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Structure and Reactivity of New Iridium Complexes with Bis(Oxazoline)-Phosphonito Ligands

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The synthesis and characterization of novel iridium(I) complexes bearing a neutral bis(oxazoline)phosphonite ligand, NOPON^{Me_2} (**I**), are reported. Numerous Ir(I) complexes have been isolated in high yields and characterized by spectroscopy and X-ray diffraction. $[Ir(\mu\text{-}Cl)(cod)]_2$ (cod = 1,5-cyclooctadiene) reacted with **I** to give the air-sensitive complex [IrCl(cod)(NOPON^{Me_2})] (**1**), which shows broad ^{1}H and $^{13}C\{^1H\}$ NMR signals due to dynamic exchange equilibria involving the cod and the NOPON^{Me_2} ligands. Reaction between a solution of **1** and CO afforded the carbonyl complex [IrCl(CO)(NOPON^{Me_2})] (**2**), whose solid-state structure has been determined by X-ray diffraction. Cationic complexes have been obtained by using NaBAr^F (BAr^F = $B[3,5\text{-}(CF_3)_2C_6H_3]_4$) as a chloride abstractor. The complex [Ir(cod)(NOPON^{Me_2})]BAr^F (**3**) displays a mononuclear structure in the solid state with ligand **I** acting as a bidentate P,N chelating ligand. This complex is a precatalyst for the hydrogenation of alkenes. Oxidative addition of H_2 to **3** occurred either in solution or in the solid-state and this reaction allowed the isolation of the 32 electron, dinuclear dihydrido-bridged iridium(III) complex $[IrH(\mu\text{-}H)(NOPON^{Me_2})]_2(BAr^F)_2$ (**4**), in which the NOPON^{Me_2} ligands exhibit a facial coordination mode. It contains only hydrides as bridging ligands and the $Ir_2(\mu\text{-}H)_2$ unit can be viewed as containing a formal Ir−Ir double bond or two 3c−2e bonds. Complex **3** has also been reacted with CO in solution and in the solid state, and this yielded the dicarbonyl derivative $[Ir(CO)_2(NOPON^{Me_2})]BAr^F$ (**5**). A transmetalation reaction between **3** and $[PdCl_2(NCPh)_2]$ afforded the cationic Pd(II) complex [PdCl(NOPON^{Me_2})]BAr^F (**6**), which has been structurally characterized.

Introduction

Phosphonite and phosphine ligands bearing oxazoline moieties have attracted much interest in the fields of inorganic and organometallic chemistry because they contain both soft (P) and hard (N) donor atoms, a feature which often allows ligand hemilability in their metal complexes and can facilitate elementary steps involved in homogeneous catalysis.[1−5] Despite the considerable number of publications dealing with iridium complexes and their catalytic properties, in particular for hydrogenation and dehydrogenation reactions, the coordination chemistry of polyfunctional ligands applied to iridium complexes is far from being exhaustively studied. In this context, iridium complexes containing P, N donor ligands have been found to be highly efficient catalytic systems for a number of organic reactions, such as asymmetric hydrogenation of alkenes,[6,7] hydrogenation of tri- and tetrasubstituted olefins,[8] alkylation of amines,[9] and formation of C−C bonds.[10] Most of these catalysts contain phosphine-, phosphonite-, or phosphoramidite functionalities combined with nitrogen donor moieties, usually pyridine or oxazoline rings, the latter being particularly convenient in asymmetric catalysis because of an easy access to enantiopure synthons. Surprisingly, to the best of our knowledge, only one iridium complex containing N,P,N chelating ligands has been described to date.[11] Moreover,

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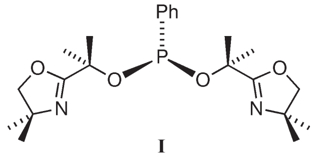
iridium complexes containing tridentate ligands, such as tris(pyrazolyl)borates and PCP pincer ligands, are well-known to be active in challenging catalytic reactions, such as C−H activation[12] and alkane dehydrogenation.[13] For these reasons, the synthesis of new iridium complexes bearing neutral N,P,N ligands was felt of interest not only for academic interest but also because of the catalytic potential of such complexes.



I

In 2001, we reported on the synthesis of the bis(oxazoline)phosphonite ligand NOPON$^{\mathrm{Me_2}}$ (**I**) and the unusual stabilization of its Pd(II) η^1-allyl complexes.[14] The complex [RuCl$_2$(NOPON$^{\mathrm{Me_2}}$)] and its carbonyl adduct, [RuCl$_2$(CO)(NOPON$^{\mathrm{Me_2}}$)], were also described together with some complexes containing an isopropyl-substituted analogue of the NOPON$^{\mathrm{Me_2}}$ ligand.[15] More recently, the NOPON$^{\mathrm{Me_2}}$ ligand has been employed for the preparation of Co(II),[16] Ni(II),[17] and Fe(II)[18] complexes, which have also been tested in the catalytic oligomerization of ethylene. These studies highlighted the versatility of the NOPON$^{\mathrm{Me_2}}$ ligand and prompted us to explore its chemistry toward Ir(I) and Ir(III). Herein, we report on the synthesis, characterization, and reactivity of new iridium complexes bearing the NOPON$^{\mathrm{Me_2}}$ ligand.

Results and Discussion

The reaction between NOPON$^{\mathrm{Me_2}}$ and the iridium(I) precursor complex [Ir(μ-Cl)(cod)]$_2$ (cod = 1,5-cyclooctadiene) in CH$_2$Cl$_2$ resulted in the formation of an orange, air-sensitive compound, exhibiting high solubility in chlorinated and aromatic solvents and moderate solubility in saturated hydrocarbons. This product could be purified by extraction of the crude in pentane followed by evaporation of the solvent. Evidence for the formation of a new complex of formula [IrCl(cod)(NOPON$^{\mathrm{Me_2}}$)] (**1**) was obtained by multinuclear magnetic resonance (NMR) and infrared (IR) spectroscopy, matrix-assisted laser desorption ionization-time-of-flight (MALDI-TOF) mass spectrometry, and elemental analysis. In particular, the ^{31}P{^{1}H} NMR spectrum of **1** in CDCl$_3$ shows a high-field shift of the phosphorus resonance from 150.5 ppm for uncoordinated NOPON$^{\mathrm{Me_2}}$ to 103.2 ppm for **1**. The ^{1}H NMR of **1** in CDCl$_3$ exhibits three sets of sharp signals due to the phenyl protons (8.0−7.3 ppm), an AB spin system for the CH$_2$ protons of the oxazoline moieties (at 3.97 and 3.85 ppm), and four singlets for the methyl protons (at 1.81, 1.75, 1.21, and 1.17 ppm). The presence of a single AB spin system for the methylene protons of the NOPON$^{\mathrm{Me_2}}$ ligand suggests that the oxazoline moieties are symmetrically coordinated to the metal center or that they are involved in a fast exchange on the NMR time scale. Similarly, only four signals for the methyl protons are observed. For comparison, the ^{1}H NMR spectrum of the free ligand displays a similar sets of signals, namely, an AB system for the diastereotopic CH$_2$ protons and four signals for the methyl groups.[14] The signals due to the vinyl protons of the cod ligand are instead very broad, suggesting a fluxional behavior of the cyclooctadiene molecule. This prompted us to perform variable temperature NMR experiments. Two different equilibria appear to exist in the coordination environment of the metal, which involve the cod and the oxazoline moieties, respectively. In particular, a comparison between the ^{1}H NMR spectra of **1** at 25 °C and at −30 °C reveals that the broad signal (5.6−3.2 ppm) due to the cod CH=CH protons is split into two signals at 5.20 and 3.52 ppm, which could correspond to the vinyl protons of the free and coordinated double bonds, respectively. As far as the resonances of the CH$_2$ protons of the oxazoline moieties are concerned, the two sharp doublets of the AB spin system change significantly by decreasing the temperature from 25 to −20 °C (see Figure S-1 of the Supporting Information). One of the two doublets becomes a broad signal, and two of the signals assigned to the methyl groups broaden. A more complex ^{1}H NMR spectrum at low temperature is consistent with the lower symmetry of the rigid structure of the complex in which the two oxazoline moieties are inequivalent. The infrared spectrum of **1** displays an absorption of medium intensity at 1662 cm^{-1} assigned to the C=N stretching vibration, which is very close to that of the free ligand. Some interesting information about the molecular structure of **1** in the solid state could be inferred from its far IR spectrum. In particular, the absorption at 304 cm^{-1} suggests the presence of an Ir−Cl bond. In the absence of single crystals suitable for X-ray diffraction, the molecular structure of the compound can only be suggested on the basis of spectroscopic data. The ^{1}H NMR spectra have shown that the cod ligand is still present in the complex and that the NOPON$^{\mathrm{Me_2}}$ ligand is coordinated through the phosphorus and the oxazoline nitrogen atoms, the latter being probably involved in a fast exchange about the metal center consistent with the documented hemilability of the NOPON$^{\mathrm{Me_2}}$ ligand.[14] We suggest that a dynamic exchange takes place in solution between the uncoordinated C=C double bond of the cod ligand and an oxazoline moiety (**1a**/**1b** in Scheme 1), as indicated by the ^{1}H NMR spectra of **1** at variable temperatures. Moreover, the far IR spectrum and the high solubility of **1** in solvents of low polarity indicate that the compound is neutral, with the chloride ligand bound to the metal. Dissociation of the chloride anion in chloroform or dichloromethane to give the cationic species [Ir(cod)(NOPON$^{\mathrm{Me_2}}$)]$^+$ appears unlikely, considering that the fragment [IrCl(NOPON$^{\mathrm{Me_2}}$)] was unambiguously observed by MALDI-TOF analysis of a dichloromethane solution of **1**. The MALDI-TOF MS spectrum of **1** shows two main peaks at m/z = 721.35 [^{193}Ir(cod)(NOPON$^{\mathrm{Me_2}}$)]$^+$ and 719.34 [^{191}Ir(cod)(NOPON$^{\mathrm{Me_2}}$)]$^+$ and a third one at m/z = 648.28 [^{193}Ir^{35}Cl(NOPON$^{\mathrm{Me_2}}$)]$^+$, which is consistent with the proposed formulation for the compound.

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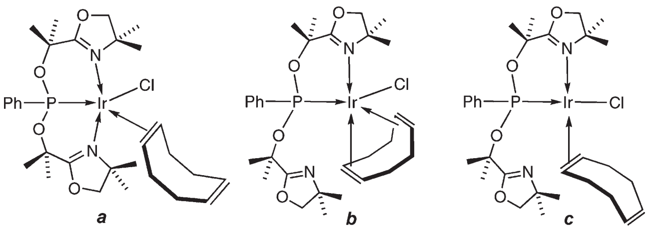
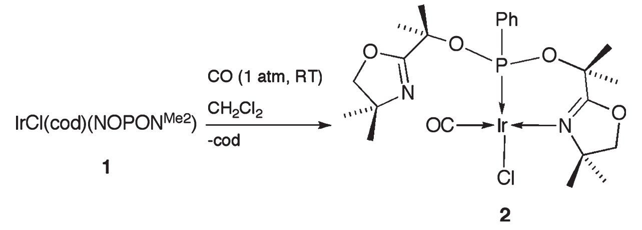
Scheme 1. Solid-State and Solution Structures of **1** Discussed in the Text



Scheme 2. Synthesis of Complex **2**



The data available for **1** are consistent with a neutral, pentacoordinated Ir(I) complex in the solid state,[19,20] with the NOPON^{Me_2} ligand acting as a tridentate ligand (Scheme 1, structure *a*) and the cod as a two electron donor, although this is very rarely encountered.[21] A pentacoordinated diolefinic complex with a chelating NOPON^{Me_2} ligand (Scheme 1, structure *b*) is not consistent with the solution data, which indicates the presence of an uncoordinated C=C double bond. Although the spectroscopic data do not strictly rule out the possibility of a tetracoordinated Ir(I) species (Scheme 1, structure *c*) where one arm of the NOPON^{Me_2} ligand is popping on and off, this appears less likely in view of the strong propensity for the cod and NOPON^{Me_2} ligands to occupy the coordination sites available, i.e., to favor pentacoordination around the Ir(I) center.

Upon treatment of complex **1** with CO at 1 atm pressure, a new compound was selectively obtained in high yield (Scheme 2). The presence of a coordinated CO molecule was clearly indicated by a strong absorption at 1989 cm^{-1} in the solid-state IR spectrum. The Ir−Cl stretching vibration gives rise to an absorption at 290 cm^{-1},[22] which disappears after treatment of the compound with LiBr in acetone solution (substitution of the Ir−Cl bond by an Ir−Br bond). The two C=N stretching absorptions at 1656 and 1608 cm^{-1} are in agreement with a P, N-bidentate behavior of the NOPON^{Me_2} ligand and the presence of a pendant oxazoline group (the C=N stretching vibration of the free ligand occurs at 1661 cm^{-1}) or with the C=N groups being coordinated in different chemical environments. These data are also consistent with the ^{1}H and ^{13}C{^{1}H} NMR spectra. In particular, the ^{1}H NMR spectrum exhibits two sets of signals for the AB spin system of the CH$_2$ protons and eight signals due to the methyl groups, thus confirming the nonequivalence of the two oxazoline arms, even in solution. Moreover, the singlet at 173.0 ppm in the ^{13}C{^{1}H} NMR spectrum of the compound is in agreement with a coordinated CO molecule. Spectroscopic evidence for the asymmetric coordination of the NOPON^{Me_2} ligand has been previously discussed in the case of Pd(II) complexes.[14]

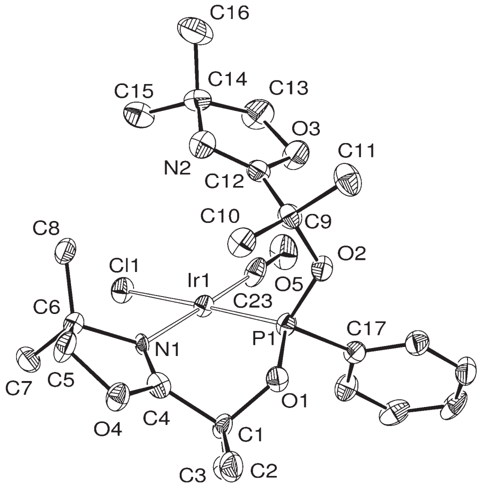


Figure 1. ORTEP of complex **2** in **2**·CH$_2$Cl$_2$ with ellipsoids drawn at the 50% probability level. Solvent molecules and hydrogen atoms are omitted for clarity.

Table 1. Selected Bond Distances (Å) and Angles (deg) for [IrCl(CO)(NOPON^{Me_2})] (**2**) in **2**·CH$_2$Cl$_2$

Ir(1)−P(1)	2.1735(19)	C(4)−N(1)	1.278(9)
Ir(1)−N(1)	2.142(6)	C(4)−O(4)	1.324(10)
Ir(1)−C(23)	1.855(9)	C(12)−N(2)	1.282(9)
Ir(1)−Cl(1)	2.4015(19)	C(12)−O(3)	1.365(9)
C(23)−O(5)	1.12(1)		
C(23)−Ir(1)−N(1)	177.3(3)	N(1)−Ir(1)−P(1)	90.14(16)
C(23)−Ir(1)−P(1)	88.6(2)	C(23)−Ir(1)−Cl(1)	88.5(2)
N(1)−Ir(1)−Cl(1)	92.94(15)	P(1)−Ir(1)−Cl(1)	175.51(7)
Ir(1)−C(23)−O(5)	178.2(7)		

A single crystal X-ray structure determination confirmed the hypotheses drawn on the basis of the spectroscopic data and allowed us to unambiguously identify the product as the neutral complex [IrCl(CO)(NOPON^{Me_2})] (**2**), see Figure 1. The crystals were grown from CH$_2$Cl$_2$/Et$_2$O and contain one molecule of dichloromethane per complex. Selected bond distances and angles are listed in Table 1.

The iridium atom lies in a slightly distorted square-planar environment as shown by the P(1)−Ir(1)−Cl(1) and N(1)−Ir(1)−C(23) bond angles of 175.51(7) and 177.3(3)°, respectively. The six-membered ring formed by the bidentate NOPON^{Me_2} ligand upon coordination adopts a boat conformation with a N(1)−Ir(1)−P(1) angle of 90.14(16)°. The C=N bond distances in the coordinated and dangling oxazoline rings are not significantly different, whereas the NC−O bond in the free oxazoline moiety is slightly longer than in the coordinated one. The metal−phosphorus distance is shorter than those reported for similar Ir(I) complexes.[9,23] As expected on the basis of the weaker trans influence of the nitrogen donor compared to the phosphorus donor, the carbonyl ligand occupies the position trans to the coordinated oxazoline ring.

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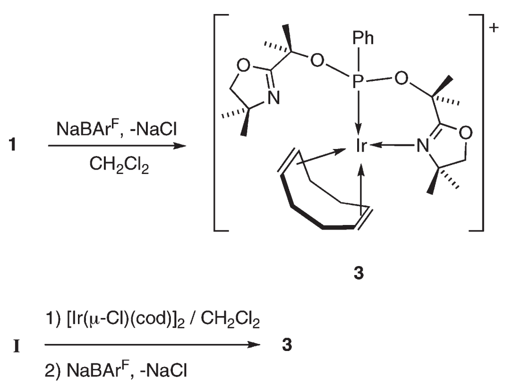
Scheme 3. Synthesis of Complex **3**



Complex **1** was reacted with NaBAr^F (BAr^F = B[3,5-(CF$_3$)$_2$C$_6$H$_3$]$_4$) in CH$_2$Cl$_2$ in order to obtain the corresponding cationic complex [Ir(cod)(NOPON^{Me_2})]BAr^F (**3**). The latter has also been prepared by reacting in situ [Ir(μ-Cl)(cod)]$_2$, NOPON^{Me_2}, and NaBAr^F (Scheme 3). Both reaction procedures led to a red-orange, air-stable compound, which is soluble in chlorinated solvents and ethers, slightly soluble in aromatic solvents, and insoluble in saturated hydrocarbons. In the ^{31}P{^{1}H} NMR spectrum of **3**, a downfield shift of 7.4 ppm is observed with respect to the neutral compound **1**, which is consistent with a decreased electron-density at the metal.

The ^{1}H and ^{13}C{^{1}H} NMR spectra of **3** are affected by a significant fluxionality of the ligands about the metal center. With the exception of the signals due to the phenyl ring and the BAr^{F-} anion, all signals are very broad. This prompted us to perform variable temperature ^{1}H NMR experiments. At −10 °C, eight singlets in the methyl region were identified, which is in agreement with a bidentate behavior of the NOPON^{Me_2} ligand. In the IR spectrum of **3**, the two bands at 1671 and 1605 cm^{-1} were attributed to the stretching vibrations of the C═N bonds of the uncoordinated and coordinated oxazoline rings, respectively.[14] After recording the NMR spectra of **1** in C$_6$D$_6$, 1 equiv of NaBAr^F was added. Formation of single crystals of [Ir(cod)(NOPON^{Me_2})]BAr^F·0.5C$_6$D$_6$ suitable for X-ray diffraction studies occurred within minutes. This confirmed the coordination of both cod and NOPON^{Me_2} ligands to the metal center, which lies in a distorted square planar environment, if the two double bonds of the cyclooctadiene, one nitrogen atom of an oxazoline ring, and the phosphorus atom are considered (see Figure 2). Selected bond distances and angles for **3** are listed in Table 2.

Similarly to the carbonyl derivative **2**, the six-membered ring formed by the bidentate NOPON^{Me_2} ligand and the iridium atom adopts a boat conformation with a N(1)−Ir(1)−P(1) angle of 84.23(14)°. Some differences between the two oxazoline moieties are noteworthy. In particular, the coordinated oxazoline ring shows a slightly longer C═N bond distance and a significantly shorter NC−O bond distance compared to the dangling oxazoline ring. The Ir−C bond distances range from 2.143(6) to 2.265(6) Å and the shortest Ir−C bonds are located, as expected, in positions trans to the nitrogen donor atom. Similarly, the cyclooctadiene C═C bond distance trans to the nitrogen atom is longer than the other one.

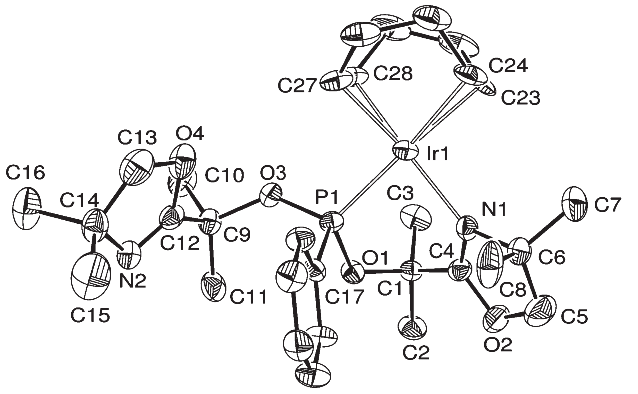


Figure 2. ORTEP of complex **3** in **3**·0.5C$_6$H$_6$ with ellipsoids drawn at the 40% probability level. The anion, solvent molecules, and hydrogen atoms are omitted for clarity.

Table 2. Selected Bond Distances (Å) and Angles (deg) for [Ir(cod)(NOPON^{Me_2})]BAr^F (**3**) in **3**·0.5C$_6$D$_6$[a]

Ir(1)−P(1)	2.2351(16)	C(23)−C(24)	1.364(9)
Ir(1)−N(1)	2.127(5)	C(27)−C(28)	1.404(9)
Ir(1)−C(23)	2.229(6)	C(12)−N(2)	1.256(8)
Ir(1)−C(24)	2.265(6)	C(12)−O(4)	1.388(7)
Ir(1)−C(27)	2.151(6)	C(4)−N(1)	1.290(7)
Ir(1)−C(28)	2.143(6)	C(4)−O(2)	1.327(7)
N(1)−Ir(1)−P(1)	84.23(14)	N(1)−Ir(1)−C(23/24)	96.7(3)
C(27/28)−Ir(1)−P(1)	93.1(3)	C(23/24)−Ir(1)−C(27/28)	85.8(3)

[a] C(23/24) and C(27/28) represent the middle of the cod double bonds, respectively.

The reactivity of **3** toward CO and H$_2$ was investigated. A rapid reaction took place when a red-orange solution of **3** in THF, dichloromethane, or chloroform was exposed to 1 atm of hydrogen at room temperature. The reaction could be visually monitored by a color change from red-orange to pale yellow, which occurred within a few minutes. Moreover, pure **3** reacted quickly with H$_2$ even in the solid state to afford a pale yellow powder. The reaction between **3** and H$_2$ was also studied in situ by multinuclear NMR spectroscopy in THF-d_8 solution. ^{31}P{^{1}H} NMR spectroscopy demonstrated that, upon exposure to H$_2$, complex **3** is quantitatively and selectively converted into a new compound with appearance of a singlet at 123.8 ppm. The ^{1}H NMR spectrum of the complex shows two sets of signals due to the oxazoline rings, namely, two AB spin systems for the CH$_2$ protons and eight resonances in the methyl region. Moreover, a doublet at −25.99 ppm ($^2J_{PH}$ = 15.0 Hz) indicates unambiguously the presence of a metal hydride, in a 1:1 ratio with the ligand. Some signals in the CH$_2$ and vinyl regions are likely to be attributed to partially hydrogenated cyclooctadiene in solution, free or bound to the metal. In this context, some Ir(III) hydrides bearing alkyl substituents have been previously reported.[24−27] Such species could explain the presence of several resonances in the methylene region. The reaction was carried out again in CD$_2$Cl$_2$ and monitored by NMR

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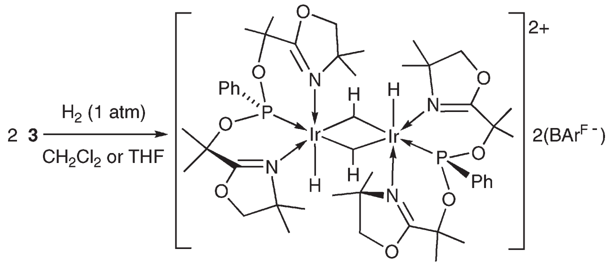
Scheme 4. Synthesis of the Tetrahydride Complex **4**[a]



4

[a] For the bonding within the $Ir_2(\mu\text{-}H)_2$ moiety, see the text.

spectroscopy, which gave the same results as those obtained in THF. The dinuclear structure drawn for **4** in Scheme 4 corresponds to that determined in the solid state by X-ray diffraction (see below). The dinuclear Ir(III) hydride complex $[IrH(\mu\text{-}H)(NOPON^{Me_2})]_2(BAr^F)_2$ (**4**·$4CH_2Cl_2$) separated out as a crystalline solid from a concentrated dichloromethane solution of **3** under H_2 (Scheme 4).

The molecular structure of this air-sensitive complex was determined by X-ray diffraction. In order to isolate **4** in higher yields, the reaction between **3** and H_2 was also performed in pentane and in the solid state. Both procedures afforded a pale yellow air-sensitive solid, which was analyzed by NMR spectroscopy and found to be identical to the compound observed by reacting **3** with H_2 in CD_2Cl_2 or THF-d_8. Dissolution of **4** led to decomposition and thus evidence for the presence of dinuclear **4** in solution could not be obtained. The fact that only one hydride resonance was observed in solution, which corresponds to one hydride per ligand, suggests that the dinuclear species forms only in the solid state by slow crystallization, a mononuclear Ir(III) monohydride being the main product in solution but its instability (see above) prevented its characterization. To the best of our knowledge, **4** represents only the second example of a structurally characterized iridium complex containing a tridentate N,P,N donor ligand (see Figure 3). The first complex of this type contained a modified scorpionate ligand, namely, a hybrid pyrazolyl/phosphane anionic ligand.[11] Although hydrido-bridged dinuclear iridium complexes are well-known, the metal centers are usually bridged by additional ligand(s), such as diphosphines,[28−30] chlorides,[31] *N*-donor ligands,[32−36] or oxygen based linkers.[37] It is noteworthy that complex **4** is one of the few iridium hydrides complexes in which the bridging ligands are all hydrides: according to the Cambridge Structural Database (CSD), structurally relevant precedents appear limited to $[\{(Ph_2PCH_2CH_2PPh_2)Ir(H)\}_2(\mu\text{-}H)_3]BF_4$,[38a] $[\{Cp^*(PMe_3)(H)Ir\}_2(\mu\text{-}H)\}]_2PF_6$,[38b] $[(Cp^*Ir)_2(\mu\text{-}H)_3]ClO_4$,[38c] $[\{(C_2F_6)_2PCH_2CH_2P(C_2F_6)_2\}(H)_2Ir(\mu\text{-}H)]_2$,[38d] $[(PhBP_3)Ir(H)(\mu\text{-}H)]_2$,[38e] $[(Cp^*Ir)(CO)(\mu\text{-}H)]_2[BAr^F]_2$,[38f] and $[(Cp^*Ir)(Cl)(\mu\text{-}H)]_2$.[38f] Selected bond distances and angles are listed in Table 3. This dicationic complex has 32 valence electrons, like $[Ir_2(\mu\text{-}\eta^2\text{-}O_2CR)(\mu\text{-}H)_2H_2(PPh_3)_4]^+$,[37] $[(Cp^*Ir)(CO)(\mu\text{-}H)]_2^{2+}$,[38f] or $[(Cp^*Ir)(Cl)(\mu\text{-}H)]_2$,[38f] and like them could be considered as containing a formal Ir−Ir double bond, which would satisfy the 18 electron rule. However, it remains clear that electronic delocalization occurs within the $Ir_2(\mu\text{-}H)_2$ unit, and this is represented in Scheme 4 by two 3c−2e bonds.

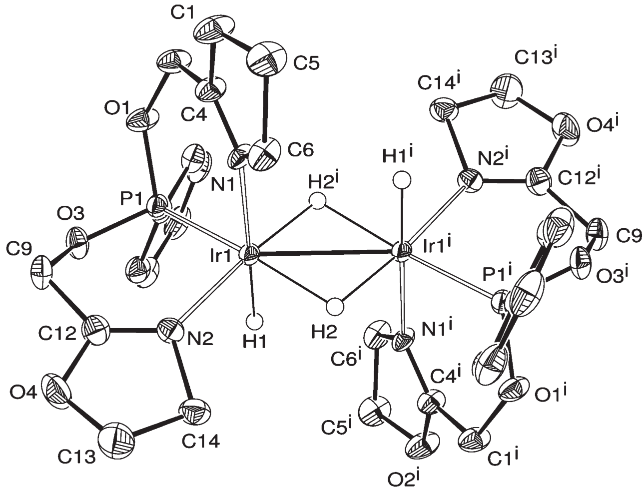


Figure 3. ORTEP of the cationic complex of **4** in **4**·$4CH_2Cl_2$ with ellipsoids drawn at the 50% probability level (methyl groups, solvent molecules, and anion are omitted for clarity). The symmetry operation generating equivalent atoms (i): -*x*, -*y*, -*z*.

Table 3. Selected Bond Distances (Å) and Angles (deg) for $[IrH(\mu\text{-}H)(NOPON^{Me_2})]_2(BAr^F)_2$ (**4**) in **4**·$4CH_2Cl_2$

Ir(1)−Ir(1)^i	2.7651(5)	Ir(1)−N(2)	2.142(5)
Ir(1)−N(1)	2.273(5)	N(1)−C(4)	1.279(8)
Ir(1)−P(1)	2.1628(15)	N(2)−C(12)	1.274(7)
N(1)−Ir(1)−P(1)	88.92(13)	N(1)−Ir(1)−Ir(1)^i	98.95(12)
N(2)−Ir(1)−P(1)	89.54(14)	P(1)−Ir(1)−Ir(1)^i	133.21(4)
N(1)−Ir(1)−N(2)	94.29(19)	N(2)−Ir(1)−Ir(1)^i	135.03(14)

The cationic unit contains a crystallographic inversion center. The data are consistent with the presence of terminal and bridging hydride ligands, as indicated in the drawings (see Experimental Section). The Ir−Ir bond distance of 2.7651(5) Å is slightly longer that in the above-mentioned complexes which contained anionic ancillary ligands, in contrast to $NOPON^{Me_2}$. The coordination spheres of the metal centers constitute two edge-sharing octahedra. The $NOPON^{Me_2}$ ligands adopt a facial arrangement with the phosphorus atoms in equatorial positions. The two terminal hydrides occupy the remaining apical positions, while the two

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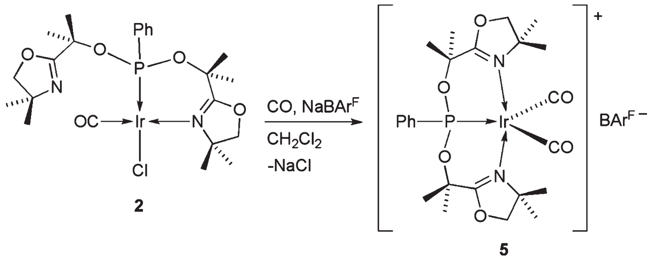
bridging hydrides lie in the equatorial plane. The Ir−N bond distances of 2.142(5) and 2.273(5) Å for the equatorial and apical bonds, respectively, are consistent with the stronger trans influence of the apical hydride compared to the bridging hydride. The N−Ir−P bond angles of 88.92(13) and 89.54(14)° for the equatorial and apical positions, respectively, are slightly distorted from the expected 90°.

Complex **4** seemed to be a good candidate for alkane transfer dehydrogenation catalysis. Therefore, a suspension of **3** was treated with hydrogen in cyclooctane in the presence of 50 equiv of *tert*-butylethylene (as a potential hydrogen acceptor), in order to eliminate the coordinated cod ligand and generate a reactive, coordinatively unsaturated Ir(III) complex. The orange suspension turned quickly pale yellow and it was then heated at 150 °C. Decomposition occurred within a few minutes as indicated by the formation of a black precipitate. Similar experiments were carried out in the absence of *tert*-butylethylene, at lower temperatures (up to 100 °C), or in the presence of H_2. Dehydrogenation of the cyclooctane to cyclooctene was never detected by gas chromatography (GC) analysis. However, we noted that the *tert*-butylethylene, which was added to the reaction as a potential hydrogen acceptor, had been hydrogenated to *tert*-butylethane when the reaction was performed under 1 atm H_2. This hence led to catalytic studies of **3** for the hydrogenation of olefinic substrates such as *cis*-cyclooctene, 1-octene, 1-methylcyclohexene, and 2-cyclohexen-1-one. Catalytic details are given in Table S-1 (Supporting Information). The experiments showed that the activity of the catalyst depends significantly on the accessibility of the C=C double bond in the substrate, i.e., on the degree of substitution of the alkene. High activities were observed in the hydrogenation of monosubstituted double bonds, such as 1-octene. The introduction of a conjugated electron-withdrawing group in the substrate did not seem to significantly affect the activity of the catalyst, as observed by comparing the hydrogenation reaction of cyclooctene and 2-cyclohexene-1-one. The best results were obtained for 1-octene in chlorobenzene (60 °C, 1.5 bar H_2, 2 h, turnover number 900). For comparison, complex **1** was also tested in hydrogenation catalysis but showed a much lower activity.

A solution of **3** in dichloromethane was reacted with 1 atm of CO at room temperature and, similarly to the reaction with H_2, the reaction took place also in the solid state to afford a yellow powder. The product of the reaction was isolated, analyzed by NMR and IR spectroscopic methods, and identified as the cationic complex $[Ir(CO)_2(NOPON^{Me_2})]BAr^F$ (**5**). The presence of coordinated CO molecules was indicated by two absorptions of medium intensity at 2096 and 2038 cm^{-1} in the solid-state IR spectrum of **5** (a weaker band at 2009 cm^{-1} is probably due to solid-state effects since it disappears when the spectrum is recorded in ether solution) and further confirmed by the $^{13}C\{^1H\}$ NMR of the complex, which exhibits a doublet due to the coordinated CO ligands at 173.9 ppm ($^2J_{PC}$ = 60.9 Hz). The $^{31}P\{^1H\}$ NMR spectrum displays a singlet at 116.5 ppm, downfield shifted by about 6 ppm with respect to complex **3**. The NMR spectra of this compound contain only sharp signals, thus indicating that the substitution of the cyclooctadiene ligand by two CO molecules has resulted in an important decrease of the fluxionality of the ligands around the metal center. In particular, the ^1H NMR spectrum of **5** exhibits two sharp doublets for the CH_2 protons of the $NOPON^{Me_2}$ (AB spin system) and four singlets for the methyl protons. This suggests that the two oxazoline arms are symmetrically coordinated to the metal, likely to be pentacoordinated as observed in several trigonal bipyramidal iridium complexes bearing two carbonyl ligands,[39] which have been known for some time.[40] The spectroscopic data are consistent with a mer arrangement of the $NOPON^{Me_2}$ ligand with the two nitrogen atoms in the apical positions and the phosphorus in the equatorial plane. Consequently, the two CO molecules should occupy two equatorial positions, in agreement with the presence of two absorption bands in the IR spectrum of the compound and with one signal due to the carbon atom of the CO in the $^{13}C\{^1H\}$ NMR spectrum. Compound **5** could also be synthesized from the carbonyl compound **2** under CO by addition of 1 equiv of $NaBAr^F$ (Scheme 5).

Scheme 5. Synthesis and Proposed Molecular Structure of Complex **5**



The availability of an uncoordinated oxazoline ring in complex **3** prompted us to attempt the synthesis of polynuclear complexes, where the $NOPON^{Me_2}$ might act as a bridging ligand between two metal centers. Hence, we reacted 2 equiv of **3** with 1 equiv of $[PdCl_2(NCPh)_2]$ in $CDCl_3$. The $^{31}P\{^1H\}$ NMR spectrum of the crude showed two sharp signals at 115.6 and 110.7 ppm, thus indicating that a new compound had formed (δ_P = 115.5 ppm) but that some iridium complex **3** remained unreacted. Slow evaporation of the solvent from the NMR tube yielded some pale yellow crystals, which were identified by X-ray diffraction as the Pd(II) cationic complex $[PdCl(NOPON^{Me_2})]BAr^F$ (**6**). Thus, transfer of the ligand from Ir(I) to Pd(II) had occurred, in preference to the formation of a heteronuclear complex.

Subsequently, compound **6** was directly prepared by reaction of $[PdCl_2(NCMe)_2]$ with $NOPON^{Me_2}$ in dichloromethane followed by addition of $NaBAr^F$ (Scheme 6). The X-ray structure of **6**$\cdot CHCl_3$ in the solid state shows that the metal center lies in an approximately square-planar coordination environment in which the $NOPON^{Me_2}$ ligand acts as a tridentate chelating ligand (see Figure 4). A terminal chloride completes the coordination on palladium. Selected bond distances and angles for **6** are reported in Table 4.

The structural features of the coordinated $NOPON^{Me_2}$ ligand are very similar to those in the dicationic complex $[Pd(NCMe)(NOPON^{Me_2})](BF_4)_2$,[14] and the bond distances involving the Pd atom are slightly longer than in this complex. This can be ascribed to the decrease in the overall charge of the cation from +2 to +1.

Conclusions

Coordination complexes of Ir(I) containing the bis(oxazoline)phosphonite ligand $NOPON^{Me_2}$ have been described and their reactivity toward H_2 and CO investigated.

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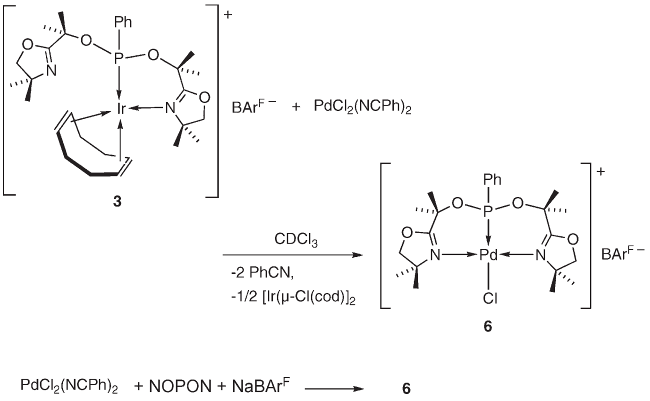
Scheme 6. Synthesis of Complex **6**



Complexes containing cod as the ancillary ligand, namely, the neutral complex **1** and its cationic analogue **3**, exhibit a significant fluxionality in solution due to fast exchange equilibria about the metal, which are facilitated by the hemilabile behavior of the NOPON^{Me_2} ligand. The cyclooctadiene molecule could be easily displaced by exposing solutions of **1** and **3** to carbon monoxide (1 atm) at room temperature, which afforded the monocarbonyl derivative **2** and the dicarbonyl derivative **5**, respectively. The molecular structures of **2** and **3** have been elucidated by X-ray diffraction analyses and display distorted square planar geometries. Addition of dihydrogen to the cationic complex **3** was achieved in pentane or in the solid state and has allowed the isolation of **4**, a 32 electron, dinuclear cationic complex of Ir(III), which shows two unusual features, namely, the presence of only hydrides as bridging ligands and a Ir$_2$(μ-H)$_2$ unit which can be viewed as containing a formal Ir−Ir double bond or two 3c−2e bonds. Furthermore, this complex is, to the best of our knowledge, only the second example of a structurally characterized iridium complex containing an N,P,N chelating ligand. Despite the chelating behavior of the NOPON^{Me_2} ligand in **3**, it was readily transferred to Pd(II) as a transmetalation reaction occurred when **3** was reacted with [PdCl$_2$(NCPh)$_2$]. Complex **3** was shown to catalyze the hydrogenation of C=C double bonds and this occurred chemoselectively in the case of 2-cyclohexene-1-one as a substrate. The versatility of the coordination modes of the NOPON^{Me_2} ligand to transition metals was further evidenced in this work. Thus, it can behave as a P, N chelate or as a N, P, N tridentate donor, occupying facial or meridional coordination sites in octahedral metal complexes.

Experimental Section

General Considerations. All operations were carried out using standard Schlenk techniques under inert atmosphere. Solvents were dried, degassed, and freshly distilled prior to use. THF and Et$_2$O were dried over sodium/benzophenone. CH$_2$Cl$_2$ was distilled from CaH$_2$. CD$_2$Cl$_2$, CDCl$_3$, and C$_6$D$_6$ were dried over 4 Å molecular sieves, degassed by freeze−pump−thaw cycles, and stored under argon. THF-d_8 was used as received. Unless otherwise stated, NMR spectra were recorded at room temperature on a Bruker AVANCE 300 spectrometer (^{1}H, 300 MHz; ^{13}C, 75.47 MHz; ^{19}F, 282.4 MHz; ^{31}P, 121.5 MHz) or on a Bruker AVANCE 400 spectrometer (^{1}H, 400 MHz; ^{13}C, 100.60 MHz, ^{31}P, 162.0 MHz,) and referenced using the residual proton solvent (^{1}H) or solvent (^{13}C) resonance. Assignments are based on DEPT135, correlation spectroscopy (COSY), heteronuclear multiple quantum coherence (HMQC), and heteronuclear multiple bond correlation (HMBC) experiments. IR spectra were recorded in the region 4000−100 cm^{-1} on a Nicolet 6700 FT-IR spectrometer equipped with a Smart Orbit ATR accessory (Ge or diamond crystals). Elemental analyses were performed by the "Service de microanalyse", Université de Strasbourg. Electrospray mass spectra (ESI-MS) were recorded on a microTOF (Bruker Daltonics, Bremen, Germany) instrument using nitrogen as the drying agent and nebulizing gas, and MALDI-TOF analyses were carried out on a Bruker AutoflexII TOF/TOF (Bruker Daltonics, Bremen, Germany), using dithranol (1,8,9-trihydroxyanthracene) as a matrix. Yields of the metal complexes are based on iridium. GC analyses were performed on a Thermoquest GC8000 Top Series gas chromatograph using a HP Pona column (50 m, 0.2 mm diameter, 0.5 μm film thickness). [Ir(μ-Cl)(cod)]$_2$ was purchased from UMICORE and used as received. [PdCl$_2$(NCPh)$_2$],[41] [PdCl$_2$(NCMe)$_2$],[42] NOPON^{Me_2},[14] and Na[B(3,5-(CF$_3$)$_2$C$_6$H$_3$)$_4$][43] were prepared according to literature methods. Other chemicals were commercially available and used as received.

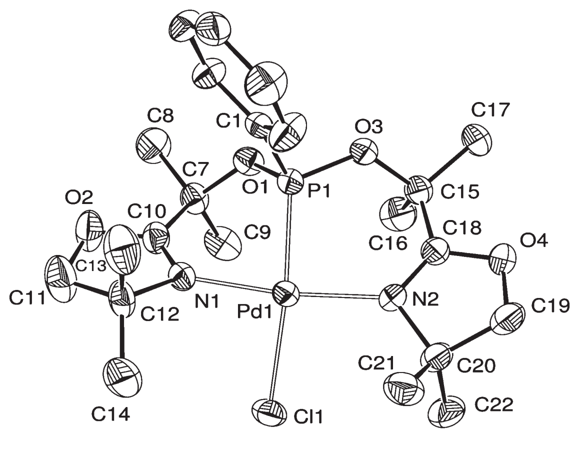


Figure 4. ORTEP of complex **6** in **6**·CHCl$_3$ with ellipsoids drawn at the 50% probability level. The anion, solvent molecules, and hydrogen atoms are omitted for clarity.

Table 4. Selected Bond Distances (Å) and Angles (deg) for [PdCl(NOPON^{Me_2})]BAr^F (**6**) in **6**·CHCl$_3$

Pd(1)−Cl(1)	2.3667(12)	C(10)−N(1)	1.289(6)
Pd(1)−P(1)	2.1811(12)	C(10)−O(2)	1.328(6)
Pd(1)−N(1)	2.049(4)	C(18)−N(2)	1.281(6)
Pd(1)−N(2)	2.068(4)	C(18)−O(4)	1.328(6)
N(2)−Pd(1)−Cl(1)	96.78(11)	N(2)−Pd(1)−P(1)	90.05(11)
N(1)−Pd(1)−P(1)	82.79(11)	N(1)−Pd(1)−Cl(1)	90.97(11)
P(1)−Pd(1)−Cl(1)	167.19(5)	N(1)−Pd (1)−N(2)	171.90(15)

Synthesis of [IrCl(cod)(NOPON^{Me_2})] (1). The complex [Ir(μ-Cl)(cod)]$_2$ (203 mg, 0.302 mmol) was dissolved in a solution of NOPON^{Me_2} (254 mg, 0.605 mmol) in CH$_2$Cl$_2$ (5 mL), and the reaction mixture was stirred overnight at room temperature. The solution was concentrated under reduced pressure to 1 mL, and pentane was added (100 mL) to afford a suspension. After the pale red solid was filtered and washed with pentane (3 × 100 mL), the combined filtrates were evaporated under reduced pressure to give a yellow-orange powder which was dried under vacuum. Yield: 270 mg (58%). Selected IR absorptions (pure, diamond attenuated total reflectance (ATR)): 2963 mw, 1662 m, 1260 s, 1108 s, 1017 vs, 968 s, 798 vs, 749 m, 697 m, 304 (Ir−Cl) cm^{-1}. ^{1}H NMR (300.13 MHz, CDCl$_3$): δ 7.95−7.87 (m, 2H, *o*-aryl), 7.41−7.38 (m, 3H, *m*- and *p*-aryl), 5.2−3.2 (vbr, 4H, CH

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[43] Yakelis, N. A.; Bergman, R. G. *Organometallics* **2005**, *24*, 3579.

cod), 3.97 and 3.85 (AB spin system, $^2J_{\mathrm{HH}}$ = 8.1 Hz, 4H, $\mathrm{OCH_2}$), 2.40−2.15 (m, 4H, $\mathrm{CH_2}$ cod), 2.05−1.85 (m, 4H, $\mathrm{CH_2}$ cod), 1.81 (s, 6H, $\mathrm{OC}(\mathrm{C}H_3)(\mathrm{CH_3})$), 1.75 (s, 6H, $\mathrm{OC}(\mathrm{CH_3})(\mathrm{C}H_3)$), 1.21 (s, 6H, $\mathrm{NC}(\mathrm{C}H_3)(\mathrm{CH_3})$), 1.17 (s, 6H, $\mathrm{NC}(\mathrm{CH_3})(\mathrm{C}H_3)$) ppm. $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (75.5 MHz, $\mathrm{CDCl_3}$): δ 166.9 (d, $^3J_{\mathrm{PC}}$ = 3.7 Hz, C=N), 137.0 (d, $^1J_{\mathrm{PC}}$ = 71.5 Hz, *ipso*-aryl), 131.6 (d, $^2J_{\mathrm{PC}}$ = 15.8 Hz, *o*-aryl), 130.9 (d, $^4J_{\mathrm{PC}}$ = 2.3 Hz, *p*-aryl), 127.9 (d, $^3J_{\mathrm{PC}}$ = 11.8 Hz, *m*-aryl), 79.4 (s, $\mathrm{O}C(\mathrm{CH_3})_2$), 79.3 (s, $\mathrm{OCH_2}$), 67.3 (s, $\mathrm{N}C(\mathrm{CH_3})_2$), 31.5 (br, $\mathrm{CH_2}$ cod), 28.3 (d, $^3J_{\mathrm{PC}}$ = 4.5 Hz, $\mathrm{OC}(C\mathrm{H_3})(\mathrm{CH_3})$), 28.1 (s, $\mathrm{NC}(C\mathrm{H_3})(\mathrm{CH_3})$), 27.8 (s, $\mathrm{NC}(\mathrm{CH_3})(C\mathrm{H_3})$), 27.0 (d, $^3J_{\mathrm{PC}}$ = 5.5 Hz, $\mathrm{OC}(\mathrm{CH_3})(C\mathrm{H_3})$) ppm. $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR (121.5 MHz, $\mathrm{CDCl_3}$): δ 103.2 (s) ppm. MALDI-TOF MS: *m*/*z* (%) 721.35 (100) $[^{193}\mathrm{Ir(cod)(NOPON^{Me_2})}]^+$, 719.34 (60) $[^{191}\mathrm{Ir(cod)(NOPON^{Me_2})}]^+$, 648.28 (15) $[^{193}\mathrm{Ir}^{35}\mathrm{Cl(NOPON^{Me_2})}]^+$. Anal. Calcd for $\mathrm{C_{30}H_{45}ClIrN_2O_4P\cdot CH_2Cl_2}$: C, 44.26; H, 5.63; N, 3.33. Found: C, 43.86; H, 5.66; N, 3.73.

Synthesis of $[\mathbf{IrCl(CO)(NOPON^{Me_2})}]$ (2). The complex $[\mathrm{Ir}(\mu\text{-}\mathrm{Cl})(\mathrm{cod})]_2$ (200 mg, 0.298 mmol) was dissolved in a solution of $\mathrm{NOPON^{Me_2}}$ (250 mg, 0.595 mmol) in $\mathrm{CH_2Cl_2}$ (5 mL) placed in a Schlenk tube. After 4 h, the flask was filled with CO. The orange solution quickly became pale yellow. The solution was concentrated to 1 mL, and pentane was added. The compound [IrCl(CO)(NOPONMe$_2$)] precipitated as a pale yellow solid which was collected by filtration and dried under vacuum. Yield: 277 mg (69%). Selected IR absorptions (pure, germanium ATR): 1989 vs, 1656 w, 1608 m, 1327 w, 1153 m, 1116 m, 973 ms, 751 ms, 290 (Ir−Cl) cm^{-1}. ^{1}H NMR (300.13 MHz, $\mathrm{CDCl_3}$): δ 8.00−7.93 (m, 2H, *o*-aryl), 7.48−7.36 (m, 3H, *m*- and *p*-aryl), 4.25 and 4.07 (AB spin system, $^2J_{\mathrm{HH}}$ = 8.2 Hz, 2H, $\mathrm{OCH_2}$ coordinated oxazoline), 4.19 and 3.97 (AB spin system, $^2J_{\mathrm{HH}}$ = 8.0 Hz, 2H, $\mathrm{OCH_2}$ uncoordinated oxazoline), 1.94 (s, 3H, $\mathrm{OC}(\mathrm{CH_3})(\mathrm{C}H_3)$ coordinated oxazoline), 1.87 (s, 3H, $\mathrm{NC}(\mathrm{C}H_3)(\mathrm{CH_3})$ coordinated oxazoline), 1.78 (s, 3H, $\mathrm{OC}(\mathrm{C}H_3)(\mathrm{CH_3})$ uncoordinated oxazoline), 1.71 (s, 3H, $\mathrm{NC}(\mathrm{CH_3})(\mathrm{C}H_3)$ coordinated oxazoline), 1.68 (s, 3H, $\mathrm{OC}(\mathrm{CH_3})(\mathrm{C}H_3)$ uncoordinated oxazoline), 1.61 (s, 3H, $\mathrm{OC}(\mathrm{C}H_3)(\mathrm{CH_3})$ coordinated oxazoline), 1.50 (s, 3H, $\mathrm{NC}(\mathrm{C}H_3)(\mathrm{CH_3})$ uncoordinated oxazoline), 1.24 (s, 3H, $\mathrm{NC}(\mathrm{CH_3})(\mathrm{C}H_3)$ uncoordinated oxazoline) ppm. $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (75.5 MHz, $\mathrm{CDCl_3}$): δ 173.0 (s, CO), 172.8 (s, C=N uncoordinated oxazoline), 166.8 (s, C=N coordinated oxazoline), 140.4 (d, $^1J_{\mathrm{PC}}$ = 108 Hz, *ipso*-aryl), 131.3 (d, $^4J_{\mathrm{PC}}$ = 2.0 Hz, *p*-aryl), 130.8 (d, $^2J_{\mathrm{PC}}$ = 14.8 Hz, *o*-aryl), 128.0 (d, $^3J_{\mathrm{PC}}$ = 11.8 Hz, *m*-aryl), 83.2 (s, $\mathrm{OCH_2}$ coordinated oxazoline), 79.2 (s, $\mathrm{OCH_2}$ uncoordinated oxazoline), 72.7 (s, $\mathrm{N}C(\mathrm{CH_3})_2$ coordinated oxazoline), 67.8 (s, $\mathrm{N}C(\mathrm{CH_3})_2$ uncoordinated oxazoline), 30.1 (s, 3H, $\mathrm{OC}(\mathrm{CH_3})(C\mathrm{H_3})$ coordinated oxazoline), 29.2 (d, $^3J_{\mathrm{CP}}$ = 7.1 Hz, 3H, $\mathrm{OC}(C\mathrm{H_3})(\mathrm{CH_3})$ uncoordinated oxazoline), 28.8 (s, $\mathrm{NC}(C\mathrm{H_3})(\mathrm{CH_3})$ uncoordinated oxazoline), 28.6 (s, 3H, $\mathrm{NC}(\mathrm{CH_3})(C\mathrm{H_3})$ coordinated oxazoline), 27.6 (s, 3H, $\mathrm{NC}(\mathrm{CH_3})(C\mathrm{H_3})$ uncoordinated oxazoline), 27.1 (s, $\mathrm{OC}(C\mathrm{H_3})(\mathrm{CH_3})$ coordinated oxazoline), 26.9 (s, $\mathrm{OC}(\mathrm{CH_3})(C\mathrm{H_3})$ uncoordinated oxazoline), 25.4 (s, 3H, $\mathrm{NC}(C\mathrm{H_3})(\mathrm{CH_3})$ coordinated oxazoline) ppm, signals of $\mathrm{O}C(\mathrm{CH_3})_2$ are masked by the peak of $\mathrm{CDCl_3}$. $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR (121.5 MHz, $\mathrm{CDCl_3}$): δ 102.1 (s) ppm. ESI-MS: *m*/*z* (%) 682.157 (100) $[^{193}\mathrm{Ir}^{35}\mathrm{ClN_2O_5PC_{23}H_{32}Li}]^+$, 680.154 (59) $[^{191}\mathrm{Ir}^{35}\mathrm{ClN_2O_5PC_{23}H_{32}Li}]^+$, 641.132 (10) $[^{193}\mathrm{IrN_2O_5PC_{23}H_{33}}]^+$. Anal. Calcd for $\mathrm{C_{23}H_{34}ClIrN_2O_5P}$: C, 40.79; H, 5.06; N, 4.14. Found: C, 40.49; H, 5.04; N, 3.78. Crystals suitable for X-ray diffraction were grown by slow diffusion of $\mathrm{Et_2O}$ in a concentrated solution of the compound in $\mathrm{CH_2Cl_2}$.

Synthesis of $[\mathbf{Ir(cod)(NOPON^{Me_2})}][\mathbf{B(3,5\text{-}(CF_3)_2C_6H_3)_4}]$ (3). The complex $[\mathrm{Ir}(\mu\text{-}\mathrm{Cl})(\mathrm{cod})]_2$ (218 mg, 0.325 mmol) was dissolved in a solution of $\mathrm{NOPON^{Me_2}}$ (272 mg, 0.647 mmol) in $\mathrm{CH_2Cl_2}$ (15 mL), and the solution was stirred for 1 h at room temperature. Solid $\mathrm{Na[B(3,5\text{-}(CF_3)_2C_6H_3)_4]}$ (580 mg, 0.654 mmol) was added and the orange solution rapidly turned red. The suspension was allowed to stir overnight at room temperature. The solvent was removed by evaporation under reduced pressure, and $\mathrm{Et_2O}$ (20 mL) was added. The resulting suspension was filtered to remove NaCl, and the volume of the solution was reduced to 3 mL. Addition of pentane afforded an orange-red precipitate, which was collected by filtration, washed with pentane (3 × 15 mL), and dried under vacuum. Yield: 940 mg (0.594 mmol, 92%). Selected IR absorptions (pure, diamond ATR): 1671 vw, 1605 w, 1353 m, 1276 vs, 1165 m, 1129 vs, 1022 w, 993 w, 965 w, 682 w cm^{-1}. ^{1}H NMR (300.13 MHz, $\mathrm{CDCl_3}$): δ 7.73 (br, 8H, *o*-BAr$^{\mathrm{F}}$), 7.62−6.47 (m, 9H, overlapping CH aryl and *p*-BAr$^{\mathrm{F}}$), 5.38 (vbr, 2H, CH cod), 4.5−3.0 (m, 6H, overlapping $\mathrm{CH_2}$ $\mathrm{NOPON^{Me_2}}$ and CH cod), 3.0−0.1 (m, 32H, overlapping $\mathrm{CH_2}$ cod and $\mathrm{CH_3}$) ppm. $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (75.5 MHz, $\mathrm{CDCl_3}$): δ 161.7 (q, $^1J_{\mathrm{BC}}$ = 49.8 Hz, *ipso*-BAr$^{\mathrm{F}}$), 134.8 (s, *o*-BAr$^{\mathrm{F}}$), 134.6 (d, $^2J_{\mathrm{PC}}$ = 69.4 Hz, *ipso*-aryl), 132.8 (d, $^4J_{\mathrm{PC}}$ = 2.4 Hz, *p*-aryl), 130.1 (d, $^2J_{\mathrm{PC}}$ = 14.9 Hz, *o*-aryl), 129.3 (d, $^3J_{\mathrm{PC}}$ = 11.6 Hz, *m*-aryl), 128.9 (qq, $^2J_{\mathrm{CF}}$ = 31.6 Hz, $^3J_{\mathrm{BC}}$ = 2.9 Hz, $C\mathrm{CF_3}$), 124.6 (q, $^1J_{\mathrm{CF}}$ = 272.5 Hz, $\mathrm{CF_3}$), 117.5 (sept, $^3J_{\mathrm{CF}}$ = 3.9 Hz, *p*-BAr$^{\mathrm{F}}$), 27.8 (s, $\mathrm{CH_3}$), 27.4 (s, $\mathrm{CH_3}$) ppm. $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR (121.5 MHz, $\mathrm{CDCl_3}$): δ 110.7 (s) ppm. $^{19}\mathrm{F}\{^1\mathrm{H}\}$ NMR (282.4 MHz, $\mathrm{CDCl_3}$): −62.8 ppm. MALDI-TOF MS: *m*/*z* (%) 720.73 (100) $[^{193}\mathrm{Ir(cod)(NOPON^{Me_2})}]^+$, 718.71 (52) $[^{191}\mathrm{Ir(cod)(NOPON^{Me_2})}]^+$. Anal. Calcd for $\mathrm{C_{62}H_{57}BF_{24}IrN_2O_4P}$: C, 47.01; H, 3.63; N, 1.77. Found: C, 47.04; H, 3.59; N, 1.92. Crystals suitable for X-ray diffraction were formed by addition of excess $\mathrm{Na[B(3,5\text{-}(CF_3)_2C_6H_3)_4]}$ to a solution of **1** in $\mathrm{C_6D_6}$.

Reaction of $[\mathbf{Ir(cod)(NOPON^{Me_2})}][\mathbf{B(3,5\text{-}(CF_3)_2C_6H_3)_4}]$ with $\mathbf{H_2}$: Isolation of $[\mathbf{IrH(\mu\text{-}H)\ (NOPON^{Me_2})}]_2[\mathbf{B(3,5\text{-}(CF_3)_2C_6H_3)_4}]_2$ (4) in the Solid State. Compound **3** (40 mg, 0.025 mmol) was dissolved in THF-d_8 (0.45 mL) in a NMR tube under Ar and placed in a Schlenk flask, which has been evacuated and filled with hydrogen. The solution quickly turned pale yellow. ^{1}H NMR (300.13 MHz, THF-d_8): δ 7.97−7.80 (m, 10H, *o*-aryl and *o*-BAr$^{\mathrm{F}}$), 7.58−7.51 (m, 7H, *m*-, *p*-aryl, and *p*-BAr$^{\mathrm{F}}$), 4.64 and 4.19 (AB spin system, 2H, $^2J_{\mathrm{HH}}$ = 8.9 Hz, $\mathrm{OCH_2}$), 4.35 and 3.94 (AB spin system, 2H, $^2J_{\mathrm{HH}}$ = 8.6 Hz, $\mathrm{OCH_2}$), 1.84 (s, 3H, $\mathrm{CH_3}$), 1.82 (s, 3H, $\mathrm{CH_3}$), 1.76 (s, 3H, $\mathrm{CH_3}$), 1.66 (s, 3H, $\mathrm{CH_3}$), 1.44 (s, 3H, $\mathrm{CH_3}$), 1.41 (s, 3H, $\mathrm{CH_3}$), 1.32 (s, 3H, $\mathrm{CH_3}$), 1.11 (s, 3H, $\mathrm{CH_3}$), −25.99 (d, 1H, $^2J_{\mathrm{PH}}$ = 15.0, Ir−H) ppm. $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (75.5 MHz, $\mathrm{CDCl_3}$): δ 167.5 (d, $^3J_{\mathrm{PC}}$ = 7.9 Hz, C=N), 165.7 (d, $^3J_{\mathrm{PC}}$ = 4.8 Hz, C=N), 160.0 (q, $^1J_{\mathrm{BC}}$ = 49.8 Hz, *ipso*-BAr$^{\mathrm{F}}$), 135.6 (d, $^2J_{\mathrm{PC}}$ = 95.15 Hz, *ipso*-aryl), 132.8 (s, *o*-BAr$^{\mathrm{F}}$), 130.7 (d, $^4J_{\mathrm{PC}}$ = 2.3 Hz, *p*-aryl), 128.6 (d, $^2J_{\mathrm{PC}}$ = 16.1 Hz, *o*-aryl), 127.2 (qq, $^2J_{\mathrm{CF}}$ = 31.5 Hz, $^3J_{\mathrm{BC}}$ = 2.8 Hz, $C\mathrm{CF_3}$), 126.5 (d, $^3J_{\mathrm{PC}}$ = 13.1 Hz, *m*-aryl), 122.7 (q, $^1J_{\mathrm{CF}}$ = 272.5 Hz, $\mathrm{CF_3}$), 115.4 (sept, $^3J_{\mathrm{CF}}$ = 3.9 Hz, *p*-BAr$^{\mathrm{F}}$), 77.9 (s, unassigned), 77.7 (d, J = 7.8 Hz, unassigned), 77.3 (s, $\mathrm{OCH_2}$), 76.4 (d, J = 6.1, unassigned), 75.9 (s, $\mathrm{OCH_2}$), 73.4 (d, J = 1.3 Hz, unassigned), 72.6 (s, $\mathrm{O}C(\mathrm{CH_3})_2$), 71.3 (s, $\mathrm{O}C(\mathrm{CH_3})_2$), 68.5 (s, $\mathrm{N}C(\mathrm{CH_3})_2$), 67.9 (s, $\mathrm{N}C(\mathrm{CH_3})_2$), 60.8 (s), 29.0−21.0 (m, $\mathrm{CH_3}$) ppm. $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR (162.0 MHz, $\mathrm{CD_2Cl_2}$): δ 123.8 (s) ppm. $^{19}\mathrm{F}\{^1\mathrm{H}\}$ NMR (282.4 MHz, $\mathrm{CDCl_3}$): −65.7 ppm. The same reaction was carried out in $\mathrm{CH_2Cl_2}$ (50 mg of **3** in 5 mL). After a few hours, colorless single crystals of $[\mathrm{Ir}(\mu\text{-}\mathrm{H})\mathrm{H(NOPON^{Me_2})}]_2[\mathrm{B(3,5\text{-}(CF_3)_2C_6H_3)_4}]_2$ formed, whose structure was determined by X-ray diffraction to be that of a dinuclear complex, **4**, too unstable in solution to be analyzed.

Synthesis of $[\mathbf{Ir(NOPON)(CO)_2}][\mathbf{B(3,5\text{-}(CF_3)_2C_6H_3)_4}]$ (5). An orange solution of **3** (150 mg, 0.095 mmol) in $\mathrm{CH_2Cl_2}$ (10 mL) was treated with CO at 1 atm. The solution quickly turned yellow. The solvent was evaporated under reduced pressure. The resulting yellow solid was washed with pentane (2 × 3 mL) and dried under vacuum. Yield: 115 mg (0.075 mmol, 79%). Selected IR absorptions (pure, germanium ATR): 2096 m, 2038 m, 2009 w, 1663 vw, 1610 mw, 1354 ms, 1276 vs, 1122 vs cm^{-1}. ^{1}H NMR (300.13 MHz, $\mathrm{CDCl_3}$): δ 7.75−7.45 (m, 17H, aromatic protons), 4.08 and 3.99 (AB spin system, $^2J_{\mathrm{HH}}$ = 8.8 Hz, 2H, $\mathrm{OCH_2}$), 1.82 (s, 6H, $\mathrm{OC}(\mathrm{C}H_3)(\mathrm{CH_3})$), 1.70 (s, 6H, $\mathrm{OC}(\mathrm{CH_3})(\mathrm{C}H_3)$), 1.26 (s, 6H, $\mathrm{NC}(\mathrm{C}H_3)(\mathrm{CH_3})$), 1.07 (s, 6H, $\mathrm{NC}(\mathrm{CH_3})(\mathrm{C}H_3)$) ppm. $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (75.5 MHz, $\mathrm{CDCl_3}$): 173.9 (d, $^2J_{\mathrm{PC}}$ = 60.9 Hz, CO),

Table 5. Crystal Data and Structure for **2**·CH_2Cl_2, **3**·0.5(C_6H_6), **4**·4(CH_2Cl_2), and **6**·$CHCl_3$

	2·CH_2Cl_2	**3**·0.5C_6H_6	**4**·4CH_2Cl_2	**6**·$CHCl_3$
formula	$C_{23}H_{33}ClIrN_2O_5P\cdot CH_2Cl_2$	$C_{62}H_{57}IrBF_{24}N_2O_4P\cdot 0.5(C_6H_6)$	$C_{108}H_{94}B_2F_{48}Ir_2N_4O_8P_2\cdot 4(CH_2Cl_2)$	$C_{54}H_{45}BClF_{24}N_2O_4PPd\cdot CHCl_3$
M_r/g mol $^{-1}$	761.06	1623.13	3295.54	1544.92
crystal system	monoclinic	monoclinic	triclinic	monoclinic
space group	$C2/c$	$P2_1/c$	$P\bar{1}$	$C2/c$
T/K	173 (2)	173 (2)	173 (2)	173 (2)
a/Å	40.250(2)	13.7530(3)	12.4044(11)	19.0888(3)
b/Å	9.0131(5)	23.6740(7)	14.6314(10)	18.4791(3)
c/Å	17.7372(5)	24.5963(6)	18.9398(17)	36.2002(7)
α/deg	90	90	71.857(4)	90
β/deg	113.674(2)	122.268 (2)	79.532(3)	100.196(1)
γ/deg	90	90	87.282(5)	90
V/Å^3	5893.0(5)	6771.5 (3)	3212.0(5)	12567.7 (4)
Z	8	4	1	8
crystal size/mm	0.08 × 0.08 × 0.04	0.15 × 0.14 × 0.09	0.14 × 0.12 × 0.07	0.35 × 0.32 × 0.30
D_{calcd}/g cm^{-3}	1.716	1.592	1.704	1.633
μ/mm^{-1}	4.89	2.11	2.39	0.61
θ max/deg	26.5	26.0	30.1	27.5
R_{int}	0.0458	0.0754	0.0948	0.0678
final R indices	$R_1 = 0.0472$	$R_1 = 0.0526$	$R_1 = 0.0702$	$R_1 = 0.0642$
[$I > 2\sigma(I)$]	$wR_2 = 0.1191$	$wR_2 = 0.1114$	$wR_2 = 0.1516$	$wR_2 = 0.1726$
no. of measd, independent, and obsvd reflns	10 079, 6109, 4497	35 689, 13 281, 8171	19 854, 19 854, 13 784	38 471, 14 298, 8344
R indices all data	$R_1 = 0.0770$ $wR_2 = 0.1447$	$R_1 = 0.1095$ $wR_2 = 0.1258$	$R_1 = 0.1207$ $wR_2 = 0.1738$	$R_1 = 0.1278$ $wR_2 = 0.2241$
S on F^2	1.049	0.999	1.069	0.995

$R_1 = \Sigma\|F_o| - |F_c\|/|\Sigma(F_o)$; $wR_2 = \Sigma w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$.

169.8 (d, $^3J_{PC}$ = 5.2 Hz, C=N), 161.7 (q, $^1J_{BC}$ = 49.8 Hz, *ipso*-BAr^F), 134.8 (s, *o*-BAr^F), 134.2 (d, $^4J_{PC}$ = 2.6 Hz, *p*-aryl), 132.0 (d, $^1J_{PC}$ = 83.7 Hz, *ipso*-aryl), 130.6 (d, $^2J_{PC}$ = 15.8 Hz, *o*-aryl), 129.7 (d, $^3J_{PC}$ = 13.0 Hz, *m*-aryl), 128.9 (qq, $^2J_{CF}$ = 31.6 Hz, $^3J_{BC}$ = 2.9 Hz, *C*CF$_3$), 124.6 (q, $^1J_{CF}$ = 272.5 Hz, CF$_3$), 117.5 (sept, $^3J_{CF}$ = 3.9 Hz, *p*-BAr^F), 83.3 (d, $^2J_{PC}$ = 9.7 Hz, O*C*-(CH$_3$)$_2$), 80.4 (s, OCH$_2$), 70.1 (s, N*C*(CH$_3$)$_2$), 28.8 (d, $^3J_{PC}$ = 6.0 Hz, OC(*C*H$_3$)(CH$_3$)), 28.2 (s, NC(CH$_3$)(*C*H$_3$)), 27.6 (d, $^3J_{PC}$ = 5.1 Hz, OC(CH$_3$)(*C*H$_3$)), 27.5 (s, NC(*C*H$_3$)(CH$_3$)) ppm. ^{31}P{^{1}H} NMR (121.5 MHz, CDCl$_3$): δ 116.5 (s) ppm. ^{19}F{^{1}H} NMR (282.4 MHz, CDCl$_3$): −62.8 ppm. MALDI-TOF MS: *m*/*z* (%) 641.13 (25) [^{193}Ir(CO)(NOPON^{Me_2}) − H]$^+$, 613.15 (100) [^{193}Ir-(NOPON^{Me_2})]$^+$, 611.15 (60) [^{191}Ir(NOPON^{Me_2})]$^+$. Anal. Calcd for $C_{56}H_{47}BF_{24}IrN_2O_6P$: C, 43.85; H, 3.09; N, 1.83. Found: C, 43.41; H, 3.21; N, 1.71.

Synthesis of [PdCl(NOPON)][B(3,5-(CF$_3$)$_2$C$_6$H$_3$)$_4$] (6). Solid [PdCl$_2$(NCMe)$_2$] (80 mg, 0.308 mmol) was dissolved in a CH$_2$Cl$_2$ solution of NOPON^{Me_2} (130 mg, 0.309 mmol) to give a pale yellow solution. After 1 h, NaBAr^F (274 mg, 0.309 mmol) was added. The mixture was stirred overnight at room temperature and then filtered to remove NaCl. The solvent was evaporated under reduced pressure, and the resulting pale yellow powder was washed with pentane (2 × 5 mL), collected by filtration, and dried under vacuum. Yield: 420 mg (94%). Selected IR absorptions (pure, diamond ATR): 1612 mw, 1376 s, 1276 vs, 1161 s, 1123 vs, 991 m, 973 m, 716 m cm^{-1}. ^{1}H NMR (300.13 MHz, CDCl$_3$): δ 7.75−7.35 (m, 17H, aromatic protons), 4.35 and 4.14 (AB spin system, $^2J_{HH}$ = 9.0 Hz, 2H, OCH$_2$), 2.30 (s, 6H, OC(CH$_3$)(C*H*$_3$)), 1.76 (s, 6H, NC(CH$_3$)(C*H*$_3$)), 1.68 (d, $^3J_{PH}$ = 2.0 Hz, 6H, OC(C*H*$_3$)(CH$_3$)), 1.47 (s, 6H, NC(C*H*$_3$)(CH$_3$)) ppm. ^{13}C{^{1}H} NMR (75.5 MHz, CDCl$_3$): δ 171.9 (d, $^3J_{PC}$ = 10.4 Hz, C=N), 161.7 (q, $^1J_{BC}$ = 49.9 Hz, *ipso*-BAr^F), 135.5 (d, $^4J_{PC}$ = 3.0 Hz, *p*-aryl), 134.8 (s, *o*-BAr^F), 130.1 (d, $^3J_{PC}$ = 14.6 Hz, *m*-aryl), 129.6 (d, $^4J_{PC}$ = 16.2 Hz, *o*-aryl), 128.9 (qq, $^2J_{CF}$ = 31.6 Hz, $^3J_{BC}$ = 2.9 Hz, *C*CF$_3$), *ipso*-aryl masked by *C*CF$_3$ signals, 124.6 (q, $^1J_{CF}$ = 272.5 Hz, CF$_3$), 117.5 (sept, $^3J_{CF}$ = 3.9 Hz, *p*-BAr^F), 83.5 (s, OCH$_2$), 83.2 (d, $^2J_{PC}$ = 5.0 Hz, O*C*(CH$_3$)$_2$), 72.7 (s, N*C*(CH$_3$)$_2$), 29.9 (d, $^3J_{PC}$ = 3.5 Hz, OC(*C*H$_3$)(CH$_3$)), 28.2 (s, NC(*C*H$_3$)(CH$_3$)), 26.9 (s, NC(CH$_3$)(*C*H$_3$)), 24.9 (d, $^3J_{PC}$ = 7.1 Hz, OC(CH$_3$)(*C*H$_3$)) ppm. ^{31}P{^{1}H} NMR (121.5 MHz, CDCl$_3$): δ 115.6 (s) ppm. ^{19}F{^{1}H} NMR (282.4 MHz, CDCl$_3$): −62.8 ppm. MALDI-TOF MS: *m*/*z* (%) 564.99 (50) [^{108}Pd^{37}Cl(NOPON^{Me_2})]$^+$, 562.99 (95) [^{106}Pd^{37}Cl(NOPON^{Me_2})]$^+$ and [^{108}Pd^{35}Cl(NOPON^{Me_2})]$^+$, 561.00 (100) [^{106}Pd^{35}Cl(NOPON^{Me_2})]$^+$, 526.03 (45) [^{106}Pd(NOPON^{Me_2})]$^+$. Anal. Calcd for $C_{54}H_{45}BClF_{24}N_2O_4PPd$: C, 45.5; H, 3.18; N, 1.97. Found: C, 43.66 ; H, 3.73; N, 1.90 (no better carbon analysis could be obtained, despite several attempts). Crystals suitable for X-ray diffraction were obtained in an NMR tube by slow evaporation of CDCl$_3$ from the solution of **1**.

X-ray Crystal Structure Analyses of 2·CH$_2$Cl$_2$, 3·0.5(C$_6$H$_6$), 4·4(CH$_2$Cl$_2$), and 6·CHCl$_3$. Suitable crystals for the X-ray analysis of all compounds were obtained as described above. The intensity data were collected at 173(2) K on a Kappa CCD diffractometer[44] (graphite monochromated Mo Kα radiation, λ = 0.710 73 Å). Crystallographic and experimental details for the structures are summarized in Table 5. The structures were solved by direct methods (SHELXS-97) and refined by full-matrix least-squares procedures (based on F^2, SHELXL-97)[45] with anisotropic thermal parameters for all the non-hydrogen atoms. The hydrogen atoms were introduced into the geometrically calculated positions (SHELXS-97 procedures) and refined riding on the corresponding parent atoms. Details about the structure refinements are summarized below.

In the crystals of **2**·CH$_2$Cl$_2$, the dichloromethane molecule was found disordered in two positions with equal occupancy factors. The disorder is probably higher, but attempts to find a satisfactory model failed. This molecule was then refined with restrained isotropic parameters and restrained C−Cl and Cl···Cl distances. The C18 atom is close to this disorder and it has been refined with restrained anisotropic parameters.

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[44] Nonius. *Kappa CCD Reference Manual*; Nonius BV: Delft, The Netherlands, 1998.

[45] Sheldrick, G. M. *SHELX-97 Program for Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, 1997.

In the crystals of **3**·0.5(C_6H_6), the CF_3 groups of the BAr^F anion were found severely disordered, the images having the carbon atom in common. In each of the three disordered CF_3 groups, the fluorine atoms were introduced in two calculated positions, tilted by 60°, and refined riding to the parent carbon (SHELXL AFIX 128). The two images have unequal occupancy factor. The F atoms were then refined with restrained anisotropic parameters. The benzene molecule was found disordered in two positions around the symmetry center, having no atom in common. The solvent was refined isotropically with ideal geometry (SHELXL AFIX 66).

An anion disorder similar to that found in **3**·0.5(C_6H_6) was observed in **4**·4CH_2Cl_2. The refinement was performed with restrains similar to those applied for **3**·0.5(C_6D_6). In addition, one of the two dichloromethane molecules was refined with restrained C−Cl distances and anisotropic parameters. The two hydrides were found in the ΔF^2 maps. They were then refined with Ir−H distances restrained to 1.8 Å.

The aforementioned disorder of the BAr^F anion was also present in **6**·$CHCl_3$. One of the CF_3 groups was disordered in two positions having the carbon atom in common and was refined with equal anisotropic displacements and with restrained geometrical parameters. A MULTISCAN[46,47] absorption correction was applied to all compounds except **6**·$CHCl_3$.

CCDC 740920−740923 contain the supplementary crystallographic data for this paper that can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

General Procedure for the Hydrogenation Experiments. In a 10 mL Schlenk tube, compound **3** (7.7 mg, 4.86 μmol) and 1-octene (0.46 mL, 293 μmol) were dissolved in PhCl (1 mL). The solution was degassed under vacuum (freeze−pump−thaw), and the Schlenk tube was connected to a hydrogen generator through its stopcock and refilled with 1.5 atm of hydrogen. The solution was then heated at 60 °C and stirred for 2 h. The hydrogen feed was always provided by the hydrogen generator. After removal of the catalyst by means of a silica column, the solution was diluted with ether and analyzed by gas chromatography using 1-heptene as an internal standard.

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Supporting Information Available: Data for hydrogenation of alkenes with **3**, ^1H NMR spectra of **1** at variable temperatures, and CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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