Three-coordinate Pt(0) η^2-complexes: electrophilic hydrogen attack through oxidative-addition of protic acids

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Abstract

Different types of products can be obtained by addition of protic acids HX (X = Cl, BF_4) to Pt(0) species of general formula [Pt(ol)(N-N)] (ol = olefin; N-N = N,N-chelate) according to the features of the two coordinated ligands. The typical attainment of four-coordinate hydrocarbyl derivatives by insertion of the alkene into the Pt–H bond is compared with the recently reported isolation of stable five-coordinate hydrides. The nature of the final product is also related to the coordinating ability of the X group. A general mechanism for the addition process is proposed.

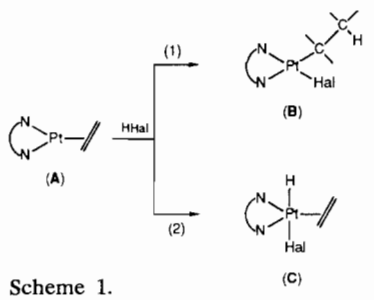
Key words: Platinum complexes; Olefin complexes; Bidentate amino ligand complexes; Chelate complexes

Introduction

It is expected [1] that protic acid addition to Pt(0)–olefin compounds (type **A**, Scheme 1) leads to the protonation of the π-coordinate olefin, with attainment of a square-planar Pt(II)–alkyl derivative (type **B**). In fact, the changing, by hydrogen addition, from the η^2 to the η^1 coordination mode is a common and well-established step [2] in many metal-assisted stoichiometric and catalytic processes involving alkenes.

On the other hand, the oxidative-addition of hydrogen halides to suitable three-coordinate [Pt(ol)(N-N)] substrates (N-N = 2,9-dimethyl-1,10-phenanthroline; ol = dimethyl-maleate or -fumarate) has been recently reported [3] to afford stable five-coordinate complexes [PtH(Hal)(ol)(N-N)] (Hal = Cl, Br, I) (type **C**) containing the H and Hal groups in the axial positions of a tbp coordinative environment.

Therefore, we intended to investigate the above depicted reaction system with the aim of getting more information on the factors affecting its evolution towards the **B** or **C** final products. In addition, it appeared of interest to ascertain if paths (1) and (2) are independent or type **B** products are formed from a type **C** precursor through a migratory hydrogen insertion.



Scheme 1.

Experimental

^1H and ^{13}C NMR spectra (see Tables 1 and 2) were recorded at 270 or 200 MHz on a Bruker AC-270 or a Varian XL-200 spectrometer, respectively. $CDCl_3$, CD_2Cl_2, $C_2D_2Cl_4$ and CD_3NO_2 were used as solvents (reference δ 7.26, $CHCl_3$ [δ 77.0 $^{13}CDCl_3$]; δ 5.32, $CHDCl_2$; δ 5.98, C_2HDCl_4; δ 4.33, CHD_2NO_2). IR spectra were recorded on a Perkin-Elmer 457 spectrophotometer in nujol mulls. Elemental analyses (see Table 3) were performed with a C. Erba elemental analyzer 1106.

Solvents and reagents were of AnalaR grade and, unless otherwise stated, were used without further

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TABLE 1. Relevant ^{1}H [^{13}C] NMR data for [Pt(N-N)(olefin)] complexes[a]

N-N	olefin	olefin-H	Me(H)–C(Het)	Others
1[b]	C_2H_4[c]	2.20(87, s, 4H)	3.33(s)	
	DMM	3.45(85, s, 2H)	3.21(s)	3.65(s, OMe)
		[23.6(490)]	[29.8]	[176.0(CO); 51.2(OMe)]
	DMF[c]	3.75(87, s, 2H)	3.18(s)	3.62(s, OMe)
		[25.0(442)]	[30.1]	[177.6(CO); 51.0(OMe)]
	MAc[c]	3.2(88, m, 1H), 2.65(74, dd, 1H),		3.63(s, OMe)
		2.38(68, dd, 1H)	3.22(s), 3.18(s)	
	AcN	2.5(98, m, 1H), 2.25([d], m, 2H)	3.29(s), 3.07(s)	
	(*Z*)-DCE[e]	4.23(75, s, 2H)	3.36(s)	
	(*E*)-DCE[e]	4.55(57, s, 2H)	3.36(s)	
2[f]	C_2H_4[c,g]	2.09(80, m, 4H)	3.28(s); 9.75(18, d)	
	DMM	3.65(82, ABq, 2H)	3.19(s), 9.68(32, d)	3.72, 3.67(s, OMe)
		[24.7(462), 22.8(462)]	[30.1; 152.6(C9)]	[176.2, 175.4(CO); 51.4, 51.1(OMe)]
	DMF[c]	3.84(90, ABq, 2H)	3.17(s); 9.50(29, d)	3.67, 3.63(s, OMe)
		[25.6(385), 24.3(418)]	[30.3; 151.8(C9)]	[177.8, 176.8(CO); 51.1, 50.8(OMe)]
	MAc[h]	3.35([d], m, 1H), 2.6([d], m, 1H),	3.27(s); 9.61(24, m)	3.67(s, OMe)
		2.35([d], m, 1H)	3.26(s); 9.71(37, m)	3.63(s, OMe)
	AcN[i]	2.6([d], m, 1H), 2.3([d], m, 2H)	3.35(s); 9.67(32, d)	
			3.16(s); 9.59(35, d)	
	(*Z*)-DCE[e]	4.23(74, ABq, 2H)	3.37(s); 9.52(27, d)	
	(*E*)-DCE[e]	4.60(57, ABq, 2H)	3.36(s); 9.53(27, d)	
3[j]	DMM	3.46(82, s, 2H)	9.53(28, d)	3.70(s, OMe)
		[23.9(450)]	[152.8(C2, C9)]	[175.8(CO); 51.3(OMe)]
	DMF	3.90(95, s, 2H)	9.50(30, d)	3.67(s, OMe)
		[25.2(387)]	[152.5(C2, C9)]	[177.2(CO); 51.1(OMe)]
4[k]	DMM	3.31(81, d, 1H), 3.50([d], d, 1H)	3.03(s)	3.65, 3.42(s, OMe)
				9.35(46, s, N=CH)
		[25.2(490), 24.6(460)]	[29.2]	[175.3, 175.1(CO); 50.8, 50.7(OMe); 162.5(N=CH)]

[a]Spectra recorded in $CDCl_3$ (reference δ 7.26, $CHCl_3$ [δ 77.0, $^{13}CDCl_3$]; the coupling constants with ^{195}Pt (Hz) are reported in parentheses. Abbreviations: s = singlet, d = doublet, q = quartet, m = multiplet. [b]The chemical shifts of the heteroaromatic 2,9-Me_2-phenanthroline protons are centered at approx. δ 8.35–8.3 (d, 2H), 7.85–7.8 (s, 2H), 7.8–7.75 (d, 2H) [^{13}C δ 162.5 (60, C2–C9), 148 (2 quat. CN), 136.5 (C4–C7), 128.0 (2 quat. C), 126–125.5 (C3–C8 and C5–C6)]. [c]See also ref. 7. [d]Coupling constant with ^{195}Pt not evaluable. [e]Spectra recorded in $C_2D_2Cl_4$ (reference δ 5.98 $C_2H_2Cl_4$). [f]The chemical shifts of the heteroaromatic 2-Me-phenanthroline protons are centered at approx. δ 8.55–8.50 (d, 1H), 8.45–8.40 (d, 1H), 7.9–7.85 (s, 2H), 7.85–7.8 (m, 1H), 7.8–7.75 (d, 1H) [^{13}C δ 163(C2), 148 (2 quat. CN), 137–136 (C4–C7), 130–125 (2 quat. C, C3–C8, C5–C6). [g]Spectrum recorded at −50 °C. [h]Two rotational isomers in approx. 3:2 ratio. [i]Two rotational isomers in approx. 1:1 ratio. [j]The chemical shifts of the heteroaromatic 1,10-phenanthroline protons are centered at approx. δ 8.5(d, 2H), 7.8 (s, 2H), 7.7 (d, 2H) [^{13}C δ 147 (2 quat. CN), 136.5 (C4–C7), 130 (2 quat. C), 127–126 (C3–C8, C5–C6)]. [k]The chemical shifts of the 6-Me-py-2-CH=NPh protons are centered at approx. δ 7.9 (t, 1H), 7.7 (d, 1H), 7.6 (d, 1H), 7.7–7.4 (m, 5 Ar–H) [^{13}C δ 162.3 (C6), 156.1 (C2), 148.8 (66, N–C_{Ph}), 137.9 (C4), 129–123 (C3, C5 and 5 Ar–C)].

purification. N-N ligands (Scheme 2) **1** and **3** are commercially available. The ligands **2** [4] and **4** [5] were prepared according to known procedures. The complex $[Pt(cod)_2]$ [6] was synthesized as previously reported. The synthesis of the three-coordinate substrates $[Pt(C_2H_4)(N\text{-}N)]$ (N-N = **1**, **2**) [7] and of the hydrides [Pt(H)Cl(DMM)dmphen)] and [Pt(H)Cl-(DMF) (dmphen)] [3] has been already reported.

Synthesis of [Pt(DMF)(N-N)] and [Pt(DMM)(N-N)] complexes

Method A (*N-N = 1–4*). $[Pt(cod)_2]$ (0.41 g, 1 mmol) was added in portions to a stirred solution of an equimolar amount of the olefin (DMF or DMM) in 20 ml of anhydrous ether within a period of 5 min. After stirring for a further 5 min, an equimolar amount of the appropriate N-N ligand was added to the filtered solution. The yellow crystalline precipitate (red, in the case of N-N = **4**) was collected by filtration after 30 min, washed with ether and dried. Yields were in the 80–85% range. Recrystallization was not required, since the products were pure according to ^{1}H NMR spectroscopy.

Method B (*N-N = 1, 2*). Solid $[Pt(C_2H_4)(N\text{-}N)]$ (*c.* 0.1 g, 0.25 mmol) was added to a solution of an equimolar amount of the olefin in 5 ml of anhydrous dichloro-

TABLE 2. Relevant ^1H NMR data for [PtCl(CHR–CH_2R')(N-N)] complexes[a]

N-N	R, R'	Pt–CHR	CH_2R'	Me(H)–C(Het)	Others
1	H, H	1.99(88, q)	0.87(42, t)	3.15(s), 2.97(s)	
	CN, H	3.71([b], q)	1.31(47, d)	3.20(s), 3.04(s)	
	COOMe, COOMe	4.30([b], dd)	2.90([b], dd) 2.55([b], dd)	3.16(s), 3.19(s)	3.60(s, OMe) 3.36(s, OMe)
2	H, H	2.26(85, q)	1.06(41, t)	3.43(s); 9.52(64, d)	
	COOMe, H	4.27(138, q)	1.21(43, d)	3.43(s); 9.89(54, d)	3.65(s, OMe)
	CN, H	3.78([b], q)	1.33(47, d)	3.40(s); 9.73(50, d)	
	COOMe, COOMe	4.20(130, dd)	3.09([b], dd), 2.68([b], dd)	3.40(s); 9.89(55, d)	3.70(s, OMe) 3.66(s, OMe)
3	H, H	2.18(84, q)	1.15(34, t)	9.84([b], d), 9.54(61, d)	
	COOMe, COOMe	4.20(121, dd)	3.14([b], dd), 2.79([b], dd)	9.97(50, d), 9.91([b], d)	3.66(s, 2 OMe)
4	COOMe, COOMe	[c]	2.63([b], dd), 2.41([b], dd)	3.18(s)	3.56(s, OMe), 3.48(s, OMe); 9.23(93, s, N=CH)

[a]Spectra recorded in $CDCl_3$ (reference δ 7.26, $CHCl_3$); the coupling constants with ^{195}Pt (Hz) are reported in parentheses. Abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, dd = double doublet. [b]Coupling constant with ^{195}Pt not evaluable. [c]Obscured by other signals.

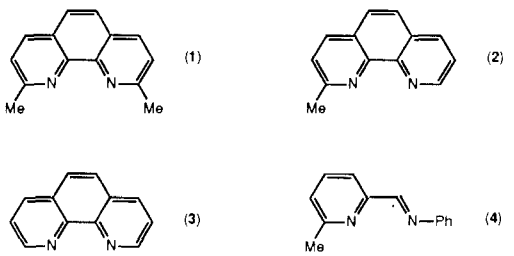
TABLE 3. Elemental analysis for some type **A** and **B** complexes

Complex	Formula	*Anal.* found (calc.)		
		C	H	N
Type **A** complexes				
[Pt(CH_2=CHCN)(dmphen)]	$C_{17}H_{15}N_3Pt$	44.65(44.74)	3.18(3.31)	9.46(9.21)
[Pt(*E*-ClCH=CHCl)(dmphen)]	$C_{16}H_{14}Cl_2N_2Pt$	38.55(38.41)	2.91(2.82)	5.64(5.60)
[Pt(*Z*-MeOOCCH=CHCOOMe)(mphen)]	$C_{19}H_{18}N_2O_4Pt$	42.65(42.78)	3.25(3.40)	5.33(5.25)
[Pt(CH_2=CHCN)(mphen)]	$C_{16}H_{13}N_3Pt$	43.51(43.44)	3.07(2.96)	9.44(9.50)
[Pt(*Z*-ClCH=CHCl)(mphen)]	$C_{15}H_{12}Cl_2N_2Pt$	37.21(37.05)	2.35(2.49)	5.75(5.76)
[Pt(*E*-MeOOCCH=CHCOOMe)(phen)]	$C_{18}H_{16}N_2O_4Pt$	41.68(41.62)	3.03(3.10)	5.30(5.39)
Type **B** complexes				
[PtCl{CH(COOMe)CH_2COOMe}(dmphen)]	$C_{20}H_{21}ClN_2O_4Pt$	40.97(41.14)	3.63(3.62)	4.75(4.80)
[PtCl{CH(COOMe)CH_2COOMe}(mphen)]	$C_{19}H_{19}ClN_2O_4Pt$	39.98(40.04)	3.40(3.36)	5.01(4.92)
[PtCl(CHMeCN)(mphen)]	$C_{16}H_{14}ClN_3Pt$	40.31(40.13)	3.01(2.95)	8.69(8.78)
[PtCl(CHMeCOOMe)(mphen)]	$C_{17}H_{17}ClN_2O_2Pt$	39.87(39.89)	3.39(3.35)	5.41(5.47)
[PtClEt(phen)]	$C_{14}H_{13}ClN_2Pt$	38.01(38.23)	3.03(2.98)	6.44(6.37)
[PtCl{CH(COOMe)CH_2COOMe}(mpan)]	$C_{19}H_{21}ClN_2O_4Pt$	39.99(39.90)	3.55(3.70)	4.78(4.90)

methane. Ethylene evolved immediately. The light orange solution was filtered on Florisil and concentrated *in vacuo*. The oily residue was crystallized by adding methanol. The yellow crystalline complexes were obtained in 75–80% yield. When N-N = **1**, this procedure could also be satisfactorily used in the case of MAc and AcN derivatives.

*Synthesis of [Pt(N-N)(ol)] complexes (N-N = **1**, **2**; ol = MAc, AcN, DCE)*

[Pt(C_2H_4)(N-N)] (*c.* 0.1 g, 0.25 mmol) was suspended in 2 ml of anhydrous toluene under nitrogen. An equimolar amount of the appropriate olefin was added and the mixture was stirred for 3 h at 0 °C. The solid residue was filtered, washed with toluene, n-hexane



Scheme 2.

and dried. The poorly soluble DCE derivatives were also washed with chloroform. The complexes were obtained in 60–70% yield as yellow–brown microcrystalline solids.

Synthesis of [Pt(MeOOCC≡CCOOMe)(phen)]

To a solution of [Pt(DMM)(phen)] (0.13 g, 0.25 mmol) in 6 ml of chloroform, an equimolar amount of the alkyne was added at room temperature. The solution was concentrated to a small volume and diluted with ether. The orange complex crystallized in 85% yield. *Anal.* Calc. for $C_{18}H_{14}N_2O_4Pt$: C, 41.78; H, 2.73; N, 5.41. Found: C, 41.56; H, 2.68; N, 5.49%. Relevant ^1H NMR data ($CDCl_3$): δ 9.91 (30, d, 2,9-H-phen), 3.93 (s, 6H, OMe).

Decomposition in solution of [Pt(H)Cl(DMM)-(dmphen)] and [Pt(H)Cl(DMF)(dmphen)]

The title complexes (0.014 g samples) were dissolved in 0.6 ml of $CDCl_3$ and ^1H NMR spectra were recorded every 24 h. After one week at room temperature, no traces of the starting hydrido complex were detected in the clear solution. [Pt(H)Cl(DMF)(dmphen)] decomposes into free olefin, [Pt(DMF)(dmphen)] (95%) and [$PtCl_2$(dmphen)] [8] (5%). [Pt(H)Cl(DMM)-(dmphen)] decomposes into free olefin, [Pt(DMM)-(dmphen)] (15%), [$PtCl_2$(dmphen)] (15%), [$PtCl_2$-(DMM)(dmphen)] [3] (50%) and another unidentified Pt–DMM complex (20%).

Reaction between [Pt(DMM)(dmphen)] and HBF_4

[Pt(DMM)(dmphen)] (0.27 g, 0.5 mmol) was suspended in 10 ml of dry toluene and an equimolar amount of $HBF_4 \cdot Et_2O$ was added under nitrogen. After 24 h stirring at room temperature, the solid residue was filtered off, washed with toluene, n-hexane and dried. [Pt{CH(COOMe)CH_2COOMe}(dmphen)]BF_4 was obtained as a pale yellow microcrystalline solid (0.24 g, 75% yield).

Anal. Calc. for $C_{20}H_{21}BF_4N_2O_4Pt$: C, 37.81; H, 3.33; N, 4.41. Found: C, 37.87; H, 3.41; N, 4.44%. ^1H NMR spectrum (CD_3NO_2): δ 8.68 (d, 1H), 8.62 (d, 1H), 8.05 (ABq, 2H), 7.92 (d, 1H), 7.85 (d, 1H), 4.57 (d, C*H*H), 4.20 (s, OMe), 3.31 (s, OMe), 3.25 (s, Me), 3.15 (dd, Pt–CH), 3.04 (s, Me), 2.55 (d, CH*H*). IR spectrum (nujol mull): 1690, 1585 cm^{-1} (CO).

When the above product was treated with an aqueous LiCl solution, the neutral complex [Pt-Cl{CH(COOMe)CH_2COOMe}(dmphen)] was obtained (see Table 2). IR spectrum (nujol mull): 1730, 1705 cm^{-1} (CO).

Reaction between [Pt(dmphen)(ol)] and $SiMe_3Cl/H_2O$ (ol = (Z)- and (E)-DCE, MAc, AcN)

The title complexes (0.014 g samples) were dissolved in 0.6 ml of $CDCl_3$ (0.002 g and $C_2D_2Cl_4$ as solvent for the DCE substrates) and the chemical changes in the solution were monitored through ^1H NMR spectra. Five-coordinate hydrido adducts formed quantitatively on adding an equimolar amount of $SiMe_3Cl$. Decomposition started immediately and was complete after several hours.

Relevant ^1H NMR data for the initially formed hydrido derivative and the composition of the decomposition mixtures are as follows.

(Z)-DCE. ^1H NMR spectrum ($C_2D_2Cl_4$): δ 3.33 (s, 6H, Me), 4.66 (s, CH=CH, J(PtH) = 94 Hz), −24.1 (s, PtH, J(PtH) = 1300 Hz); decomposition mixture: free olefin, [$PtCl_2$(dmphen)] (40%), [Pt(*Z*-DCE) (dmphen)] (20%) and [$PtCl_2$(*Z*-DCE)(dmphen)] (40%).

(E)-DCE. ^1H NMR spectrum ($C_2D_2Cl_4$): δ 3.44 (s, 6H, Me), 5.10 (ABq, CH=CH), −23.4 (s, PtH, J(PtH) = 1255 Hz); decomposition mixture: free olefin, [$PtCl_2$(dmphen)] (50%), [$PtCl_2$(*E*-DCE)(dmphen)] (40%) and an another unidentified Pt–DCE complex (10%).

MAc. ^1H NMR spectrum ($CDCl_3$): δ 3.67 (s, OMe), 3.37 (s, Me), 3.36 (s, Me), 3.9 (m, =CH), 3.45 (d, =C*H*H), J(PtH) = 50 Hz), 3.12 (d, =CH*H*, J(PtH) = 81 Hz), −27.1 (s, PtH, J(PtH) = 1199 Hz); decomposition mixture: platinum black, free olefin and dmphen (35%), [$PtCl_2$(dmphen)] (40%), [$PtCl_2$(MAc)(dmphen)] (25%) and traces of a possible four-coordinate insertion product.

AcN. ^1H NMR spectrum ($CDCl_3$): δ 3.46 (s, Me), 3.30 (s, Me), 3.03 (d, =CH*H*, J(PtH) = 76 Hz), −25.8 (s, PtH, J(PtH) = 1185 Hz); decomposition mixture: [$PtCl_2$(AcN)(dmphen)] (35%), [PtCl(CHMeCN)-(dmphen)] (65%, see Table 2).

Authentic samples of the five-coordinate [$PtCl_2$(DCE)(dmphen)], [$PtCl_2$(AcN)(dmphen)] and [$PtCl_2$(MAc)(dmphen)] complexes were obtained by chlorine oxidative-addition to the corresponding three-coordinate compounds, according to a previously reported method [3] for [$PtCl_2$(DMM)(dmphen)].

[$PtCl_2$(Z-DCE)(dmphen)]. *Anal.* Calc. for $C_{16}H_{14}Cl_4N_2Pt$: C, 33.64; H, 2.47; N, 4.90. Found: C, 33.71; H, 2.39; N, 4.76%. ^1H NMR spectrum ($C_2D_2Cl_4$):

δ 8.45 (d, 2H), 7.95 (s, 2H), 7.88 (d, 2H), 5.25 (s, CH=CH, J(PtH) = 81 Hz) 3.47 (s, 6H, Me).

[$PtCl_2$(E-DCE)(dmphen)]. *Anal.* Calc. for $C_{16}H_{14}Cl_4N_2Pt$: C, 33.64; H, 2.47; N, 4.90. Found: C, 33.75; H, 2.48; N, 4.85%. ^{1}H NMR spectrum ($C_2D_2Cl_4$): δ 8.45 (d, 2H), 7.93 (s, 2H), 7.90 (d, 2H), 5.66 (s, CH=CH, J(PtH) = 68 Hz), 3.47 (s, 6H, Me).

[$PtCl_2$(MAc)(dmphen)]. *Anal.* Calc. for $C_{18}H_{18}Cl_2N_2O_2Pt$: C, 38.58; H, 3.24; N, 5.00. Found: C, 38.72; H, 3.29; N, 5.03%. ^{1}H NMR spectrum ($CDCl_3$): δ 8.38 (d, 1H), 8.35 (d, 1H), 7.88 (s, 2H), 7.85 (d, 1H), 7.82 (d, 1H), 4.93 (dd, CH, J(PtH) = 84 Hz), 4.28 (d, C*H*H, J(PtH) = 61 Hz), 3.76 (s, OMe), 3.70 (d, CH*H*), 3.62 (s, Me), 3.46 (s, Me).

[$PtCl_2$(AcN)(dmphen)]. *Anal.* Calc. for $C_{17}H_{15}Cl_2N_3Pt$: C, 38.72; H, 2.87; N, 7.97. Found: C, 38.48; H, 3.01; N, 7.78%. ^{1}H NMR spectrum ($CDCl_3$): δ 8.40 (d, 2H), 7.93 (ABq, 2H), 7.88 (s, 1H), 7.85 (d, 1H), 4.08 (dd, CH), 3.93 (d, C*H*H), 3.71 (d, CH*H*), 3.54 (s, Me), 3.41 (s, Me).

Reaction between [Pt(C_2H_4)(dmphen)] and $SiMe_3Cl/H_2O$

(a) [Pt(C_2H_4)(dmphen)] (0.015 g) was dissolved in 0.7 ml of CD_2Cl_2 and an equimolar amount of $SiMe_3Cl$ was added. ^{1}H NMR spectra of the reaction mixture were recorded every 5 min. A five-coordinate hydrido derivative formed immediately and was present in the reaction mixture in higher than 80% amount. (Relevant resonances in the ^{1}H NMR spectrum δ: 3.33 (s, 6H, Me), 2.74 (app. d, 2H, J(PtH) = 85 Hz), −27.4 (s, PtH, J(PtH) = 1250 Hz).) After 30 min the hydrido species was reduced to 30% and a 40% amount of the four-coordinate [PtClEt(dmphen)] was observed. 24 h later the reaction mixture had the approximate composition: [$PtCl_2$(dmphen)], 30%; [$PtCl_2$(C_2H_4)(dmphen)] [8], 30%; [PtCl(CD_2Cl)(C_2H_4)(dmphen)] [7], 40%.

(b) [Pt(C_2H_4)(dmphen)] (0.015 g) was dissolved in 0.7 ml of C_2H_4-saturated CD_2Cl_2 and an equimolar amount of $SiMe_3Cl$ was added. ^{1}H NMR spectra of the reaction mixture were recorded every 5 min. The five-coordinate hydrido derivative formed immediately and was present in the reaction mixture in an amount similar to that given above. After 24 h the reaction mixture had the approximate composition: [$PtCl_2$(dmphen)], 40%; $PtCl_2$(C_2H_4)(dmphen)], 10%; [PtCl(CD_2Cl)(C_2H_4)(dmphen)], 10%; [PtClEt(C_2H_4)-(dmphen)] [9], 40%.

Reaction between [Pt(ol)(N-N)] and $SiMe_3Cl/H_2O$ (N-N = 2–4, ol = C_2H_4, MAc, AcN, DMM)

An equimolar amount of $SiMe_3Cl$ was added to a chloroform solution (0.020 g/ml) of the three-coordinate Pt(0) complex at room temperature (dichloromethane in the case of the C_2H_4 derivative). After 15 min, the solution was filtered through Celite and diluted with ether. The four-coordinate complexes [PtCl(CHR–CH_2R')(N-N)] crystallized in 50–70% yields. Comparable yields were obtained when the reactions were performed in toluene suspension. The products were recovered by work-up of the reaction mixture after 24 h stirring at room temperature.

Reaction between [Pt(ol)(mphen)] and $SiMe_3Cl/H_2O$ (ol = (E)-DCE, (Z)-DCE)

An equimolar amount of $SiMe_3Cl$ was added to a toluene suspension (0.020 g/ml) of the three-coordinate Pt(0) complex. After 24 h stirring at room temperature, the solid residue was filtered off, washed with toluene, n-hexane and dried. The product was formulated as [$PtCl_2$(mphen)] on the basis of its ^{1}H NMR spectrum.

^{1}H NMR spectrum ($C_2D_2Cl_4$): δ 10.0 (d, 1H), 8.61 (d, 1H), 8.45 (d, 1H), 7.93 (s, 2H), 7.85 (m, 1H), 7.70 (d, 1H), 3.38 (s, 3H).

An authentic sample of [$PtCl_2$(mphen)] was obtained as reported for [$PtCl_2$(mphen)] in ref. 8.

Reaction between [Pt(C_2H_4)(phen)] and $SiMe_3Cl/H_2O$

[Pt(cod)$_2$] (0.205 g, 0.5 mmol) was suspended in 2 ml of dry toluene at 0 °C under ethylene. After 10 min, an equimolar amount of phen was added in portions to the clear yellow solution at the same temperature. A red solution was obtained and the temperature was raised to 20 °C to remove excess ethylene. An equimolar amount of $SiMe_3Cl$, dissolved in 2 ml of wet toluene, was added. A yellow–brown solid formed on stirring. After 15 min, the mixture was concentrated to dryness and the residue was purified by column chromatography on Florisil using methylene dichloride as eluant. [PtCl(Et)(phen)] (0.088 g, 40% yield) was obtained as a yellow crystalline solid.

Reaction between [Pt(DMM)(phen)] and [Pt(DMF)(phen)] with HBF_4

The title complexes (0.26 g, 0.5 mmol) were suspended in 10 ml of dry toluene and an equimolar amount of $HBF_4 \cdot Et_2O$ was added under nitrogen. After 24 h stirring at room temperature, the solid residue was filtered off, washed with toluene, n-hexane and dried. [Pt{CH(COOMe)CH_2COOMe}(phen)]BF_4 was obtained as a yellow microcrystalline solid (0.24 g, 75% yield).

Anal. Calc. for $C_{18}H_{17}BF_4N_2O_4Pt$: C, 35.60; H, 2.82; N, 4.61. Found: C, 35.62; H, 2.88; N, 4.55%. ^{1}H NMR spectrum (CD_3NO_2): δ 9.58 (d, 1H, J(PtH) = 60 Hz), 9.22 (d, 1H), 8.9 (m, 2H), 8.22 (s, 1H), 8.20 (s, 1H), 8.2 (m, 1H), 8.05 (m, 1H), 4.33 (s, OMe), 3.63 (s, OMe), 3.74 (d, 1H, J(PtH) = 88 Hz, C*H*H), 3.23 (dd, 1H, Pt–CH), 2.88 (d, 1H, CH*H*). IR spectrum (nujol mull): 1690, 1585 cm^{-1} (CO).

When the above product was treated with an aqueous LiCl solution, the neutral complex [Pt-Cl{CH(COOMe)CH_2COOMe}(phen)] was obtained (see Table 2). IR spectrum (nujol mull): 1730, 1705 cm^{-1} (CO).

Reaction between [Pt(MeOOCC≡CCOOMe)(phen)] and HBF_4/LiCl

The title complex (0.13 g, 0.25 mmol) was suspended in 5 ml of dry toluene and an equimolar amount of $HBF_4 \cdot Et_2O$ was added under nitrogen. After 24 h stirring at room temperature, the solid residue was removed by filtration, washed with toluene, n-hexane and dried. The crude product was dissolved in the minimum amount of chloroform/nitromethane (1:1) and the solution treated with the same volume of LiCl-saturated water. The organic phase was separated and dried over Na_2SO_4. The volume of the solution was reduced *in vacuo* and the product [PtCl-{C(COOMe)CHCOOMe}(phen)] was crystallized in 70% yield by careful addition of ether.

Anal. Calc. for $C_{18}H_{17}ClN_2O_4Pt$: C, 38.89; H, 3.08; N, 5.04. Found: C, 38.80; H, 3.02; N, 4.97%. ^1H NMR spectrum ($CDCl_3$): δ 9.75 (d, 1H), 9.70 (d, 1H), 8.65 (m, 2H), 8.0 (s, 2H), 7.95 (m, 1H), 7.8 (m, 1H), 6.04 (s, 1H, J(PtH) = 68 Hz), 3.80 (s, OMe), 3.72 (s, OMe).

Results

Synthesis of three-coordinate Pt(0) complexes

The synthesis and the properties of some three-coordinate platinum(0) complexes of general formula [Pt(ol)(N-N)] have been already described in previous work [7]. Here we report the extension of the synthesis to other N-N ligands and olefins, and present a better spectroscopic characterization of both known and new species.

Three-coordinate [Pt(ol)(N-N)] complexes (N-N = 2,9-Me_2-1,10-phenanthroline (dmphen, **1**), 2-Me-1,10-phenanthroline (mphen, **2**), 1,10-phenanthroline (phen, **3**), 6-Me-py-2-CH=N-Ph (mpan, **4**) (see Scheme 2); ol = (*E*)- and (*Z*)-MeOOCCH=CHCOOMe (DMF and DMM), (*E*)- and (Z)-ClCH=CHCl (DCE), CH_2=CHCOOMe (MAc), CH_2=CHCN (AcN) and C_2H_4) were prepared by using two experimental procedures: method (i) dissolution of finely powdered [Pt(cod)$_2$] (cod = 1,5-cyclooctadiene) into a solution of the olefin in diethyl ether, followed by the N-N ligand addition, or method (ii) olefin exchange on [Pt(C_2H_4)(N-N)] complexes in toluene suspension.

(i) $Pt(cod)_2 + ol + N\text{-}N = Pt(ol)(N\text{-}N) + 2cod$
(ol = C_2H_4, DMM, DMF)

(ii) $Pt(C_2H_4)(N\text{-}N) + ol = Pt(ol)(N\text{-}N) + C_2H_4$

Method (i) gave satisfactory results in the synthesis of DMF or DMM derivatives, while method (ii) was used in all the other cases. Although it is reported [10] that a (*Z*) to (*E*) isomerization of the olefin can be observed upon coordination to Pt(0) derivatives, no indication of such a process was detected in the syntheses of **A** complexes.

All the compounds were obtained as red to yellow microcrystalline solids and were identified by the usual procedures (the complete list is reported in Table 1, together with NMR characterization data). With the exception of the ethylene derivatives, the three-coordinate complexes show a fairly good stability in the solid state as well as in a solution of chlorinated solvents. Attempts to isolate the ethylene complex of the N-N ligand **3** in the solid state were unsuccessful. However, its formation was clearly inferred by the results obtained on treating the red reaction mixture, obtained using method (i), with protic acids (*vide infra*).

The ^1H NMR data show the expected high field shift of the olefin protons resonance, which is consistent with a higher π-backdonation when comparison is made with the corresponding Pt(II) derivatives in a five-coordinate environment [9]. It should also be noted that in the cases where N-N has chemically non-equivalent nitrogen atoms (**2** and **4**), hindered rotation of the unsaturated ligand around the Pt–alkene bond is indicated by the non-equivalence of the olefin protons of a symmetrically disubstituted olefin ligand or by the presence of two stereoisomers for monosubstituted alkenes (Table 1).

Reactions with protic acids

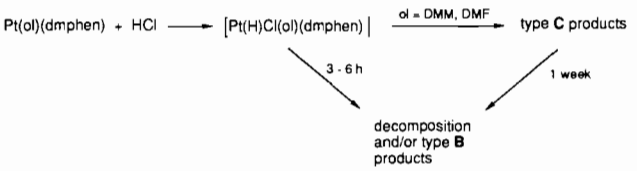
The above-described three-coordinate substrates were allowed to react with HX (X = Cl, BF_4) in chlorinated solvents or in toluene suspension at room temperature. Fluoroboric acid was used as etherate. In the case of the hydrogen chloride, the acid was admitted as anhydrous gas into the reaction vessel or was formed *in situ* by adding the stoichiometric amount of $SiMe_3Cl$ to the reaction mixture*. Since these two procedures gave identical results, the latter was largely preferred because of an easier evaluation of the reagent amount. The reactions were monitored by ^1H NMR spectroscopy and the obtained products were identified by the usual procedures.

Dmphen and mpan derivatives

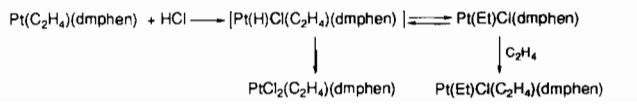
A downfield shift of the resonances of the olefin protons and the appearance of a new signal at δ −24

*The water content in the AnalaR grade solvents is quite sufficient to allow the formation of the HCl required amount ($2SiMe_3Cl + H_2O = (SiMe_3)_2O + 2HCl$) at the used substrate concentration level.

to −27 (J(PtH) = 1050–1300 Hz) were at once observed in the ^{1}H NMR spectra when HCl was added to the three-coordinate complexes of dmphen. Therefore, it was inferred that a hydrido/olefin complex was formed as the first product for all the used unsaturated ligands. When the olefin was DMM or DMF, the decomposition of the first product occurred very slowly. Thus, the five-coordinate adducts (type **C**) could be isolated in the solid state, as previously reported [3]. Alternatively, after one week standing in a solution of the adducts, the known [$PtCl_2$(dmphen)], [$PtCl_2$(ol)(dmphen)] and [Pt(ol)(dmphen)] were detected as the main decomposition products (see 'Experimental').



In all the other cases the decomposition of the type **C** hydrido derivative started immediately, going to completion after a few hours. The initial formation of a type **C** complex was simply argued by comparing the general features of the ^{1}H NMR spectral patterns of the reaction mixtures with those of the pure DMM and DMF hydrido complexes [3]. The nature of the final decomposition products was strongly dependent on the properties of the alkene bound to platinum. In the case of the *Z*- and *E*-DCE–Pt(0) precursors the mixture of the decomposition products was analogous to that reported above for the DMM and DMF derivatives. With the MAc–Pt(0) substrate, extensive decomposition to platinum metal was observed: free olefin and dmphen, together with [$PtCl_2$(dmphen)] and [$PtCl_2$(MAc)(dmphen)] complexes were the only species clearly identified in solution. In the case of the AcN derivative the initial formation of the Pt–H bond is followed by a hydrogen addition on the coordinated olefin and the square-planar [PtCl(MeCHCN)-(dmphen)] complex (type **B**) was identified in solution. A similar behavior was observed when the olefin was ethylene. The isolation of the square-planar [PtCl(Et)(dmphen)] complex in the solid state proved to be difficult owing to a subsequent β-elimination process and ultimate formation of the five-coordinate compound [$PtCl_2(C_2H_4)$(dmphen)]. However, the Pt–C_2H_5 fragment could be successfully trapped by admitting free ethylene into the reaction vessel to give the stable five-coordinate adduct [PtCl(Et)(C_2H_4)-(dmphen)].



A side reaction involving a solvent oxidative-addition can occur when the highly reactive [Pt(C_2H_4)(dmphen)] is treated with HCl in chlorinated solvents, thus accounting for the reported formation of the [PtCl(CH_nCl_{3-n})(C_2H_4)(dmphen)] (n = 1, 2) as significant by-product [7, 11].

$$Pt(C_2H_4)(dmphen) + CH_nCl_{4-n} = PtCl(CH_nCl_{3-n})(C_2H_4)(dmphen)$$

We wish to point out that when HCl was allowed to react with [Pt(DMM)(mpan)], which contains a N-N ligand with fairly good five-coordination stabilizing properties [9], a well defined type **C** five-coordinate hydrido adduct was detected in solution. This species slowly disappeared affording the final type **B** complex [PtCl{CH(COOMe)CH_2COOMe}(mpan)].

Other N-N ligands derivatives

Both 1,10-phenanthroline and its 2-Me derivative differ from the 2,9-Me_2 homologue in that they present a markedly diminished or no five-coordination stabilizing effect, respectively [9]. When the corresponding [Pt(ol)(N-N)] complexes were allowed to react with HCl, no significant amount of the five-coordinate Pt–hydrido species could be generally detected in solution by ^{1}H NMR spectroscopy. Type **B** square-planar complexes [PtCl(CHR-CH_2R′)(N-N)] (see Table 2), deriving from a fast hydrogen addition on the double bond, were usually formed:

$$Pt(CHR{=}CHR')(N\text{-}N) + HCl = PtCl(CHR{-}CH_2R')(N\text{-}N)$$

In the case of the asymmetric mphen, only one of the two possible geometrical isomers, i.e. that with the Pt–C σ bond *trans* to the nitrogen in the 2-Me-substituted ring, was obtained. The only exceptions to the above reported reaction pathway were represented by the DCE and DMF derivatives. In these cases a noticeable olefin release was observed and the corresponding [$PtCl_2$(N-N)] compounds were identified as the main reaction products. However, it should be noted that monitoring of the reaction between [Pt(DMF)(phen)] and HCl by ^{1}H NMR spectroscopy showed the formation of a labile species containing a Pt–H σ bond in the early stages of the process.

In the case of monosubstituted olefins, i.e. MAc or AcN, the hydrogen migration is regioselective, involving the less substituted carbon atom of the coordinated olefin. In this respect, it is worth mentioning that the insertion of AcN into metal–hydride bonds is well known and the alternative formation of 1-cyanoethyl or 2-cyanoethyl derivatives has already been related to the polarity of the metal–hydride bond [12].

Reactions with HBF_4

A few experiments, sufficient to allow some comparison with the behaviour of HCl, were performed with a protic acid yielding a non-coordinating anion, i.e. HBF_4. The reactions with [Pt(DMM)(dmphen)] and [Pt(DMF)(dmphen)] were performed in toluene suspension in order to rule out the possibility of halide abstraction from the chlorinated solvent. Thus, no monitoring of the reaction course by ^1H NMR spectroscopy was possible and the product was purified and identified by standard procedures. The same ionic complex $[Pt\{CH(COOMe)CH_2COOMe\}(dmphen)]BF_4$, which is the product of hydrogen addition on the double bond (type $\mathbf{B}^+$), was isolated in both cases. The organic moiety acts as a bidentate ligand through coordination of a carbonyl group to the metal. This arrangement is indicated by the presence of two very different stretching modes of the carbonyl groups in the IR spectra [13] (1690 and 1580 cm^{-1}) together with a marked downfield shift (δ *c.* 4.2) of one methoxy group in the ^1H NMR spectra. Actually, a four- or a five-membered platinate ring could form, according to the coordination mode of the C=O group to the metal, i.e. in α- or in β-position with respect to the Pt–CH σ bond. Inspection of the ^1H NMR spectra of both the cationic compound and the corresponding neutral chloro derivative obtained by LiCl treatment shows the absence of the geminal coupling between the CH_2 protons in the former species, thus indicating the formation of a five-membered ring.

Fast hydrogen addition on the double bond was also obtained when HBF_4 was allowed to react with the DMM and DMF substrates of the less hindered phen. The ionic square-planar product $[Pt\{CH(COOMe)CH_2COOMe\}(phen)]BF_4$ was isolated in both cases and its NMR features were very similar to those reported above for the dmphen analogue.

It is expected that in the case when the olefin bound in the three-coordinate substrate lacks suitable donor groups, the type $\mathbf{B}^+$ product formed upon addition of HBF_4 could not be stabilized by chelation of the organic ligand. The coordination vacancy could possibly be occupied by a solvent molecule or another donor. In fact, when HBF_4 was added to [Pt(AcN)(dmphen)] in presence of acetonitrile with subsequent treatment with LiCl, a complex mixture of products, including the insertion derivative [PtCl(CHMeCN)(dmphen)], was obtained.

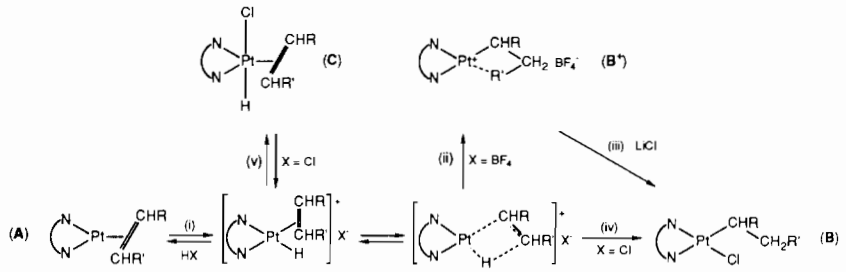
Discussion

A comprehensive scheme of the reaction between the [Pt(ol)(N-N)] substrates and a protic acid HX is depicted in Scheme 3. All the complexes, except those reported in brackets, have been isolated and identified. The particular fate of each three-coordinate substrate after addition of HX is dependent on several factors. These are the steric properties of the N-N and of the olefin ligands, the coordinating ability of the X group, the solvent medium and the reaction time. However, a common feature is represented by the HX addition rate to the Pt(0)–olefin substrates, which is fast in every case.

Several competing mechanisms (three-center *cis* addition, S_N2, ionic and radical paths) have been proposed [14] for the oxidative addition of class **B** electrophiles to transition metal compounds. In our case, whatever activated complex is formed on the approach between the two reagents, a first reaction step (i) involving the protonation at the metal center and the formation of a cationic four-coordinate hydrido–olefin Pt(II) intermediate can account for all the reported results. Actually, we have no direct evidence of the presence of such an intermediate in our reaction system. However, it is worth mentioning that similar species [15] have been recently obtained and fully characterized in the reaction between $[Pt(C_2H_4)(P\text{-}P)]$ (P-P = chelating diphosphine) and HBF_4.

The evolution of the proposed hydrido–olefin cationic intermediate would depend on the coordinating ability of the X^- counterion. In case of a non-coordinating anion such as BF_4^- the attainment of a five-coordinated type **C** product is obviously disfavored. Thus, cationic type $\mathbf{B}^+$ products are formed by hydrogen migratory insertion (ii) onto the coordinated double bond. Such species can be easily isolated in the solid state and fully characterized when the olefin is DMM or DMF. In these cases, the Pt(II) σ-bound organic moiety acts as a chelating ligand through C=O coordination to the metal, thus stabilizing the whole complex. Alternatively, a subsequent treatment of the reaction mixture with LiCl (iii) can allow the isolation of the corresponding neutral type **B** complexes.

The possibility that type **B** compounds could not ensue from a migratory hydrogen insertion, being instead involved in an intermolecular hydrogen attack, is not consistent with the results obtained by adding HBF_4 to [Pt(MeOOCC≡CCOOMe)(phen)]. After LiCl treatment of the reaction mixture, the σ-vinyl derivative $[PtCl\{C(COOMe)=CHCOOMe\}(phen)]$ was isolated. The ^1H NMR of the product shows a singlet at $\delta = 6.04$ ($^3J(PtH) = 68$ Hz), which can be attributed to the olefin proton. By comparing these spectral data with those reported [16] for Pt(II)–alkenyl derivatives a *cis* ar-



Scheme 3.

rangement of the Pt moiety and of the =CH hydrogen is inferred. This stereochemistry agrees with an intramolecular hydrogen addition.

In the case of X=Cl two different reaction paths are possible and are related to the five-coordination stabilizing properties of the N-N ligand in the substrate. The insertion path (iv) can be overwhelmed by a faster halogen uptake (v) and a type **C** five-coordinate olefin–hydrido–Pt(II) species (N-N = **1**) is clearly identified as the main product at the early reaction stages. These five-coordinate adducts look to be unstable on standing in chlorinated solvents, their meanlife seeming dependent on the sterical demand of the substituents on the double bond. In fact, only in the case of the derivatives of the disubstituted ethenes DMM and DMF could the corresponding five-coordinate hydrido complexes be isolated in the solid state [3]. The decomposition pattern can be easily rationalized if the Pt–Cl bond in these five-coordinate adducts undergoes a dissociative equilibrium, thus restoring the above-cited cationic intermediate (see Scheme 3). It must be considered that the hydrogen migratory insertion rate decreases on increasing the substitution degree and/or the bulkiness of the substituents on a double bond [17]. Concerning the 'in plane' hindrance of N-N, it is well ascertained [9] that the presence of dmphen substantially disfavors the attainment of square-planar geometries.

Thus, type **B** products are ultimately formed only in the case of ethylene and AcN derivative, while even moderately fast paths involving the formation of five-coordinate $[PtCl_2(ol)(dmphen)]$, four-coordinate $[PtCl_2(dmphen)]$ and three-coordinate [Pt(ol)-(dmphen)] species prevail in the other cases. Excess of HCl in the reaction medium or chlorine abstraction from the chlorinated solvent can account for the formation of the two former products. For example, we recall that treatment of the DMM hydrido complex with a strong excess of HCl resulted in the formation of dimethylsuccinate and of a highly insoluble platinum product, formulated as $[PtCl_4(dmphen)]$ [3].

When other N-N ligands (**2**, **3** or **4**) are present in the coordination sphere, square-planar geometries are more accessible or no longer disfavored. Thus, type **B** products are obtained also in the case of the more sterically hindered DMM. However, the *E*-DCE and *Z*-DCE derivatives containing **2** yield $[PtCl_2(mphen)]$ instead of the insertion product.

We note that the possibility that the hydrogen insertion or the other decomposition ways could take place on the five-coordinate tbp hydrido adduct **C** itself cannot be in principle ruled out. However, theoretical calculations [18] on d^8 ions have shown that this geometry is less suitable to a migratory insertion than the square-planar one.

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