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Five-coordinate hydrido-complexes [PtX(H)(*N*,*N*-chelate)(olefin)] (X = Cl, Br or I). Crystal structure of [PtCl(H)(2,9-Me_2-1,10-phenanthroline)(dimethyl maleate)]

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Abstract

The title compounds were obtained by oxidative addition of hydrogen halides to suitable [Pt(*N*,*N*-chelate)(olefin)] species. The properties of the ligands and of the electrophile which allow the isolation of stable products must meet very strict requirements. The crystal structure of [PtCl(H)(2,9-Me_2-1,10-phenanthroline)(dimethyl maleate)] was determined by single-crystal X-ray diffraction. Substitution, insertion, and elimination reactions were performed on one hydride complex.

Key words: Platinum; Hydride; Alkene; Oxidative addition

1. Introduction

The role of the hydrido-derivatives of the metals of Group 10 as intermediates in hydrogenation, hydrosilation, and hydrocyanation processes is well established [1]. Furthermore, several stable hydrido-complexes [2] of this group, and mainly of platinum, have been isolated and/or characterized.

However, according to the general trend, most derivatives of d^8 ions in the group are coordinatively unsaturated $16e^-$ species, and few $18e^-$ five-coordinate compounds [3] are known. Some results on catalytic processes suggest the involvement of five-coordinate intermediates [4] with a metal–hydrogen bond, thus prompting further investigations of coordinatively saturated hydrides.

Previous studies have been devoted to the identification of stable trigonal bipyramidal Pt^{II} and Pd^{II} complexes with halo or hydrocarbyl groups as anionic axial ligands X in neutral species of the type [Pt(halide)X(*N*,*N*-chelate)(olefin)] (**I**) [5,6]. Following a similar synthetic approach, we have found that stable type I (X = H) hydrido-complexes can be obtained through the oxidative addition of protic acids to three-coordinate compounds [Pt(*N*,*N*-chelate)(olefin)] (**II**) [7].

We report here the synthesis, coordination environment requirements and the characterization of the five-coordinate hydrides. The X-ray structure determination of [PtCl(H)(dmphen)(dimethyl maleate)] (dmphen = 2,9-Me_2-1,10-phenanthroline) is also described. Some aspects of the reactivity of this hydride derivative have also been investigated.

2. Results and discussion

2.1. Synthetic procedure and ligand requirements

Within the synthetic procedures yielding type **I** complexes [8] only the one involving oxidative addition to a trigonal precursor appears to be suitable for the attainment of hydrido derivatives. In fact, other potential precursors of these species, such as [PtX(H)(*N*,*N*-

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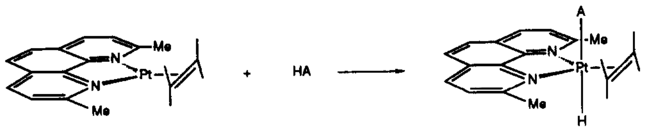


Scheme 1.

chelate)], are not yet available. The preparation of the new complexes is illustrated by Scheme 1.

An equivalent amount of Me_3SiX was used as a source of HX, generated by hydrolysis in the presence of water-containing commercial Analar grade solvents. This avoids the tedious preparation of freshly titrated solutions of HX in the organic solvents.

Accepting that several type **II** complexes yield type **I** hydrides as transient products upon addition of HX [9], our results show that only a careful choice of the chelate, of the unsaturated ligand and of the electrophile HX allows the isolation of the five-coordinate species.

Very strict requirements for the chelate ligand seem to be necessary. Indeed, only 2,9-dimethyl-1,10-phenanthroline (dmphen), which is known to give the highest stabilization for a variety of other type **I** species [10], yields stable hydrides. Even the derivatives of 6,6′-dimethyl-2,2′-bipyridine (with the same "in plane" hindrance, but more "flexible") are unstable.

Second, there is a restricted choice of the unsaturated ligand in the three-coordinate precursor. Among the compounds tested only maleate and fumarate esters afforded isolable compounds.

Finally, even in presence of the appropriate equatorial ligands, the reaction pathway definitely seems to be dictated by the nature of the protic acid. In fact, in preliminary screening experiments, we observed that if the conjugate anion of the strong acid has poor or moderate coordination ability (*e.g.* BF_4^-) a clean insertion reaction of the olefin in the Pt–H bond is observed [7] and an alkyl derivative is produced. For the only weak acid whose parent anion is a good ligand that we tested, HCN, the most abundant reaction product was still the insertion product and no significant amount of type **I** product was observed. These insertion processes are likely to involve unstable hydrides of type I [9]. No reaction of the Pt^0 species was observed when other weak acids such as CH_3COOH were used.

Thus, only when HX was a strong acid, generating an anion with good coordinating ability (Cl^-, Br^- or I^-), was it possible to isolate the hydrides which are the object of this work.

2.2. NMR spectroscopic characterization

Relevant features of the ^1H NMR spectra of complexes I (which are not electrolytes in chloroform) are reported in Table 1. The spectra of maleate derivatives show equivalence of the two halves of the *N-N* ligand and of the olefin. This is not observed in the spectra of dimethyl fumarate complexes, which lack the mirror plane bisecting the olefin double bond. These general features, suggesting five-coordination and *tbp* arrangement of the ligands, have been discussed elsewhere

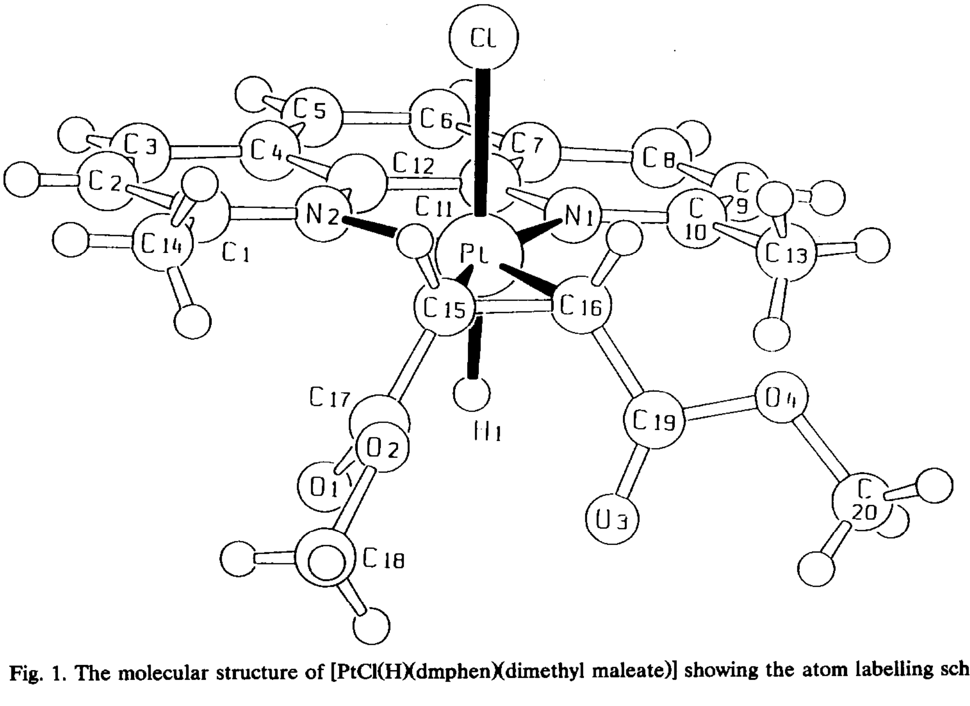


Fig. 1. The molecular structure of [PtCl(H)(dmphen)(dimethyl maleate)] showing the atom labelling scheme.

TABLE 1. Selected ^{1}H NMR [δ (ppm), J (Hz)], IR (cm^{-1}) and analytical data [a] for the five-coordinate complexes [PtX(H)(dmphen)(olefin)]

		Pt–H [b]	Olefin–H [c]	Me–C (Het)	Others	Analysis (found (calcd.) (%))		
						C	H	N
Ia	[PtCl(H)(dmphen)(*Z*-MeOOCCH=CHCOOMe)]	−25.70(1178, 1H) [2290]	4.08(83, 2H)	3.35(6H)	3.71(MeO, 6H)	41.30 (41.14)	3.69 (3.62)	4.73 (4.80)
Ib	[PtCl(H)(dmphen)(*E*-MeOOCCH=CHCOOMe)]	−25.90(1070, 1H) [2260]	4.70(71, d, 1H) 4.43(74, d, 1H)	3.47(3H) 3.37(3H)	3.76(MeO, 3H) 3.67(MeO, 3H)	41.23 (41.14)	3.59 (3.62)	4.75 (4.80)
Ic	[PtCl(H)(dmphen)(*Z*-t-BuOOCCH=CHCOOt-Bu)]	−25.93(1191, 1H) [2330]	3.95(81, 2H)	3.38(6H)	1.47(*t*-BuO, 18H)	46.70 (46.74)	5.10 (4.98)	4.06 (4.19)
Id	[PtBr(H)(dmphen)(*Z*-MeOOCCH=CHCOOMe)]	−24.70(1205, 1H) [2250]	4.20(84, 2H)	3.39(6H)	3.72(MeO, 6H)	38.11 (38.23)	3.29 (3.37)	4.38 (4.46)
Ie	[PtBr(H)(dmphen)(*E*-MeOOCCH=CHCOOMe)]	−24.94(1106, 1H) [2250]	4.69(80, d, 1H) 4.51(86, d, 1H)	3.47(3H) 3.38(3H)	3.77(MeO, 3H) 3.68(MeO, 3H)	38.31 (38.23)	3.25 (3.37)	4.55 (4.46)
If	[PtI(H)(dmphen)(*Z*-MeOOCCH=CHCOOMe)]	−22.94(1215, 1H) [2240]	4.34(84, 2H)	3.37(6H)	3.70(MeO, 6H)	35.85 (35.57)	3.26 (3.13)	4.30 (4.15)

[a] The NMR spectra were recorded at 270 or 200 MHz. CDCl$_3$ was used as solvent and CHCl$_3$ (δ = 7.26 ppm) as internal standard. Abbreviations: d, doublet; no attribute, singlet. IR frequencies (nujol mull) are reported in brackets.

[b] ^1J(Pt–H) in parentheses.

[c] ^2J(Pt–H) in parentheses.

[10]. We note here that, in principle, two stereoisomers can be obtained with dimethyl maleate derivatives, because of the hindered rotation of the unsaturated ligand. Actually, only one rotamer is observed in solution. In the ^{1}H NMR spectra of the related five-coordinate complexes [PtX(hydrocarbyl)(*N*,*N*-chelate)(olefin)] a higher ^2J(PtH) coupling constant was observed [11] for RCH = protons when opposite the axial halogen. If this correlation is retained in the hydrido-derivatives, by comparing the ^{1}H NMR data (see Table 1) of dimethyl maleate and dimethyl fumarate compounds we infer that the isomer formed is the one in which the carbomethoxy groups are opposite the axial hydrogen. This conclusion is supported by the X-ray determination of the configuration of maleate in Ia.

TABLE 2. Selected bond lengths (Å) and angles (deg) for [PtCl(H)(dmphen)(dimethylmaleate)]

Pt–C(15)	2.037(7)
Pt–C(16)	2.064(6)
Pt–N(2)	2.175(5)
Pt–N(1)	2.205(6)
Pt–Cl	2.464(3)
Pt–H(1)	1.63(7)
C(15)–C(16)	1.450(10)
C(15)–C(17)	1.498(10)
C(16)–C(19)	1.486(10)
C(17)–O(1)	1.189(9)
C(17)–O(2)	1.357(9)
O(2)–C(18)	1.422(11)
C(19)–O(3)	1.197(11)
C(19)–O(4)	1.364(11)
O(4)–C(20)	1.435(12)
C(16)–C(15)–C(17)	120.2(6)
C(15)–C(16)–C(19)	119.9(7)

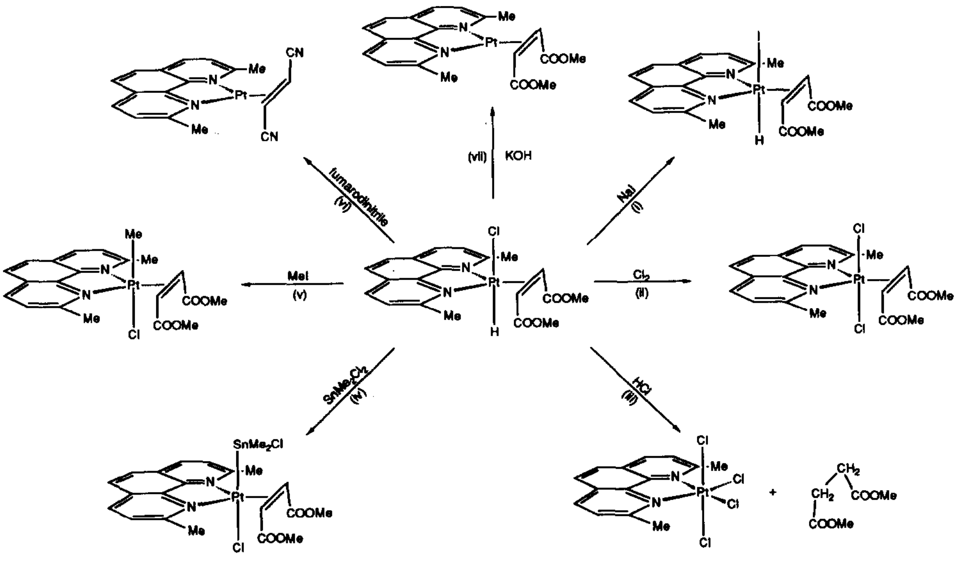
2.3. The molecular structure of [PtCl(H)(dmphen)(dimethyl maleate)]

The molecular structure of the title compound is given in Fig. 1, relevant bond distances and angles are reported in Table 2. The coordination geometry around the Pt atom is trigonal bipyramidal with the hydride and chloride in axial positions. The dimethyl maleate is coordinated through the C = C double bond and the C(O)OMe groups are oriented, with respect to equatorial plane, on the same side as the hydride ligand. The coordination polyhedron has approximate C$_s$ symmetry but the molecule as a whole is asymmetric because the C(O)OMe groups adopt different conformations about the C(olefin)–C(carboxyl) axes in order to avoid close contacts between oxygen atoms. The platinum–ligand interactions are normal, *viz.*

(i) The dmphen is strictly planar and in the equatorial coordination plane, the deviations from the average plane not exceeding 0.04 Å. The Pt–N distances [2.175, 2.205(6), av. 2.19 Å] are in the range of those found in similar compounds, whose average value for Pt–N(sp^2) is 2.23 Å [8]. The slightly shorter value found in this structure may be significant because it indicates stronger donation to the metal in the presence of a good π-acceptor olefin (see iv, below);

(ii) The Pt–H distance [1.63(7) Å] is normal but, due to the high standard deviation, is not worth discussing (see Section 3);

(iii) The Pt–Cl distance [2.464(3) Å] is longer than the average value in these species [av. 2.30 Å] but consistent with what is found when a strong *trans*



Scheme 2.

ligand occupies the opposite coordination site [av. 2.47 Å] [8];

(iv) The Pt–C (maleate) distances [2.064, 2.037(7), av. 2.05 Å] fall at the lower limit of the range of experimental values [av. 2.08 Å] [8]. The coordinated C=C double bond, on the other hand, [1.450(10) Å] is longer than the mean value found in similar compounds [1.43 Å] [8]. These facts can be ascribed to the electron-withdrawing effect of the carboxyl substituents that enhance platinum–olefin back-bonding. Note that the plane of the C(17)–C(15)–C(16)–C(19) skeleton is tilted outward, and that the dihedral angle with the equatorial coordination plane is 112.0(6)°. This is comparable to that observed for maleic anhydride in [PdCl(Me)(dmphen)($C_4H_2O_3$)] [114.7°] [12] and is attributed to some rehybridization of the orbitals of the coordinated carbon atoms.

The conformations of the C(O)OMe groups deserve comment. One of the two is almost coplanar with the C–C–C–C plane [torsion around C(16)–C(19), 12.6(5)°] and the other almost orthogonal [torsion around C(15)–C(17), 96.4(5)°]. This is a minimum energy conformation because no angular strain is present [average C–C–C angle at C(15) and C(16), 120°]. The same conformation has been found in the maleate dianion [13] and in the adduct of maleic acid with the macrocyclic polyether 18-crown-6 [14]. Crystals of maleic acid contain planar molecules stabilized by an intramolecular hydrogen bond [15].

2.4. *Reactions of the hydrides*

The hydrides are fairly stable at room temperature in solutions of reagent grade chloroform and methylene chloride, in the presence of air. Significant decomposition could be detected only after several h in chloroform solution at room temperature. The principal reactions are the formation of dihalo complexes lacking coordinated hydride and the reductive elimination of HCl.

The chemical behaviour of **Ia** is displayed in Scheme 2. In some cases the reactivity of Ia is similar to that of other complexes of the general type **I**. Otherwise, the reaction course is in some way related to the presence of the Pt–H bond.

As previously found for hydrocarbyl species [8] the exchange of the apical halide with another anionic ligand, does not involve a change of configuration of the olefin. Accordingly, the addition of two molar equivalents of NaI in acetone solution to solid Ia affords 60% of the iodo complex **If** in 3 h.

Addition of the equimolar amount of Cl_2 to **Ia** in chloroform solution yields the five-coordinate complex [$PtCl_2$(dmphen)(dimethyl maleate)]. This product is also obtained through oxidative addition of Cl_2 to the platinum(0) complex [Pt(dmphen)(dimethyl maleate)]. Treatment of a hydrocarbyl type **I** complex with Cl_2 affords a complex mixture of compounds which were not identified.

If HCl is bubbled through a $CDCl_3$ solution of Ia for 20 min, the solution contains only dimethylsuccinate 48 h later, and all the platinum is recovered as a highly insoluble yellow precipitate, possibly a platinum(IV) complex. Proton NMR spectra obtained during the experiment showed the presence in solution of **Ia** only and of the succinate. No reaction is observed when type **I** hydrocarbyl derivatives react with an excess of HCl. An attractive hypothesis concerning the insertion of double hydrogen proposes undetectable amounts of an insertion product of the type recalled above [7], [Pt(*N-N*)Cl(CHCOOMeCH$_2$COOMe)], in equilibrium with Ia. The irreversible protolysis of the alkyl derivative by HCl would easily account for the succinate.

The reaction of **Ia** in chloroform solution with one equivalent of $SnMe_2Cl_2$ affords the five-coordinate complex [PtCl($SnMe_2Cl$)(dmphen)(dimethyl maleate)], previously prepared by an oxidative addition reaction [16]. The same single isomer is obtained by both procedures.

The products of the reaction of **Ia** with MeI, as monitored by ^1H NMR spectroscopy, are a mixture of four five-coordinate platinum(II) complexes with methyl in axial position. There are two isomers each of [PtCl(Me)(dmphen)(dimethyl maleate)] and [PtI(Me)(dmphen)(dimethyl maleate)], owing to hindered rotation of the olefin around the platinum–double bond axis. A similar result was obtained when the olefin was dimethyl fumarate (**Ib**), but, of course, the two products, [PtCl(Me)(dmphen)(dimethyl fumarate)] and [PtI(Me)(dmphen)(dimethyl fumarate)], did not have isomers. For both the olefins the first product seems to be the chloro-derivative, which converts to the corresponding iodo-species.

For sake of completeness two previous results [7] are also included in Scheme 2. One concerns the reaction of fumarodinitrile and **Ia** in equimolar amounts, to give [Pt(dmphen) (fumarodinitrile)] and HCl. The driving force for this reaction appears to be the poor solubility of the three-coordinate product. Treatment of **Ia** with KOH in absolute ethanol regenerates the three-coordinate precursor by removal of HCl.

3. Experimental details

^1H NMR spectra were recorded at 270 or 200 MHz on a Bruker AC-270 and Varian XL-200 spectrometers, respectively. IR spectra were recorded in Nujol mulls between KBr plates on a Perkin-Elmer 457 spectrophotometer. The syntheses of [Pt(dmphen)(dimethyl maleate)] [16], [Pt(dmphen)(dimethyl fumarate)] [5] and [Pt(dmphen)(di-*t*-butyl maleate)] [17] were described previously. Solvents and reagents were of Analar grade and were used without further purification.

3.1. Structure determination of [PtCl(H)(dmphen)(dimethyl maleate)]

Crystals suitable for X-ray diffraction were precipitated by slow diffusion of toluene in a dichloromethane solution of the complex. Crystal data and experimental details are reported in Table 3. The diffraction experiments were carried out on an Enraf-Nonius CAD-4 diffractometer. The diffraction intensities were corrected for Lorentz polarization and decay effects; an absorption correction was also applied on the basis of azimuthal scan data [18]. The calculations were performed with the SHELX92 package of programs [19]. The structure was solved by the Patterson method which gave the position of the Pt atom, and Fourier syntheses that allowed the detection of all the non-hydrogen atoms. The structure model behaved well during least-squares calculations, using the anisotropic model of thermal motion. Subsequent difference-Fourier syntheses revealed most of the hydrogen atoms and some residual density (not exceeding 3 eÅ^{-3}) around the inversion centre at 0.5, 0.5, 0.0. The void space [20] in this region was about 180 Å^3 and presumably arises from solvent but no reasonable molecular model could be fitted to the experimental peaks. Therefore this detail of the crystal structure was disregarded. The hydrogen atoms of the methyl groups were placed in idealized positions (C–H 0.96 Å) on the basis of the approximate ones detected in the difference Fourier map. All the hydrogen atoms were introduced in the structure model but not refined. The hydride was not detected in the early stages of refinement but, when the refinement of the structure model was almost complete, a small peak appeared in the expected region. The final cycle of least-squares refinement was performed by restraining the distance between H(1) and Pt, the ethylene carbons (average), and the nitrogens (average) to three target values with $\sigma = 0.02$, in order to estimate the standard deviations for the atomic coordinates of H(1). The list of the positional parameters, obtained from the final least-squares calculations are given in Table 4. Full lists of atomic coordinates,

TABLE 3. Crystal geometry, data collection, and structure refinement details for [PtCl(H)(dmphen)(dimethylmaleate)]

Empirical formula	$C_{20}H_{21}ClN_2O_4Pt$
Formula weight	583.93
Temperature	298(2) K
Wavelength	0.71069 Å
Crystal system	triclinic
Space group	$P\bar{1}$ (No. 2)
Unit cell dimensions	a = 9.300(10) Å alpha = 98.11(5) deg.
	b = 9.355(10) Å beta = 100.08(5) deg.
	c = 14.128(10) Å gamma = 102.55(5) deg.
Volume	1161(2) Å^3
Z	2
Density (calculated)	1.67 g cm^{-3}
Absorption coefficient (Mo Kα)	24.98 cm^{-1}
F(000)	564
Crystal size	0.32 × 0.20 × 0.20 mm
Theta range for data collection	2.27 to 30.96 deg.
Index ranges	$-13 <= h <= 13$, $-13 <= k <= 13$, $0 <= l <= 16$
Scan mode	ω
Scan width	$1 + 0.35 \tan\theta$
Prescan acceptance $\sigma(I)/I$	0.5
Required $\sigma(I)/I$	0.02
Maximum scan time	60 s
Reflections collected	6863
Independent reflections	6580
Refinement method	Full-matrix least-squares on F
Data/restraints/parameters	6547/9/266
Goodness-of-fit	1.058
Final R indices [I > 2sigma(I)]	R = 0.0447
Extinction coefficient	0.037(2)
Largest diff. peak and hole	2.62 and −1.72 eÅ^{-3}

TABLE 4. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for [PtCl(H)(dmphen)(dimethyl maleate)]. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor

	x	y	z	U_{eq}
Pt	2423(1)	635(1)	3026(1)	39(1)
Cl	856(2)	2424(2)	3222(1)	49(1)
N(1)	2787(6)	477(6)	4588(4)	44(2)
N(2)	4430(5)	2406(5)	3705(4)	40(2)
C(1)	5219(7)	3353(7)	3252(5)	49(3)
C(2)	6472(8)	4476(8)	3778(6)	58(3)
C(3)	6942(8)	4623(8)	4750(6)	58(3)
C(4)	6121(7)	3654(7)	5257(5)	49(3)
C(5)	6506(8)	3755(9)	6280(5)	57(4)
C(6)	5677(9)	2771(9)	6718(5)	57(4)
C(7)	4416(7)	1638(8)	6177(5)	51(3)
C(8)	3556(9)	575(10)	6600(6)	61(4)
C(9)	2380(9)	−473(10)	6020(6)	64(4)
C(10)	1971(7)	−506(8)	5004(6)	53(3)
C(11)	4006(7)	1537(7)	5164(5)	42(3)
C(12)	4877(7)	2555(6)	4688(5)	43(3)
C(13)	658(9)	−1652(10)	4384(7)	68(4)
C(14)	4702(11)	3223(11)	2174(6)	70(5)
C(15)	1640(7)	216(7)	1549(5)	46(3)
C(16)	682(7)	−815(7)	1990(6)	54(3)
C(17)	2568(8)	−342(8)	884(5)	55(4)
O(1)	3856(7)	−373(8)	1081(4)	72(3)
O(2)	1737(7)	−736(7)	−46(4)	66(3)
C(18)	2468(13)	−1300(11)	−766(7)	76(7)
C(19)	648(8)	−2426(8)	1800(7)	64(4)
O(3)	1509(8)	−2976(7)	1428(6)	87(4)
O(4)	−522(8)	−3238(7)	2113(6)	85(4)
C(20)	−707(15)	−4822(11)	1944(13)	114(8)
H(1)	3559(73)	−467(68)	2965(52)	47

thermal parameters, *etc.*, have been deposited with the Cambridge Crystallographic Data Centre.

3.2. Synthesis of the hydrides.

To a solution of a three-coordinate precursor (0.10 mmol) in 3 ml of dichloromethane (chloroform for **Ib** and **Ie**) Me_3SiX was added in excess (1.5 : 1 molar ratio). After 2 min, 3 ml of hexane was added dropwise to the solution and the volume then reduced under vacuum to afford white-yellow micro-crystals of the complex. These were collected by filtration, washed with hexane and dried *in vacuo*. The poorly soluble complex **If** crystallized from the reaction mixture and hexane was added to complete the crystallization (yield 80–90%).

3.3. Reactions of **Ia**

3.3.1. With NaI

To 0.10 mmol (0.058 g) of **Ia** two molar equivalents of NaI dissolved in 2 ml of acetone was added at 273 K. After 3 h stirring the solid was filtered, washed with acetone and dried. A portion of the residue, extracted with $CDCl_3$ and monitored via NMR spectroscopy, revealed the presence of both hydrido complexes Ia and If.

3.3.2. With Cl_2

To 0.10 mmol (0.058 g) of **Ia** in 1.5 ml of chloroform an equimolar amount of Cl_2 was added. After 1 min crystallization of [$PtCl_2$(dmphen)(dimethyl maleate)] began and 1 ml methanol was added dropwise to achieve precipitation of the product. This was filtered, washed with methanol and dried (yield: 60%). Selected ^1H NMR data [in $CDCl_3$; $CHCl_3$ ($\delta = 7.26$ ppm) as internal standard; ^2J(Pt–H) (Hz) in parentheses]: 4.79(76, = CH,2H), 3.80(MeO,6H), 3.55(NCMe,6H) ppm.

3.3.3. With HCl

Gaseous HCl was bubbled for 20 min through a solution of Ia (0.10 mmol, 0.058 g) in 3 ml of $CDCl_3$. After 48 h the supernatant contained only dimethyl succinate in appreciable amount, as determined by ^1H NMR spectroscopy.

3.3.4. With $SnMe_2Cl_2$

The reaction was monitored with ^1H NMR spectroscopy. To 0.10 mmol (0.058 g) of **Ia** in 2.5 ml of $CDCl_3$ an equimolar amount of $SnMe_2Cl_2$ was added. After three days the reaction was complete, as suggested by comparison with the ^1H NMR spectrum of an authentic sample of [PtCl($SnMe_2Cl$)(dmphen)(dimethyl maleate)] [16].

3.3.5. With MeI

To 0.036 mmol (0.021 g) of **Ia** in 0.6 ml $CDCl_3$, 0.042 mmol (0.006 g) of MeI was added. After 16 h the reaction mixture was analysed by ^1H NMR spectroscopy. Selected ^1H NMR data [in $CDCl_3$; $CHCl_3$ ($\delta = 7.26$ ppm) as internal standard; ^2J(Pt–H) (Hz) in parentheses]: [PtCl(Me)(dmphen)(dimethyl maleate)] (48% yield): 3.45(75, = CH,2H), 0.30(64,Me,3H) ppm. [PtCl(Me)(dmphen)(dimethyl maleate)] (15% yield, isomer): 4.35(84, = CH,2H), 0.38(70,Me,3H) ppm. [PtI(Me)(dmphen)(dimethyl maleate)] (22% yield): 3.39(75, = CH,2H), 0.47(60,Me,3H) ppm. [PtI(Me)(dmphen)(dimethyl maleate)] (15% yield, isomer): 4.71(85, = CH,2H), 0.57 (70,Me,3H) ppm.

3.3.6. With fumarodinitrile

To 0.10 mmol (0.058 g) of **Ia** in 1.5 ml $CHCl_3$, an equimolar amount of fumarodinitrile (0.008 g) was added. After a few minutes the poorly soluble complex [Pt(dmphen)(fumarodinitrile)] [7] began to crystallize and after 1 h it was collected on a filter, washed with chloroform and dried (yield 65%).

3.3.7. With KOH

To a suspension of **Ia** (0.10 mmol, 0.058 g) in 2 ml absolute ethanol one equivalent of KOH (0.006 g) dissolved in the minimum amount of the same solvent was added. After 15 min stirring the residue was filtered, washed with absolute ethanol and dried *in vacuo*. The resulting solid was then extracted with 3 ml of chloroform and the solvent removed under vacuum to give [Pt(dmphen)(dimethyl maleate)] in 90% yield.

3.4. Addition of Cl_2 to [Pt(dmphen)(dimethyl maleate)]

To 0.10 mmol (0.055 g) of [Pt(dmphen)(dimethyl maleate)] in 1.5 ml $CHCl_3$ an equimolar amount of Cl_2 was added. The solution became almost colourless and the complex [$PtCl_2$(dmphen)(dimethyl maleate)] was crystallized by adding 1 ml of methanol to the reaction mixture. The light-yellow crystals were filtered, washed with methanol and dried *in vacuo* (Yield: 60%).

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