Synthesis and Spectroscopic Properties of the Complexes $[M_2(DIEN)_2(NIPHOS)_2][SbF_6]_2$ (M = Ir, DIEN = 1,5-Cyclooctadiene, COD; M = Rh, DIEN = Norbornadiene, NBD; NIPHOS = 2-(2′-Pyridyl)-4,5-dimethylphosphinine). X-ray Crystal Structure of $[Ir_2(COD)_2(NIPHOS)_2][SbF_6]_2$

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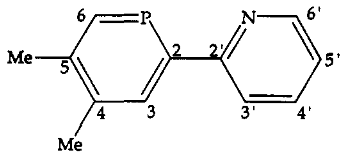
The ligand 2-(2′-pyridyl)-4,5-dimethylphosphinine, NIPHOS, reacts with the compounds $[Ir_2Cl_2(COD)_2]$ (COD = 1,5-cyclooctadiene) and $[Rh_2Cl_2(NBD)_2]$ (NBD = norbornadiene) to give the binuclear cations $[Ir_2(COD)_2(NIPHOS)_2]^{2+}$ and $[Rh_2(NBD)_2(NIPHOS)_2]^{2+}$, respectively, which were isolated as their $[SbF_6]^-$ salts. These complexes were fully characterized in solution by ^1H, ^{13}C, and ^{31}P NMR spectroscopy. The crystal structure of $[Ir_2(COD)_2(NIPHOS)_2][SbF_6]_2$ was determined by X-ray crystallography and showed that the two iridium atoms are bridged by the two phosphinine P atoms. These and the two iridium atoms are almost coplanar. The NIPHOS molecules and the Ir_2P_2-plane are arranged in a "boat" conformation. The crystals belong to space group $P2_1/n$ with $Z = 4$, $a = 17.979$ (1) Å, $b = 11.817$ (2) Å, $c = 21.513$ (2) Å, $\beta = 99.677$ (10)°, and $V = 4505.5$ (11) Å^3. The structure was refined to $R = 0.0411$ for the 7980 observed reflections.

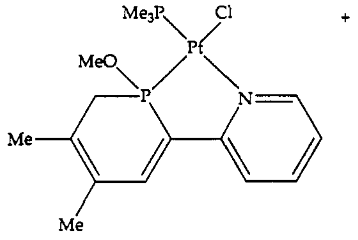
Introduction

The number of publications about transition metal complexes with 2,2′-bipyridine (bpy), mainly of ruthenium(II), has increased almost exponentially over the last decade.[2] Furthermore, there has been also a growing interest in complexes with multidentate ligands containing bpy units.[3] Considerably less attention has been paid to the preparation of complexes with phosphorus analogues of bpy,[4–7] probably because of the difficulties encountered in the synthesis of these ligands.

In an earlier paper[8] we reported synthetic and reactivity studies of platinum(II) and palladium(II) complexes with the ligand 2-(2′-pyridyl)-4,5-dimethylphosphinine, NIPHOS, of the type $[MC(L)(NIPHOS)][MCl_3(L)]$ (M = Pt and Pd; L = tertiary phosphine or arsine). The cations in these complexes readily add one molecule of water at the P–C6 double bond. Several cationic complexes of the type $[MCl(PMe_3)(NIPHOSPH{\cdot}Y)]^+$ (Y = OH, OR and SR), obtained by addition of the appropriate HY molecule to the above cations, were characterized in solution. Furthermore, the crystal structure of $[PtCl(PMe_3)(NIPHOSH{\cdot}OMe)][SbF_6]$ (NIPHOSPH·OMe = 2-(2′-pyridyl)-1-methoxy-4,5-dimethyl-6-hydrophosphinine ($[1][SbF_6]$) was determined by X-ray crystallography. The structure of the cation is



NIPHOS



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The high reactivity of coordinated NIPHOS toward water was ascribed to an increase in positive charge on the phosphorus atom upon complexation to platinum(II) and palladium(II), coupled with the poor π-back-bonding abilities of these two metal centers. Therefore, in order to obtain stable NIPHOS complexes with metals of the platinum group, iridium(I) and rhodium(I) were chosen as they are known to be better π-donors than platinum(II) or palladium(II).

We report here the synthesis and characterization of complexes of the type $[M_2(DIEN)_2(NIPHOS)_2][SbF_6]_2$ (M = Ir, DIEN = COD; M = Rh, DIEN = NBD) together with the X-ray crystal structure of $[Ir_2(COD)_2(NIPHOS)_2][SbF_6]_2$, the first example of a complex containing a bridging phosphinine.

Results

Synthesis of $[Ir_2(COD)_2)NIPHOS)_2][SbF_6]_2$ ($[2][SbF_6]_2$ and $[Rh_2(NBD)_2)(NIPHOS)_2][SbF_6]_2$)($[3][SbF_6]_2$). The ligand NIPHOS reacts with $[Ir_2Cl_2(COD)_2]$ (4) and $[Rh_2Cl_2(NBD)_2]$ (5), according to eq 1, giving the binuclear cationic complexes

$$\underset{\substack{\textbf{4}:\ M = Ir;\ DIEN = COD\\ \textbf{5}:\ M = Rh;\ DIEN = NBD}}{[M_2Cl_2(DIEN)_2]} + 2NIPHOS \rightarrow \underset{\substack{\textbf{2}:\ M = Ir;\ DIEN = COD\\ \textbf{3}:\ M = Rh;\ DIEN = NBD}}{[M_2(DIEN)_2(NIPHOS)_2]^{2+}} + 2Cl^- \quad (1)$$

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(1) (a) Laboratorium für Anorganische Chemie, ETH-Zentrum. (b) Institut für Kristallographie und Petrographie, ETH-Zentrum. (c) CDPH Ecole Polytechnique.

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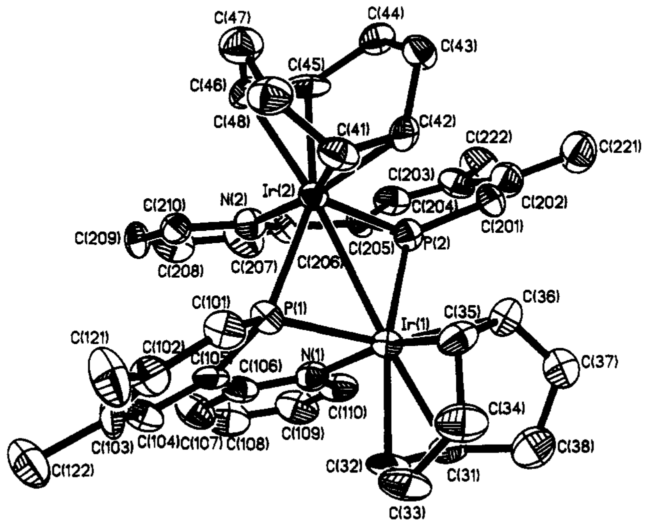


Figure 1. ORTEP view of the cationic complex $[\mathrm{Ir_2(COD)_2(NIPHOS)_2}]^{2+}$ ($[\mathbf{2}]^{2+}$). (The hydrogen atoms have been omitted.)

$[\mathrm{Ir_2(COD)_2(NIPHOS)_2}]^{2+}$ (**2**) and $[\mathrm{Rh_2(NBD)_2(NIPHOS)_2}]^{2+}$ (**3**), respectively. These were isolated as their $[\mathrm{SbF_6}]^-$ salts in 74% and 68% yields, respectively. As the chloride ion liberated during reaction 1 appears to facilitate the decomposition of the cationic species **2** and **3**, high yields of these $[\mathrm{SbF_6}]$ salts are obtained only by minimizing the time required for the precipitation of the products, i.e., by adding NIPHOS to a methanolic suspension of $\mathrm{Na[SbF_6]}$ and the olefin–chloro complex.

Cations **2** and **3** could also be obtained by reacting NIPHOS with $[\mathrm{Ir(COD)(bpy)}]^+$ (**6**) and $[\mathrm{Rh(NBD)(bpy)}]^+$ (**7**), respectively (eq 2), indicating that NIPHOS binds more strongly to Ir(I) and Rh(I) than bpy.

$$2[\mathrm{M(DIEN)(bpy)}]^+ + 2\mathrm{NIPHOS} \rightarrow$$

6: M = Ir; DIEN = COD
7: M = Rh; DIEN = NBD

$$[\mathrm{M_2(DIEN)_2(NIPHOS)_2}]^{2+} + 2\mathrm{bpy} \quad (2)$$

2: M = Ir; DIEN = COD
3: M = Rh; DIEN = NBD

The salts $[\mathbf{2}][\mathrm{SbF_6}]_2$ and $[\mathbf{3}][\mathrm{SbF_6}]_2$ were obtained as black powders. However, solutions of the former compound have an intensely dark green color whereas those of the latter have a beautiful turquoise color.

The UV/vis spectra of solutions of both compounds (see Experimental Section) show several maxima, the most intense absorption being in the near-UV in both cases. The values of the extinction coefficients are in the range 10 000–30 000 $\mathrm{M^{-1}\,cm^{-1}}$, indicating that these transitions must be of the charge-transfer type.

X-ray Crystal Structure of $[\mathrm{Ir_2(COD)_2(NIPHOS)_2}][\mathrm{SbF_6}]_2$ ($[\mathbf{2}][\mathrm{SbF_6}]_2$). The structure of $[\mathbf{2}][\mathrm{SbF_6}]_2$ consists of discrete cations and $[\mathrm{SbF_6}]^-$ anions without significant interaction between them. An ORTEP view of the cation is shown in Figure 1. A selection of bond lengths and angles in cation **2** are given in Table I.

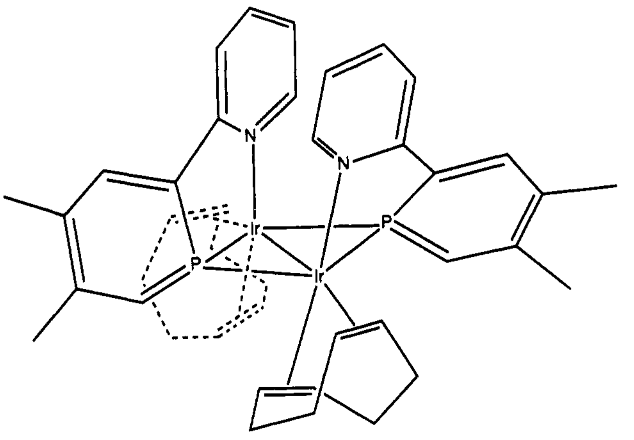
The cationic complex is binuclear and the two iridium atoms are bridged by the phosphorus atoms of the two NIPHOS molecules, these four atoms being approximately coplanar, the most remarkable feature of this structure being the coordination of the phosphinine P-atoms which are simultaneously bonded to two iridium atoms. To our knowledge this type of connectivity has not been observed before. The relative positions of the two NIPHOS molecules are best seen in the following line drawing:

Table I. Selection of Bond Lengths (Å) and Angles (deg) in $[\mathbf{2}][\mathrm{SbF_6}]_2$[a]

Ir(1)–Ir(2)	2.894 (1)	Ir(2)–C(41)	2.215 (15)
Ir(1)–P(1)	2.371 (4)	Ir(2)–C(42)	2.240 (15)
Ir(1)–P(2)	2.424 (4)	Ir(2)–C(45)	2.127 (13)
Ir(2)–P(1)	2.424 (4)	Ir(2)–C(46)	2.163 (15)
Ir(2)–P(2)	2.377 (4)	Ir(2)–C(41m)	2.12 (2)
Ir(1)–N(1)	2.128 (12)	Ir(2)–C(42m)	2.03 (2)
Ir(2)–N(2)	2.098 (12)	P(1)–C(101)	1.727 (14)
Ir(1)–C(31)	2.193 (16)	P(1)–C(105)	1.743 (15)
Ir(1)–C(32)	2.144 (13)	C(105)–C(106)	1.470 (20)
Ir(1)–C(35)	2.230 (14)	P(2)–C(201)	1.698 (14)
Ir(1)–C(36)	2.248 (14)	P(2)–C(205)	1.729 (14)
Ir(1)–C(31m)	2.04 (2)	C(205)–C(206)	1.483 (21)
Ir(1)–C(32m)	2.11 (1)		

Ir(1)–P(1)–Ir(2)	74.2 (1)	P(2)–Ir(2)–C(41m)	106.4 (5)
Ir(1)–P(2)–Ir(2)	74.1 (1)	P(2)–Ir(2)–C(42m)	113.5 (5)
P(1)–Ir(1)–P(2)	104.1 (1)	N(1)–Ir(1)–P(1)	80.8 (3)
P(1)–Ir(2)–P(2)	103.9 (1)	N(1)–Ir(1)–P(2)	86.3 (3)
P(1)–Ir(1)–C(31m)	114.2 (5)	N(1)–Ir(1)–C(31m)	85.1 (5)
P(1)–Ir(1)–C(32m)	106.9 (5)	N(1)–Ir(1)–C(32m)	169.4 (5)
P(2)–Ir(1)–C(31m)	139.1 (5)	N(2)–Ir(2)–P(1)	86.8 (3)
P(2)–Ir(1)–C(32m)	97.8 (5)	N(2)–Ir(2)–P(2)	80.8 (3)
P(1)–Ir(2)–C(41m)	99.8 (5)	N(2)–Ir(2)–C(41m)	168.4 (5)
P(1)–Ir(2)–C(42m)	139.6 (5)	N(2)–Ir(2)–C(42m)	84.5 (5)

[a] C(31m), C(32m), C(41m), and C(42m) are the midpoints of the double bonds of the two COD molecules in $[\mathbf{2}][\mathrm{SbF_6}]$.



If one neglects the metal–metal bond, the coordination polyhedron at each iridium atom can be described as being trigonal bipyramidal.

The pyridine units of the two NIPHOS molecules are approximately parallel to each other on the same side of the $\mathrm{Ir_2P_2}$ unit. The phosphinine and pyridine rings are not coplanar and the corresponding dihedral angles are 17 (1) and 21 (1)°.

The Ir–Ir distance (2.894 (1) Å) is indicative of direct metal–metal interaction as this distance in metallic iridium is 2.72 Å.[9] The Ir–P distances are not equal, two of them being 2.371 (4) and 2.377 (4) Å and the other two being 2.424 (4) Å, the shorter value being that observed for the iridium atom which is also coordinated to the nitrogen atom of the same NIPHOS molecule. The shorter distances fall within the range for Ir–P bonds with chelating ligands such as $\mathrm{Ph_2PCH_2CH_2PPh_2}$ (2.33–2.38 Å).[10] The P–C, C–C, and C–N distances in **2** (see Table II) are similar to those found in $[\mathrm{Cr(CO)_4(NIPHOS)}]$ (**8**)[4] and $[\mathrm{Cr(CO)_4(BIPHOS)}]$ (BIPHOS = 4,4′,5,5′-tetramethyl-2,2′-biphosphinine) (**9**),[7] at least within the limits imposed by the magnitudes of the standard deviations.

The Ir–N distances (average value of 2.113 (27) Å) fall in the upper range for Ir–N bonds (2.039–2.115 Å) for compounds

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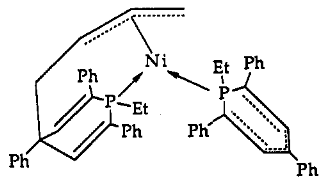
Table II. Selection of Bond Lengths (Å) and Angles (deg) for [**2**]$[SbF_6]_2$, $[Cr(CO)_4(NIPHOS)]$ (**8**),[4] $[Cr(CO)_4(BIPHOS)]$ (**9**),[7] $[Cr(CO)_5(TPP)]$ (TPP = 2,4,6-Triphenylphosphinine) (**13**),[24] [**1**]$[SbF_6]$,[8] and (1–3-η^3-(4-(1-Ethyl-1,4-dihydro-2,4,6-triphenyl-1λ^3-phosphinin-4-yl)butenyl-*P*))(1-ethyl-2,4,6-triphenyl-1λ^5-phosphinin-1-yl)nickel–Tetrahydrofuran(**14**)[25]

	2[a]	8	9	13	1	14[b]
M–P	2.374 (7) 2.424 (4)	2.280 (1)	2.295 (1)	2.372 (4)	2.189 (1)	2.187 (3) 2.212 (3)
M–N	2.11 (3)	2.193 (4)			2.153 (4)	
P–C(101)	1.71 (3)	1.707 (5)	1.711 (3)	1.73 (1)	1.810 (5)	1.815
P–C(105)	1.74 (2)	1.709 (4)	1.737 (2)	1.73 (1)	1.782 (5)	1.821
C(101)–C(102)	1.40 (2)	1.385 (6)	1.385 (4)	1.39 (2)	1.517 (6)	1.35
C(102)–C(103)	1.44 (3)	1.411 (7)	1.400 (3)	1.41 (2)	1.352 (7)	1.39 (1)
C(103)–C(104)	1.34 (2)	1.393 (7)	1.395 (4)	1.41 (2)	1.456 (7)	1.40 (1)
C(104)–C(105)	1.40 (2)	1.384 (6)	1.392 (3)	1.38 (2)	1.337 (7)	1.34
C(101)–P–C(105)	103.6 (9)	104.2 (2)	104.3 (1)	102.2 (6)	101.5 (2)	100.9
P–M–N	80.8 (3)	76.7 (1)	77.15 (3)		83.8 (1)	

[a] Average values. [b] Schematic view of **14**.



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containing chelating bpy.[10] Also, the Ir–C(alkene) distances (2.138–2.239 Å) appear to be normal for iridium(I)–COD complexes.[10]

NMR Studies. The NMR data are fully consistent with the dimeric structure found in the solid state by X-ray analysis, and thus, they are best discussed on the basis of that structure.

The ^{31}P NMR spectrum of **2** shows a singlet at 108 ppm, a chemical shift value which is outside of the range reported so far for σ-coordinated phosphinines (140–200 ppm).[11] This observation can, however, be explained given the known tendency of iridium to shift the ^{31}P resonances of, e.g., phosphines considerably to higher field compared to those of isostructural complexes of other platinum metals.[12] The analogous rhodium complex **3** shows a triplet at 155 ppm with ^1J(Rh,P) = 92.5 Hz. This multiplicity demonstrates that in solution complex **3** remains a dinuclear species, a result confirmed by extensive ^{103}Rh–^{31}P multiple-quantum NMR spectroscopic studies.[13]

The dinuclear nature of the complexes can also be derived from ^{13}C NMR spectroscopy, where most of the signals, in particular those of the "aromatic" fragment, show multiplets, which can be analyzed as arising from AXX′ spin systems involving the two magnetically inequivalent phosphorus nuclei. The A part (^{13}C in this context) corresponding to such a spin system consists in principle of six lines;[14] however, the outermost lines are generally of low intensity and are often buried in the noise of the spectrum, while the two innermost lines are often not resolved, thus resulting in a triplet-like appearance of those resonances. The separation of the outer intense lines of such a "triplet" corresponds to the sum of the coupling constants *J*(P,C) and *J*(P′,C) and these are the values quoted in the Experimental Section. For **3** one would expect to see further splitting of the signals due to ^{103}Rh; however, these long-range coupling constants are apparently too small to be resolved under the experimental conditions used. The assignment of the carbon resonances of the "aromatic" fragments in **2** and **3** was achieved by means of DEPT[15] spectra and by comparison with data of the free NIPHOS ligand and of the complex $[Mo(CO)_4(NIPHOS)]$.[4]

The eight types of resonances observed for the COD ligand in **2** are consistent with the asymmetric environment found in the crystal structure, the chemical shifts (see Experimental Section) being consistent with such a type of ligand. In contrast, the ^{13}C NMR spectra of **3** exhibit only half of the expected NBD resonances, namely two broad multiplets for the olefinic carbons and one each for the two bridgeheads and the methylene bridge. This apparently higher local symmetry of the diolefinic ligand could arise from a dynamic process involving the rotation of the NBD ligand, a conclusion which is supported by ^1H NMR spectroscopy.[16] When the spectrum is recorded in CD_3CN solution at room temperature, the olefinic and the bridgehead protons appear as an ill-defined broad absorption centered at ca. 3.61 ppm. The same compound shows somewhat better dispersion in acetone-d_6, where two types of olefinic protons can be distinguished, while the bridgehead and the methylene protons are rendered equivalent by diolefin rotation, in agreement with the ^{13}C spectra. However, the two bridgehead protons become diastereotopic at lower temperature (–40 °C) as do the methylene protons of the bridge, the latter showing an AB pattern in the spectrum. The two olefinic resonances observed at room temperature split at this temperature into a total of four lines consistent with the expected nonequivalence of the four hydrogens in a static structure analogous to the type found in the crystal structure of **2**.

The shapes of the signals of the six "aromatic" protons of **2** and **3** in the ^1H NMR spectrum are identical; only the chemical shifts are different. The two magnetically nonequivalent but homotopic protons H6 form a AA′XX′ spin system with the two magnetically nonequivalent P atoms giving a three-line multiplet. The same is true for the homotopic protons H3. ^{31}P-decoupled ^1H NMR spectra of **2** and **3**, respectively, show two singlets instead of the two three-line multiplets. The other "aromatic signals" are not affected by the decoupling. The data of the aromatic protons of the complexes are given in the Experimental Section.

Reactivity of $[Ir_2(COD)_2(NIPHOS)_2][SbF_6]_2$ ([2][SbF$_6$]$_2$). Solutions of this salt in acetone or acetonitrile do not react either with H_2 or CO under standard conditions or with PPh_3 or NBD. However, the complex $[Ir_2(NBD)_2(NIPHOS)_2][SbF_6]_2$

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(16) A reviewer, citing unpublished observations, points out that "...the broadening seen in the ^1H NMR spectrum for the NBD complex 3 is quite general." Similar behavior has also been observed in our laboratory in some iridium complexes with COD and chelating diphosphines (unpublished).

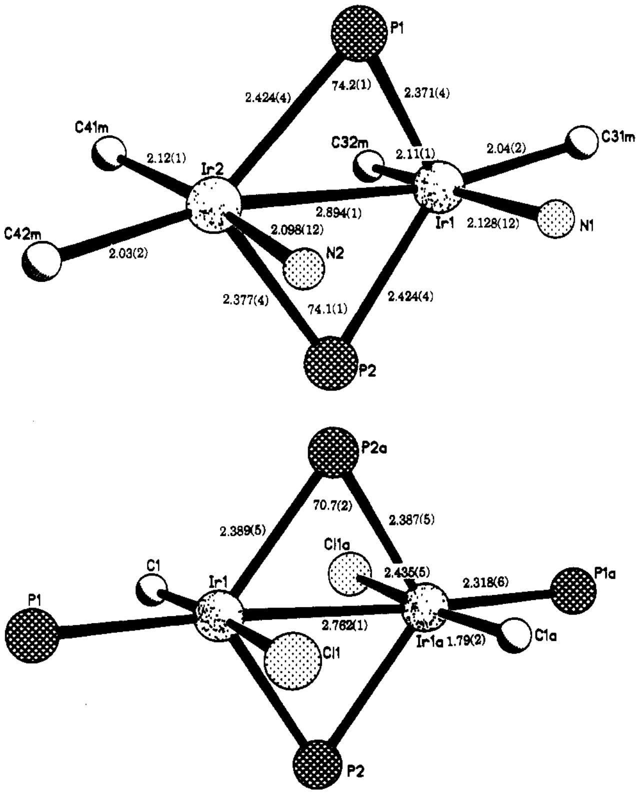

Figure 2. Comparison of the Coordination Polyhedra in (a, top) $[Ir_2(COD)_2(NIPHOS)_2]^{2+}$ ($[\mathbf{2}]^{2+}$) and (b, bottom) $[(CO)(PEt_3)ClIr(\mu\text{-}PCy_2)_2IrCl(PEt_3)\,(CO)]$ (**11**).

($[\mathbf{10}][SbF_6]_2$) is formed upon heating an acetonitrile solution of $[\mathbf{2}][SbF_6]_2$ with a large excess of NBD. The values of the ^{31}P NMR chemical shift of **2** and **10** are identical, i.e., 108 ppm. A comparison of the ^1H NMR spectra of **2** and **10** shows that the resonances of the "aromatic" protons of the former lie at lower field than those of the latter, but the values of the chemical shifts in the two compounds follow the same trend. Solutions of **2** in dichloromethane or chloroform, when exposed to air, undergo a slow transformation: they gradually become yellow and in their NMR spectra the signal/noise ratio decreases until the signals eventually disappear. It is likely that paramagnetic species are formed. This decomposition appears to be more rapid when chloride is added to the acetonitrile solution.

Discussion

As mentioned earlier, the most remarkable feature of the structure of cation **2** is its bimetallic nature containing bridging phosphinine P atoms. In this respect the coordination polyhedron around each iridium atom, which approximates a trigonal bipyramid, is similar to that found in two phosphido-bridged compounds $[(CO)(PEt_3)ClIr(\mu\text{-}PCy_2)_2IrCl(PEt_3)(CO)]$ (**11**)[17] and $[(COD)Ir(\mu\text{-}pz)(\mu\text{-}PPh_2)_2Ir(C_8H_{13})]$ (pz = pyrazolyl, C_8H_{13} = 1-σ-4,5-η^2-C_8H_{13}) (**12**).[18] As the structural features of **2** are closer to those of **11**, only a comparison between these two species will be made. Their salient bonding parameters are shown in Figure 2. As can be seen there, the coordination polyhedra of the two systems are quite similar. Significant differences are as follows:

(1) Ir–Ir distances are longer in **2** than in **11** (2.894 (1) and 2.762 (1) Å, respectively) indicating a weaker Ir–Ir interaction in the former compound.

(2) The P(1)–Ir–P(2) angles in **2** (104.1 (1) and 103.9 (1)°) are smaller than those in **11** (109.4 (2)°) as expected from the longer Ir–Ir separation and the comparable Ir–P distances in the two compounds (2.371–2.424 (**2**) and 2.387–2.389 Å (**11**)).

(3) The deviations from regular trigonal bipyramidal structure are greater in **2** than in **11** and are presumably associated with the chelating nature of NIPHOS and COD.

Nonetheless, it is remarkable that the two structures are so closely related despite the fact that the P atom of the phosphinine is, at least formally, a two-electron donor while that of PCy_2^- is a four-electron donor.

These observations raise the question as to whether it is appropriate to consider the phosphinine P atom as a two-electron donor. For this purpose it is useful to compare interligand bond lengths and angles in **2** and in several compounds containing either NIPHOS itself or related ligands. A selection of such data is collected in Table II. As can be seen there, there is a close correspondence between the bond distances in the phosphinine rings in **2** and those in the complexes $[Cr(CO)_4(L)]$ (L = NIPHOS and BIPHOS (see Table II, entries for **8** and **9**, respectively). Furthermore, this pattern differs from that found in cation **1** and compound **14** which have "four-coordinate" phosphorus atoms (see the appropriate entries in Table II). Thus, it must be concluded that there is no significant difference in bonding pattern of the coordinated phosphinine ring between **2**, where the P atom is bonded simultaneously to two metals, and **8**, **9**, and **13**, where it is bonded to one metal center forming a normal σ-bond.

It is generally recognized that the driving force for "dimer formation", e.g. in compound **11**, is due to the coordinative unsaturation of the four-coordinated monomeric fragment, in this case $(PEt_3)(CO)ClIr(PR_2)$, and the presence of a pair of electrons on each phosphide ligand on the above fragment. This idea could be extended to rationalize "dimer formation" in cation **2** by taking into account the results of CNDO/2 MO calculation on phosphinine by Oehling et al.[19] which indicate that (1) "aromatic" π-bonding has a significant amount of 3d-character, (2) the P lone pair has a greater s character than the corresponding lone pair in pyridine, and (3) the P lone pair is more diffuse and has less directed character than that of pyridine. Thus, the phosphinine lone pair, because of its nature, could give rise to the formation of two Ir–P bonds and thus to the dimerization of the coordinatively unsaturated [Ir(COD)(NIPHOS)] species.

A comment is also required about the mutual arrangement of the two NIPHOS molecules. As mentioned earlier, these constitute the two sides of a "boatlike" structure, and as can be seen in Figure 2, the two pyridine rings face each other and give raise to numerous short C···C distances (3.4–3.5 Å). These interactions may help to stabilize the boatlike configuration in cation **2**.

The formation of a dicationic bimetallic unit raises also the question as to why this is preferred to the uncharged five-coordinated mononuclear species [IrCl(COD)(NIPHOS)] as there are no obvious steric reasons preventing the formation of the latter. However, an answer to this question could be obtained only by carrying out an appropriate MO calculation.

As mentioned earlier, the P- and N-aromatic rings of NIPHOS in **2** are not coplanar. This contrasts the observation of coplanarity of the two rings in $[Cr(CO)_4(NIPHOS)]$ (**8**). However, no reliable deductions can be made on the basis of these structural differences as NIPHOS in the latter complex is coordinated in a "normal" bidentate fashion, while in the former in addition to the classical chelate coordination it is also acting as a bridging ligand through its P atom.

It is interesting to compare the values of the "coordination chemical shift", $\Delta\delta$, defined as $\Delta\delta = \delta(\text{complex}) - \delta(\text{free ligand})$, of atoms C(2) and C(6) of complexes **2** and **3**: these are strongly negative for **2** (−11.9 and −17.4 ppm, respectively) and

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Table III. Experimental Data for the X-ray Diffraction Studies of $[\mathbf{2}][SbF_6]_2$

formula	$C_{40}H_{48}F_{12}Ir_2N_2P_2Sb_2$	Z	4
mol wt	1474.68	ρ_{calc}, gcm^{-3}	2.174
cryst syst	monoclinic	μ, cm^{-1}	72.12
space group	$P2_1/n$	T, °C	20
a, Å	17.979 (3)	λ, Å	0.710 73 (graphite monochromated, Mo Kα)
b, Å	11.817 (2)		
c, Å	21.513 (2)		
β, deg	99.677 (10)	R^a	0.0411
V, Å^3	4505.5 (11)	$R_w{}^b$	0.0490
		GOF^c	1.05

[a] $R = \sum(|F_o| - 1/k|F_c|)/\sum|F_o|$; $R_w = [\sum w(|F_o| - 1/k|F_c|)^2/\sum w|F_o|^2]^{1/2}$, where $w = [\sigma^2(F_o)]^{-1}$.

significantly negative for **3** (−8.2 and −6.9, respectively). The same tendency was also observed by Brêque et al.[4] in the complexes $[M(CO)_4(NIPHOS)]$ (M = Cr, Mo, W).

Given the apparent stability of this dimeric unit it is not surprising that cation **2** does not react, at least under normal conditions, with either H_2 or CO.

In conclusion, although only two types of metal centers have been examined, i.e. d^6 (Cr(0), Mo(0), and W(0)) and d^8 (Pt(II), Rh(I), and Ir(I)), the formation of "normal" coordination compounds by NIPHOS appears to be more the exception than the rule, at least for the complexes with metal centers of the latter type.

Experimental Section

All reactions were carried out under argon unless other stated. Methanol was dried with magnesium and distilled under N_2. $CHCl_3$ was passed through a column with Al_2O_3, activity I, and immediately used. All other solvents were dried prior to use and distilled under N_2.

The NMR spectra were recorded on a Bruker AC200 spectrometer operating at 200.13, 81.0 and 50.3 MHz for ^1H, ^{31}P, and ^{13}C, respectively. Chemical shifts are given relative to external H_3PO_4 for ^{31}P and TMS for ^{13}C and ^1H, respectively. In the latter cases, the residual solvent resonance was used as a secondary standard (using $\delta(H) = 1.94$ for CHD_2CN and 2.05 for acetone-d_5 and $\delta(C) = 1.2$ for CD_3CN). A negative spin denotes a shift upfield of the reference. The values given in parentheses (ΣJ) in the experimental part corresponds to the sums of the coupling constants $^nJ(^{31}P,X) + {}^{n+2}J(^{31}P',X)$, where X = ^{13}C or ^1H.

The UV/vis spectra were recorded on a Kontron Uvikon 810 spectrometer.

Elemental analyses were performed at the "Organisch-Chemisches Mikrolaboratorium, ETH Zürch".

A. Syntheses. Bipyridine was obtained from Fluka and used as received. $Na[SbF_6]$ was obtained from ALfa Products and used without further purification. The ligand NIPHOS was prepared as previously described, while $[Ir_2Cl_2(COD)_2]$,[20] $[Rh_2Cl_2(NBD)_2]$,[21] $[Ir(COD)(bpy)][PF_6]$, and $[Rh(NBD)(bpy)][SbF_6]$[22] were prepared as described in the appropriate references.

$[Ir_2(COD)_2(NIPHOS)_2][SbF_6]_2$ ($[\mathbf{2}][SbF_6]_2$). Reaction 1. Solid $[Ir_2Cl_2(COD)_2]$ (114 mg, 0.17 mmol) was added to a filtered solution of $Na[SbF_6]$ (181 mg, 0.70 mmol) in methanol. The orange-red suspension formed was treated dropwise with a solution of NIPHOS (71 mg, 0.35 mmol) in chloroform. The last drop was added 3 min after the beginning. After the mixture was stirred for another 2 min, the black precipitate was filtered off, washed once with methanol, twice with diethyl ether, and twice with pentane, and dried under vacuum (186 mg, 74%). This complex is quite soluble in acetonitrile and acetone and sparingly soluble in methanol, ethanol, chloromethane, and chloroform. It is air stable both in the solid state and in solution. Anal. Calcd for $C_{40}H_{48}F_{12}Ir_2N_2P_2Sb_2$ (M_r = 1474.68): C, 32.58; H, 3.28; N, 1.90. Found: C, 32.64; H, 3.24; N, 2.03. ^1H NMR (200 MHz, CD_3CN): 8.71 (m, ΣJ = 25.1 Hz, 2 H, H6); 8.37 (d, J_{obs} = 5.7 Hz, 2 H, H6′); 8.00 (m, ΣJ = 19.5 Hz, 2 H, H3); 7.50 (2m, 4 H, H3′ and H4′); 6.71 (m, 2 H, H5′); 4.50 (br, 2 H, olefinic H); 3.80 (br, 4 H, olefinic H); 2.95 (br, 2 H, olefinic H); 2.70 (s, 6 H, Me–C5); 2.47 (s, 6 H, Me-C4); 3–2 (br, 16 H, aliphatic H). ^{13}C NMR (50 MHz, CD_3CN): 162.1 (m, ΣJ = ca. 16 Hz, C2′); 155.3 (m, C6′): 154.0 (m, ΣJ = 32.0 Hz, C2); 153.6 (m, ΣJ = 10.6 Hz, C5); 142.2 (s, C4′); 139.8 (m, ΣJ = 6.7 Hz, C3); 139.6 (s, C4); 137.2 (m, ΣJ = 33.6 Hz, C6); 126.9 (s, C5′); 122.8 (m, J = 10.5 Hz, C3′); 83.1, 80.8, 79.3 (s, olefinic C of COD); 74.9 (m, olefinic C of COD); 35.1, 34.4, 32.3, 31.2 (s, aliphatic C of COD); 24.5 (m, ΣJ = 10.3 Hz, Me–C5); 22.9 (s, Me–C4). ^{31}P NMR (81 MHz, CD_3CN): 108.0. UV/vis (acetone, 3×10^{-5} M): 706 (13 200); 581 (8530); 432 (10 530); 388 (16 400).

Table IV. Final Positional Parameters (×10^4), Their Estimated Standard Deviations, and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3) for $[\mathbf{2}][SbF_6]_2$

atom	x	y	z	U_{eq}
Ir(1)	3235 (1)	2116 (1)	384 (1)	32 (1)
Ir(2)	1866 (1)	960 (1)	560 (1)	29 (1)
P(1)	3159 (2)	353 (3)	895 (2)	35 (1)
C(101)	3496 (8)	-175 (13)	1638 (6)	39 (5)
C(102)	3954 (8)	−1140 (13)	1737 (7)	45 (6)
C(121)	4136 (11)	−1548 (15)	2408 (8)	68 (7)
C(103)	4214 (9)	−1724 (12)	1241 (8)	45 (6)
C(122)	4688 (10)	−2800 (15)	1418 (9)	74 (8)
C(104)	4055 (8)	−1398 (14)	628 (8)	48 (6)
C(105)	3616 (7)	−463 (12)	399 (6)	35 (5)
C(106)	3566 (7)	−78 (13)	−256 (7)	36 (5)
C(107)	3687 (9)	−813 (16)	−741 (7)	53 (6)
C(108)	3617 (10)	−362 (18)	−1349 (8)	67 (8)
C(109)	3450 (9)	776 (17)	−1459 (7)	56 (7)
C(110)	3345 (8)	1442 (15)	−960 (7)	45 (6)
N(1)	3381 (6)	1016 (11)	−369 (5)	36 (4)
P(2)	1965 (2)	2437 (3)	−172 (2)	34 (1)
C(201)	1545 (8)	3725 (12)	−287 (6)	35 (5)
C(202)	1107 (9)	4068 (15)	−853 (8)	50 (6)
C(221)	529 (10)	3802 (16)	−2003 (8)	69 (8)
C(203)	957 (8)	3328 (15)	−1394 (7)	44 (6)
C(222)	776 (10)	5234 (15)	−879 (9)	71 (8)
C(204)	1182 (8)	2256 (15)	−1364 (7)	44 (6)
C(205)	1614 (7)	1710 (12)	−856 (7)	35 (5)
C(206)	1698 (8)	462 (13)	−837 (7)	36 (5)
C(207)	1626 (10)	−199 (17)	−1390 (8)	61 (7)
C(208)	1733 (10)	−1360 (17)	−1332 (8)	61 (7)
C(209)	1914 (9)	−1857 (131)	−734 (8)	49 (6)
C(210)	1959 (8)	−1167 (12)	−211 (8)	45 (6)
N(2)	1874 (6)	−18 (10)	−253 (5)	38 (4)
C(31)	4185 (9)	3095 (14)	147 (8)	49 (6)
C(32)	4444 (7)	2171 (15)	574 (8)	48 (6)
C(33)	4750 (8)	2359 (17)	1278 (7)	58 (7)
C(34)	4250 (8)	3079 (16)	1604 (7)	58 (7)
C(35)	3417 (8)	3038 (13)	1302 (7)	42 (5)
C(36)	3076 (9)	3780 (12)	852 (6)	37 (5)
C(37)	3457 (9)	4674 (14)	526 (8)	55 (6)
C(38)	4188 (10)	4322 (16)	346 (8)	61 (7)
C(41)	1846 (8)	1293 (13)	1570 (7)	43 (6)
C(42)	1496 (8)	2224 (13)	1222 (7)	39 (5)
C(43)	649 (7)	2415 (14)	1080 (8)	48 (6)
C(44)	245 (7)	1829 (13)	477 (7)	45 (6)
C(45)	674 (7)	804 (15)	316 (7)	46 (6)
C(46)	938 (8)	−93 (13)	731 (7)	40 (5)
C(47)	784 (9)	−123 (15)	1396 (7)	56 (6)
C(48)	1454 (9)	341 (15)	1860 (7)	51 (6)
Sb(1)	1774 (1)	6485 (1)	1369 (1)	53 (1)
F(11)	1554 (8)	6705 (13)	2173 (5)	120 (7)
F(12)	1427 (9)	5022 (10)	1351 (8)	130 (8)
F(13)	1988 (8)	6239 (11)	552 (6)	110 (6)
F(14)	2128 (8)	7949 (10)	1346 (7)	110 (6)
F(15)	2732 (7)	5986 (12)	1712 (6)	113 (6)
F(16)	818 (7)	7008 (11)	1024 (6)	107 (6)
Sb(2)	6825 (1)	4636 (1)	1642 (1)	63 (1)
F(21)	7020 (11)	5729 (13)	1110 (7)	167 (10)
F(23)	6510 (12)	3638 (15)	995 (8)	179 (10)
F(22)	6607 (15)	3587 (20)	2175 (8)	254 (15)
F(24)	7165 (15)	5589 (10)	2280 (8)	236 (14)
F(25)	7800 (11)	4147 (18)	1670 (15)	258 (18)
F(26)	5881 (10)	5094 (19)	1542 (16)	280 (20)

$[Ir_2(COD)_2(NIPHOS)_2][PF_6]_2$ ($[\mathbf{2}][PF_6]_2$). Reaction 2. A solution of NIPHOS (20.0 mg, 0.10 mmol) in 1 mL of $CHCl_3$ was added to a solution of $[Ir(COD)(bpy)][PF_6]$ (60.0 mg, 0.10 mmol) in 5 mL of dichloromethane. The resulting deep green solution was immediately

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treated with 20 mL of diethyl ether. The black precipitate was filtered off, washed twice with diethyl ether and pentane, and dried under vacuum (35 mg, 54%). Anal. Calcd for $C_{40}H_{48}N_2F_{12}P_4Ir_2$ (M_r = 1293.10): C, 37.15; H, 3.74; N, 2.17. Found: C, 37.18; H, 3.83; N, 2.12.

[Ir_2(NBD)$_2$(NIPHOS)$_2$][SbF_6]$_2$ ([8][SbF_6]$_2$). To a solution of [**2**][SbF_6]$_2$ (14.6 mg, 0.01 mmol) in 2 mL of acetonitrile were added 3 drops of NBD. The solution was heated at reflux for 4 h, and after it was cooled to room temperature, 20 mL of diethyl ether was added. The precipitate was filtered off, washed with diethyl ether and pentane, and dried under vacuum. ^{1}H NMR (200 MHz, acetone-d_6): 9.27 (m, H6); 8.29 (d, H6′); 8.25 (m, H3); 7.62 (2m, H3′ and H4′); 6.95 (m, H5′); 4.32 (br); 4.20 (br); 4.07 (br); 3.88 (br, olefinic H); 3.60 (br, olefinic H); 2.90 (s, Me–C5); 2.50 (s, Me–C4); 1.35 (m, bridge-H) ^{31}P NMR (81 MHz, acetone-d_6): 107.9.

[Rh_2(NBD)$_2$(NIPHOS)$_2$][SbF_6]$_2$ ([3][SbF_6]$_2$). Reaction 1. This was prepared as its iridium analogue [**2**][SbF_6]$_2$ as a black powder. Yield: 68%. Anal. Calcd for $C_{38}H_{40}N_2F_{12}P_2Sb_2Rh_2$ (M_r = 1263.96): C, 36.11; H, 3.19; N, 2.22. Found: C, 35.70; H, 3.14; N, 2.20. ^{1}H NMR (200 MHz, CD_3CN): 9.24 (m, ΣJ = 28.3 Hz, 2 H, H6); 8.11 (m, ΣJ = 17.2 Hz, 2 H, H3); 7.49 (d, J_{obs} = 5.9 Hz, 2 H, H6′); 7.34 (2m, 4 H, H3′ and H4′); 6.72 (m, 2 H, H5′); 4.24 (s, 4 H, bridgehead-H); 3.61 (very br, 8 H, olefinic H); 2.83 (s, 6 H, Me–C5); 2.60 (s, 6 H, Me–C4); 1.31 (s, 4 H, bridge-H). ^{13}C NMR (50 MHz, CD_3CN): 160.5 (m, ΣJ = 18.5 Hz, C2′); 157.7 (m, ΣJ = 22.1 Hz, C2); 153.2 (s, C6′); 151.6 (m, ΣJ = 12.1 Hz, C5); 147.7 (m, ΣJ = 20.1 Hz, C6); 141.6 (m, ΣJ = 21.1 Hz, C4); 141.0 (s, C4′); 139.9 (m, ΣJ = 9.6 Hz, C3); 125.5 (s, C5′); 121.0 (m, ΣJ = 10.1 Hz, C3′); 62.8 (2s, bridge-C); 58.9 (br, olefinic C); 54.7 (br, olefinic C); 48.4 (s, bridgehead-C); 24.3 (m, ΣJ = 10.1 Hz, Me–C5); 23.0 (s, Me–C4). ^{31}P NMR (81 MHz, CD_3CN): 154.9 (t, ^1J(Rh,P) = 92.5 Hz). UV/vis (acetone, 1.2×10^{-5} M): 624 (16 300); 348 (27 670).

[Rh_2(NBD)$_2$(NIPHOS)$_2$][SbF_6]$_2$ ([3][SbF_6]$_2$). Reaction 2. It was carried out as described for [**2**][PF_6]$_2$ in the presence of Na[SbF_6]. Yield: 83%.

B. Crystallography. Crystals of [**2**][SbF_6]$_2$ were obtained by the following procedure: [**2**][SbF_6]$_2$ (5 mg) was dissolved in 1.0 mL of acetone and the solution filtered into a shortened NMR tube. The NMR tube was then placed in flask which contained a little diethyl ether. The flask was stoppered and stored in a refrigerator (–25 °C) for 5 days. After the solvent was decanted, the crystals were washed with diethyl ether and dried in the air

A dark black crystal was put on a Nicolet R3M diffractometer which was then used for the determination of lattice parameters, space group, and data collection. The cell parameters were obtained by a least-squares fit of the 2θ values of 27 high-angle reflections (20.0° $\leq 2\theta \leq$ 30.0°). The crystallographic data are listed in Table III.

A total of 8671 reflections were measured in the 2θ-array of 2–50°. During data collection three standard reflections (8,0,0; 0,7,–1; 0,0,10) were measured every 69 reflections. No significant variations of the intensities were observed. Data were corrected for Lorentz and polarization factors, and no empirical absorption correction was applied. Reflections having $I \geq 6\sigma(I)$ were considered as observed and so 7980 reflections were used for the solution and refinement of the structure.

The structure was solved by direct and Fourier methods using the SHELXTL-PLUS system. Refinement was carried out by full-matrix least-squares; the function minimized was $\sum w(|F_o| - 1/k|F_c|)^2$. The positions of the hydrogen atoms were calculated but not refined. Anisotropic temperature factors were used for all non-hydrogen atoms. Scattering factors were taken ref 23. The final positions of the atoms and the most important bond lengths and bond angles are listed in Tables IV and I, respectively. The large thermal parameters of the atoms of one [SbF_6]$^-$ are like to be due to disorder of this anion.

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Supplementary Material Available: A full table of X-ray experimental data and tables of bond lengths and angles (8 pages). Ordering information is given on any current masthead page.

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