, Et; L = tertiary phosphine) were reported to occur in the range 1530–1570 cm^{-1}.[16] Complexes IIa–c show two $\nu(PdCl)$ bands in the range 280–316 cm^{-1}, which are indicative of a cis geometry.[8] The ^1H NMR spectra of IIa–c display the $-SCH_2-$ protons downfield (δ 3.76–4.14) with respect to the $-NCH_2-$ protons (δ 2.99–3.40). In the related aminothiocarbene $Cp(CO)_2Fe(\overline{CSCH_2CH_2NH})PF_6$[5b] the $-SCH_2-$ and $-NCH_2-$ resonances are observed at δ 4.45 and 3.69, respectively. Complexes IIa–c give rise to four distinct multiplets for the ring protons of the carbene ring at 400 MHz.

Reactions of Oxirane. Synthesis of Five-Membered Cyclic Aminooxycarbene Complexes. In contrast to the reactions of aziridine and thiirane with coordinated RNC ligands, oxirane alone fails to convert the isocyanide group in Pd(II) and Pt(II) complexes to the cyclic aminooxycarbene ligand. Thus, reactions of *cis*-$Cl_2(Ph_3P)M(CNC_6H_4\text{-}p\text{-}OMe)$ (M = Pd, Pt) with excess oxirane (ca. 4 mL) in THF gave no evidence of the formation of the cyclic aminooxycarbene complexes *cis*-$Cl_2(Ph_3P)M{=}\overline{CN(C_6H_4\text{-}p\text{-}OMe)CH_2CH_2O}$, the starting compounds being recovered unchanged after 24 h of stirring at room temperature. However, treatment of each of the complexes *cis*-$Cl_2(Ph_3P)Pt(CNC_6H_4\text{-}p\text{-}OMe)$, *trans*-$[(PPh_3)_2Pt(CNC_6H_4\text{-}p\text{-}OMe)Cl]BF_4$, and *cis*-$Cl_2Pt(CNC_6H_4\text{-}p\text{-}OMe)_2$ in 2-chloroethanol with excess oxirane in the presence of NaCl leads to the slow conversion (3 days) of one isocyanide ligand to afford the cyclic aminooxycarbene compounds IIIa–c (Scheme III), respectively.

Reactions of the oxirane–NaCl system with Pd(II)–isocyanide complexes such as *cis*-$Cl_2(Ph_3P)Pd(CNC_6H_4\text{-}p\text{-}OMe)$ in 2-chloroethanol, under experimental conditions similar to those described above for the synthesis of IIIa–c, fail to give any aminooxycarbene derivative. In all cases, red solutions were obtained in which no $\nu(N{\equiv}C)$ absorptions of the starting isocyanide or $\nu(N{=}C)$ of the carbene product were present, thereby suggesting the formation of Pd(0) species as proposed for the reactions of cationic Pd(II)–isocyanide complexes with 2-bromoethanol and *n*-BuLi.[2]

The IR and ^1H NMR data for IIIa–c are reported in Table II, while the ^{31}P NMR data are given in Table III. Elemental analyses are reported in the Experimental Section. Complexes IIIa–c show strong $\nu(C{=}N)$ absorptions in the range 1510–1539 cm^{-1} as observed for other cyclic aminooxycarbene complexes of Pt(II).[2] For IIIc $\nu(N{\equiv}C)$ of the coordinated isocyanide is observed at 2203 cm^{-1} as a strong absorption. The cis configuration of IIIa and IIIc has been assigned by the presence of two $\nu(Pt\text{–}Cl)$ bands of medium to weak intensity in the region 294–334 cm^{-1}. Also the value of $^1J(Pt\text{–}P)$ (3908 Hz) for IIIa is consistent with a configuration in which a PPh_3 ligand is trans to a halide.[17] The trans geometry of IIIb has been confirmed by its ^{31}P NMR spectrum. Compounds IIIa–c show $\nu(C\text{—}O)$ bands of medium intensity in the range 1250–1300 cm^{-1}. These last assignments were made by comparison with $\nu(C\text{—}O)$ absorptions of several Pt(II) alkoxycarbenes, which were reported to occur around 1300 cm^{-1}.[18]

The aminooxycarbene complex IIIa shows four distinct multiplets for the carbene ring protons in the ^1H NMR spectrum. The $-OCH_2-$ protons are assigned downfield (δ 4.74 and 4.39) with respect to the $-NCH_2-$ protons (δ 3.74 and 3.36), as is also observed for other cyclic aminooxycarbene complexes of Pt(II).[2] The cationic carbene compound IIIb shows two triplets (AA'BB' type) for the ring protons at δ 3.75 ($-OCH_2-$) and 3.30 ($-NCH_2-$). The related complex *trans*-$\{(PPh_3)_2Pt[\overline{CN(C_6H_4\text{-}p\text{-}Me)CH_2CH_2O}]X\}BF_4$ (X = Cl, Br) shows the $-OCH_2-$ and $-NCH_2-$ protons as triplets at δ 3.71 and 3.37, respectively.[2] For this latter compound an X-ray structural determination has been also carried out.[2] Compound IIIc displays two multiplets for the $-OCH_2-$ and $-NCH_2-$ resonances centered at δ 4.97 and 4.21, respectively.

Discussion

The possible mechanism for the isocyanide–cyclic carbene conversion by aziridine outlined in Scheme I could proceed in the first step by a nucleophilic attack of the entering amine on the electrophilic carbon of the coordinated RNC ligand to give the intermediate iminometal(II) species I*. The subsequent step to give the final complex I could involve C–N ring opening of the coordinated heterocycle, which may occur by intramolecular attack of the nucleophilic imino nitrogen on the adjacent methylene group of aziridine in a four-membered cyclic transition state. We have no evidence of the proposed intermediate I*, which has been proposed[6] for the reactions of Pd(II)-coordinated isocyanides with

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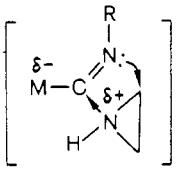
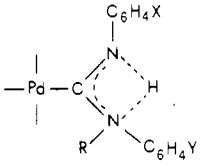


I*

various amines and for the cyclization reactions of RNC ligands in metal isocyanide complexes with 2-bromoethylamine.[3] A four-membered cyclic transition state has been proposed in the proton-transfer step for the formation of aminocarbene complexes of Pd(II) from reactions of RNC ligands with arylamines[6] (see structure A).



A

The present isocyanide cyclization reaction may be related to the conversion of CO and CS ligands to five-membered cyclic carbene derivatives by aziridine in the presence of a halide salt.[5] Typically, it has been found[5b] that one CO group in $Cp(CO)_3Fe^+$ can be converted to an aminooxycarbene ligand as in $Cp(CO)_2Fe(\overline{COCH_2CH_2NH})^+$ by reaction in CH_3CN solvent with equivalent amounts of aziridine and $[BrCH_2CH_2NH_3]Br$ in higher yields and shorter reaction times compared to other methods.[4,19] It has been demonstrated that Br^- is a catalyst for the reaction.[5b] For $M(CO)_5Br$ (M = Mn, Re) complexes, it has been shown that, even in the absence of any added Br^- salt, one CO group reacts with excess $H\overline{NCH_2CH_2}$ in CH_3CN to form the corresponding aminooxycarbene derivatives. However, this reaction takes a longer time to complete and consumes aziridine, which is partly lost due to polymerization.[5c] It is also observed that the reaction of aziridine with $M(CO)_5Br$ (M = Mn, Re) depends upon the nature of the solvent and on the halide ion used as catalyst.[5c] As for the isocyanide reactions with aziridine, we note that the addition of Cl^- ions does not affect the rate and the yield of the isocyanide–carbene conversion. This has been shown (see Experimental Section) by reacting each of the complexes *cis*-$Cl_2(Ph_3P)Pd(CNR)$ (R = *t*-BuNC, *p*-$MeOC_6H_4$) with aziridine (1 equiv) and LiCl (1 equiv) in THF solvent to afford the corresponding cyclic diaminocarbene complexes Ia and Ib, respectively.

The difference in reactivity between CO and CNR ligands toward aziridine may be tentatively explained in terms of the combined effects of the basicity of the imino nitrogen in I* (Scheme I) and the susceptibility of aziridine to undergo ring opening by external attack of a nucleophile with consequent relief of strain. The nucleophilic character of the imino nitrogen in I* may be illustrated by the reactions of the imidoyl ligands M—C(R)=NR with electrophiles (E^+) to form the aminocarbene complexes M=C(R)—N(E)R^+.[20] Recently, it has been shown that the aminooxycarbene $Cp(CO)_2Fe(\overline{COCH_2CH_2NH})^+$[21] and the diaminocarbenes *trans*-$\{(PPh_3)_2M[\overline{CN(R)CH_2CH_2NH}]\}^+$ (M = Pd, Pt; R = aryl)[3] react with bases (NaH, K_2CO_3, *n*-BuLi) to give the intermediate imino complexes $Cp(CO)_2Fe(\overline{COCH_2CH_2N}:)$ and *trans*-$\{(PPh_3)_2M[\overline{CN(R)CH_2CH_2N}:]\}$, whose nitrogen atoms readily react with electrophiles such as alkyl halides RX to afford the corresponding N-R-substituted aminocarbene complexes. As for the stability of aziridine toward ring opening by external attack of a nucleophile, it is known that this process is slow.[22] However, addition of electrophiles such as protons and Lewis acids leads to the formation of quaternary ammonium salts, which are usually reactive toward nucleophiles.[22] In our case (Scheme I), the isocyanide carbon acts as an electrophile coordinating to the imine nitrogen of aziridine and thus facilitating the ring-breaking process of the heterocycle to yield the final five-membered cyclic carbene.

A reaction intermediate similar to that described for the aziridine reactions (I*) may be suggested for the reactions of thiirane with coordinated RNC ligands to give cyclic aminothiocarbene compounds (Scheme II).

As for the formation of cyclic aminooxycarbene compounds from reactions of RNC ligands and oxirane (Scheme III), two possible mechanisms may be considered. Mechanism A may involve initial chloride attack on oxirane to produce the haloalkoxide ion $^-OCH_2CH_2Cl$, which subsequently attacks the electrophilic RNC ligand to yield the aminooxycarbene compound via intramolecular cyclization of the imidoyl intermediate by imino nitrogen displacement of the Cl^- ion. Mechanism B could involve attack of oxirane on the electrophilic carbon of the RNC ligand to form an isocyanide–oxirane adduct, which may be attacked by Cl^- ion at an oxirane carbon, resulting in ring opening to yield an imidoyl intermediate. This latter species could then rearrange to the final carbene product as described for mechanism A.

Mechanisms analogous to mechanisms A and B have been proposed for the related conversion of CO ligands to dioxycarbene ligands by oxirane and halide ion.[5b] As reported for the CO systems, and also for the reactions of RNC ligands with oxirane and Cl^- ion, none of the intermediates involved in Scheme III could be detected. It must be noted, however, that ring opening of oxirane by Cl^- attack to produce the haloalkoxide ion (mechanism A) is supported by other studies in which the halide ion acts as catalyst to produce ring opening in certain organic reactions.[23-25] Furthermore, the haloalkoxide ion $^-OCH_2CH_2X$ (X = Cl, Br) has been shown to attack electrophilic RNC[2] and CO[4] ligands to give cyclic carbenes.

It is likely that only mechanism A is operative for the reactions of Pd(II)- and Pt(II)–isocyanide complexes with oxirane in the presence of halide ions. In fact, route A in contrast to route B provides a reliable explanation for the failure of Pd(II)–isocyanide complexes to give Pd(II)–carbene derivatives when reacted with haloalkoxide ions.[2] As noted earlier,[2] the alkoxide ion preferentially attacks the metal rather than the bound isocyanide ligand, leading to the formation of unstable Pd–alkoxide derivatives that subsequently decompose to Pd(0) species.[26]

Experimental Section

General Procedures and Materials. All reactions were carried out under an N_2 atmosphere. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl under N_2. All other solvents were of reagent grade purity and used without further purification. ^1H NMR spectra of the starting isocyanide metal complexes **1–12** (Table I) were recorded on a Varian FT-80A spectrometer. The ^1H NMR spectra of all the carbene complexes of the type I–III (Table II) were obtained on a Bruker AM-400 spectrometer. ^{31}P NMR spectra were recorded on a Varian FT-80A spectrometer. IR spectra were taken on a Perkin-Elmer 983 spectrophotometer. The fast atom bombardment (FAB) mass spectra were obtained on a VG ZAB2F instrument operating with a Xe atom beam energy of 8 keV. Melting points (uncorrected) of the compounds were determined in air on a hot-plate apparatus. Elemental analyses were performed by the Department of Analytical Chemistry of the University of Padua. Aziridine was prepared according to a reported procedure[27a]

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with subsequent modification.[27b] Thiirane and oxirane were commercially available products and were used as received. As aziridine, thiirane, and oxirane are toxic substances, all preparations were carried out in an efficient hood.

Starting Complexes. The isocyanide complexes **1–12** (Table I) were prepared according to literature procedures, which are outlined in ref 28.

Reactions of Aziridine. Synthesis of *cis*-$Cl_2(Ph_3P)Pd[\overline{CN(t\text{-}Bu)CH_2CH_2NH}]$ (Ia). To a suspension of *cis*-$Cl_2(Ph_3P)Pd(CN\text{-}t\text{-}Bu)$ (334 mg, 0.64 mmol) in THF (15 mL) was added aziridine (0.048 mL, 0.96 mmol) and the reaction mixture stirred at 0 °C for 1 h. The stirring was then continued while the temperature of the bath was allowed to rise slowly to room temperature to give a clear solution. After 20 h of reaction time, a white precipitate formed. An IR spectrum of the solution showed that almost all the starting complex had reacted. The solid was then filtered, washed with *n*-hexane (3 × 5 mL), and dried under vacuum: yield 252 mg (70%); mp 280–283 °C. Anal. Calcd for $C_{25}H_{29}N_2Cl_2PPd$: C, 53.07; H, 5.16; N, 4.95; Cl, 12.53. Found: C, 52.60; H, 5.27; N, 4.77; Cl, 12.28. In a separate experiment *cis*-$Cl_2(Ph_3P)Pd(CN\text{-}t\text{-}Bu)$ (130 mg, 0.25 mmol) was reacted in THF (10 mL) with aziridine (0.014 mL, 0.27 mmol) in the presence of LiCl (10 mg, 0.25 mmol) and the reaction mixture stirred at 0 °C for 45 min. The course of the reaction was monitored by IR spectroscopy, by observing the decrease of $\nu(N{\equiv}C)$ at 2224 cm^{-1}. After 20 h of stirring at room temperature, no residual $\nu(N{\equiv}C)$ was present. The white solid formed, Ia, was filtered, washed with MeOH (2 × 3 mL) and *n*-hexane (2 × 5 mL), and dried under vacuum; yield 100 mg (70%).

***cis*-$Cl_2(Ph_3P)Pd[\overline{CN(C_6H_4\text{-}p\text{-}OMe)CH_2CH_2NH}]$ (Ib).** To a suspension of *cis*-$Cl_2(Ph_3P)Pd(CNC_6H_4\text{-}p\text{-}OMe)$ (331 mg, 0.58 mmol) in THF (10 mL) was added aziridine (0.043 mL, 0.86 mmol) and the reaction mixture stirred at 0 °C for 15 min and at room temperature for 45 min to give a clear solution. An IR spectrum of the solution did not reveal any bands due to the starting isocyanide complex. The white precipitate formed during this time was filtered and washed with a mixture of *n*-hexane–Et_2O (1:1 v/v) (3 × 5 mL): yield 214 mg (60%); mp 265–268 °C dec. Anal. Calcd for $C_{28}H_{27}N_2Cl_2POPd$: C, 56.41; H, 4.42; N, 4.55. Found: C, 54.43; H, 4.36; N, 4.35. The same reaction was repeated in the presence of LiCl (10 mg, 0.25 mmol) by starting from *cis*-$Cl_2(Ph_3P)Pd(CNC_6H_4\text{-}p\text{-}OMe)$ (143 mg, 0.25 mmol) and aziridine (0.014 mL, 0.27 mmol) in THF (10 mL). The reaction mixture was stirred at 0 °C for 15 min and then at room temperature for 45 min. After this time no $\nu(N{\equiv}C)$ at 2207 cm^{-1} of the starting isocyanide complex was detected in the IR spectrum. The solid formed, Ib, was filtered, washed with MeOH (2 × 3 mL) and *n*-hexane (2 × 5 mL), and dried under vacuum; yield 84 mg (55%).

***cis*-$Cl_2(PhMe_2P)Pd[\overline{CN(t\text{-}Bu)CH_2CH_2NH}]$ (Ic).** This compound was prepared as described for Ia by starting from *cis*-$Cl_2(PhMe_2P)Pd(CN\text{-}t\text{-}Bu)$ (219 mg, 0.55 mmol) and aziridine (0.033 mL, 0.66 mmol) in THF (10 mL): yield 166 mg (69%); mp 265–268 °C dec. Anal. Calcd for $C_{15}H_{25}N_2Cl_2PPd$: C, 40.79; H, 5.70; N, 6.34. Found: C, 40.66; H, 5.78; N, 6.16.

***cis*-$Cl_2(PhMe_2P)Pd[\overline{CN(C_6H_4\text{-}p\text{-}OMe)CH_2CH_2NH}]$ (Id).** This compound was prepared as described for Ia by starting from *cis*-$Cl_2(PhMe_2P)Pd(CNC_6H_4\text{-}p\text{-}OMe)$ (250 mg, 0.56 mmol) and aziridine (0.033 mL, 0.66 mmol) in THF (10 mL). Reaction time for completing the reaction was 15 h at room temperature: yield 160 mg (58%); mp 260–263 °C dec. Anal. Calcd for $C_{18}H_{22}N_2Cl_2POPd$: C, 43.97; H, 4.71; N, 5.69. Found: C, 43.84; H, 4.62; N, 5.42. The mass spectrum showed M^+ at *m/e* 491.

***cis*-$Cl_2(Ph_3P)Pt[\overline{CN(C_6H_4\text{-}p\text{-}OMe)CH_2CH_2NH}]$ (Ie).** This compound was prepared by starting from *cis*-$Cl_2(Ph_3P)Pt(CNC_6H_4\text{-}p\text{-}OMe)$ (304 mg, 0.46 mmol) and aziridine (0.034 mL, 0.68 mmol) in THF (20 mL). After 2 h of reaction time no residual $\nu(N{\equiv}C)$ absorption of the starting complex was present. The white solid formed during this time was filtered, washed with *n*-hexane (2 × 10 mL), and dried under vacuum: yield 170 mg (53%); mp >300 °C. Anal. Calcd for $C_{28}H_{27}N_2Cl_2POPt$: C, 47.73; H, 3.86; N, 3.97. Found: C, 47.79; H, 3.89; N, 3.89.

***cis*-$Cl_2(Ph_3P)Pt[\overline{CN(C_6H_4\text{-}p\text{-}Me)CH_2CH_2NH}]$ (If).** This compound was prepared as described for Ie by starting from *cis*-$Cl_2(Ph_3P)Pt(CNC_6H_4\text{-}p\text{-}Me)$ (230 mg, 0.35 mmol) and aziridine (0.026 mL, 0.52 mmol) in THF (10 mL). Reaction time was 0.5 h: yield 190 mg (78%); mp >300 °C. Anal. Calcd for $C_{28}H_{27}N_2Cl_2PPt$: C, 48.84; H, 3.95; N, 4.06. Found: C, 48.53; H, 3.87; N, 3.92.

***cis*-$Cl_2(t\text{-}BuNC)Pd[\overline{CN(t\text{-}Bu)CH_2CH_2NH}]$ (Ig).** To a solution of *cis*-$Cl_2Pd(CN\text{-}t\text{-}Bu)_2$ (243 mg, 0.70 mmol) in THF (20 mL) at 0 °C was added aziridine (0.042 mL, 0.84 mmol). An IR spectrum of the solution showed $\nu(N{\equiv}C)$ at 2209 cm^{-1}, while the starting bis(isocyanide) complex showed $\nu(N{\equiv}C)$ at 2243 and 2225 cm^{-1} in THF solvent. An absorption of medium intensity at 1509 cm^{-1} corresponding to $\nu(N{=}C)$ was also observed. The ice bath was removed, and stirring was continued for 20 h. During this time a white solid precipitated. The solution was then concentrated under reduced pressure to ca. 10 mL and Et_2O (10 mL) added. The white solid formed was filtered, washed with Et_2O (3 × 5 mL), and dried under vacuum: yield 190 mg (70%); mp 295–298 °C. Anal. Calcd for $C_{12}H_{23}N_2Cl_2Pd$: C, 37.27; H, 5.99; N, 10.87; Cl, 18.34. Found: C, 36.95; H, 6.06; N, 10.62; Cl, 17.83.

***cis*-$Cl_2Pd[\overline{CN(C_6H_4\text{-}p\text{-}OMe)CH_2CH_2NH}]_2$ (Ih).** To a solution of *cis*-$Cl_2Pd(CNC_6H_4\text{-}p\text{-}OMe)_2$ (290 mg, 0.65 mmol) in THF (20 mL) was added aziridine (0.069 mL, 1.38 mmol) and the reaction mixture stirred for 1 h at 0 °C. After 30 min an IR spectrum of the solution showed the presence of only one $\nu(N{\equiv}C)$ absorption at 2185 cm^{-1} together with a band at 1511 cm^{-1} corresponding to $\nu(N{=}C)$. Stirring was continued at room temperature until no band at 2185 cm^{-1} was present (ca. 15 h). During this time a white precipitate formed, which was filtered, washed with *n*-hexane (2 × 5 mL), and dried under vacuum: yield 140 mg (40%); mp 180–183 °C. Anal. Calcd for $C_{20}H_{24}N_4Cl_2O_2Pd$: C, 45.34; H, 4.56; N, 10.57; Cl, 13.38. Found: C, 45.16; H, 5.01; N, 10.69; Cl, 12.98. The mass spectrum showed a peak of low abundance corresponding to M^+ at *m/e* 529 and peaks of medium to high abundance corresponding to $[M - Cl]^+$ and $[M - 2\ Cl]^+$ at *m/e* 494 and 459, respectively.

Reactions of Thiirane. Synthesis of *cis*-$Cl_2(Ph_3P)Pd[\overline{CN(C_6H_4\text{-}p\text{-}OMe)CH_2CH_2S}]$ (IIa). Thiirane (0.039 mL, 0.65 mmol) was added to a stirred solution of *cis*-$Cl_2(Ph_3P)Pd(CNC_6H_4\text{-}p\text{-}OMe)$ (254 mg, 0.44 mmol) in THF (10 mL) at 0 °C. The ice bath was removed, and stirring was continued at room temperature for 10 h. During this time a white precipitate formed. An examination of the IR spectrum of the solution did not reveal any $\nu(N{\equiv}C)$ band due to the starting complex. The solid was filtered, washed with Et_2O (2 × 5 mL), and dried under vacuum: yield 110 mg (38%); mp 262–265 °C dec. Anal. Calcd for $C_{28}H_{26}NSCl_2POPd$: C, 53.14; H, 4.14; N, 2.21. Found: C, 52.90; H, 4.13; N, 2.12.

***cis*-$Cl_2(PhMe_2P)Pd[\overline{CN(C_6H_4\text{-}p\text{-}OMe)CH_2CH_2S}]$ (IIb).** This compound was prepared by starting from *cis*-$Cl_2(PhMe_2P)Pd(CNC_6H_4\text{-}p\text{-}OMe)$ (391 mg, 0.87 mmol) in THF (10 mL) at 0 °C and thiirane (0.078 mL, 1.31 mmol). The reaction mixture was stirred initially at 0 °C for 10 min, and then stirring was continued at room temperature for 12 h. The white solid formed was filtered, recrystallized from CH_2Cl_2–*n*-hexane, and dried under vacuum: yield 331 mg (75%); mp 233–236 °C dec. Anal. Calcd for $C_{18}H_{22}NSCl_2POPd$: C, 42.50; H, 4.36; N, 2.75. Found: C, 42.05; H, 4.36; N, 2.67. The mass spectrum showed peaks at *m/e* 473 and 438 corresponding to $[M - Cl]^+$ and $[M - 2\ Cl]^+$, respectively.

***cis*-$Cl_2(C_6H_{11}NC)Pd[\overline{CN(C_6H_{11})CH_2CH_2S}]$ (IIc).** Thiirane (0.115 mL, 1.93 mmol) was added to a stirred solution of *cis*-$Cl_2Pd(CNC_6H_{11})_2$ (255 mg, 0.64 mmol) in THF (10 mL) at room temperature. An IR spectrum of the solution showed only one $\nu(N{\equiv}C)$ absorption at 2221 cm^{-1}, while the starting bis(isocyanide) complex showed in THF $\nu(N{\equiv}C)$ absorptions at 2233 and 2242 cm^{-1}. A medium to weak band at 2138 cm^{-1} corresponding to $\nu(N{\equiv}C)$ of free isocyanide was also detected. The solution was stirred for 2 days at room temperature, and the band at 2221 cm^{-1} slowly decreased during this time. The white precipitate formed after this time was filtered, washed with Et_2O (2 × 5 mL), and dried under vacuum: yield 60 mg (21%); mp 208–211 °C. Anal. Calcd for $C_{16}H_{26}N_2SCl_2Pd$: C, 42.16; H, 5.75; N, 6.14. Found: C, 41.83; H, 5.68; N, 5.60. The mass spectrum showed a peak of low abundance corresponding to M^+ at *m/e* 455 and a peak of medium abundance corresponding to $[M - 2\ Cl]^+$ at *m/e* 385.

Reactions of Oxirane. Synthesis of *cis*-$Cl_2(Ph_3P)Pt[\overline{CN(C_6H_4\text{-}p\text{-}OMe)CH_2CH_2O}]$ (IIIa). To a solution of *cis*-$Cl_2(Ph_3P)Pt(CNC_6H_4\text{-}p\text{-}OMe)$ (285 mg, 0.43 mmol) in 2-chloroethanol (10 mL) at 0 °C were added solid NaCl (126 mg, 2.15 mmol) and subsequently oxirane (4 mL). The reaction mixture was stirred 3 days at room temperature. The solution was then evaporated to dryness under vacuum. The oily residue was taken up with CH_2Cl_2 (20 mL), the solution filtered, and the filtrate concentrated to ca. 10 mL. On addition of Et_2O (40 mL), a white solid formed, which was filtered, washed with acetone (5 mL), MeOH (5 mL), and Et_2O (3 × 5 mL), and dried under vacuum: yield 198 mg (66%); mp 247–250 °C dec. Anal. Calcd for $C_{28}H_{26}NO_2Cl_2PPt$: C, 47.67; H, 3.71; N, 1.98. Found: C, 47.68; H, 3.72; N, 2.08.

***trans*-$\{(PPh_3)_2Pt[\overline{CN(C_6H_4\text{-}p\text{-}OMe)CH_2CH_2O}]Cl\}BF_4$ (IIIb).** This

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compound was prepared as described for IIIa by starting from *trans*-$[(PPh_3)_2Pt(CNC_6H_4$-*p*-$OMe)Cl]BF_4$ (482 mg, 0.49 mmol), NaCl (144 mg, 2.47 mmol), and oxirane (4 mL) in 2-chloroethanol (5 mL). After it was stirred for 3 days at room temperature, the reaction mixture was evaporated to dryness, dissolved in CH_2Cl_2 (10 mL), and filtered. The filtrate was treated with Et_2O (50 mL) to give a white precipitate of the product, which was filtered and dried under vacuum: yield 233 mg (47%); mp 229–232 °C. Anal. Calcd for $C_{46}H_{41}NO_2ClP_2BF_4Pt$: C, 51.13; H, 3.92; N, 1.26. Found: C, 51.48; H, 3.86; N, 1.22.

***cis*-Cl_2(*p*-$MeOC_6H_4NC)Pt[CN(C_6H_4$-*p*-$OMe)CH_2CH_2O]$ (IIIc).** This compound was prepared as described for IIIa by starting from *cis*-$Cl_2Pt(CNC_6H_4$-*p*-$OMe)_2$ (251 mg, 0.47 mmol), NaCl (81 mg, 1.41 mmol), and oxirane (4 mL) in 2-chloroethanol (5 mL): yield 63 mg (23%); mp 179–182 °C dec. Anal. Calcd for $C_{18}H_{18}N_2Cl_2O_3Pt$: C, 37.51; H, 3.14; N, 4.86. Found: C, 37.04; H, 3.10; N, 4.80.

Acknowledgment. R.A.M. thanks Prof. R. J. Angelici, Department of Chemistry, Iowa State University, for helpful discussions.

Registry No. **1**, 115268-38-7; **2**, 38883-39-5; **3**, 115226-76-1; **4**, 115226-77-2; **5**, 115226-78-3; **6**, 111140-04-6; **7**, 34710-33-3; **8**, 29827-46-1; **9**, 40927-13-7; **10**, 40927-16-0; **11**, 76376-35-7; **12**, 27902-71-2; Ia, 115226-79-4; Ib, 115244-43-4; Ic, 115226-80-7; Id, 115226-81-8; Ie, 115226-82-9; If, 115226-83-0; Ig, 115226-84-1; Ih, 115226-85-2; IIa, 115226-86-3; IIb, 115226-87-4; IIc, 115226-88-5; IIIa, 115244-44-5; IIIb, 115244-46-7; IIIc, 115226-89-6; *trans*-$[(PPh_3)_2Pt(CNC_6H_4$-*p*-$OMe)]BF_4$, 110313-73-0; aziridine, 151-56-4; thiirane, 420-12-2; oxirane, 75-21-8.

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Photoassisted Catalysis of the 1-Pentene Isomerization by $Fe(CO)_5$ Physisorbed onto Porous Vycor Glass

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Received December 29, 1987

UV photolysis of $Fe(CO)_5$ physisorbed onto porous Vycor glass under a 1-pentene atmosphere leads to quantitative formation of $Fe(CO)_4$(1-pentene). Continued photolysis leads to an active, catalytic intermediate capable of promoting alkene isomerization. Diffuse-reflectance FTIR spectra reveal intermediates that closely resemble those found in low-temperature hydrocarbon matrices. Although the spectral similarities and isomerization quantum yield, 152 ± 23, indicate a thermally activated ground-state catalyst, the cis/trans product ratio varies with irradiation time and differs from the expected thermodynamic ratio.

Introduction

Catalytic activity of iron carbonyls requires vacant or labile coordination site(s) where the substrate(s) can bind and undergo chemical transformation.[1-3] In the isomerization of olefins, for example, current data suggest $Fe(CO)_3$ as a key intermediate. Mechanistic studies performed by Grevels, Fleckner, and Hess implicate $Fe(CO)_3$ as the recurring catalytic intermediate in the thermally activated isomerization of 1-pentene.[4] Similar results occur in the photoactivated isomerization of 1-pentene, although the identity of the actual catalytic intermediate remains somewhat controversial. Chase and Weigert assign a band at 1969 cm^{-1} to active intermediate generated during photolysis of $Fe(CO)_5$ in neat 1-pentene.[5] Grant and co-workers identify $Fe(CO)_3(C_5H_{10})$ (C_3H_{10} = pentene) as the phenomenological catalyst and suggest that the catalyst lifetime, 0.2 s in neat 1-pentene, is determined by olefin dissociation, which yields a fragment that rapidly degrades to an inactive form.[6] Wrighton and co-workers propose the involvement of $Fe(CO)_3(1\text{-}C_5H_{10})_2$[7,8] and, on the basis of photolyses in low-temperature hydrocarbon matrices, suggest that the π-allyl complex $HFe(CO)_3(\eta^3\text{-}C_5H_9)$ is potentially the essential intermediate in the catalytic cycle.[9,10] In spite of the uncertainty with respect to the molecularity of the alkene, quantum yields of isomerization in excess of unity suggest that, although the compound is generated photochemically, the actual isomerization of the alkene is accomplished by a thermally activated ground-state species.[7-10]

Recent studies have focused on the catalytic activity of hybrid systems where the precursor, $Fe(CO)_5$ or a substituted analogue, is on a support. Wrighton and co-workers have used the photocatalyzed isomerization of 1-pentene to examine the activity of iron carbonyl anchored to a styrene microporous resin.[11] UV photolysis of the surface-confined species, principally $Fe(CO)_4L$ and $Fe(CO)_3L_2$ where L designates the triarylphosphine anchor, results in CO loss and formation of a catalytic intermediate capable of effecting a number of isomerizations.[11] The cis/trans ratio obtained with the hybrid system, relative to that obtained with the analogues $Fe(CO)_4(PPh_3)$ and $Fe(CO)_3(PPh_3)_2$ in homogeneous solution, suggests controlling product distribution by surface modification.[11] Similar results are described by Suib and coworkers for the photocatalyzed isomerization of 1-pentene by $Fe(CO)_5$ adsorbed onto the outer surfaces of small-pore zeolites and in the supercages of large-pore zeolites.[12] Although decomposition of the precursor complex to either an oxidized species and/or a cluster clouds the mechanistic interpretation, this hybrid system alters both the percent conversion and the product ratio,[12] relative to those for the photoactivated isomerization in homogeneous solution.

The development of hybrid systems, particularly an understanding of their differences from homogeneous systems, rests on the characterization of the surface-confined species. Experiments in this laboratory have shown that UV photolysis of $Fe(CO)_5$ physisorbed onto Corning's Code 7930 porous Vycor glass (PVG)

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