Articles

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Synthesis and Reactivity of Platinum and Palladium Complexes with a Phosphorus Analogue of 2,2′-Bipyridine, NIPHOS. X-ray Crystal Structure of $[PtCl(NIPHOSH{\cdot}OMe)(PMe_3)][SbF_6]$

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The cations $[MCl(NIPHOS)(L)]^+$ (M = Pt (**3**), L = PPh_3, $PMePh_2$, PMe_2Ph, PMe_3, P-*n*-Bu_3; M = Pd (**7d**), L = PMe_3; NIPHOS = 2-(2-pyridyl)-4,5-dimethylphosphinine) were prepared and characterized by NMR spectroscopy (^1H, ^{31}P, ^{195}Pt). It is shown that the chemical shift of the phosphorus atom of the coordinated NIPHOS is only slightly affected by variations of the ligand L. Complexes of the types **3** and **7** add water, alcohols, or thiols regioselectively at the P–C6 double bond forming complexes of the type $[MCl(NIPHOSH{\cdot}Y)(L)]^+$ (M = Pt, Y = OH, L as above and $AsMe_2Ph$; M = Pt, Y = OMe, O-*i*-Pr, O-*i*-Am, OPh, SPh, L = PMe_3; M = Pd, Y = OH, OMe, L = PMe_3) in which the Y moiety is bonded to the phosphorus atom. They were characterized by NMR spectroscopy (^1H, ^{31}P, ^{195}Pt). The X-ray crystal structure of $[PtCl(NIPHOSH{\cdot}OMe)(PMe_3)][SbF_6]$ was determined. The crystals belong to space group $P\bar{1}$ with $Z = 2$, $a = 8.493$ (1) Å, $b = 11.588$ (1) Å, $c = 12.754$ (1) Å, $\alpha = 73.763$ (8)°, $\beta = 80.384$ (6)°, $\gamma = 81.948$ (8)°, and $V = 1182.4$ (2) Å^3. The structure was refined to $R = 0.027$ for the 4254 observed reflections. The platinum atom shows normal square-planar geometry. The platinum–phosphinite bond distance is comparable with that found in platinum(II) phosphite complexes.

Introduction

The synthesis of 2-(2-pyridyl)-4,5-dimethylphosphinine, NIPHOS (**1**), was reported by Mathey and co-workers[2] in 1982. Although one would have expected a lot of interest in the donor properties of this ligand, in view of the importance of 2,2′-bipyridine, bpy, in coordination chemistry[3] or in photochemistry,[4] only one class of compounds containing NIPHOS, i.e., $[M(CO)_4(NIPHOS)]$ (M = Cr, Mo, W), appears to have been prepared.[5]

In contrast, the coordination chemistry of unidentate phosphinines has been more extensively studied over the last 20 years.[6-11] However, most of the compounds prepared contain group 6 metal centers and CO as auxiliary ligands although there is a communication reporting the preparation of phosphinine complexes of the platinum metals,[12] i.e., the compounds $[RuCl_2L_2]$, $[RhClL_3]$, and $[PdCl_2L_2]$, where L is 2,4,6-triphenylphosphinine.

As the above results led one to expect that NIPHOS also could show an interesting coordination chemistry with platinum metal centers, a research program was undertaken to explore the donor properties of this ligand with these centers. We report here the synthesis and characterization of some platinum(II) complexes of the types $[PtCl(NIPHOS)(L)][PtCl_3(L)]$ (L = PPh_3, $PMePh_2$, PMe_2Ph, PMe_3, P-*n*-Bu_3) and $[PtCl(NIPHOSH{\cdot}Y)(L)][X]$ (Y = OH, L = as above and $AsMe_2Ph$, X = $[PtCl_3(L)]^-$; Y = OMe, O-*i*-Pr, O-*i*-Am, OPh, SPh, L = PMe_3, X = $[PtCl_3(L)]^-$, SbF_6^-). The X-ray crystal structure of $[PtCl(NIPHOSH{\cdot}OMe)(PMe_3)][SbF_6]$ is reported. The palladium complexes $[PdCl(NIPHOS)(PMe_3)][PdCl_3(PMe_3)]$ and $[PdCl(NIPHOSH{\cdot}Y)(PMe_3)][X]$ (Y = OH, OMe, X = $[PdCl_3(PMe_3)]^-$, SbF_6^-) have also been prepared.

Table I. ^{31}P NMR and ^{195}Pt NMR Chemical Shifts δ (ppm) and Coupling Constants J (Hz) of Complexes $[PtCl(NIPHOS)(L)][PtCl_3(L)]$ ([**3**][**4**]) and $[PtCl(bpy)(L)][PtCl_3(L)]$([**5**][**4**]), in $CDCl_3$

	L				
	PPh_3	$PMePh_2$	PMe_2Ph	PMe_3	P-*n*-Bu_3
cation	**3a**	**3b**	**3c**	**3d**	**3e**
δ(P′(NIPHOS))	155.1	155.0	154.8	152.0	151.6
$^1J(^{195}Pt, ^{31}P')$	4526	4582	4634	4658	4536
δ(P(L))	5.2	−5.0	−17.5	−20.4	7.6
$^1J(^{195}Pt, ^{31}P)$	3244	3137	3025	2967	2964
$^2J(^{31}P', ^{31}P)$	20.5	20.5	21.4	22.9	22.0
δ(Pt)	−4350	−4336	−4326	−4356	−4371
anion	**4a**	**4b**	**4c**	**4d**	**4e**
δ(P(L))	7.0	−10.0	−23.8	−28.8	−4.9
$^1J(^{195}Pt, ^{31}P)$	3967	3865	3779	3677	3744
δ(Pt)	−3500	−3486	−3478	−3475	−3507
cation	**5a**	**5b**	**5c**	**5d**	**5e**
δ(P(L))	12.0	−3.0	−15.2	−28.0	−2.8
δ(Pt)	−3535	−3510	−3501	−3533	−3467

Results

The Complexes $[PtCl(NIPHOS)(L)][PtCl_3(L)]$ ([3][4]). Attempts to prepare $[PtCl_2(NIPHOS)]$ (NIPHOS = 2-(2-pyridyl)-4,5-dimethylphosphinine) from starting materials such as $[PtCl_2(CH_3CN)_2]$, $[PtCl_2(COD)]$, and *cis*-$[PtCl_2(styrene)_2]$ were not successful. Thus, addition of NIPHOS to these complexes gave several products. ^{31}P NMR examination of the crude reaction mixtures showed that only one or two of the compounds obtained contained platinum as they showed appropriate ^{195}Pt satellites. The other ^{31}P signals were indicative of ligand decomposition reactions which had occurred either during the re-

(1) (a) ETH-Zentrum. (b) Università di Milano. (c) CDPH Ecole Polytechnique.
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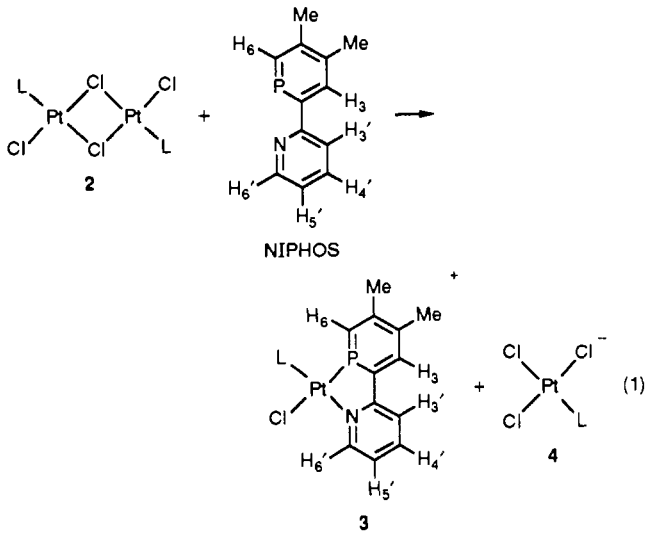
Table II. ^{1}H NMR Chemical Shifts δ (ppm) of the Aromatic Protons of **3d** and **5d** and of NIPHOS and bpy, in $CDCl_3$

	δ(**3d**)	δ(NP)	$\Delta\delta^a$	δ(**5d**)	δ(bpy)	$\Delta\delta$
H6′	9.33	8.68	+0.65	9.31	8.69	+0.62
H6	8.39 (22.8)[b]	8.50 (39.6)[b]	−0.11			
H5′	7.43	7.21	+0.22	7.77	7.31	+0.46
H4′	8.21	7.70	+0.51	8.36	7.82	+0.54
H3′	8.60	7.89	+0.71	8.97	8.40	+0.57
H3	8.37 (19.7)[c]	8.37 (5.0)[c]	0.00			

[a] $\Delta\delta$ = coordination chemical shift = δ(complex) − δ(free ligand). [b] In parentheses ^2J(P, H6) in Hz. [c] In parentheses ^3J(P, H3) in Hz.

action itself or during workup. Only the NIPHOS-containing platinum complexes described below could be prepared.

NIPHOS reacts with compounds of the type $[Pt_2Cl_4L_2]$ (L = PPh_3, $PMePh_2$, PMe_2Ph, PMe_3, P-*n*-Bu_3) (**2a–e**), respectively, according to eq 1, giving salts which contain the cations [PtCl(NIPHOS)(L)]$^+$ (**3a–e**), respectively, with the anions $[PtCl_3(L)]^-$ (**4a–e**), respectively. It did not prove possible to isolate these compounds as analytically pure solids: attempts to precipitate them out of solution by addition of solvents or other counterions resulted in the formation of intractable oils which gradually decomposed. Therefore, structural assignments in the salts [**3**][**4**] were made on the basis of their ^{1}H, ^{31}P, and ^{195}Pt NMR spectra. The ^{31}P and ^{195}Pt data are summarized in Table I.



The ^{31}P NMR spectra of the NIPHOS-containing cations **3a–e** are most informative. They show one set of resonances (P′) at low field with δ = 152–155 ppm, typical of σ-coordinated phosphinines, which differ significantly from the chemical shifts of π-coordinated phosphinines, the latter being in the range 0–20 ppm.[6,13] A second set of resonances in these cations, due to P (L), showed δ values in the range +8 to −20 ppm. The ^2J(P′, P) values are small (20.5–22.9 Hz), indicating the mutually *cis* position of the two P atoms. The ^{31}P NMR chemical shifts of the phosphines L in the cations **3a–e** have values comparable to those observed in the corresponding complexes containing bpy, i.e., [PtCl(bpy)(L)]$^+$ (**5a–e**). These data are listed in Table I.

The ^{195}Pt NMR spectra of the NIPHOS-containing cations **3a–e** appear as doublet of doublets consistent with the structure postulated above. The values of the chemical shifts, ranging from −4235 to −4370 ppm (relative to $[PtCl_6]^{2-}$), are more upfield than the corresponding values for the bpy cations **5a–e**, these being between −3467 and −3535 ppm (see also Table I).

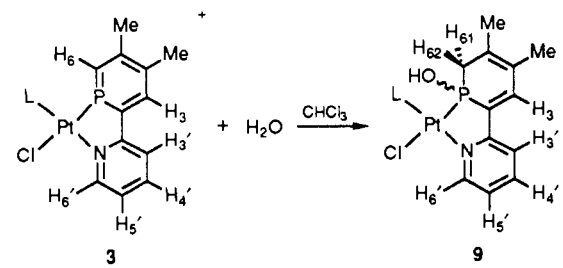
Information about nature of the NIPHOS ligand in the cations **3a–e** is provided by their ^{1}H NMR spectra. These are best discussed for the cation [PtCl(NIPHOS)(PMe_3)]$^+$ (**3d**), as the absence of aryl substituents on the ligand L allows a clear observation of the "aromatic" protons of coordinated NIPHOS. These data are reported in Table II. As can be seen there, the chemical shifts of the "pyridine protons" H3′, H4′, H5′, and H6′ have values comparable to those found for the ring in the *trans* position to PMe_3 in the cation [PtCl(bpy)(PMe_3)]$^+$ (**5d**).

In complex **3d** the coupling of platinum and H6′ could not be observed as the resonances were unusually broad. This is in contrast to what is observed for the cation [PtCl(bpy)(PMe_3)]$^+$ (**5d**), where the platinum satellites could be recognized, although these resonances were not especially sharp either.

In order to test further the complexing properties of NIPHOS, its reaction with $[Pd_2Cl_4(PMe_3)_2]$ (**6d**) was carried out. This gave the salt [PdCl(NIPHOS)(PMe_3)][$PdCl_3(PMe_3)$] ([**7d**][**8d**]). It did not prove possible to isolate this salt as it was even more easily decomposed than the corresponding platinum salt [**3**][**4**], and therefore, it was characterized in solution by ^{31}P and ^{1}H NMR spectroscopy. The ^{31}P NMR spectrum of complex **7d** shows three resonances, one centered at 169 ppm, a second at 14 ppm, and the third at 3 ppm. The first two are assigned to NIPHOS and PMe_3 coordinated to the cationic species, while the latter arises from PMe_3 in the anion. The signals from the P atoms in the cation were broad, indicating dynamic behavior in solution. On lowering of the temperature to −50 °C, the NIPHOS signal split up into a doublet with a ^2J(P′, P) value of 6.4 Hz whereas the second signal remained unchanged under these conditions, the line width being 13.2 Hz.

The ^{1}H NMR resonances of **7d** were very broad at room temperature. On lowering of the temperature to −50 °C, they remained broad and no assignements were possible. A ^{31}P-decoupled spectrum, however, allowed the identification of the signals arising from H3 and H6: their chemical shifts are 8.48 and 8.42 ppm, respectively, the coupling constants J(P, H) being almost equal for both protons, i.e., 21 Hz.

Reaction of [PtCl(NIPHOS)(L)]$^+$ (3) with Water and Alcohols. The NIPHOS-containing cationic complexes [PtCl(NIPHOS)(L)]$^+$ (**3**) reacted with moisture, giving the corresponding cations to which one molecule of water had been added, which proved to have the composition [PtCl(NIPHOSH·OH)(L)]$^+$ (**9**). These were immediately produced when one drop of water was added to $CDCl_3$ solutions of the salts [PtCl(NIPHOS)(L)][$PtCl_3$(L)] ([**3**][**4**]) (eq 2). The reaction was accompanied by a color change from deep red to yellow. The products were characterized in solution by multinuclear NMR spectroscopy, and the data are given in Table III. The anionic complexes remained unaltered.



The ^{31}P NMR spectra of cations **9** showed that the resonance due to the P atom of NIPHOS was replaced by a broad resonance between 53 and 55 ppm with ^1J(Pt, P′) values ranging from 3987 to 4152 Hz. However, the δ values for L in [PtCl(NIPHOSH·OH)(L)]$^+$ (**9**) did not change significantly although there

Table III. ^{31}P NMR and ^{195}Pt NMR Chemical Shifts δ (ppm) and Coupling Constants J (Hz) of Complexes [PtCl(NIPHOSH·OH)(L)]$^+$ (**9**), in $CDCl_3$

	L					
	PPh_3	$PMePh_2$	PMe_2Ph	PMe_3	P-*n*-Bu_3	$AsMe_2Ph$
compd	**9a**	**9b**	**9c**	**9d**	**9e**	**9f**
δ(P′(NIPHOSH·OH))	50.9	53.5	52.8	54.7	54.5	55.0
$^1J(^{195}Pt, ^{31}P')$	3936	3987	4002	4059	4152	3873
δ(P(L))	6.0	−5.9	−18.5	−24.7	2.0	
$^1J(^{195}Pt, ^{31}P)$	3618	3460	3368	3248	3261	
$^2J(^{31}P', ^{31}P)$	20.3	21.4	22.4	23.7	23.3	
δ(Pt)	−4443	−4447	−4446	−4437	−4478	*a*

[a] Not measured.

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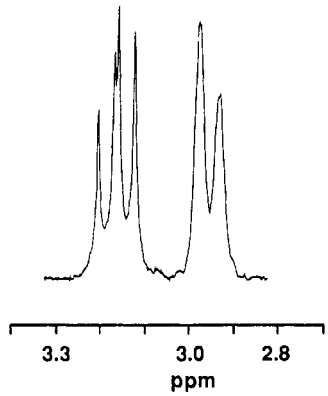


Figure 1. Resonance of the CH_2 group in the ^1H NMR spectrum (250 MHz, $CDCl_3$) of complex $[PtCl(NIPHOSH·OH)(PMe_3)]^+$ (**9d**).

was a marked increase in the ^1J(Pt, P) values.

The ^1H NMR spectra were also informative. Once again the cation **9d** was investigated in more detail because of the absence of "aromatic protons" on the ligand L. While there were no marked differences in the signals due to the pyridine ring, significant changes had occurred to the hydrogen resonances of the phosphinine ring. The multiplet associated with C6 gave a pattern consistent with an ABX spin system centered at ca. 3 ppm; see Figure 1. The presence of two hydrogen atoms on C6 was confirmed by a $^{13}C\{^1H\}$ DEPT NMR spectrum, which gave a δ(C) of 36.9 ppm with ^1J(P′, C) = 57.1 Hz. On the other hand, the resonance of H3 had shifted from 8.37 to 7.18 ppm. The very broad resonance at 5.8 ppm is assigned to the proton of the hydroxyl group bonded to the P atom.

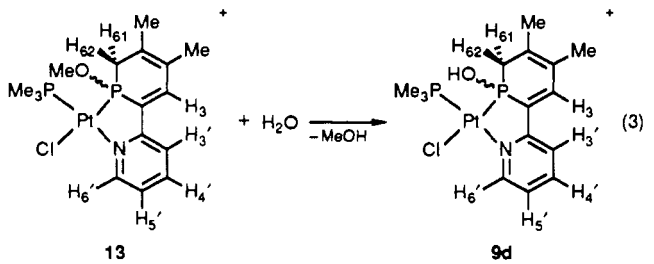
A complex cation of type **9** could also be obtained when the ligand L was a tertiary arsine. During the attempted preparation of $[PtCl(NIPHOS)(AsMe_2Ph)]^+$ by reaction of $[Pt_2Cl_4(AsMe_2Ph)_2]$ with NIPHOS as described for cations **3**, one observed the transient formation of a red color which quickly turned to yellow, indicating the formation of $[PtCl(NIPHOSH·OH)(AsMe_2Ph)]^+$ (**9f**). The ^{31}P NMR spectrum showed a broad resonance at 55 ppm with a ^1J(Pt, P) coupling constant of 3873 Hz.

A palladium complex containing NIPHOSH·OH as a ligand was also characterized: The cation $[PdCl(NIPHOSH·OH)(PMe_3)]^+$ (**10d**) was obtained by addition of water to a solution of [**7d**][**8d**]. The ^{31}P NMR spectrum of **10d** showed two broad resonances, centered at 75.5 and 3.3 ppm, respectively.

The cation $[PtCl(NIPHOS)(PMe_3)]^+$ (**3d**) reacted even with alcohols and thiophenol, giving addition compounds analogous to those with water. Also in these cases the reaction was accompanied by a color change from deep red to yellow. The products were characterized by ^{31}P NMR spectroscopy, and the data are given in Table IV. The ^{31}P NMR spectra of the cations showed two sharp doublets: one between 30 and 80 ppm, assigned to the coordinated phosphinite, and the other at ca. −22 ppm, due to PMe_3, with ^2J(P′, P) values of ca. 23 Hz.

The cation $[PtCl(NIPHOSH·OMe)(PMe_3)]^+$ (**13**) was isolated with $[SbF_6]^-$ as a counterion in 82% yield by adding an excess of Na[SbF_6] to a methanolic solution of **13**. The analogous palladium complex **18** was isolated in 89% yield using the same procedure.

Solutions of "methoxy" complexes [**13**][SbF_6] and [**18**][SbF_6], respectively, reacted with water according to eq 3, giving complexes



13 9d (3)

Table IV. ^{31}P NMR Chemical Shifts δ (ppm) and Coupling Constants J (Hz) for Cations $[PtCl(NIPHOSH·Y)(PMe_3)]^+$, in $CDCl_3$

	YH				
	MeOH	*i*-PrOH	*i*-AmOH	PhOH	PhSH
cation	**13**[a]	**14**	**15**	**16**	**17**
δ(P′(NIPHOSH·Y))	80.0	72.0	75.4	80.4	28.6
$^1J(^{195}Pt, ^{31}P')$	4156	4138	4162	4296	3872
δ(P(PMe_3))	−21.4	−22.5	−22.2	−22.1	−23.2
$^1J(^{195}Pt, ^{31}P)$	3117	3139	3141	3095	3105
$^2J(^{31}P', ^{31}P)$	24.5	22.4	23.6	23.5	20.2

[a] In CD_3CN.

9d and **10d**, respectively. The rate of hydrolysis depends on the concentration of water and on the solvent. In acetone the hydrolysis of **13** with 30 equiv of water was complete after 3 h, while in acetonitrile the completion of the reaction took 10 h under the same conditions. The rate of hydrolysis is accelerated by OH^- as well as by H^+, the former being the more efficient catalyst. The reaction of **13** with 30 equiv of 0.1 M NaOH in acetonitrile was complete after 90 min, whereas the reaction with 30 equiv of 0.1 M CF_3SO_3H took twice as long.

In the ^{31}P NMR spectrum of a solution of $[PtCl(NIPHOSH·OH)(PMe_3)]^+$ (**9d**) in CD_3CN the heterocyclic P resonance appeared as a sharp doublet centered at 60.5 ppm. Upon addition of 1 equiv of diisopropylethylamine to this solution, this doublet shifted to 30 ppm. However, the resonance at −23 ppm, due to coordinated PMe_3, was only slightly affected. The ^1J(Pt, P) values of these two new signals were almost equal at 3620 Hz. These changes are attributed to the formation of the complex $[PtCl(NIPHOSH·O)(PMe_3)]$ (**19d**). When 1 equiv of CF_3SO_3H was added to a solution of **19d**, the resonance of the heterocyclic P atom appeared again at 60.5 ppm, indicating the regeneration of cation **9d**.

Addition of 1 equivalent of CF_3COOH (pK_a = 0.3) to a solution of **19d** in CD_3CN gave a spectrum showing two doublets at 43.6 and −24.6 ppm, respectively. The former resonance lies in the middle between the resonances of **9d** and **19d**, indicating that the ratio of these two complexes is ca. 1:1 and thus the pK_a of **9d** is comparable to that of CF_3COOH, which is 0.3 in aqueous solution.

Discussion

Although the synthesis of NIPHOS (**1**) was first reported in 1982,[2] its coordination chemistry has remained unknown except for the original report of the group VI metal carbonyl derivatives.[5] It is likely that the multistep ligand synthesis may have deterred the study of its coordination chemistry. As mentioned earlier, given the recent significant developments of the coordination chemistry of 2,2′-bipyridine with the platinum metal centers, there is an obvious interest in the corresponding compounds containing NIPHOS.

Platinum(II) was chosen as the first center to be investigated because of the NMR information obtainable due to presence of the ^{195}Pt nucleus. Earlier attempts to obtain complexes using various starting materials led to the production of intractable mixtures, as it was not recognized that *coordinated* NIPHOS is very susceptible to nucleophilic attack by water and alcohols. The NIPHOS-containing products which could be directly characterized, albeit only in solution, were derived from the addition of NIPHOS to the dinuclear complexes $[Pt_2Cl_4L_2]$ (L = tertiary phosphines) (see eq 1). However, their structure could be unambigously established by ^{31}P and ^1H NMR spectroscopy. Thus, the bidentate nature of NIPHOS in $[PtCl(NIPHOSH)(PMe_3)]^+$ was apparent from the values of the $^1J(^{195}Pt, ^{31}P^1)$ coupling constants (P^1 = P(NIPHOS)) (see Table I) and the chemical shifts of the "pyridine protons", which are similar to those in $[PtCl(bpy)(PMe_3)]^+$ (see Table II). As mentioned earlier, the counterions $[PtCl_3(L)]^-$ were easily identified by comparison with independently prepared salts containing them.

It is interesting to compare the values of the "coordination chemical shift", $\Delta\delta$, defined as $\Delta\delta$ = δ(complex) − δ(free ligand), of complexes **3d** and **5d**. These are given in Table II. As can be

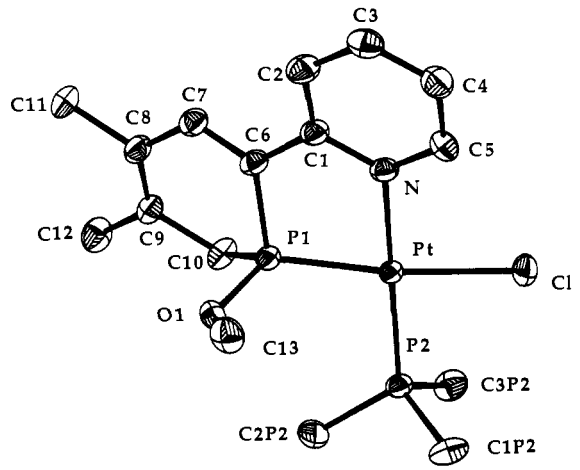


Figure 2. ORTEP view of the cation in $[PtCl(NIPHOSH{\cdot}OH)(PMe_3)][SbF_6]$ ($[13][SbF_6]$).

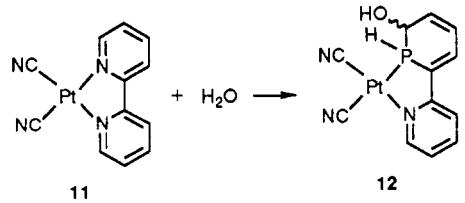
seen there, they are either zero or have small negative values for the aromatic protons of the phosphinine ring and significant to larger values for those of the pyridine ring. This tendency was also observed by Brêque et al.[5] in the complexes $[M(CO)_4(NIPHOS)]$ (M = Cr, Mo, W).

The values of the coupling constants J(P, H) of the phosphinine protons in the **3d** cation, however, have changed relative to the free ligand **1**; the ^2J(P, H6) value decreased from 39.6 to 22.8 Hz, whereas the ^3J(P, H3) value increased from 5.0 to 19.7 Hz. The latter value is in agreement with the formulation of a σ-bonded NIPHOS, as in π-coordinated phosphinines the ^3J(P, H3) values are in the range 4.5–8 Hz.[6,11]

The palladium(II) cation $[PdCl(NIPHOSH)(PMe_3)]^+$ could be obtained as described for its platinum analogue, but it proved to be even more reactive than the latter.

A comparison of the chemical shifts of the corresponding platinum and palladium complexes, **3d** and **7d**, respectively, shows that the resonance for the latter lies at lower field than that of the former. This observation is in agreement with literature data: the resonances of phosphinine complexes of metals of the second transition series occur at lower fields than those of the corresponding complexes of the third series.[5,7]

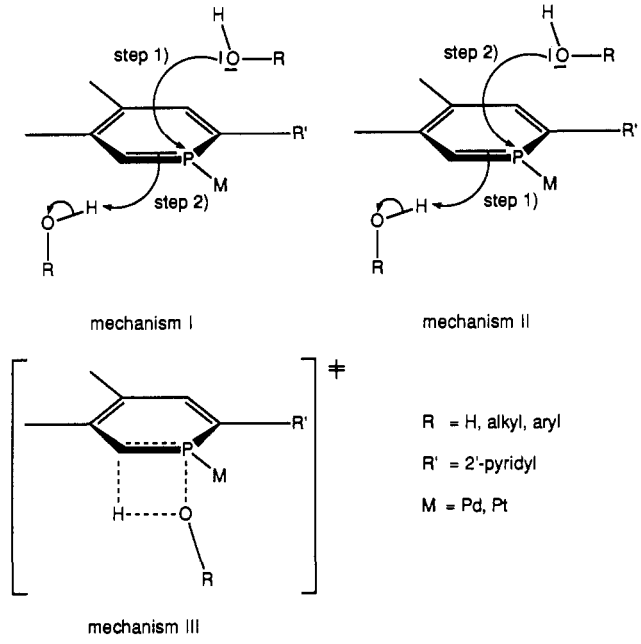
The most unexpected feature of the coordination of NIPHOS to platinum(II) and palladium(II) is the great ease with which this coordinated ligand reacts with nucleophiles. To our knowledge, the addition of water to coordinated NIPHOS had not been previously observed. Furthermore, there do not appear to be any reports in the literature about other phosphinine transition-metal complexes showing similar behavior. However, some complexes of bpy show an apparently similar reactivity toward water. Thus, Gillard et al.[15] found that $[Pt(CN)_2(bpy)]$ (**11**) adds water regioselectively and reversibly (eq 4). In this case, however,



11 12 (4)

the OH group adds on the α–C atom. The different regioselectivity can be explained by comparing the charge distribution in pyridine and phosphinine. Calculations by Oehling et al.[14] show that the phosphorus atom in phosphinine carries a distinct positive charge whereas the nitrogen atom in pyridine is negatively charged. If one assumes that (1) the polarity of the P–C bond in NIPHOS and that of the N–C bond in bpy are not changed relative to those of the corresponding monocyclic systems and that (2) the coordination of NIPHOS and bpy to platinum does not alter the signs of the charges, then a dipolar molecule like water would add as observed to complexes **3** and **11**. Furthermore, the coordination of NIPHOS to palladium or platinum should increase the positive charge on the P atom and, therefore, make the addition of water more favorable compared to the reaction of free NIPHOS with water.

The mechanism of the addition of water (or alcohols) to the coordinated NIPHOS in complexes **3** and **7d**, respectively, could occur either by nucleophilic attack of OH^- (RO^-) or H_2O (ROH) to the phosphinine (P′) followed by protonation of C6 (mechanism I) or by protonation of C6 and subsequent attack by OH^- (RO^-)



at P′ (mechanism II). It is also conceivable that the reaction proceeds via a concerted mechanism (mechanism III). If one assumes that H_2O or ROH react with the same pathway, then mechanism I is the most likely.

After the addition of OH^- or RO^- groups to the NIPHOS P atom in complexes **3** or **7d** this atom becomes chiral, i.e., racemic mixtures of complexes **9**, **13**–**17**, and **10d** are formed. The ^{31}P NMR spectrum of the solution obtained by adding the enantiomeric pure alcohol (2*S*)-methylbutanol (Am-*i*-OH) to complex **3d** showed two doublets at 75.5 and 75.4 ppm with identical ^1J(Pt, P′) and ^2J(P′, P) values which were assigned to the two diastereomeric complexes *SS*-$[PtCl(NIPHOSH{\cdot}O\text{-}i\text{-}Am)(PMe_3)]^+$ (**15**) and *SR*-$[PtCl(NIPHOSH{\cdot}O\text{-}i\text{-}Am)(PMe_3)]^+$ (**15′**). The intensities of the signals indicated that they had formed exactly in a 1:1 ratio. It is likely that chiral induction might have occurred if a chiral phosphine L had been used. However, no mechanistic information would have resulted from this experiment.

X-ray Crystal Structure of $[PtCl(NIPHOSH{\cdot}OMe)(PMe_3)][SbF_6]$ ($[13][SbF_6]$). The structure of $[13][SbF_6]$ consists of discrete cations and $[SbF_6]^-$ anions. An ORTEP view of the cation with the atomic numbering scheme is shown in Figure 2, while a selection of bond lengths and angles is given in Table V. The platinum shows a square-planar coordination with slight distortion toward tetrahedral geometry. The two phosphorus atoms occupy mutually *cis* positions.

The Pt–Cl distance (2.354 (1) Å) is at the lower end of the range found in the corresponding complexes having PR_3 in a *trans* position (2.355 (2)–2.369 (2) Å),[16] but it is comparable with, or

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Table V. Relevant Bond Distances (Å) and Bond Angles (deg) for the Complex [PtCl(NIPHOSH·OMe)(PMe$_3$)][SbF$_6$]([13][SbF$_6$])

Pt–N	2.153 (4)	C8–C11	1.533 (7)
Pt–Cl	2.354 (1)	C8–C7	1.456 (7)
Pt–P2	2.250 (1)	C7–C6	1.337 (7)
Pt–P1	2.189 (1)	C6–C1	1.468 (7)
P1–O1	1.593 (3)	C1–C2	1.415 (7)
P1–C6	1.782 (5)	C2–C3	1.380 (8)
P1–C10	1.810 (5)	C3–C4	1.384 (8)
C10–C9	1.517 (6)	C4–C5	1.378 (7)
C9–C12	1.505 (7)	C5–N	1.335 (6)
C9–C8	1.352 (7)	N–C1	1.370 (6)
Cl–Pt–P1	171.6 (0.05)	Pt–P1–O1	119.0 (0.13)
Cl–Pt–P2	87.5 (0.05)	Pt–P1–C6	102.1 (0.16)
Cl–Pt–N	92.3 (0.11)	Pt–P1–C10	122.8 (0.17)
P1–Pt–P2	97.6 (0.04)	O1–P1–C6	109.3 (0.20)
P1–Pt–N	83.8 (0.11)	O1–P1–C10	100.4 (0.23)
P2–Pt–N	170.6 (0.11)	C6–P1–C10	101.51 (0.24)

longer than, the distance found where the *trans* ligand is a phosphite, e.g., P(OPh$_3$),[16a] P(OMe)$_3$,[17] or PPh$_2$(OR) (R = 2-methylcyclopropyl).[16b] The Pt–N distance (2.153 (1) Å) is normal for this type of bond.[18]

The Pt–P2 distance (2.250 (1) Å) is somewhat longer than the corresponding distance in, e.g., *trans*-[PtCl$_2$(benzoquinoline)-(PEt$_3$)][18a] (2.226 (1) Å), the latter value being typical of complexes containing a monodentate nitrogen heterocycle coordinated in *trans* position to a tertiary phosphine.[18] The Pt–P1 distance, however, is significantly shorter (2.189 (1) Å) than Pt–P2, being the same as the Pt–P(OPh)$_3$ distance in *cis*-[PtCl$_2$(PEt$_3$)(P(OPh)$_3$)].[16a] Nevertheless, this should be considered in the context of distances ranging from 2.155 (3) Å (for P(OMe)$_3$[17]) to 2.224 (3) Å (for PPh$_2$(OR)[16b]). Thus, it appears that P1 can be considered as a donor more similar to a phosphite than to a phosphine in agreement with the type of substituents attached to the P atom. The P1–O bond length is typical for that found in phosphite complexes (1.60 (2) Å average).[19]

Two of the donor–Pt–donor bond angles deviate significantly from 90°, i.e., N–Pt–P1 (83.8 (1)°) and P1–Pt–P2 (97.6 (4)°). This is likely to be due to the bite angle of the NIPHOS·OMe ligand. This bite angle can be even smaller; e.g., the N–Cr–P angle in [Cr(CO)$_4$(NIPHOS)][5] is 76.7 (1)° presumably because of the longer Cr–P and Cr–N bond lengths (2.280 (1) and 2.193 (4) Å, respectively). Another contributory cause is the longer P1–C6 distance in **13** relative to the corresponding distance in the chromium compound (1.709 (4) Å). As a consequence, the P1–Pt–P2 angle is increased relative to that of the chromium compound.

The atom P1 has a very distorted tetrahedral structure, two of the angles being ca. 120° and another ca. 100° (see Table V). The P–C distances are significantly different and are likely to reflect the difference in C hybrids, i.e., sp^3 for C10 and sp^2 for C6. The C–C distances in the P-containing ring show the expected values for a diene structure, i.e., C10—C9=C8—C7=C6—C1 (see Table V). These are in good agreement with those calculated from literature data.[20] It should be noted that the coordinated P-containing ring in [Cr(CO)$_4$(NIPHOS)] does not show these alternations.[5] While the structure of coordinated NIPHOS·OMe does not show any unexpected features, a more detailed discussion is not possible because of lack of appropriate comparison data.

Finally, the pyridine ring does not show any unusual features and the bonding parameters also correspond to those found in the chromium compound above.

Experimental Section

Starting Materials and Solvents. [Pt$_2$Cl$_4$(L)$_2$] compounds (L = PPh$_3$, PMePh$_2$, PMe$_2$Ph, PMe$_3$, P-*n*-Bu$_3$, AsMe$_2$Ph) were prepared by the method of Goodfellow and Venanzi,[21] while [Pd$_2$Cl$_4$(PMe$_3$)$_2$] was prepared by the method of Chatt and Venanzi.[26] 1-Thio-1-phenyl-2-(2-pyridyl)-4,5-dimethyl-1-phospha-2,4-cyclohexadiene was prepared as described by Alcaraz et al.[2] Kerosene (boiling range 200–250 °C), bipyridine, and nickel powder obtained from Fluka AG were used as received. Na[SbF$_6$] was obtained from Alfa Products and used without further purification. Methanol was dried with magnesium and distilled under N$_2$. CDCl$_3$ was passed through a column with Al$_2$O$_3$, activity I, and immediately used. All other solvents were dried prior to use and distilled under N$_2$. All reactions were carried out under argon unless otherwise stated.

Instrumentation. The ^{1}H NMR spectra were recorded at 200.13, 250.13, or 300.13 MHz on an AC 200, WM 250, or AM 300 Bruker instrument, respectively. Chemical shifts were referenced to the residual proton signal of the deuteriated solvent. The following values were used: δ = 7.26 for CDCl$_3$, 5.32 for CD$_2$Cl$_2$, and 1.94 for CD$_3$CN. ^{13}C NMR spectra were recorded at 50.32 MHz on a Bruker AC 200 instrument. Chemical shifts were referenced to the the signal of the deuteriated solvent. The following values were used: δ = 77.2 for CDCl$_3$ and 1.2 for CD$_3$CN. ^{31}P NMR spectra were recorded at 81.015 or 101.21 MHz on a AC 200 or WM 250 Bruker instrument, respectively. Chemical shifts are given relative to external 85% H$_3$PO$_4$. ^{195}Pt NMR spectra were recorded at 53.53 MHz on a Bruker WM 250 instrument. The concentrations of the solutions were 0.1 M. Chemical shifts are given relative to external 0.1 M [PtCl$_6$]$^{2-}$. A negative sign denotes a shift upfield of the reference. Elemental analyses were performed at the "Organisch-Chemisches Mikrolaboratorium ETH Zürich".

Preparation of the Compounds. NIPHOS. The last step of its synthesis was carried out by the following modification of the published procedure.[2] Strict adherance to the details given below is essential to obtain the yields of products reported here. 1-Thio-1-phenyl-2-(2-pyridyl)-4,5-dimethyl-1-phospha-2,4-cyclohexadiene (500 mg, 1.6 mmol), nickel powder (1.2 g, 20 mmol), and 20 mL of kerosene were added into a 50-mL flask containing a magnetic stirring bar (14 mm × 5 mm). The flask was purged with argon for 15 min and then fitted with a reflux condenser sealed with a Teflon sleeve. The flask was heated on a graphite bath to 240 °C. After 16 h the flask was allowed to cool to room temperature and the reaction mixture was filtered through Celite to remove solid materials. The filtrate was shaken with 10 mL of 1 M hydrochloric acid. The two layers were separated, and a sodium carbonate solution was added to the aqueous layer until bubbling ceased. The orange suspension was extracted with four 20-mL portions of CH$_2$Cl$_2$. The combined CH$_2$Cl$_2$ extract was dried over sodium sulfate and the solvent evaporated under reduced pressure. The brown oily residue upon treatment with 5 mL of methanol gave an orange crystalline byproduct, which was separated by filtration. The filtrate, after evaporation of the solvent, was purified by flash chromatography (silica gel, 7:1 hexane/ethyl acetate), affording NIPHOS (70–90 mg, 22–28%) as an almost colorless oil. Filtration and extraction were not carried out under an inert atmosphere. ^{31}P NMR (81 MHz, CDCl$_3$): δ 187.8 (lit.[2] δ 184.9). ^{1}H NMR (200 MHz, CDCl$_3$): δ 8.68 (m, H6′), 8.50 (d, ^2J(P, H) = 39.6 Hz, H6), 8.37 (d, ^3J(P, H) = 5.0 Hz, H3), 7.89 (m, H3′), 7.70 (m, H4′), 7.21 (m, H5′), 2.42 (s, Me), 2.41 (s, Me). The ^{13}C NMR data correspond to those given in ref 2.

[PtCl(NIPHOS)(PMe$_3$)][PtCl$_3$(PMe$_3$)] ([3d][4d]). Solid [Pt$_2$Cl$_4$-(PMe$_3$)$_2$] (68 mg, 0.1 mmol) was added to a stirred solution of NIPHOS (20 mg, 0.1 mmol) in 0.5 mL of CHCl$_3$. The platinum complex dissolved within seconds, giving a red-brown cloudy solution. As previous experiments had shown that the salt [PtCl(NIPHOS)(PMe$_3$)][PtCl$_3$(PMe$_3$)] could not be obtained as a solid, solid [PBu$_4$][SbF$_6$] (45 mg, 0.1 mmol) was added, resulting in the formation of a deep red solution. As no precipitate formed by storing this solution at −25 °C for ca. 12 h, the solvent was evaporated under high vacuum. However, the residual foamy gel could not be induced to crystallize before decomposition of the cationic complex occurred (indicated by a color change to yellow). Therefore, solutions of [3d][4d] for NMR studies were prepared as follows: solid [Pt$_2$Cl$_4$(PMe$_3$)$_2$] (68 mg, 0.1 mmol) was added to a stirred solution

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of NIPHOS (20 mg, 0.1 mmol) in 0.5 mL of $CDCl_3$. Within seconds a deep red solution was obtained. The ^{31}P and ^{195}Pt NMR data are given in Table I. ^1H NMR (250 MHz, $CDCl_3$): δ 9.32 (m, H6'), 8.59 (m, H3'), 8.39 (d, ^2J(P, H) = 22.8 Hz, H6), 8.37 (d, ^3J(P, H) = 19.7 Hz, H3), 8.21 (m, H4'), 7.43 (m, H5'), 2.48 (s, Me–C5), 2.21 (s, Me–C4), 2.19 (d, ^2J(P, H) = 12.3 Hz, Me–P (**3d**)), 1.48 (d, ^2J(P, H) = 11.8 Hz, Me–P (**4d**)). The ^{31}P NMR spectra of these solutions show that the cation **3d** is not stable (see Discussion), and signals of this cation are accompanied by those of an unknown compound as well as by those of [**9d**][**4d**], the relative amounts of the latter two increasing with time.

[PtCl(NIPHOS)(L)][$PtCl_3$(L)] (L = PPh_3, $PMePh_2$, PMe_2Ph, P-*n*-Bu_3) ([3a–c,e][4a–c,e]). Solutions of these complexes were prepared as described for [**3d**][**4d**]. The ^{31}P and ^{195}Pt NMR spectral data are also given in Table I.

[PtCl(bpy)(L)][$PtCl_3$(L)] (L = PPh_3, $PMePh_2$, PMe_2Ph, PMe_3, P-*n*-Bu_3) ([5][4]). Solutions of these salts were prepared by the same procedure as for the salts [**3**][**4**] and characterized by ^{31}P and ^{195}Pt NMR spectroscopy (see Table I). The ^1H NMR data for **4d** are given in Table II.

[PtCl(NIPHOSH·OH)(PMe_3)][$PtCl_3$(PMe_3)] ([9d][4d]). Water (2 mg, 0.1 mmol) was added to the solutions of the salt [**3d**][**4d**] prepared as described above. The color of the solution turned immediately yellow. The yellow solid which gradually precipitated out was filtered off. Anal. Calcd for $C_{18}H_{32}NO_3Cl_4Pt_2$ (M_r = 903.35): C, 23.93; H, 3.57; N, 1.55. Found: C, 23.71; H, 3.51; N, 1.59. ^1H NMR (300 MHz, $CDCl_3$): δ 9.55 (m, H6'), 8.1–7.95 (2 m, H3' and H4'), 7.36 (m, H5'), 7.18 (d, ^3J(P, H) = 24.3 Hz, H3), 5.8 (br, H–OP), 3.0 (ABX system, ^2J(H, H) = 17.5 Hz, H61 and H62), 2.06 (s, Me–C5), 1.98 (s, Me–C4), 1.94 (d, ^2J(P, H) = 12.0 Hz, Me–P (**6d**)), 1.49 (d, ^2J(P, H) = 12.0 Hz, Me–P (**4d**)). The ^{31}P and ^{195}Pt NMR data are given in Table III.

[PtCl(NIPHOSH·O)(PMe_3)] (19d). A solution of this salt was obtained by adding NEt(*i*-Pr)$_2$ (3.45 μL, 0.02 mmol) to [**9d**][SbF_6] (15 mg, 0.02 mmol) in 0.5 mL of CD_3CN. For the ^{31}P NMR data of this compound, see Discussion.

Estimation of the pK_a of 9d. To a solution of [PtCl(NIPHOSH·O)(PMe_3)] (**19d**), prepared as described above, was added CF_3COOH (1.5 μL, 0.02 mmol). The ^{31}P NMR data of the resulting solution are given in the Discussion.

[PtCl(NIPHOSH·OH)(L)][$PtCl_3$(L)] (L = PPh_3, $PMePh_2$, PMe_2Ph, P-*n*-Bu_3) ([9a–c,e,f][4a–c,e,f]). Solutions of these were prepared as described for [**9d**][**4d**]. They were characterized by ^{31}P and ^{195}Pt NMR spectroscopy, and the data are given in Table III.

[PtCl(NIPHOSH·Y)(PMe_3)][$PtCl_3$(PMe_3)] (Y = O-*i*-Pr, O-*i*-Am, OPh, SPh) ([14–17][4]). Solutions of these salts for ^{31}P NMR studies were prepared by adding the corresponding alcohol (0.1 mmol) to $CDCl_3$ solutions of [**3d**][**4d**] prepared as described above. The ^{31}P NMR data are given in Table IV.

[PtCl(NIPHOSH·OMe)(PMe_3)][SbF_6] ([13][SbF_6]). Solid [Pt_2Cl_4(PMe_3)$_2$] (171 mg, 0.25 mmol) was added to a stirred solution of NIPHOS (50 mg, 0.25 mmol) in 3 mL of methanol in a 10-mL Schlenk tube. A deep red solution was formed which gradually changed to yellow. After 10 s most of the solid had dissolved. After filtration the solution was treated dropwise with a filtered solution of Na[SbF_6] (78 mg, 0.30 mmol) in 2 mL of methanol. The bright yellow product which formed slowly was filtered off, washed twice with ether and twice with pentane, and dried under vacuum (159 mg, 82%). Anal. Calcd for $C_{16}H_{25}ClF_6NOP_2PtSb$ (M_r = 775.59): C, 24.78; H, 3.25; N, 1.81. Found: C, 24.77; H, 3.31; N, 1.79. ^1H NMR (250 MHz, CD_2Cl_2): δ 9.76 (m, H6'), 8.12 (t, J_{obs} = 7.7 Hz, H4'), 7.96 (m, H3'), 7.55 (m, H5'), 7.38 (d, ^3J(P, H) = 24.1 Hz, H3), 3.52 (d, ^3J(P, H) = 14.1 Hz, Me–OP), 3.3–3.0 (2 m, H61 and H62), 2.15 (s, Me–C5); 2.10 (s, Me–C4), 1.95 (d, ^2J(P, H) = 11.9 Hz, ^3J(Pt, H) = 38.7 Hz, Me–P). ^{31}P NMR (81 MHz, CD_3CN): δ 80.0 (d, ^1J(Pt, P') = 4156 Hz, ^2J(P', P) = 24.2 Hz, P'), –21.4 (d, ^1J = 3117 Hz, ^2J = 24.7 Hz, P).

Studies of the Hydrolysis of [13][SbF_6]. Uncatalyzed Reaction. To a solution of [**13**][SbF_6] (8 mg, 0.01 mmol) of 0.5 mL of deuteriated solvent was added H_2O (5.4 μL, 0.3 mmol). The end of the reaction was determined by the total disappearance of the signal of the Me–OP group of **13** in the ^1H NMR spectrum.

Catalyzed Reaction. To a solution of [**13**][SbF_6] (15.5 mg, 0.02 mmol) in 0.5 mL CD_3CN were added 0.1 M NaOH and CF_3SO_3H, respectively (1.8 μL, 0.1 mmol). The end of the reaction was determined as described above. For data, see Discussion.

[PdCl(NIPHOS)(PMe_3)][$PdCl_3$(PMe_3)] ([7d][8d]). A solution of this salt for NMR studies was prepared as described for its platinum analogue [**3d**][**4d**]. The ^1H and ^{31}P NMR parameters are given in the Discussion.

[PdCl(NIPHOSH·OH)(PMe_3)][$PdCl_3$(PMe_3)] ([10d][8d]). This was prepared as its platinum analogue [**9d**][**4d**]. For ^{31}P NMR data, see Discussion. ^1H NMR (200 MHz, CD_3CN): δ 9.40 (m, H6'), 8.15–7.95 (2 m, H3' and H4'), 7.50 (m, H5'), 7.38 (d, ^3J(P, H) = 24.2 Hz, H3), 3.2 (2 m, H61 and H62), 2.08 (s, Me–C5), 2.03 (s, Me–C4), 1.83 (dd, ^2J(P, H) = 12.6 Hz, ^4J(P, H) = 1.6 Hz, Me–P (**10**)), 1.45 (dd, ^2J = 12.8 Hz, ^4J = 2.4 Hz, Me–P (**8d**)).

[PdCl(NIPHOSH·OMe)(PMe_3)][SbF_6] ([18][SbF_6]). This was prepared as its platinum analogue [**13**][SbF_6] as a yellow powder. Yield: 89%. Anal. Calcd for $C_{16}H_{25}NClF_6SbPd$ (M_r = 686.92): C, 27.98; H, 3.67; N, 2.04; Cl, 5.16. Found: C, 27.95; H, 3.89; N, 2.30; Cl, 5.23. ^1H NMR (200 MHz, CD_3CN): δ 9.45 (m, H6'), 8.2–7.9 (2 m, H3' and H4'), 7.54 (m, H5'), 7.53 (d, ^3J(P, H) = 23.9 Hz, H3), 3.51 (d, ^3J(P, H) = 14.1 Hz, Me–OP), 3.15 (2 m, H61 and H62), 2.11 (s, Me–C5), 2.05 (s, Me–C4), 1.86 (dd, ^2J(P, H) = 12.6 Hz, ^4J(P, H) = 1.7 Hz, Me–P). ^{31}P NMR (81 MHz, CD_3CN): δ 107.7 (d, ^2J(P', P) = 10.4 Hz, P'), 5.8 (d, ^2J = 10.4 Hz, P).

Crystallography. Crystals of [**13**][SbF_6] were obtained by the following procedure: [**13**][SbF_6] (10 mg) was dissolved in 0.6 mL of CH_2Cl_2, and the solution was placed in an NMR tube. A layer of cyclohexane was placed on top of the solution, and after being capped,

Table VI. Experimental Data for the X-ray Diffraction Studies of [PtCl(NIPHOSH·OMe)(PMe_3)][SbF_6]([13][SbF_6])

formula	$C_{16}H_{25}NClF_6OP_2SbPt$
mol wt	775.59
cryst syst	triclinic
space group	$P\bar{1}$
a, Å	8.493 (1)
b, Å	11.588 (1)
c, Å	12.754 (1)
α, deg	73.763 (8)
β, deg	80.384 (6)
γ, deg	81.948 (8)
Z	2
V, Å^3	1182.4 (2)
δ(calcd), g cm^{-3}	2.175
μ, cm^{-1}	74.24
T, °C	22
λ, Å	0.710 69 (graphite monochromated, Mo K$\bar{\alpha}$)
R^a	0.027
$R_w{}^b$	0.037

$^a \sum||F_o| - 1/k|F_c|/\sum|F_o|$. $^b [\sum w(|F_o| - 1/k|F_o|)^2/\sum w|F_o|^2]^{1/2}$, where $w = [\sigma^2(F_o)]^{-1}$ and $\sigma(F_o) = [\sigma^2(F_o^2) + f^2(F_o^2)]^{1/2}/2F_o$ with f = 0.040.

Table VII. Final Positional Parameters and Their Estimated Standard Deviations for [PtCl(NIPHOSH·OH)(PMe_3)][SbF_6]

atom	x	y	z	B,^{a} Å^2
Pt	0.33984 (2)	0.19686 (2)	0.08643 (2)	2.592 (4)
Sb	0.16149 (5)	0.27943 (4)	0.55263 (3)	3.834 (9)
Cl	0.1082 (2)	0.2063 (2)	0.0041 (1)	4.14 (3)
P1	0.5490 (2)	0.2171 (1)	0.1573 (1)	2.73 (3)
P2	0.2255 (2)	0.0638 (1)	0.2345 (1)	3.04 (3)
O	0.6772 (4)	0.1033 (3)	0.1901 (3)	4.56 (8)
F1	0.1602 (5)	0.3277 (4)	–0.6011 (3)	6.5 (1)
F2	–0.0270 (8)	0.3692 (7)	–0.4247 (6)	12.4 (2)
F3	0.0426 (7)	0.1551 (5)	–0.4392 (5)	10.3 (2)
F4	0.2826 (6)	0.4035 (4)	–0.4599 (4)	9.0 (1)
F5	0.3500 (7)	0.1826 (6)	–0.4709 (6)	11.2 (2)
F6	0.8323 (8)	–0.2285 (6)	0.2996 (4)	9.8 (2)
N	0.4647 (5)	0.2984 (4)	–0.0651 (4)	3.1 (1)
C1	0.6034 (7)	0.3439 (5)	–0.0599 (5)	3.3 (1)
C2	0.7018 (8)	0.3963 (6)	–0.1584 (5)	4.1 (1)
C3	0.6534 (9)	0.4052 (6)	–0.2595 (6)	4.4 (2)
C4	0.5111 (8)	0.3602 (6)	–0.2596 (6)	4.2 (1)
C5	0.4210 (7)	0.3065 (5)	–0.1625 (5)	3.4 (1)
C6	0.6427 (6)	0.3319 (5)	0.0507 (5)	3.1 (1)
C7	0.7368 (7)	0.4014 (5)	0.0757 (5)	3.5 (1)
C8	0.7713 (7)	0.3942 (5)	0.1861 (5)	3.6 (1)
C9	0.6792 (6)	0.3381 (5)	0.2785 (5)	3.4 (1)
C10	0.5321 (7)	0.2781 (5)	0.2750 (5)	3.7 (1)
C11	0.9151 (8)	0.4581 (6)	0.1883 (6)	4.8 (2)
C1P2	0.0311 (8)	0.1190 (6)	0.2932 (6)	4.4 (2)
C12	0.7061 (9)	0.3326 (7)	0.3934 (5)	4.7 (2)
C13	0.7296 (9)	0.0283 (6)	0.1174 (6)	4.7 (2)
C2P2	0.3363 (9)	0.0005 (7)	0.3508 (6)	5.5 (2)
C3P2	0.1940 (9)	–0.0660 (6)	0.1921 (6)	4.7 (2)

^{a} B values for anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

the tube was stored in a refrigerator (-25 °C) for 2 weeks. After decanting of the solvent, the crystals were washed with diethyl ether.

A small prismatic crystal was mounted at a random orientation on a glass fiber for both space group and cell constant determination. The data were collected using a Nonius CAD4 diffractometer. Cell constants were obtained by least-square fit of 25 high-angle reflections ($9.9 < \theta < 17.2$) using the CAD4 centering routines.

Crystallographic and experimental data are listed in Table VI and in the supplementary material, Table S1. Three reflections were chosen as standards to check the decay of the crystal and the stability of the experimental conditions and measured every 1 h; the crystal orientation was checked by measuring three standards every 300 reflections. No significant variation was observed.

Data were collected at variable scan speeds to ensure constant statistical precision of the measured intensities. A total of 5125 reflections ($\pm h, \pm k, +l$) were measured and corrected for Lorentz and polarization factors.[23] An absorption correction was then calculated using the ψ scans of five reflections at high χ angles ($\chi > 84°$). A total of 4254 reflections were considered as observed having $F_o^2 \geq 2.0\sigma(F^2)$, while $F_o^2 = 0.0$ was given to those reflections having negative net intensities.

The structure was solved by standard Patterson and Fourier methods and refined by full-matrix least square minimizing the function $\sum(w(F_o - 1/kF_c)^2)$. An isotropic extinction parameter was refined but found to be negligible and not considered in the final refinement. The scattering factors used, corrected for the anomalous dispersion,[24] were taken from tabulated values.[24] Anisotropic temperature parameters were used for all atoms, and the contribution of the hydrogen atoms, held fixed at their calculated positions (C-H = 0.95 Å, B_{iso} = 5.0 Å^2), was also taken into account but not refined. Upon convergence a Fourier difference map showed no significant features. All calculations were carried out using the Nonius SDP package.[25] Final positional parameters are listed in Table VII.

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Registry No. **1**, 82884-19-3; **2a**, 17522-96-2; **2b**, 94992-93-5; **2c**, 59599-36-9; **2d**, 17522-93-9; **2e**, 15282-39-0; **2f**, 136984-68-4; [**3a**][**4a**], 136953-68-9; [**3b**][**4b**], 136953-70-3; [**3c**][**4c**], 136953-72-5; [**3d**][**4d**], 136953-74-7; [**3e**][**4e**], 136953-76-9; [**4a**][**5a**], 136984-63-9; [**4a**][**9a**], 136953-86-1; [**4b**][**5b**], 136953-78-1; [**4b**][**9b**], 136953-88-3; [**4c**][**5c**], 136953-80-5; [**4c**][**9c**], 136953-90-7; [**4d**][**5d**], 136953-82-7; [**4d**][**9d**], 136953-92-9; [**4d**][**13**], 136953-96-3; [**4d**][**14**], 137036-74-9; [**4d**][**15**], 136953-98-5; [**4d**][**16**], 136954-00-2; [**4d**][**17**], 136954-02-4; [**4e**][**5e**], 136953-84-9; [**4e**][**9e**], 136953-94-1; [**4f**][**9f**], 136984-44-6; **6d**, 17522-86-0; [**7d**][**8d**], 136984-65-1; [**8d**][**10d**], 136954-05-7; [**13**][SbF_6], 136954-03-5; [**18**][SbF_6], 136984-67-3; **19d**, 136954-06-8; PhSH, 108-98-5; H_2O, 7732-18-5; 1-thio-1-phenyl-2-(2-pyridyl)-4,5-dimethyl-1-phospha-2,4-cyclohexadiene, 82884-21-7.

Supplementary Material Available: Tables of X-ray experimental data (Table S1) and anisotropic thermal parameters (Table S2) and an extended list of bond lengths and angles (Table S3) (6 pages); a table of observed and calculated structure factors (Table S4) (43 pages). Ordering information is given on any current masthead page.

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Nucleophilic Attacks of 1,2-Diaminoethane on MeCN Ligands: Synthesis, X-ray Structure, and Spectral and Electrochemical Properties of $[Ru_2(\mu\text{-}O)(\mu\text{-}O_2CAr)_2\{NH_2CH_2CH_2NHC(Me)NH\}_2(PPh_3)_2](ClO_4)_2$ (Ar = C_6H_4-*p*-X; X = H, Me, OMe, Cl)

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The diruthenium(III) complex $[Ru_2O(O_2CAr)_2(MeCN)_4(PPh_3)_2](ClO_4)_2$ (**1**), on reaction with 1,2-diaminoethane (en) in MeOH at 25 °C, undergoes nucleophilic attacks at the carbon of two facial MeCN ligands to form $[Ru_2^{III}O(O_2CAr)_2\{NH_2CH_2CH_2NHC(Me)NH\}_2(PPh_3)_2](ClO_4)_2$ (**2**) (Ar = C_6H_4-*p*-X, X = H, Me, OMe, Cl) containing two seven-membered amino-amidine chelating ligands. The molecular structure of **2** with Ar = C_6H_4-*p*-OMe was determined by X-ray crystallography. Crystal data are as follows: triclinic, $P\bar{1}$, a = 13.942 (5) Å, b = 14.528 (2) Å, c = 21.758 (6) Å, α = 109.50 (2)°, β = 92.52 (3)°, γ = 112.61 (2)°, V = 3759 (2) Å^3, and Z = 2. The complex has an $\{Ru_2(\mu\text{-}O)(\mu\text{-}O_2CAr)_2^{2+}\}$ core. The Ru-Ru and average Ru-O_{oxo} distances and the Ru-O-Ru angle are 3.280 (2) Å, 1.887 [8] Å, and 120.7 (4)°, respectively. The amino group of the chelating ligand is trans to the μ-oxo ligand. The nucleophilic attacks take place on the MeCN ligands cis to the μ-oxo ligand. The visible spectra of **2** in $CHCl_3$ display an absorption band at 565 nm. The ^{1}H NMR spectra of **2** in $CDCl_3$ are indicative of the formation of an amino-amidine ligand. Complex **2** exhibits metal-centered quasireversible one-electron oxidation and reduction processes in the potential ranges +0.9 to +1.0 V and -0.3 to -0.5 V (vs SCE), respectively, involving the $Ru^{III}_2/Ru^{III}Ru^{IV}$ and $Ru^{III}_2/Ru^{II}Ru^{III}$ redox couples in CH_2Cl_2 containing 0.1 M TBAP. The mechanistic aspects of the nucleophilic reaction are discussed.

Introduction

The discovery[1] of a (μ-oxo)bis(μ-carboxylato)diiron core in the active sites of a number of non-heme metalloproteins has generated considerable current interest[2-4] in the synthesis of low molecular weight transition-metal complexes with a similar core structure. The role of facial as well as bridging ligands in tuning and controlling the electronic structure of the dimetallic core is an interesting aspect of this chemistry. It is a general observation that

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