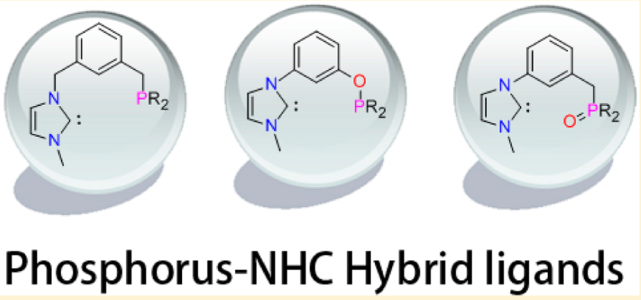
Inorganic Chemistry
Article
pubs.acs.org/IC

Complexes with Hybrid Phosphorus-NHC Ligands: Pincer-Type Ir Hydrides, Dinuclear Ag and Ir and Tetranuclear Cu and Ag Complexes

Xianghao Liu and Pierre Braunstein*

Laboratoire de Chimie de Coordination, Institut de Chimie, UMR 7177 CNRS, Université de Strasbourg, 4 rue Blaise Pascal, CS 90032, 67081 Strasbourg Cedex, France

Supporting Information

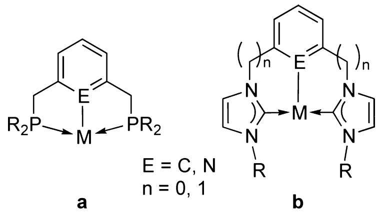


ABSTRACT: Three types of hybrid phosphorus-imidazolium salts, 1-methyl-3-(3-((diphenylphosphino)methyl)benzyl)-1*H*-imidazol-3-ium hexafluorophosphate ($\mathbf{2}\cdot\mathrm{PF}_6$), 1-methyl-3-(3-(di-*tert*-butylphosphinooxy)phenyl)imidazolium iodide (**8a**), and 3-(3-((diphenylphosphoryl)methyl)phenyl)-1-methyl-1*H*-imidazol-3-ium iodide (**11**) have been prepared and used as precursors to phosphine-NHC, phosphinite-NHC, and phosphoryl-NHC metal complexes, respectively. The structure of **11** has been determined by X-ray diffraction. The Ag(I) and Ir(I) complexes of the phosphine-NHC ligand, $[\mathrm{Ag}(\mu\text{-P-NHC},\kappa C,\kappa P)]_2(\mathrm{PF}_6)_2$ (**3**) and $[\mathrm{Ir}(\mathrm{cod})(\mu\text{-P-NHC},\kappa C,\kappa P)]_2(\mathrm{PF}_6)_2$ (**4**), were obtained and characterized by NMR, ESI-MS, elemental analysis, and X-ray diffraction. Both complexes are dinuclear and dicationic, with two P-NHC ligands bridging the two metal centers. The presence of the P donor led for **3** to an unprecedented structure compared to that of related Ag(I) complexes with trans spanning bis-NHC ligands. Complex **4** is the first example of a dinuclear iridium complex with a hybrid P-NHC ligand. The new hydrido, Ir(III) pincer-type complex $[\mathrm{IrH}(\mathrm{C_{NHC}CC_{NHC}})(\mathrm{MeCN})]\mathrm{PF}_6$ (**7**) is suggested to have a square-pyramidal structure. The tetranuclear Ag(I) complex with the phosphinite-NHC ligand, $[\mathrm{Ag}_2(\mu_3\text{-I})(\mu\text{-PO-NHC},\kappa P,\kappa C_{\mathrm{NHC}})]_2$ (**9a**) has a cubane-type structure, with alternating silver and iodine apexes and two PO-NHC ligands bridging opposite edges of the Ag_4 tetrahedron. The Ir(III) pincer complexes $[\mathrm{IrH(I)}(\text{PO-NHC},\kappa P,\kappa C,\kappa C_{\mathrm{NHC}})^{\mathrm{Me}}]$ (**10a**) and $[\mathrm{IrH(I)}(\text{PO-NHC},\kappa P,\kappa C,\kappa C_{\mathrm{NHC}})^{n\text{-Bu}}]$ (**10b**), with Me or *n*-Bu substituents on the nitrogen atom, respectively, have been prepared and characterized. Ag(I) and Cu(I) complexes with the phosphoryl-NHC ligand are reported and the centrosymmetric structure of the latter, $[\mathrm{Cu}(\text{OP-NHC},\kappa C_{\mathrm{NHC}})_2(\mu\text{-I})\{\mathrm{Cu}(\mu\text{-I})\}]_2$ (**13**), was established by X-ray diffraction and consists of a central $\mathrm{Cu}_2(\mu\text{-I})_2$ rhombus connected by single iodide bridges to two $\mathrm{Cu}(\text{OP-NHC},\kappa C_{\mathrm{NHC}})_2$ moieties. The Ir(III) hydride pincer complexes **10a,b** were tested as catalyst precursors for the C−H bond activation of alkanes. Although their efficiency was significantly lower for transfer dehydrogenation from cyclooctane (coa) to *t*-butylethylene (tbe) than that of known PCP-Ir systems, these results represent the first attempts to study the catalytic properties of hybrid P-NHC iridium pincer complexes.

INTRODUCTION

Since the seminal work of Shaw and Moulton,[1] phosphorus-based pincer-type complexes have been increasingly studied because of their intrinsic interest and involvement in numerous aspects of fundamental and applied modern organometallic chemistry (Chart 1a).[2,3] Many of them display interesting structural/electronic properties and behave as efficient catalysts in a number of reactions.[4−7] Another family of ligands, the N-heterocyclic carbenes (NHC), has received increasing attention over the past few years in coordination/organometallic chemistry and homogeneous catalysis where they behave as valuable alternatives to phosphorus ligands for transition metals because of their strong σ-donating and weak π-accepting properties which limit their dissociation from the metal center to which they are coordinated.[8,9] With the objective to associate within the same molecule the beneficial properties of each class of ligands, a diversity of metal complexes with pincer-type NHC ligands have been prepared (Chart 1b) (with, e.g., $\mathrm{C_{NHC}CC_{NHC}}$[10−23] or $\mathrm{C_{NHC}{}^{\wedge}N^{\wedge}C_{NHC}}$[24−33] donor sets). NHC metal complexes generally exhibit advantages over their

Chart 1. Pincer-Type Complexes with Phosphorus (a) or NHC Donor Groups (b)

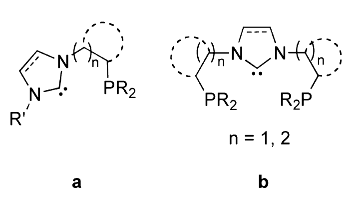


Received: December 28, 2012

phosphorus analogues in terms of, for example, improved air and thermal stability, which are highly desirable properties in organometallic chemistry and homogeneous catalysis.[34,35]

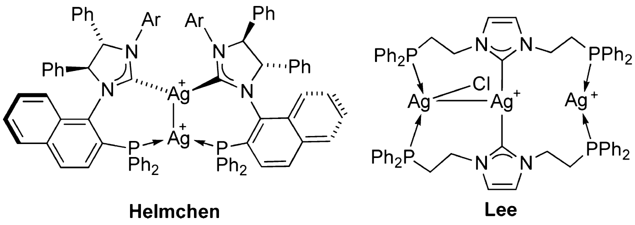
Consistent with the often unique properties that hybrid ligands, that is, which contain chemically different donor functions, confer to their metal complexes,[36−39] phosphorus-based hybrid ligands have attracted considerable interest,[37,40] while the importance of NHC-based hybrid ligands in metal-catalyzed reactions has been recently emphasized.[41] There are still relatively few examples of hybrid phosphine-NHC ligands,[42] and they include bidentate[43−70] (Chart 2a), tridentate $PC_{NHC}P$[71−77] (Chart 2b), and macrocyclic $P_2(C_{NHC})_2$ (Chart 2c) ligands.[78] This triggered our interest for the synthesis and coordination chemistry of such PC_{NHC} ligands. The ligand backbone was chosen to consist in a 1,3-disubstituted aryl ring that could potentially be metalated at the 2-position and thus lead to a pincer-type system.

Chart 2. Examples of Hybrid Phosphine-NHC Ligands



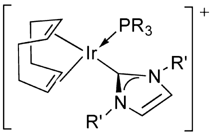
In terms of synthetic efforts, Ag(I)-NHC complexes have received most attention among the coinage metal-NHCs owing to their ease of preparation, from an imidazolium precursor and Ag_2O, and their ability to transfer the resulting NHC ligand to other metal centers by a transmetalation reaction.[79] This is particularly useful when a convenient, high yield direct synthesis of a transition metal-NHC complex is not available. In the case of hybrid phosphorus/NHC ligands, Helmchen et al. synthesized the rhodium complex of a chiral P-functionalized NHC ligand by a transmetalation reaction from the corresponding dinuclear silver complex (Chart 3),[45] and Lee et al. used the trinuclear Ag(I) complex of a tridentate pincer phosphine/NHC ligand to prepare the corresponding Pd(II),[80] Ru(II),[72] and Rh(I)[81] complexes (Chart 3).

Chart 3. Previously Reported Ag(I) Complexes with P-NHC Hybrid Ligands Used for Transmetalation Reactions



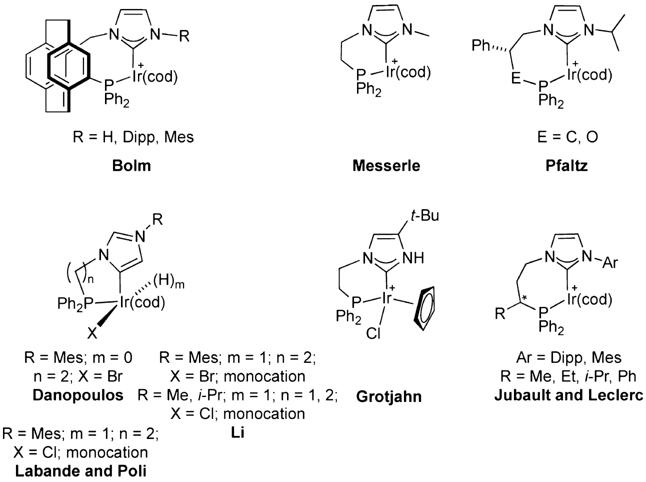
Among the transition metals which have been most investigated, besides silver for the reasons given above, those with potential applications in homogeneous catalysis have attracted special attention. Much research has been performed on iridium complexes, in particular since the report of Crabtree's hydrogenation catalyst,[82] and of new applications found for iridium complexes in the dehydrogenation of alkanes.[83,84] For the latter, significant progress has been made recently which has led to more active catalysts as a result of their relatively higher stability compared to the corresponding Rh and Co complexes.[85] The combined use of monodentate phosphine and NHC ligands in iridium complexes was first reported by Buriak and coworkers,[86] and this was followed by other research groups[87−94] (Chart 4). We were interested to extend these studies by connecting these donor functions within the same ligand and to synthesize new metal complexes, in particular of iridium, containing P-functionalized NHCs because of the conceivable diversity and tunability of such ligands and the beneficial contribution of the chelate effect.

Chart 4. General Formula of Ir Complexes Containing Monodentate Phosphine and NHC Ligands



Although the first P-NHC iridium complex was developed for asymmetric hydrogenation by Bolm in 2004,[53] iridium complexes with hybrid P-NHC ligands remain rare. Except for Bolm's complex (Chart 5),[53] they all contain an alkyl chain as spacer between the P and NHC donor groups of the chelating P-NHC ligand.[52,57,59,65,70,95−98] We will describe below the first example, to the best of our knowledge, of a dinuclear Ir complex with a hybrid P-NHC ligand, which extends the range of known P-NHC Ir complexes to a new class of dimetallacyclic complexes.

Chart 5. Relevant Ir Complexes with P-NHC Hybrid Ligands (See Text)



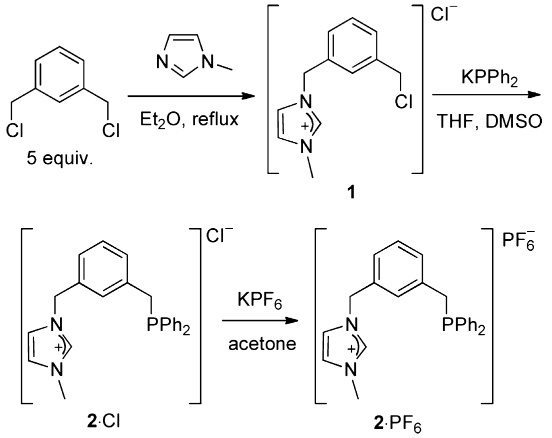
To vary the nature of the phosphorus donor function associated with the NHC moiety, we have used two different P(III) functions (phosphine and phosphinite) and one P(V) donor (phosphine oxide). We thus report the synthesis of: (*i*) 1-methyl-3-(3-((diphenylphosphino)methyl)benzyl)-1*H*-imidazol-3-ium hexafluorophosphate and its use as precursor to a phosphine-NHC hybrid ligand that could behave in a bidentate or a pincer-type manner in Ag(I) and Ir(I) complexes; (*ii*) 1-methyl-3-(3-(di-*tert*-butylphosphinooxy)phenyl)imidazolium iodide and its use as precursor to a phosphinite-NHC hybrid ligand that could also behave in a bidentate or a pincer-type manner in Ag(I) and Ir(I) complexes, and (*iii*) 3-(3-((diphenylphosphoryl)methyl)phenyl)-1-methyl-1*H*-imidazol-

3-ium iodide and its use as precursor to a phosphoryl-NHC hybrid ligand in Cu(I) and Ag(I) complexes.

RESULTS AND DISCUSSION

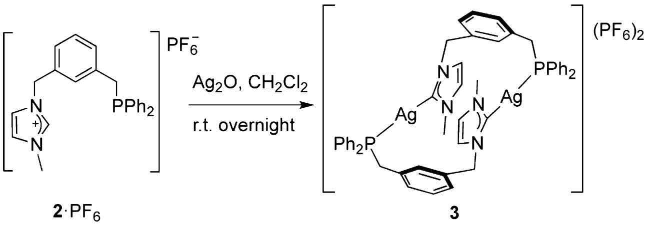
Phosphine-NHC Hybrid Ligand. The phosphine-imidazolium salt **2**·PF_6 was prepared from 1,3-bis(chloromethyl)-benzene by modifying a reported procedure (Scheme 1).[99] To limit possible problems associated with the air-sensitivity of an uncoordinated phosphine group, we introduced the P-donor moiety in the final step of the preparation. Diethyl ether was used as the solvent in the first step of the synthesis to precipitate the monosubstituted derivative **1**, thus preventing further substitution even though 1,3-bis(chloromethyl)benzene was present in large excess. Highly hygroscopic **2**·Cl was treated with KPF_6 to give the phosphine-imidazolium salt associated with the noncoordinating hexafluorophosphate anion, which is easier to handle.

Scheme 1. Synthesis of the Phosphine-Imidazolium Precursor



To obtain the corresponding Ag(I) NHC complex, a dichloromethane solution of the phosphine-imidazolium salt was reacted with 0.5 equiv of Ag_2O at room temperature under the protection against light. This reaction afforded a white precipitate of the Ag(I) complex **3** (Scheme 2). Its $^{31}P\{^1H\}$ NMR spectrum contains a doublet of doublets resonance at δ 12.19 ppm [$^1J(P-^{107}Ag)$ = 488 Hz, $^1J(P-^{109}Ag)$ = 555 Hz)]. Single crystals of this complex suitable for X-ray diffraction were obtained by slow diffusion of diethyl ether into a saturated acetonitrile solution of the complex.

Scheme 2. Synthesis of the Ag(I) Complex [Ag(μ-P-NHC,κP,κC_{NHC})]$_2$(PF_6)$_2$ (3)



In the centrosymmetric structure of the cationic complex, the two phosphine-NHC ligands bridge two Ag metal centers (Ag···Ag 6.304(6) Å), which have a linear coordination geometry defined by the Ag−P and Ag−C_{NHC} bonds [C1−Ag1−P1^i 172.94(2)°] (Figure 1). As a result, the aromatic rings of the spacer are thus parallel to each other, their mean planes being 6.607 Å apart and their centroids separated by 6.783 Å, and the P−Ag−C_{NHC} vectors are in a mutual antiparallel orientation. A comparison between this structure and that of other Ag(I) complexes containing either phosphorus or NHC ligands (Chart 6a-c)[99−101] demonstrates the structural diversity brought about by the hybrid P-NHC ligands. When halides are present, they usually behave as ligands in neutral Ag(I) complexes, whereas noncoordinating anions such as OTf$^-$,

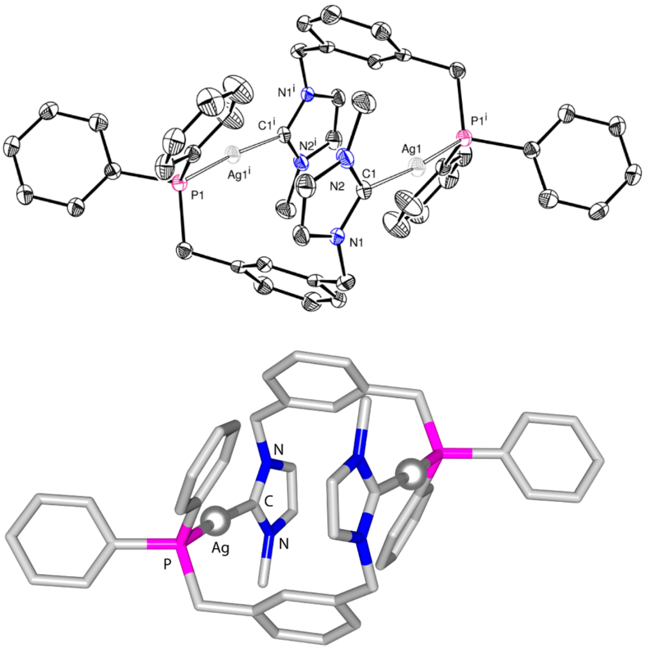
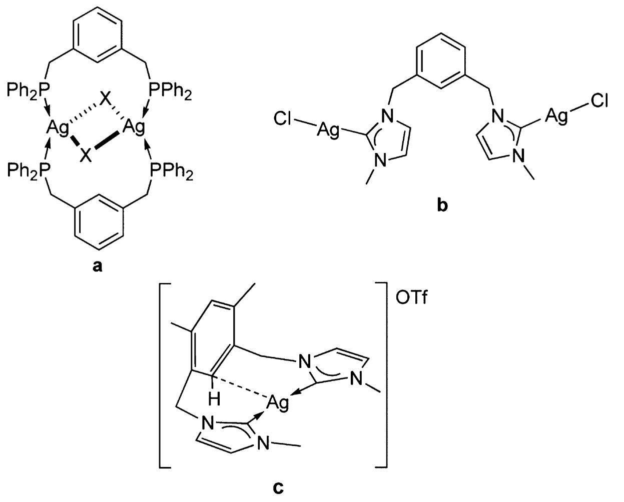


Figure 1. (top): ORTEP of the molecular structure of the dicationic complex [Ag(μ-P-NHC,κP,κC_{NHC})]$_2$ in **3** with 30% probability thermal ellipsoids. Hydrogen atoms and anions omitted for clarity. Selected bond lengths [Å] and angles (deg): Ag1−C1 2.104(5), Ag1−P1i 2.366(1); C1−Ag1−P1i 172.94(2), C1−N1−C3 104.7(5). (bottom) Perspective view of the molecular structure of **3** (Diamond software).

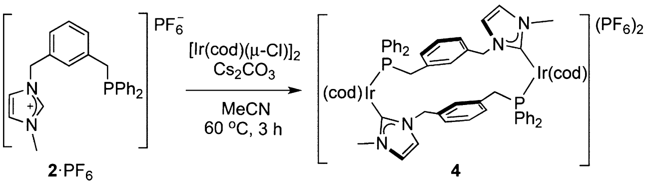
Chart 6. Ag(I) Complexes with Phosphorus or NHC Ligands Related to the Hybrid Ligand Present in 3



PF_6^-, or BF_4^- favor the linear coordination of neutral donors around a cationic metal center.[101−103]

The poor solubility of the Ag(I) complex **3** hampered further transmetalation reactions. This triggered our efforts for a direct synthesis of iridium complexes from **2**·PF_6. Thus, a solution of **2**·PF_6 was reacted with $[Ir(cod)(\mu\text{-}Cl)]_2$ and Cs_2CO_3 in acetonitrile for 3 h, which gave an Ir(I) complex in excellent yield (Scheme 3). A singlet appeared in the $^{31}P\{^1H\}$ NMR spectrum at δ 16.88 ppm (low field shifted from the value of δ −7.74 ppm for the free ligand). The $^{13}C\{^1H\}$ NMR spectrum contained a resonance at δ 175.1 ppm for the NHC carbon coordinated to Ir. Single crystals of **4**·2THF suitable for X-ray diffraction studies were obtained by slow diffusion of tetrahydrofuran (THF) in a saturated CH_2Cl_2 solution of the complex.

Scheme 3. Synthesis of the Dinuclear Ir(I) Complex 4



The centrosymmetric structure of the dinuclear cation in **4** is shown in Figure 2. Each Ir(I) center is chelated by a cod ligand and coordinated by a phosphorus and a carbene donor from two different P-NHC ligands, thus reaching a 16e environment. The separation between the two Ir centers is 9.725(6) Å. This dicationic, 18-membered dimetallacycle with μ-P-NHC units is obviously preferred to a mononuclear 9-membered ring structure with P-NHC chelating ligands. Similary to the Ag(I) complex **3**, the aromatic rings which separate the NHC and P donor groups in each ligand are parallel to each other, the distance between their mean planes is 1.585 Å and that between their centroids is 7.054 Å. The two bridging ligands are in an extended-type conformation in comparison to **3** where it is more "contracted". In Crabtree's work on Ir complexes, it was shown that imidazolium salts associated with a halogen anion led preferentially to classical NHCs, whereas non-coordinating anions, such as BF_4^- or PF_6^-, mostly give rise to abnormal NHCs.[104] However, here we did not observe the formation of any abnormal NHC.

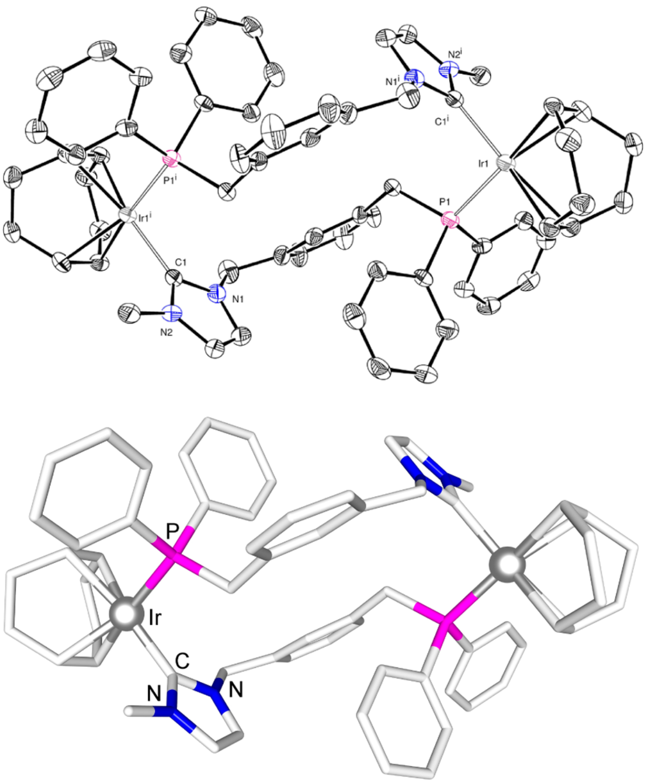
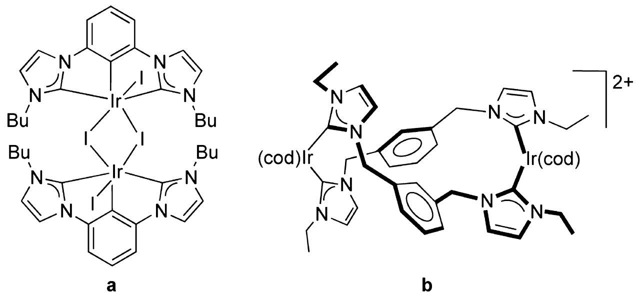


Figure 2. Top: ORTEP of the molecular structure of the dicationic complex $[Ir(cod)(\mu\text{-}P\text{-}NHC,\kappa P,\kappa C_{NHC})]_2$ in **4**·2THF with 30% probability thermal ellipsoids. The 2 molecules of THF, the anions, and the hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [deg]: Ir1i−C1 2.043(7), Ir1i−P1i 2.316(2); C1−Ir1i−P1i 91.5(2), N1−C1−N2 104.0(6). Bottom: Perspective view of the molecular structure of the dicationic complex in **4** (Diamond software).

It is interesting to compare the structure of **4** with that of two other dinuclear iridium complexes: (a) the dinuclear pincer-type Ir(III) complex $[Ir(\mu\text{-}I)(I)(C_{NHC}CC_{NHC})]_2$ with iodides as bridging ligands (Chart 7a), obtained by transmetalation from a Zr(IV) intermediate;[19] (b) a dimetallacyclic, helical Ir(I) complex with an arrangement of the 20-membered ring formed by the bis-carbene bridging ligands resulting in a *figure-of-eight* conformation, which was obtained by in situ deprotonation of the imidazolium precursor (Chart 7b).[23]

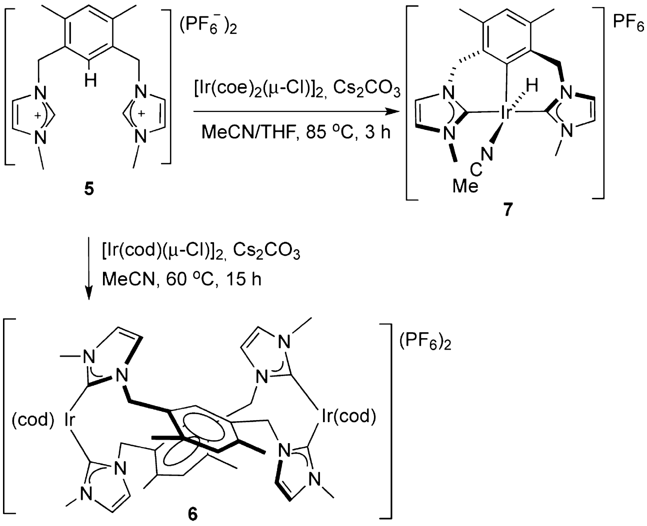
Chart 7. Dinuclear Ir(III) (a) and Ir(I) (b) Complexes with Chelating or Bridging Bis-carbene Ligands



In the course of studies extending the latter system to the iridium(I) complex **6**, obtained from the bis-imidazolium salt **5** having methyl substituents in the 4 and 6 positions of the aryl ring (Scheme 4),[100] and of ^1H NMR investigations of the stereodifferentiation in solution of its *P* and *M* enantiomers,[105] we noted that using the more labile precursor $[Ir(coe)_2(\mu\text{-}Cl)]_2$ led instead to a pincer-type iridium hydride complex, formulated as **7**.

Whereas the ^1H NMR spectra of complexes **5** and **6** were consistent with a symmetrical structure, that of **7** suggested a nonsymmetrical conformation. In addition to the AB spin system observed for the NCH_2 protons, consistent with the lack of symmetry element passing through this group, a doubling of all the resonances was observed, except for the arene hydrogen (C<u>⋯</u>CH<u>⋯</u>C), which shifted from δ 7.23 (ligand) to 6.47 ppm. This would be consistent with the two twisted NHC arms being inequivalent, which in turn suggests for **7** a square-pyramidal coordination geometry with transoid H and MeCN ligands, similar to the situation observed in recently reported Ir(III) NHC pincer complexes.[11] Moreover, the resonance of the hydrogen attached to the arene carbon C2 has disappeared and a singlet at δ −22.09 ppm provided

Scheme 4. Synthesis of Ir(I) or Ir(III) Complexes as a Function of the Metal Precursor



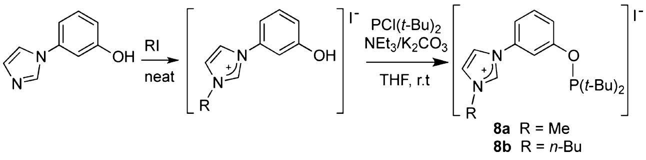
evidence for the formation of an Ir−H bond. MS-ESI data presented a main peak at (m/z) 528.2 $[M\text{-PF}_6]^+$ and another peak at (m/z) 487.1 $[M\text{-MeCN-PF}_6]^+$, indicating coordination of a neutral solvent molecule (MeCN) to the metal center, giving rise to a penta-coordinated complex. Unfortunately, we could not obtain single crystals of this complex suitable for X-ray diffraction.

These results illustrate the influence that the iridium-coordinated ligands cod or coe of the precursor complexes may have on their reactivity. In complex **6**, the cod ligand remains chelated to the Ir center and the two bridging bis-NHC ligands connect the Ir(I) centers in such a way that each metal is bonded to two mutually cis carbene donors. This results in a dicationic 20-membered dimetallacycle. Because coe is a more labile olefin than cod, it was easily displaced by the solvent molecule MeCN, which coordinates to the Ir center through its nitrogen atom in complex **7**. The requirement for shorter reaction times (compared to the reaction using $[\mathrm{Ir(cod)}(\mu\text{-Cl})]_2$ also indicated the higher lability of the complex due to a more weakly bound coe ligand compared to cod. Unlike the situation in **6**, with its *figure-of-eight* loop structure, the aromatic ring has been metalated in complex **7**, as a result of oxidative-addition and formation of Ir−C and Ir−H bonds. Mixtures of solvents were used to increase the solubility of the ligand (soluble in MeCN) and $[\mathrm{Ir(coe)_2}(\mu\text{-Cl})]_2$ (soluble in THF). Interestingly, MeCN appears to have significantly stabilized the pincer-type Ir(III) hydride complex **7** because when the bis-imidazolium dibromide precursor, which is soluble in THF, was treated under similar conditions but in the absence of MeCN, only decomposition of the iridium precursor was observed.

The chelating cod ligand in the Ir complexes **4** and **6** and in that of Chart 7b is responsible for the mutual cis arrangement of the NHC donors (in **6** and Chart 7b) and of the P and NHC donor functions (in **4**), while in the Ag(I) complex **3**, there is no constraint preventing the P-NHC ligands to adopt a conformation allowing a trans arrangement of the P and NHC donor groups and a linear coordination geometry about the Ag(I) centers.

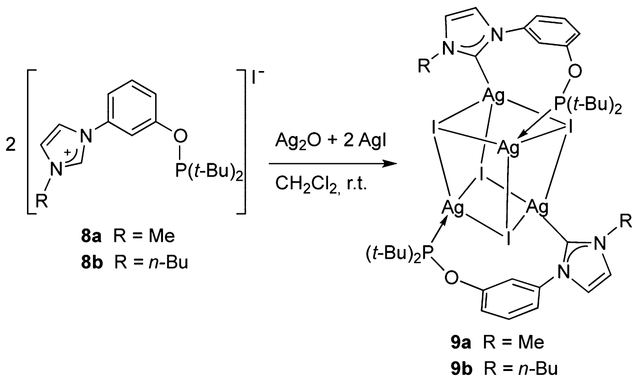
Phosphinite-NHC Hybrid Ligands. To examine the consequences of replacing the $\mathrm{CH_2}$ spacer between the phosphorus and the aryl ring with an isoelectronic oxygen atom, we prepared the imidazolium salts **8a** and **8b**, with slight modifications for the former of the procedure reported earlier for **8b** (Scheme 5).[106]

Scheme 5. Synthesis of the Phosphinite-Imidazolium Salts



By analogy with the reaction with **8b**,[106] 2 equiv of the N-methyl substituted ligand **8a** were reacted with $\mathrm{Ag_2O}$ in the presence of 2 equiv of AgI to afford the cubane-type silver cluster **9a** (Scheme 6), which was characterized by X-ray diffraction (Figure 3).

Scheme 6. Synthesis of the Silver PO-NHC Cluster $[\mathrm{Ag_2}(\mu_3\text{-I})(\mu\text{-PO-NHC},\kappa P,\kappa C_{\mathrm{NHC}})]_2$ (9a)



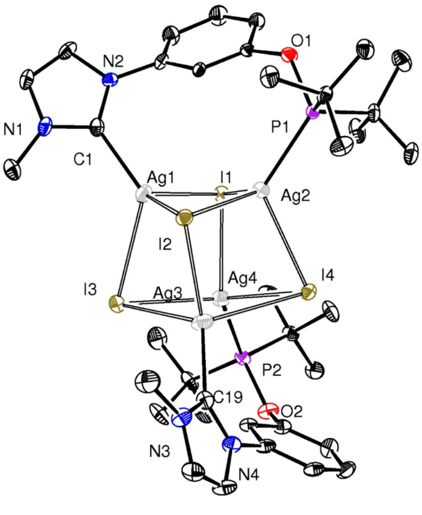


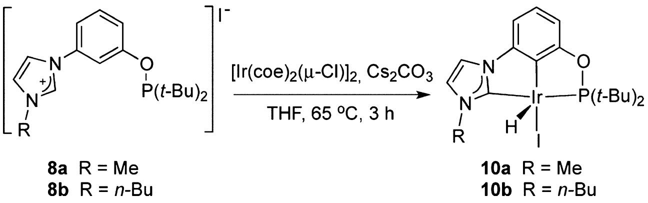
Figure 3. ORTEP of **9a** in **9a**·$\mathrm{CH_2Cl_2}$ with 30% probability thermal ellipsoids. Hydrogen atoms omitted for clarity. Selected bond lengths [Å] and angles [deg]: Ag1−C1 2.176(8), Ag2−P1 2.451(2), Ag3−C19 2.156(9), Ag4−P2 2.460(2), Ag1−I1 2.9740(9), Ag1−I2 2.887(1), Ag1−I3 2.987(1), Ag1−Ag2 3.084(1), Ag3−Ag4 3.045(1); N1−C1−N2 103.3(7), C1−Ag1−I1 104.5(2), C1−Ag1−I2 123.4(2), C1−Ag1−I3 127.6(2), I1−Ag1−I2 113.96(3), I1−Ag1−I3 93.80(3), I2−Ag1−I3 90.29(3).

The molecular structure of **9a** is similar to that of known **9b**[106] and exhibits a rare ligand/metal arrangement, despite the diversity encountered in the structural chemistry of Ag-NHC complexes.[79,102,103] The distorted Ag_4I_4 cubane-like core, with alternating Ag and I vertices, features iodide ligands capping three metal centers and two PO-NHC ligands bridging opposite edges of the Ag_4 tetrahedron. The corresponding Ag···Ag distances of 3.084(1) and 3.045(1) Å are compatible with the existence of d^{10}-d^{10} interactions.[107] The Ag···Ag distances and the P−Ag bond lengths are in the range of the corresponding values in $[Ag_4I_4(PPh_3)_4]$.[108,109] The pronounced deformation of the pseudocubane arrangement in **9a** is due to I···I separations being significantly longer than the Ag···Ag ones. The NHC-Ag distances (Ag1−C1 2.176(8) and Ag3−C19 2.156(9) Å) are similar to those in **9b**. The $^{31}P\{^1H\}$ NMR spectrum of **9a** exhibits a broad signal at 158.3 ppm, and the two ^1J(P−Ag) couplings were not resolved.

The similarities between **9a** and **9b** show that PO-NHC ligands with different N-substituents behave as bridging rather than chelating ligands and that the change of N-substituent from *n*-Bu to methyl does not significantly affect the structure of the corresponding tetrasilver complexes obtained according to Scheme 6.

Since attempts to use **9a** for transmetalation to Ir(I) complexes failed, we attempted the direct synthesis of what should be the first examples of iridium complexes with a P-containing NHC pincer ligand. We reacted the corresponding imidazolium salts **8a,b** with the Ir(I) precursor complex in the presence of weak bases, as detailed in Scheme 7, and obtained the corresponding Ir(III) complexes **10a,b**.

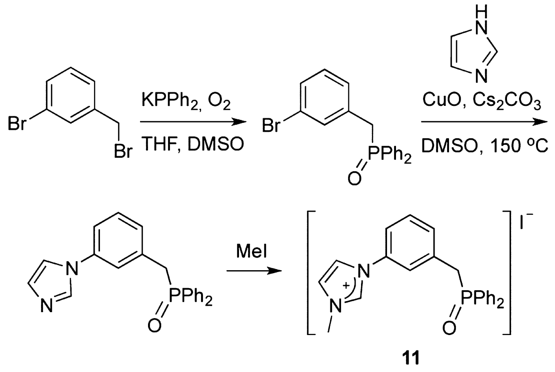
Scheme 7. Synthesis of Iridium(III) Pincer Complexes [IrH(I)(PO-NHC,*κP*,*κ*C,*κ*C_{NHC})] (10a,b) with a PO-NHC Ligand



Like in the case of **7**, the ^1H NMR spectrum of **10a,b** revealed the presence of a hydride resonance at δ −26.88 (d, ^2J(PH) = 17.6 Hz) and −31.72 (br s) ppm, respectively. Compared with the spectrum of **8a,b**, the two *tert*-butyl groups of **10a,b** appeared nonidentical (both in the ^1H and ^{13}C NMR). The $^{31}P\{^1H\}$ NMR resonance is downfield shifted from δ 159.9 (**8a**) and 159.5 (**8b**) to 174.6 (**10a**) and 173.1 (**10b**) ppm, respectively. Although the poor quality of the crystals available and of the X-ray diffraction data of **10b** prevented a full refinement of the structure, tridentate coordination of the pincer ligand and iodide coordination trans to carbon were unambiguously established. We thus assume for **10a,b** a square pyramidal coordination geometry similar to those reported for PCP and POCOP pincer iridium hydride complexes, which also contain a halide ligand trans to carbon.[110−113]

Phosphoryl-NHC Hybrid Ligand. To evaluate the influence of the chelate or of the pincer ring size and of the nature of the donor atom associated with the NHC function on the structure and properties of the metal complexes, a precursor to a phosphoryl-NHC hybrid ligand was synthesized according to Scheme 8.

Scheme 8. Synthesis of the Precursor to a Phosphoryl-NHC Hybrid Ligand



The salt **11** was characterized by X-ray diffraction (Figure 4). Whereas no intramolecular H-bonding interaction involving the oxygen atom was detected, some intermolecular interactions between the oxygen atom and the imidazole olefinic hydrogen atom of an adjacent molecule were detected (CH···O═P: 3.100 Å). It is interesting to compare the X-ray structure of this salt, which contains a C−P═O linkage, with that of **8b** and its C−O−P moiety.[106] Whereas the imidazolium and aromatic rings are coplanar in **11**, their mean planes formed an angle of 22.7(2)° in **8b**. The iodide counterion in both **8b** and **11** forms an intramolecular contact with the NC*H*N hydrogen (CH···I: 3.672 and 3.760 Å respectively). In **11**, another iodide (belonging to another entity) is situated in the vicinity of C3 and C10 (C3H···I: 3.122 Å and C10H···I: 3.061 Å). Other metrical data within the cation are as expected.

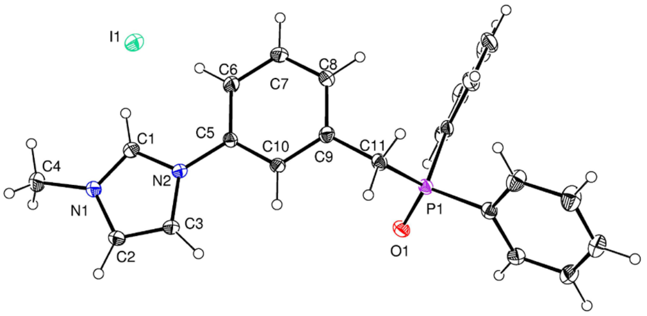
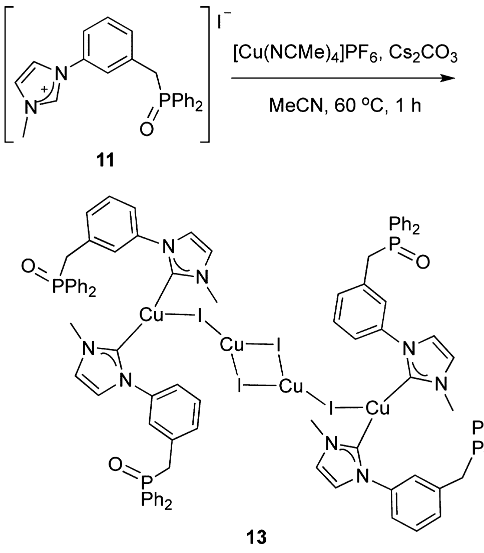


Figure 4. ORTEP of **11** with 30% probability thermal ellipsoids. Selected bond lengths [Å] and angles [deg]: N1−C1 1.312(3), N2−C1 1.337(4), P1−O1 1.483(2); N1−C1−N2 109.2(3), C11−P1−O1 114.1(1).

To synthesize the corresponding NHC silver complex, the salt **11** was reacted with 0.5 equiv of Ag_2O in dichloromethane at room temperature, under the protection against light. Although we could not obtain single crystals of the product formed, it was characterized by NMR spectroscopy and elemental analysis and formulated as $[Ag(\mathbf{11}_{-H})I]_n$ (**12**). The value of the $^{31}P\{^1H\}$ NMR chemical shift (27.72 ppm) is almost identical to that in **11** (27.67 ppm), indicating that the oxygen is not coordinated to the metal. We are lacking sufficient data to suggest a structure for **12**, and we will see below that the Cu(I) complex with this ligand has indeed an unexpected structure, while retaining a 1:1 M/NHC ratio.

We then attempted to prepare the corresponding Cu(I) complex and, unexpectedly, obtained in high yield a complex, **13**, of which the structure could fortunately be established by X-ray diffraction. Complex **13** has a centrosymmetric, tetranuclear structure, with a central $Cu_2(\mu\text{-}I)_2$ unit (Scheme 9).

Scheme 9. Synthesis of the Tetranuclear Cu(I) Complex $[Cu(OP\text{-}NHC,\kappa C_{NHC})_2(\mu\text{-}I)\{Cu(\mu\text{-}I)\}]_2$ (13)



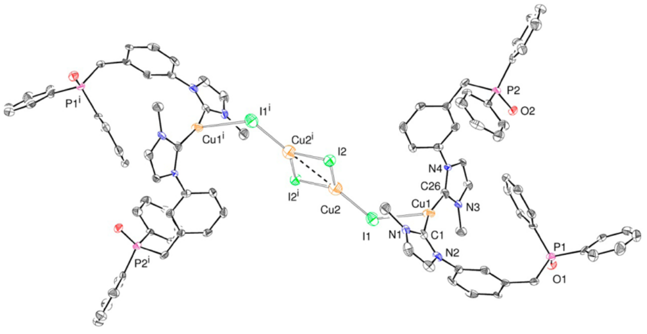
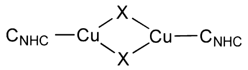


Figure 5. ORTEP of the Cu(I) complex **13** with 30% probability thermal ellipsoids. Hydrogen omitted for clarity. Selected bond lengths [Å] and angles [deg]: Cu1−C1 1.912(8), Cu1−C26 1.930(9), Cu1−I1 3.119(1), Cu2−I1 2.522(2), Cu2−I2, 2.576(2); C1−Cu1−C26 162.6(4), C1−Cu−I1 97.7(3), Cu1−I1−Cu2 121.99(5), I2−Cu2−I2^i 108.37(6).

As shown in Figure 5, there are two types of coordination environments for the Y-shaped coordinated Cu(I) centers: (1) Cu1 is surrounded by two NHC ligands and an iodide; (2) Cu2 has three iodide ligands. All the P═O functions are dangling. Despite the structural diversity encountered with NHC Cu(I) complexes containing halide ligands, most published examples containing a $Cu_2(\mu\text{-}X)_2$ core have the NHC ligand directly coordinated to this unit (Chart 8).[114−126]

The structure of **13** may be viewed as constituted of two $Cu(NHC)_2$-type cations associated with a $[Cu_2(\mu\text{-}I)_2I_2]^{2-}$ dianion. This is consistent with the bending of the C_{NHC}−Cu−C_{NHC} angle (162.6(4)°). It is interesting to compare the M/NHC/I ratio of 4:2:4 in the Ag(I) cubane-type complexes **9a,b** with that of 4:4:4 in **13**. Since the additional P═O functionality in **13** does not participate in the bonding to the metals, the structural arrangement observed in **13** could have a more widespread occurrence.

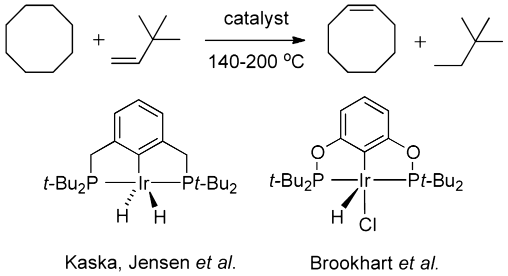
Chart 8. Structural Unit Generally Encountered in Cu(I)-NHC Complexes with Bridging Halides



Attempted Transfer Dehydrogenation of Cyclooctane Using the Iridium Complexes 4, 6, 7, 10a, and 10b as Precatalysts. Iridium complexes of the PCP pincer-type ligands have shown very promising properties in catalytic C−H bond activation of alkanes.[127−129] Considering that complexes with NHC ligands generally exhibit higher thermal stability than their phosphine analogues, and that an increased electronic density around the metal center would be beneficial for the C−H oxidative-addition of the C−H bond,[35] NHC-based Ir complexes could represent good candidates for the homogeneous catalytic dehydrogenation of alkanes.

Since the initial reports of transfer dehydrogenation of cyclooctane (coa) using PCP[130,131] and POCOP[132,133] iridium pincer complexes these systems have served as benchmarks for this reaction (Scheme 10).[83,85,112,134−146]

Scheme 10. Transfer Dehydrogenation of coa in the Presence of tbe



Preliminary studies using the dicationic Ir(I) complexes **4** and **6** or the cationic Ir(III) hydride complex **7** revealed no catalytic activity, probably because of their poor solubility in neat alkanes. The synthesis of a neutral Ir(III) dihydride complex from **7** using KO*t*-Bu in the presence of dihydrogen was also unsuccessful, because of decomposition initiated by the reactivity of the CH_2 position under such basic conditions.

The solubility of the neutral iridium complexes **10a** and **10b**, however, is significantly better than that of **6** or **7**, and these were tested for the transfer dehydrogenation of coa. Each of these precatalysts was tested for 5 and 10 h reaction time. The results of the catalytic experiments are summarized in Table 1.

Table 1. Catalytic Transfer Dehydrogenation of Cyclooctane in the Presence of *tert*-Butylethene with 10a and 10b

entry	catalyst	time/h	TOF/h^{-1}
1	**10a**	5	0.85
2	**10a**	10	0.52
3	**10b**	5	1.27
4	**10b**	10	1.46

In a preliminary investigation, a red suspension of **10a** (6.4 mg, 10 μmmol) or **10b** (6.8 mg, 10 μmmol) in a mixture of cyclooctane (coa; 4.0 mL, 30.3 mmol) and *tert*-butylethene (tbe; 0.45 mL, 3.5 mmol), in sealed tubes under argon, was heated to 200 °C. Gas chromatographic analysis of the products indicated that, for entry 4 (Table 1) 0.48% of the cyclooctane was converted to *cis*-cyclooctene (coe) at a turnover freguency (TOF) of 1.46 h^{-1}, indicating that the transfer dehydrogenation reaction did occur, although at a rate significantly lower than previously found in PCP-Ir systems.[112,130−133,144] Such low catalytic activities compared with those of PCP-Ir systems operating at similar temperatures and thus with similar concentrations of tbe cannot be due to a too low concentration of tbe in solution at 200 °C. According to the observations made with PCP pincer complexes, high concentrations of tbe tend to inhibit the catalytic reaction.[130,131,147] The stronger σ-donor properties of the NHC ligands compared to phosphines should facilitate the C−H oxidative-addition step while disfavoring the reductive elimination of the product during the catalytic cycle. Further work is needed to improve the catalytic performances.

■ CONCLUSION

The coordination chemistry of functional NHC ligands associated with three different types of phosphorus donors, of the phosphine, phosphinite, and phosphine-oxide type, has been explored. The phosphine-NHC ligand present in the Ag(I) and Ir(I) complexes **3** and **4**, respectively, behaved as a bidentate, bridging ligand and did not form PCC$_{\text{NHC}}$ pincer-type complexes. The presence of the P donor led for **3** to an unprecedented structure when compared to that of related trans-spanning bis-NHC donors (Chart 6c). The steric bulk of the diphenylphosphino group may be responsible for the formation of a dinuclear rather than a mononuclear Ag complex.[101] It is interesting to compare the metal/NHC/halide ratios in complexes **9a,b** (4:2:4) with that in **12** (4:4:4). Since the additional P═O functionality does not participate in the bonding to the metals, the structural arrangement found in **12** could have a more widespread occurrence in complexes with a formula of the common type MX(NHC). We observed that the use of NHC Ag(I) complexes as transmetalating agents suffers from limitations, which may be due to their low solubility, as with **3**, or to a lack of reactivity, as with **9a**, where the stability of the cubane structure may disfavor NHC transfer. In both cases however, a direct access to Ir NHC complexes was successful, which reduces the number of steps.

The reactivity of the pincer-type iridium(III) hydrido complexes **10a,b** deserves further investigations. Preliminary experiments performed with the latter as catalyst precursors for the C−H bond activation of alkanes showed that they were less active than PCP-Ir systems. These experiments still provide the first attempts to study the catalytic properties of hybrid P-NHC iridium pincer complexes and remain promising.

■ EXPERIMENTAL SECTION

General Considerations. All reactions were performed under a dry argon atmosphere using standard Schlenk techniques. All solvents were distilled under argon from the appropriate drying agents and stored under argon. ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectra were recorded on a Bruker AV-300 spectrometer at 300.13, 75.48, and 121.49 Hz, respectively, using TMS as external standard, with downfield shifts reported as positive. All NMR spectra were measured at 298 K, unless otherwise specified. Elemental analyses were performed by the "Service de microanalyses", Université de Strasbourg. Electrospray mass spectra (ESI-MS) were recorded on a microTOF (Bruker Daltonics, Bremen, Germany) instrument using nitrogen as drying agent and nebulizing gas. The syntheses of **5**, **6**, **8b**, and **9b** have been reported before.[100,105,106]

Synthesis of 1-(3-(Chloromethyl)benzyl)-1*H*-imidazol-3-ium Chloride (1). *N*-methyl-imidazole (0.165 g, 158 μL, 2.01 mmol) was added to a Et_2O solution (10 mL) of *m*-xylene dichloride (1.751 g, 10.00 mmol) at room temperature. After it was refluxed for 7 days, the suspension was allowed to cool to room temperature and filtered. The crude solid was washed with Et_2O (2 × 10 mL) leading to an off-white product. (0.190 g, 0.736 mmol, 37% based on *N*-methyl-imidazole). ^{1}H NMR ($CDCl_3$): δ 10.84 (1H, s, NCHN), 7.52 (1H, s), 7.45 (1H, m), 7.40−7.37 (3H, m), 7.35−7.33 (1H, m), 5.61 (2H, s, N−CH_2), 4.55 (2H, s, Cl-CH_2), 4.03 (3H, s, N−CH_3); ^{13}C{^{1}H} NMR ($CDCl_3$): δ 138.8 (s, C$_{\text{arom.}}$), 138.0 (s, C$_{\text{arom.}}$), 133.9 (s, C$_{\text{arom.}}$), 129.9 (s, C$_{\text{arom.}}$), 129.6 (s, C$_{\text{arom.}}$), 129.0 (s, C$_{\text{arom.}}$), 129.0 (s, C$_{\text{arom.}}$), 123.7 (s, C$_{\text{imid.}}$), 122.0 (s, C$_{\text{imid.}}$), 52.8 (s, N−CH_2), 45.6 (s, Cl-CH_2), 36.6 (s, N−CH_3) ppm. ESI-MS (*m*/*z*): 221.1 [*M*-Cl]$^{+}$. The hygroscopic nature of this compound prevented the recording of satisfactory elemental analyses.

Synthesis of 1-Methyl-3-(3-((diphenylphosphino)methyl) benzyl)-1*H*-imidazol-3-ium Hexafluorophosphate (2·PF_6). A THF solution of potassium diphenylphosphide (0.500 M, 2.00 mL, 1.00 mmol) was added dropwise to a solution of **1** (0.258 g, 1.00 mmol) in dimethylsulfoxide (DMSO, 5 mL). The mixture was stirred at room temperature for 3 h, and DMSO was removed under reduced pressure. Methanol (5 mL) was then added and after the mixture was stirred for 20 min, all volatiles were removed under reduced pressure. The residue was then dissolved in dichloromethane (15 mL), and the suspension was filtered to remove inorganic salts. The solvent was then removed under vacuum to afford 1-methyl-3-(3-((diphenylphosphino)methyl) benzyl)-1*H*-imidazol-3-ium chloride as a foam after washing with diethyl ether (3 × 10 mL). This product was used directly for the synthesis of the PF_6 salt, and a large excess of KPF_6 (0.900 g, 4.89 mmol) was added to its suspension in acetone (10 mL). The mixture was stirred at room temperature for 8 h. Acetone was then removed under reduced pressure and dichloromethane (15 mL) was added to this residue. A clear solution was obtained after filtration. Removal of the solvent followed by addition of diethyl ether gave an oil which solidified slowly at room temperature in Et_2O to give **2**·PF_6 a white solid (0.346 g, 0.668 mmol, 67% based on **1**). ^{1}H NMR (d_6-DMSO): δ 9.13 (1H, br s, NCHN), 7.71 (1H, pseudo t, ^{3}J(HH) = ^{4}J(HH) = 1.7 Hz, CH$_{\text{imid}}$), 7.61 (1H, pseudo t, ^{3}J(HH) = ^{4}J(HH) = 1.7 Hz, CH$_{\text{imid}}$); 7.45−7.35 (10H, m, CH$_{\text{arom.}}$), 7.24 (1H, pseudo q, ^{3}J(HH) = ^{4}J(HH) = ^{5}J(HH) = 7.8 Hz, $C\underline{\cdots}CH\underline{\cdots}C$), 7.18−7.13 (3H, m, CH$_{\text{arom.}}$), 5.31 (2H, s, NCH_2), 3.87 (3H, s, NCH_3), 3.54 (2H, s, P-CH_2); ^{13}C{^{1}H} NMR (DMSO): δ 138.6 (d, *J*(PC) = 8.1 Hz, C$_{\text{arom.}}$), 137.6 (d, *J*(PC) = 15.5 Hz, C$_{\text{arom.}}$), 136.5 (s, C$_{\text{arom.}}$), 134.6 (s, C$_{\text{arom.}}$), 132.6 (d, *J*(PC) = 18.8 Hz, C$_{\text{arom.}}$), 130.6 (d, *J*(PC) = 9.2 Hz, C$_{\text{arom.}}$), 129.5 (d, *J*(PC) = 6.8 Hz, C$_{\text{arom.}}$), 128.9 (d, *J*(PC) = 6.5 Hz, C$_{\text{arom.}}$), 128.8 (s, C$_{\text{arom.}}$), 128.7 (d, *J*(PC) = 1.3 Hz, C$_{\text{arom.}}$), 128.5 (d, *J*(PC) = 6.6 Hz, C$_{\text{arom.}}$), 125.7 (d, *J*(PC) = 2.4 Hz, C$_{\text{arom.}}$), 123.9 (s, C$_{\text{imid}}$), 122.2 (s, C$_{\text{imid}}$), 51.7 (s, NCH_2), 35.8 (s, NCH_3), 34.1 (d, *J*(PC) = 15.1 Hz, PCH_2); ^{31}P{^{1}H} NMR (d_6-DMSO): δ −7.74 (s, PPh_2), −143.10 (sept, ^{1}J(PF) = 711 Hz, PF_6) ppm. ESI-MS (*m*/*z*): 371.2 [M-PF_6]$^{+}$. Anal. Calcd for $C_{24}H_{24}F_6N_2P_2$ (516.40): C, 55.82; H, 4.68; N, 5.42. Found: C, 55.58; H, 4.80; N, 5.70%.

Synthesis of [Ag(μ-P-NHC,κ*P*,κC$_{\text{NHC}}$)]$_2$(PF_6)$_2$ (3). Solid Ag_2O (0.023 g, 0.10 mmol) was added to a Schlenk tube containing a CH_2Cl_2 solution of **2**·PF_6 (0.103 g, 0.199 mmol) under argon. The Schlenk tube was protected against light, and the solution was stirred at room temperature until the black solid disappeared and a white precipitate formed. The solid was collected by filtration and redissolved in MeCN. The solution was filtered again to remove any unreacted Ag_2O and concentrated to 5 mL. Diethyl ether (15 mL) was added to precipitate an off-white solid, which was collected and washed with diethyl ether to afford the product. (0.157 g, 0.126 mmol, 63%). Single crystals suitable for X-ray diffraction studies were obtained by slow diffusion of diethyl ether into a saturated acetonitrile solution of the complex. ^{1}H NMR (CD_3CN): δ 7.57−7.42 (10H, m,

$CH_{arom.}$), 7.21 (1H, d, J(HH) = 7.1 Hz, $CH_{arom.}$), 7.08 and 7.05 (2H, AB spin system, $CH_{imid.}$, ^3J(HH) = 1.6 Hz), 7.04 (1H, overlap, $CH_{arom.}$), 6.96 (1H, d, J(HH) = 6.8 Hz, $CH_{arom.}$), 6.87 (1H, s, C⋯CH⋯C), 4.93 (2H, s, NCH_2), 3.87 (3H, s, NCH_3), 3.71 (2H, br, PCH_2); $^{13}C\{^1H\}$ NMR (CD_3CN): δ 138.4 (s, $C_{arom.}$), 136.3 (s, $C_{arom.}$), 134.1 (s, $C_{arom.}$), 134.0 (s, $C_{arom.}$), 132.0 (s, $C_{arom.}$), 130.2 (s, $C_{arom.}$), 130.1 (s, $C_{arom.}$), 130.0 (s, $C_{arom.}$), 129.5 (s, $C_{arom.}$), 126.9 (s, $C_{arom.}$), 123.9 (s, $C_{imid.}$), 122.8 (s, $C_{imid.}$), 55.1 (s, NCH_2), 39.2 (s, NCH_3), 34.1 (s, PCH_2), the resonance of the coordinated NHC carbon could not be observed, probably because of the poor solubility of the complex in CD_3CN; $^{31}P\{^1H\}$ NMR (CD_3CN): δ 12.22 (dd, ^1J(P-^{107}Ag) = 488 Hz, ^1J(P-^{109}Ag) = 555 Hz), −142.91 (sept., ^1J(PF) = 711 Hz, PF_6) ppm. ESI-MS (m/z): 371.2 (ligand), 477.1 $[1/2(M-2PF_6)]^+$. Anal. Calcd for $C_{48}H_{46}N_4P_4F_{12}Ag_2$ (1246.52): C, 46.25; H, 3.72; N, 4.49. Found: C, 45.95; H, 3.90; N, 4.55%.

Synthesis of [Ir(cod)(*μ*-P-NHC,*κP*,*κ*C_{NHC})]$_2$(PF_6)$_2$ (4). Solid **2**·PF_6 (0.103 g, 0.200 mmol), $[Ir(cod)(\mu\text{-}Cl)]_2$ (0.067 g, 0.10 mmol), and Cs_2CO_3 (0.098 g, 0.30 mmol) were mixed and heated in acetonitrile (15 mL) at 60 °C for 3 h. The suspension was then allowed to cool to room temperature and the solvent was removed under reduced pressure. The orange solid was dissolved in CH_2Cl_2 (10 mL), and the solution was filtered, concentrated to 5 mL, and diethyl ether was added to precipitate an orange solid. (0.13 g, 0.080 mol, 80%). Single crystals of **4**·2THF suitable for X-ray diffraction studies were obtained by slow diffusion of THF into a saturated CH_2Cl_2 solution of the complex. ^1H NMR (CD_3CN): δ 7.51−7.48 (3H, m, $CH_{arom.}$), 7.40−7.32 (6H, m, $CH_{arom.}$), 7.25 (1H, d, ^3J(HH) = 2.0 Hz, $CH_{imid.}$), 7.19−7.11 (4H, m, $CH_{arom.}$), 6.78 (1H, d, ^3J(HH) = 2.0 Hz, $CH_{imid.}$), 5.94 (1H, br s, C⋯CH⋯C), 5.80 (1H, A part of an AB spin system, simulated, ^2J(HH) = 14.9 Hz, NC*H*H), 5.03 (1H, B part of an AB spin system, simulated, ^2J(HH) = 14.9 Hz, NCH*H*), 4.51 (4H, m, cod), 4.07 (3H, s, N−CH_3), 3.87 (2H, m, cod), 3.68 (2H, m, cod), 3.56 (1H, A part of an AB spin system, simulated, ^2J(HH) = 7.7 Hz, PC*H*H), 3.51 (2H, B part of an AB spin system, simulated, ^2J(HH) = 7.7 Hz, PCH*H*), 3.10 (2H, m, cod), the other cod protons are partly masked by the solvent; $^{13}C\{^1H\}$ NMR (CD_3CN): δ 175.1 (NCN), 136.4 (d, J(PC) = 12.2 Hz, $C_{arom.}$), 135.8 (s, $C_{arom.}$), 133.6 (d, J(PC) = 10.0 Hz, $C_{arom.}$), 132.9 (s, $C_{arom.}$), 131.9 (s, $C_{arom.}$), 130.9 (d, J(PC) = 3.8 Hz, $C_{arom.}$), 130.0 (d, J(PC) = 4.2 Hz, $C_{arom.}$), 129.8 (s, $C_{arom.}$), 129.7 (s, $C_{arom.}$), 129.6 (s, $C_{arom.}$), 125.3 (s, $C_{imid.}$), 122.9 (s, $C_{imid.}$), 88.8 (d, J = 11.8 Hz, cod), 87.3 (d, J = 11.8 Hz, cod), 82.3 (s, cod), 79.0 (s, cod), 55.0 (s, NCH_2), 38.6 (s, NCH_3), 37.1 (d, J(PC) = 26.2 Hz, PCH_2), 33.2 (d, J(PC) = 41.6 Hz, cod), 29.4 (d, J(PC) = 48.0 Hz, cod); $^{31}P\{^1H\}$ NMR (CD_3CN): δ 16.88 (s, PPh_2), −143.44 (sept, ^1J(PF) = 706 Hz, PF_6) ppm. ESI-MS (m/z): 671.2 $[M-2(PF_6)]^{2+}$. Anal. Calcd for $(C_{32}H_{35}F_6IrN_2P_2)_2$ (1631.58): C, 47.11; H, 4.32; N, 3.43. Found: C, 46.82; H, 4.28; N, 3.33%.

Synthesis of [IrH(C_{NHC}CC_{NHC})(MeCN)]PF_6 (7). Solid 1,1′-((4,6-dimethyl-1,3-phenylene)bis(methylene)) bis (3-methyl-1*H*-imidazol-3-ium) dihexafluorophosphate (**5**) (0.231 g, 0.394 mmol), $[Ir(coe)_2(\mu\text{-}Cl)]_2$ (0.180 g, 0.200 mmol) and Cs_2CO_3 (0.326 g, 1.00 mmol) were mixed and heated in a stirred solution of acetonitrile (35 mL) and THF (15 mL) at 85 °C for 3 h. The suspension was then allowed to cool to room temperature and the solution was filtered. The filtrate was concentrated to 5 mL and ether was added to precipitate a pale yellow solid. (0.201 g crude, 0.299 mmol, 75.8% yield based on Ir). ^1H NMR (CD_3CN): δ 7.27 (1H, d, ^3J(HH) = 1.9 Hz, $CH_{imid.}$), 7.26 (1H, d, ^3J(HH) = 1.9 Hz, $CH_{imid.}$), 7.07 (1H, d, ^3J(HH) = 1.9 Hz, $CH_{imid.}$), 7.01 (1H, d, ^3J(HH) = 1.9 Hz, $CH_{imid.}$), 6.47 (1H, s, $CH_{arom.}$), 5.19 (2H, m, A part of an AB spin system, ^2J(HH) = 13.9 Hz, C*H*H), 5.16 (2H, m, a part of an AB spin system, ^2J(HH) = 15.0 Hz, C*H*H), 5.06 (2H, m, b part of an AB spin system, ^2J(HH) = 15.0 Hz, CH*H*), 4.38 (2H, m, B part of an AB spin system, ^2J(HH) = 13.9 Hz, C*H*H), 3.88 (3H, s, N−CH_3), 3.67 (3H, s, N−CH_3), 2.30 (3H, s, C−CH_3), 2.27 (3H, s, C−CH_3), −22.07 (1H, s, Ir−H); $^{13}C\{^1H\}$ NMR (CD_3CN): δ 164.5 (NCN), 164.1 (NCN), 139.0 ($C_{arom.}$), 138.7 ($C_{arom.}$), 135.0 ($C_{arom.}$), 132.5 ($C_{arom.}$), 131.9 ($C_{arom.}$), 127.2 ($C_{arom.}$), 122.4 ($C_{imid.}$), 122.0 ($C_{imid.}$), 121.9 ($C_{imid.}$), 121.4 ($C_{imid.}$), 56.1 (CH_2), 53.4 (CH_2), 38.2 (NCH_3), 37.2 (NCH_3), 20.6 (CH_3), 20.5 (CH_3); $^{31}P\{^1H\}$ NMR (CD_3CN): δ −144.71 (sept., ^1J(PF) = 709 Hz, PF_6) ppm. ESI-MS (m/z): 528.2 $[M\text{-}PF_6]^+$, 487.1 $[M\text{-}MeCN\text{-}PF_6]^+$. Anal. Calcd for $C_{20}H_{25}F_6IrN_5P$ (672.63): C, 35.71; H, 3.75; N, 10.41. Found: C, 35.10 ; H, 3.30 ; N 9.90%. Despite several attemps, no better analysis data were obtained, owing to the air- and moisture-sensitivity of this complex.

Synthesis of 1-Methyl-3-(3-hydroxyphenyl)imidazolium Iodide. Solid 1-(3-hydroxyphenyl)-imidazole (0.512 g, 3.20 mmol) and iodomethane (5.0 mL) were mixed and stirred for 3 h. The suspension was filtered. The crude solid was washed with Et_2O (2 × 30 mL) leading to a gray product. Recrystallization from MeOH/Et_2O/pentane yielded the product as a white solid (0.863 g, 2.86 mmol, 89%). ^1H NMR (d_6-DMSO): δ 10.23 (1H, br s, OH), 9.72 (1H, br s, NCHN), 8.25 (1H, br s, $CH_{imid.}$), 7.95 (1H, br s, $CH_{imid.}$), 7.44 (1H, t, ^3J(HH) = 6.7 Hz, $CH_{arom.}$), 7.18 (1H, d, ^2J(HH) = 6.7 Hz, $CH_{arom.}$), 7.11 (1H, s, $CH_{arom.}$), 6.98 (1H, d, ^2J(HH) = 6.7 Hz, CH $CH_{arom.}$), 3.95 (3H, s, NCH_3); $^{13}C\{^1H\}$ NMR (d_6-DMSO): δ 159.2 (C−OH), 136.3 ($C_{arom.}$), 136.2 (NCN), 131.6 ($C_{arom.}$), 124.9 ($C_{imid.}$), 121.4 ($C_{imid.}$), 117.1 ($C_{arom.}$), 112.6 ($C_{arom.}$), 109.3 ($C_{arom.}$), 36.7 (NCH_3) ppm. ESI-MS (m/z): 175.1 $[M\text{-}I]^+$. Anal. Calcd for $C_{10}H_{11}IN_2O$ (302.11): C, 39.76; H, 3.67; N, 9.27. Found: C, 39.73; H, 3.81; N, 9.06%.

Synthesis of 1-Methyl-3-(3-(di-*tert*-butylphosphinooxy)-phenyl)imidazolium Iodide (8a). 1-Methyl-3-(3-hydroxyphenyl) imidazolium iodide (0.863 g, 2.86 mmol) and excess NEt_3 (1.00 mL, 7.17 mmol) were mixed in THF (50 mL). Di-*tert*-butyl-chlorophosphine (0.584 mL, 3.00 mmol) was added via a syringe and the reaction mixture was stirred at room temperature for 15 h. The resulting suspension was filtered, and the solvent was removed in vacuo. The crude solid was recrystallized from THF/Et_2O, yielding the pure product as a white solid. (0.597 g, 1.34 mmol, 47%). ^1H NMR ($CDCl_3$): δ 10.60 (*pseudo* t, ^4J(HH) = 1.5 Hz, 1H, NCHN), 7.64 (*pseudo* t, ^3J(HH) = ^4J(HH) = 1.7 Hz, 1H, $CH_{imid.}$), 7.61 (*pseudo* t, ^3J(HH) = ^4J(HH) = 1.7 Hz, 1H, $CH_{imid.}$), 7.44−7.51 (m, 2H), 7.39−7.43 (m, 2H), 4.29 (s, 3H, NCH_3), 1.20 [d, ^3J(PH) = 12.0 Hz, 18H, CH_3, P(*t*-Bu)$_2$]; $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 161.3 (d, ^2J(PC) = 4.9 Hz, C−O), 136.1 ($C_{arom.}$), 135.3 (NCN), 131.5 ($C_{arom.}$), 124.3 ($C_{imid.}$), 120.7 ($C_{imid.}$), 120.2 (d, ^3J(PC) = 11.8 Hz, $C_{arom.}$), 115.0 ($C_{arom.}$), 111.8 (d, ^3J(PC) = 11.2 Hz, $C_{arom.}$), 37.4 (NCH_3), 35.7 [d, ^1J(PC) = 25.0 Hz, $C_{quart.}$, 2 × P(*t*-Bu)$_2$], 27.1 [d, ^2J(PC) = 15.4 Hz, CH_3, 2 × P(*t*-Bu)$_2$]; $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 159.92 ppm. ESI-MS (m/z): 319.2 $[M\text{-}I]^+$. Anal. Calcd for $C_{18}H_{28}IN_2OP$ (446.31): C, 48.44; H, 6.32; N, 6.28. Found: C, 48.17; H, 6.29; N, 6.07%.

Synthesis of the Tetranuclear Silver Cluster [Ag$_2$(*μ*$_3$-I)$_2$(*μ*-OP-NHC,*κP*,*κ*C_{NHC})]$_2$ (9a). In a Schlenk tube, Ag_2O (0.023 g, 0.10 mmol) and AgI (0.047 g, 0.20 mmol) were added to a solution of 1-methyl-3-(3-(di-*tert*-butylphosphinooxy)phenyl)imidazolium iodide (0.089 g, 0.20 mmol) in CH_2Cl_2 (15 mL). The mixture was stirred at room temperature for 15 h. The solvent was removed in vacuo, and the solid obtained was recrystallized from CH_2Cl_2/Et_2O, yielding the product as a colorless solid (0.16 g, 0.087 mmol, 87%). Single crystals of **9a**·CH_2Cl_2 suitable for X-ray diffraction studies were obtained by slow diffusion of Et_2O into a saturated dichloromethane solution of the complex. ^1H NMR (CD_2Cl_2): δ 7.55 (br s, 1H, $CH_{arom.}$), 7.38 (t, ^3J(HH) = 8.0 Hz, 1H, $CH_{arom.}$), 7.20 (d, ^3J(HH) = 1.8 Hz, 1H, $CH_{imid.}$), 7.11−7.16 (m, 2H, $CH_{arom.}$), 7.10 (d, ^3J(HH) = 1.8 Hz, 1H, $CH_{imid.}$), 3.97 (s, 3H, NCH_3), 1.41 [d, ^3J(PH) = 14.6 Hz, 18H, P(*t*-Bu)$_2$]; $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 158.6 (C−O), 142.1 (C−N), 130.2 ($C_{arom.}$), 122.3 ($C_{imid.}$), 121.7 ($C_{imid.}$), 121.1 (d, ^3J(PC) = 2.7 Hz, $C_{arom.}$), 119.4 ($C_{arom.}$), 118.0 (d, ^3J(PC) = 8.1 Hz, $C_{arom.}$), 39.5 (NCH_3), 39.2 [d, ^1J(PC) = 0.8 Hz, $C_{quart.}$, 2 × P(*t*-Bu)$_2$], 28.2 [d, ^2J(PC) = 10.0 Hz, CH_3, 2 × P(*t*-Bu)$_2$], the resonance of the coordinated NHC carbon could not be observed, probably because of the poor solubility of the complex in CD_2Cl_2; $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 158.33 (br, ^1J(P−Ag) not resolved) ppm. ESI-MS (m/z): 1576.6 $[M+H]^+$, 1468.7 $[M+2H-Ag]^+$, 1340.8 $[M+H-AgI]^+$, 1234.9 $[M\text{-}AgI_2]^+$. Anal. Calcd for $C_{36}H_{54}Ag_4I_4N_4O_2P_2\cdot 3CH_2Cl_2$ (1830.68): C, 25.59; H, 3.30; N, 3.06. Found: C, 25.14; H, 3.26; N, 3.15%.

Synthesis of [IrH(I)(PO-NHC,*κP*,*κC*,*κ*C_{NHC})^{Me}] (10a). Solid **8a** (0.178 g, 0.399 mmol), $[Ir(coe)_2(\mu\text{-}Cl)]_2$ (0.180 g, 0.200 mmol), and

Cs_2CO_3 (0.163 g, 0.500 mmol) were mixed and heated in THF (50 mL) at 65 °C for 3 h. The suspension was then allowed to cool to room temperature, and the solvent was removed in vacuo. Toluene (15 mL) was added to extract the product, and the suspension was filtered. The filtrate was concentrated to 3 mL and layered with pentane to give some red crystals at 0 °C in low yield (0.020 g, 0.031 mmol, 7.7% based on Ir). ^{1}H NMR ($C_6D_5CD_3$): δ 6.84 (2H, m, $CH_{arom.}$), 6.58 (1H, br s, $CH_{imid.}$), 6.40 (1H, d, $^{3}J(HH)$ = 7.3 Hz, $CH_{arom.}$), 5.99 (1H, br s, $CH_{imid.}$), 3.98 (3H, s, NCH_3), 1.48 (9H, d, $^{3}J(PH)$ = 13.9 Hz, $C(CH_3)_3$), 1.33 (9H, d, $^{3}J(PH)$ = 14.1 Hz, $C(CH_3)_3$), −26.88 (1H, d, $^{2}J(PH)$ = 17.6 Hz, IrH). $^{13}C\{^{1}H\}$ NMR ($C_6D_5CD_3$): δ 175.2 (NCN), 166.2 ($C_{arom.}$−O), 145.0 ($C_{arom.}$−N), 122.1 ($C_{imid.}$), 120.7 (d, $^{3}J(PC)$ = 4.7 Hz, $C_{arom.}$), 114.8 ($C_{imid.}$), 107.6(d, $^{3}J(PC)$ = 9.6 Hz, $C_{arom.}$), 105.0 ($C_{arom.}$), 43.5 [d, $^{1}J(PC)$ = 15.1 Hz, $C_{quart.}$, P(*t*-Bu)$_2$], 39.7 [d, $^{1}J(PC)$ = 21.0 Hz, $C_{quart.}$, P(*t*-Bu)$_2$], 37.7 (NCH_3), 27.2 [CH_3, P(*t*-Bu)$_2$], 27.0 [CH_3, P(*t*-Bu)$_2$], the resonance of one of the aromatic carbon (supposed to be present around δ 130 ppm) may overlap with the solvent peaks; $^{31}P\{^{1}H\}$ NMR ($C_6D_5CD_3$): δ 174.61 ppm. Anal. Calcd for $C_{18}H_{28}IIrN_2OP$ (638.52): C, 33.86; H, 4.42; N, 4.39. Found: C, 33.35 ; H, 4.10: N, 4.15. The air- and moisture-sensitivity of this complex precluded better elemental analysis data to be obtained.

Synthesis of [IrH(I)(PO-NHC,*κP*,*κC*,*κ*C_{NHC})$^{n\text{-}Bu}$] (10b). Solid 1-butyl-3-(3-(di-*tert*-butylphosphinooxy)phenyl) imidazolium iodide (**8b**) (0.195 g, 0.399 mmol), $[Ir(coe)_2(\mu\text{-}Cl)]_2$ (0.180 g, 0.200 mmol), and Cs_2CO_3 (0.163 g, 0.500 mmol) were mixed and heated in THF (50 mL) at 65 °C for 3 h. The suspension was then allowed to cool to room temperature, and the solvent was removed in vacuo. Toluene (15 mL) was added to extract the product, and the suspension was filtered. The filtrate was concentrated to 3 mL and layered with pentane to give some dark red crystals at 0 °C in low yield (0.025 g, 0.037 mmol, 9.2% based on Ir). Their poor quality and that of the X-ray diffraction data prevented a full refinement of the structure (a = 10.7577(5) Å, b = 20.0596(13) Å, c = 11.8999(7) Å, $\alpha = \gamma$ = 90.00°, β = 113.069(3)°, V = 2362.6(2) Å^3, Z = 4). However, tridentate coordination of the pincer ligand and iodide coordination trans to carbon were unambiguously established. ^{1}H NMR ($C_6D_5CD_3$): δ 6.84 (2H, m, $CH_{arom.}$), 6.67 (1H, br s, $CH_{imid.}$), 6.43 (1H, d, $^{3}J(HH)$ = 7.1 Hz, $CH_{arom.}$), 6.26 (1H, br s, $CH_{imid.}$), 4.97 (1H, br s, A part of an AB spin system, NC*H*H), 4.49 (1H, br s, B part of an AB spin system, NCH*H*), 1.75 (2H, m, NCH_2CH_2), 1.48 (11H, m, CH_2CH_3 + $C(CH_3)_3$), 1.36 (9H, d, $^{3}J(PH)$ = 14.9 Hz, $C(CH_3)_3$), 0.92 (3H, t, CH_2CH_3), −31.72 (1H, br s, IrH); $^{13}C\{^{1}H\}$ NMR ($C_6D_5CD_3$): δ 175.4 (NCN), 166.7 ($C_{arom.}$−O), 146.1 ($C_{arom.}$−N), 122.7 ($C_{imid.}$), 120.1 (d, $^{3}J(PC)$ = 2.7 Hz, $C_{arom.}$), 114.7 ($C_{imid.}$), 107.5(d, $^{3}J(PC)$ = 8.1 Hz, $C_{arom.}$), 104.7 ($C_{arom.}$), 51.3 (NCH_2), 43.4 [d, $^{1}J(PC)$ = 14.4 Hz, $C_{quart.}$, P(*t*-Bu)$_2$], 40.3 [d, $^{1}J(PC)$ = 18.2 Hz, $C_{quart.}$, P(*t*-Bu)$_2$], 34.6 (CH_2), 27.3 [CH_3, P(*t*-Bu)$_2$], 27.1 [CH_3, P(*t*-Bu)$_2$], 21.9 (CH_2), 14.3 (CH_3), the resonance of one of the aromatic carbon (supposed at around δ 130 ppm) may be masked by the solvent peaks; $^{31}P\{^{1}H\}$ NMR ($C_6D_5CD_3$): δ 173.13 ppm. ESI-MS (*m*/*z*): 594.2 $[M\text{-}I+2H\ +K]^+$, 552.2 $[M\text{-}HI]^+$. Anal. Calcd for $C_{21}H_{34}IIrN_2OP$ (680.60): C, 37.06; H, 5.04; N, 4.12. Found: C, 36.55 ; H, 4.70: N, 3.85. The air- and moisture-sensitivity of this complex precluded better elemental analysis data to be obtained.

Synthesis of (3-Bromobenzyl)diphenylphosphine Oxide. A solution of potassium diphenylphosphide in THF (0.50 M, 10 mL, 5.0 mmol) was added dropwise to a solution of 1-bromo-3-(bromomethyl)benzene (1.25 g, 5.00 mmol) in DMSO (10 mL). The mixture was stirred at 60 °C overnight and then cooled to room temperature. Dichloromethane (50 mL) was added, and the mixture was washed with brine (20 mL). The organic layer was collected and dried with anhydrous Na_2SO_4. Air was bubbled through the filtered solution, and stirring was maintained for 1 h. The solvent was then removed under vacuum to afford (3-bromobenzyl)diphenylphosphine oxide as a white solid after washing with diethyl ether (3 × 10 mL). (0.76 g, 2.0 mmol, 41%). ^{1}H NMR ($CDCl_3$): δ 7.72−7.66 (5H, m, $CH_{arom.}$), 7.52−7.43 (5H, m, $CH_{arom.}$), 7.31−7.29 (1H, m, $CH_{arom.}$), 7.24−7.18 (2H, m, $CH_{arom.}$), 7.08 (1H, s, $CH_{arom.}$), 3.60 (2H, d, $^{2}J(PH)$ = 13.6 Hz, PCH_2); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 133.08 (d, $J(PC)$ = 7.9 Hz), 132.59 (d, $J(PC)$ = 5.3 Hz), 132.05, 131.61 (d, $J(PC)$ = 2.8 Hz), 131.42 (d, $J(PC)$ = 5.3 Hz), 131.35 (d, $J(PC)$ = 5.5 Hz), 130.69 (d, $J(PC)$ = 9.2 Hz), 129.53 (d, $J(PC)$ = 2.9 Hz), 129.40 (d, $J(PC)$ = 2.5 Hz), 128.35 (d, $J(PC)$ = 5.1 Hz), 128.18 (d, $J(PC)$ = 11.8 Hz), 128.16, 37.38 (d, $J(PC)$= 65.7 Hz, PCH_2); $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ 29.32 ppm; ESI-MS (*m*/*z*): 371.0 $[M+H]^+$. Anal. Calcd for $C_{19}H_{16}BrOP$ (371.21): C, 61.48; H, 4.34. Found: C, 61.80; H, 4.45%.

Synthesis of 3-(3-((Diphenylphosphoryl)methyl)phenyl)-1-methyl-1*H*-imidazol-3-ium Iodide (11). First, (3(1*H*-imidazol-1-yl)benzyl)diphenylphosphine oxide was prepared by reacting (3-bromobenzyl)diphenylphosphine oxide (1.12 g, 3.02 mmol), imidazole (0.336 g, 4.94 mmol), K_2CO_3 (0.692 g, 5.00 mmol), and CuO (0.046 g, 0.58 mmol) in DMSO (5 mL). The solution was heated at 150 °C for 48 h. The mixture was cooled, and the DMSO was distilled off under reduced pressure. CH_2Cl_2 (15 mL) was added, and the suspension was filtered. The filtrate was concentrated to 5 mL, and diethyl ether (15 mL) was added to precipitate an off-white solid, which was collected and dried. Then, to a flask containing a larger quantity of (3-(1*H*-imidazol-1-yl)benzyl)diphenylphosphine oxide (1.79 g, 5.00 mmol) iodomethane (10 mL) was added, and the suspension was stirred at room temperature for 3 h until the color of the solid turned to light yellow. It was then filtered, washed with diethyl ether (3 × 30 mL), and an off-white solid was obtained. (1.50 g, 3.00 mmol, 60%). ^{1}H NMR (d_6-DMSO): δ 9.66 (1H, s, NCHN), 8.10 (1H, s, $CH_{imid.}$), 7.94 (1H, s, $CH_{imid.}$), 7.84 (4H, m, $CH_{arom.}$), 7.66 (1H, s, $CH_{arom.}$), 7.55 (8H, m, $CH_{arom.}$), 7.30 (1H, m, $CH_{arom.}$), 4.05 (2H, d, $^{2}J(P{-}H)$ = 13.8 Hz, PCH_2), 3.94 (3H, s, NCH_3); $^{13}C\{^{1}H\}$ NMR (d_6-DMSO): δ 135.80 ($C_{arom.}$), 135.04 (d, $J(P{-}C)$ = 8.1 Hz, $C_{arom.}$), 134.30 (d, $J(PC)$ = 2.6 Hz, $C_{arom.}$), 133.54 ($C_{arom.}$), 132.24 ($C_{arom.}$), 131.73 (d, $J(PC)$ = 2.5 Hz, $C_{arom.}$), 131.05 (d, $J(PC)$ = 5.3 Hz, $C_{arom.}$), 130.60 (d, $J(P{-}C)$ = 9.3 Hz, $C_{arom.}$), 129.74 (d, $J(PC)$ = 2.1 Hz, $C_{arom.}$), 128.58 (d, $J(PC)$ = 11.5 Hz, $C_{arom.}$), 124.55 (C_{imid}), 123.27 (d, $J(PC)$ = 5.1 Hz, $C_{arom.}$), 120.65 (C_{imid}), 119.91 (d, $J(PC)$ = 2.7 Hz, $C_{arom.}$), 36.13 (NCH_3), 35.79 (d, $J(PC)$ = 64.9 Hz, PCH_2); $^{31}P\{^{1}H\}$ NMR (d_6-DMSO): δ 27.67 ppm. ESI-MS (*m*/*z*): 373.2 $[M{-}I]^+$. Anal. Calcd for $C_{23}H_{22}IN_2OP$ (500.31): C, 55.21; H, 4.43; N, 5.60. Found: C, 55.27; H, 4.50; N, 5.53%.

Synthesis of the Ag(I) Complex of the Phosphoryl-NHC Ligand (12). Ag_2O (0.023 g, 0.099 mmol) was added to a CH_2Cl_2 solution of **11** (0.100 g, 0.200 mmol). The suspension was stirred at room temperature overnight under the protection against light. It was then filtered to remove unreacted Ag_2O, and the filtrate was concentrated to 5 mL. Diethyl ether (30 mL) was added, and an off-white solid precipitated. The solid was collected through filtration, yielding the Ag(I) complex **12** (0.089 g, 0.15 mmol, 73%). ^{1}H NMR (d_6-DMSO): δ 7.86−7.79 (4H, m, $CH_{arom.}$), 7.66 (1H, br s, $CH_{imid.}$), 7.59 (1H, br s, $CH_{imid.}$), 7.58−7.46 (8H, m, $CH_{arom.}$), 7.27−7.22 (2H, m, $CH_{arom.}$), 3.98 (2H, d, $^{2}J(P{-}H)$ = 13.8 Hz, PCH_2), 3.82 (3H, s, NCH_3), the broadness of some resonances could be due to some dynamic behavior; $^{13}C\{^{1}H\}$ NMR (d_6-DMSO): δ 139.27 (d, $J(P{-}C)$ = 2.8 Hz, $C_{arom.}$), 134.43 (d, $J(P{-}C)$ = 7.9 Hz, $C_{arom.}$), 133.75 (s, $C_{arom.}$), 132.50 (s, $C_{arom.}$), 131.68 (d, $J(PC)$ = 3.0 Hz, $C_{arom.}$), 130.55 (d, $J(PC)$ = 9.1 Hz, $C_{arom.}$), 129.18 (d, $J(PC)$ = 2.8 Hz, $C_{arom.}$), 128.85 (s, $C_{arom.}$), 128.58 (d, $J(PC)$ = 11.6 Hz, $C_{arom.}$), 128.16 (s, $C_{arom.}$), 125.39 (d, $J(PC)$ = 7.4 Hz, $C_{arom.}$), 124.05 (s, $C_{imid.}$), 122.88 (s, $C_{arom.}$), 121.80 ($C_{imid.}$), 38.39 (s, NCH_3), 35.66 (d, $J(PC)$ = 65.0 Hz, PCH_2); $^{31}P\{^{1}H\}$ NMR (d_6-DMSO): δ 27.72 ppm. ESI-MS (*m*/*z*): 373.1 $[M{-}AgI]^+$. Anal. Calcd for $C_{23}H_{21}AgIN_2OP$ (607.17): C, 45.50; H, 3.49; N, 4.61. Found: C, 45.01; H, 3.58; N, 4.31%. Despite several attempts, no better elemental analysis data could be obtained.

Synthesis of the Phosphoryl-NHC Cu(I) Complex [Cu(OP-NHC,*κ*C_{NHC})$_2$(μ-I){Cu(μ-I)}]$_2$ (13). A suspension of **11** (0.100 g, 0.200 mmol), $[Cu(NCMe)_4]PF_6$ (0.074 g, 0.20 mmol) and Cs_2CO_3 (0.098 g, 0.30 mmol) in acetonitrile (10 mL) was stirred at 60 °C for 1 h under an inert atmosphere. The suspension was then allowed to cool to room temperature, and the solvent was removed under vacuum. The resulting colorless solid was then treated with CH_2Cl_2 (10 mL), and the solution was filtered. The filtrate was concentrated to 5 mL, and diethyl ether was added to precipitate a white solid.

Table 2. X-ray Data Collection and Structure Refinement Parameters

compound	3	4·2THF	9a·CH_2Cl_2	11	13
chemical formula	$C_{48}H_{46}Ag_2N_4P_2·2PF_6$	$C_{64}H_{70}Ir_2N_4P_2·C_8H_{16}O_2·2PF_6$	$C_{36}H_{54}Ag_4I_4N_4O_2P_2·CH_2Cl_2$	$C_{23}H_{22}IN_2OP$	$C_{92}H_{84}Cu_4I_4N_8O_4P_4$
formula Mass	1246.51	1775.73	1660.78	500.30	2251.31
crystal system	monoclinic	triclinic	monoclinic	triclinic	triclinic
a/Å	11.9233(3)	10.0347(6)	20.4549(6)	9.4993(7)	13.0030(7)
b/Å	10.5074(5)	14.2909(6)	12.3814(2)	11.2175(9)	13.7427(8)
c/Å	19.8377(8)	14.4418(7)	25.1919(6)	12.0230(15)	14.3145(6)
α/deg	90.00	62.225(3)	90.00	108.775(2)	72.152(3)
β/deg	93.315(2)	72.114(3)	123.518(2)	107.405(2)	76.698(3)
γ/deg	90.00	85.688(3)	90.00	103.001(2)	63.608(2)
unit cell volume/Å^3	2481.17(17)	1738.17(15)	5319.2(2)	1081.80(18)	2167.82(19)
temperature/K	173(2)	173(2)	193(2)	173(2)	173(2)
space group	$P2_1/n$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
Z	2	1	4	2	1
absorption coefficient, μ/mm^{-1}	1.003	3.997	3.966	1.570	2.522
no. of reflections measured	8209	10687	34450	14190	12341
no. of independent reflections	4855	6819	12190	5231	7685
R_{int}	0.0348	0.0423	0.0691	0.0359	0.0529
final R1 values ($I > 2\sigma(I)$)	0.0530	0.0530	0.0619	0.0306	0.0759
final wR(F^2) values ($I > 2\sigma(I)$)	0.1402	0.1082	0.1502	0.0581	0.1614
final R1 values (all data)	0.0837	0.0801	0.0998	0.0517	0.1317
final wR(F^2) values (all data)	0.1743	0.1210	0.1667	0.0638	0.1810
goodness of fit on F^2	1.139	1.030	1.101	1.029	1.041

Recrystallization was carried out by layering Et_2O onto a MeCN solution of the white solid, which afforded colorless crystals (0.10 g, 0.044 mmol, 88%). Single crystals suitable for X-ray diffraction studies were obtained by slow vapor diffusion of pentane into a saturated dichloromethane solution of the complex. ^{1}H NMR (CD_3CN): δ 7.77−7.70 (4H, m, $CH_{arom.}$), 7.54−7.44 (8H, m, $CH_{arom.}$), 7.18−7.12 (4H, m, $CH_{arom.}$), 3.75 (2H, d, ^2J(PH) = 13.6 Hz, PCH_2), 3.69 (3H, s, NCH_3); ^{31}P{^{1}H} NMR (CD_3CN): δ 27.46 ppm. The broadness of the ^{13}C{^{1}H} NMR resonances, probably because of quadrupolar effects and/or dynamic behavior of the Cu(I) complex, prevented their full identification. Anal. Calcd for $C_{92}H_{84}Cu_4I_4N_8O_4P_4$ (2251.40): C, 49.08; H, 3.76; N, 4.98. Found: C, 48.85 ; H, 3.45 ; H, 4.85.

X-ray Data Collection and Structure Refinement for All Compounds. Suitable crystals for the X-ray analysis were obtained as described above. The intensity data were collected at 173(2) K on a Kappa CCD diffractometer[148] (graphite monochromated Mo−Kα radiation, λ = 0.71073 Å). Crystallographic and experimental details for the structures are summarized in Table 2. The structures were solved by direct methods (SHELXS-97) and refined by full-matrix least-squares procedures (based on F^2, SHELXL-97)[149] with anisotropic thermal parameters for all the non-hydrogen atoms. CCDC 852587−852591 contain the supplementary crystallographic data for this paper that can be obtained free of charge from the Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The CIF of compounds **3**, **4**·2THF, **9a**·CH_2Cl_2, **11**, and **13**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: braunstein@unistra.fr.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank the Centre National de la Recherche Scientifique, the Ministère de l′Enseignement Supérieur et de la Recherche (Paris), the Université de Strasbourg, and the **I**nternational **C**enter for **F**rontier **R**esearch in **C**hemistry, Strasbourg (icFRC, www.icfrc.fr), the China Scholarship Council and the French Embassy in Beijing (grant to X.L.) for financial support. We are very grateful to Johnson Matthey PLC for the loan of iridium salts and to Drs. Roberto Pattacini and the Service de Radiocristallographie, Institut de Chimie, Strasbourg, for the resolution of the structures by X-ray diffraction and to Dr. A. A. Danopoulos for discussions.

■ REFERENCES

(1) Moulton, C. J.; Shaw, B. L. *Dalton Trans.* **1976**, 1020.

(2) Cazin, C. S. J. *N-Heterocyclic Carbenes in Transition Metal Catalysis and Organocatalysis*, 1st ed.; Springer: Dordrecht, The Netherlands, 2011.

(3) Themed issue: Pincers and other hemilabile ligands. *Dalton Trans.* **2011**, *40*, 8713−9052.

(4) Rybtchinski, B.; Milstein, D. *Angew. Chem., Int. Ed.* **1999**, *38*, 870.

(5) Albrecht, M.; van Koten, G. *Angew. Chem., Int. Ed.* **2001**, *40*, 3750.

(6) Singleton, J. T. *Tetrahedron* **2003**, *59*, 1837.

(7) van der Boom, M. E.; Milstein, D. *Chem. Rev.* **2003**, *103*, 1759.

(8) Herrmann, W. A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1290.

(9) Crabtree, R. H. *J. Organomet. Chem.* **2005**, *690*, 5451.

(10) Öfele, K. *J. Organomet. Chem.* **1968**, *12*, P42.

(11) Schultz, K. M.; Goldberg, K. I.; Gusev, D. G.; Heinekey, D. M. *Organometallics* **2011**, *30*, 1429.

(12) Godoy, F.; Segarra, C.; Poyatos, M.; Peris, E. *Organometallics* **2011**, *30*, 684.

(13) Cho, J.; Hollis, T. K.; Valente, E. J.; Trate, J. M. *J. Organomet. Chem.* **2011**, *696*, 373.

(14) Kose, O.; Saito, S. *Org. Biomol. Chem.* **2010**, *8*, 896.

(15) Chianese, A. R.; Mo, A.; Lampland, N. L.; Swartz, R. L.; Bremer, P. T. *Organometallics* **2010**, *29*, 3019.

(16) Raynal, M.; Pattacini, R.; Cazin, C. S. J.; Vallée, C.; Olivier-Bourbigou, H.; Braunstein, P. *Organometallics* **2009**, *28*, 4028.
(17) Raynal, M.; Cazin, C. S. J.; Vallée, C.; Olivier-Bourbigou, H.; Braunstein, P. *Dalton Trans.* **2009**, 3824.
(18) Andavan, G. T. S.; Bauer, E. B.; Letko, C. S.; Hollis, T. K.; Tham, F. S. *J. Organomet. Chem.* **2005**, *690*, 5938.
(19) Bauer, E. B.; Andavan, G. T. S.; Hollis, T. K.; Rubio, R. J.; Cho, J.; Kuchenbeiser, G. R.; Helgert, T. R.; Letko, C. S.; Tham, F. S. *Org. Lett.* **2008**, *10*, 1175.
(20) Rubio, R. J.; Andavan, G. T. S.; Bauer, E. B.; Hollis, T. K.; Cho, J.; Tham, F. S.; Donnadieu, B. *J. Organomet. Chem.* **2005**, *690*, 5353.
(21) Lv, K.; Cui, D. *Organometallics* **2008**, *27*, 5438.
(22) Zuo, W. W.; Braunstein, P. *Organometallics* **2010**, *29*, 5535.
(23) Raynal, M.; Cazin, C. S. J.; Vallée, C.; Olivier-Bourbigou, H.; Braunstein, P. *Chem. Commun.* **2008**, 3983.
(24) Tu, T.; Malineni, J.; Bao, X.; Dötz, K. H. *Adv. Synth. Catal.* **2009**, *351*, 1029.
(25) Maron, L.; Bourissou, D. *Organometallics* **2009**, *28*, 3686.
(26) Kuroda, J.-i.; Inamoto, K.; Hiroya, K.; Doi, T. *Eur. J. Org. Chem.* **2009**, 2251.
(27) Inamoto, K.; Kuroda, J.-i.; Kwon, E.; Hiroya, K.; Doi, T. *J. Organomet. Chem.* **2009**, *694*, 389.
(28) Danopoulos, A. A.; Pugh, D.; Smith, H.; Sassmannshausen, J. *Chem.—Eur. J.* **2009**, *15*, 5491.
(29) Brown, D. H.; Nealon, G. L.; Simpson, P. V.; Skelton, B. W.; Wang, Z. *Organometallics* **2009**, *28*, 1965.
(30) Pugh, D.; Boyle, A.; Danopoulos, A. A. *Dalton Trans.* **2008**, 1087.
(31) Danopoulos, A. A.; Tsoureas, N.; Green, J. C.; Hursthouse, M. B. *Chem. Commun.* **2003**, 756.
(32) Danopoulos, A. A.; Wright, J. A.; Motherwell, W. B. *Chem. Commun.* **2005**, 784.
(33) Danopoulos, A. A.; Pugh, D.; Wright, J. A. *Angew. Chem., Int. Ed.* **2008**, *47*, 9765.
(34) Peris, E.; Crabtree, R. H. *Coord. Chem. Rev.* **2004**, *248*, 2239.
(35) Jacobsen, H.; Correa, A.; Poater, A.; Costabile, C.; Cavallo, L. *Coord. Chem. Rev.* **2009**, *253*, 687.
(36) Bader, A.; Lindner, E. *Coord. Chem. Rev.* **1991**, *108*, 27.
(37) Braunstein, P. *J. Organomet. Chem.* **2004**, *689*, 3953.
(38) Braunstein, P.; Naud, F. *Angew. Chem., Int. Ed.* **2001**, *40*, 680.
(39) Slone, C. S.; Weinberger, D. A.; Mirkin, C. A. *Prog. Inorg. Chem.* **1999**, *48*, 233.
(40) Braunstein, P. *Chem. Rev.* **2006**, *106*, 134.
(41) Tornatzky, J.; Kannenberg, A.; Blechert, S. *Dalton Trans.* **2012**, *41*, 8215.
(42) Gaillard, S.; Renaud, J.-L. *Dalton Trans.* **2013**, *42*, 7255.
(43) Wanzlick, H. W.; Schönherr, H. J. *Angew. Chem., Int. Ed.* **1968**, *7*, 141.
(44) Yang, C.; Lee, H. M.; Nolan, S. P. *Org. Lett.* **2001**, *3*, 1511.
(45) Bappert, E.; Helmchen, G. *Synlett* **2004**, *10*, 1789.
(46) Becht, J. M.; Bappert, E.; Helmchen, G. *Adv. Synth. Catal.* **2005**, *347*, 1495.
(47) Cabeza, J. A.; Damonte, M.; García-Álvarez, P.; Kennedy, A. R.; Pérez-Carreño, E. *Organometallics* **2011**,, *30*, 826.
(48) Canac, Y.; Lepetit, C.; Abdalilah, M.; Duhayon, C.; Chauvin, R. *J. Am. Chem. Soc.* **2008**, *130*, 8406.
(49) Danopoulos, A. A.; Tsoureas, N.; Macgregor, S. A.; Smith, C. *Organometallics* **2007**, *26*, 253.
(50) Danopoulos, A. A.; Winston, S.; Gelbrich, T.; Hursthouse, M. B.; Tooze, R. P. *Chem. Commun.* **2002**, 482.
(51) Debono, N.; Labande, A.; Manoury, E.; Daran, J.-C.; Poli, R. *Organometallics* **2010**, *29*, 1879.
(52) Field, L. D.; Messerle, B. A.; Vuong, K. Q.; Turner, P. *Organometallics* **2005**, *24*, 4241.
(53) Focken, T.; Raabe, G.; Bolm, C. *Tetrahedron: Asymmetry* **2004**, *15*, 1693.
(54) Gischig, S.; Togni, A. *Eur. J. Inorg. Chem.* **2005**, 4745.
(55) Gischig, S.; Togni, A. *Organometallics* **2005**, *24*, 203.
(56) Lee, C. C.; Ke, W. C.; Chan, K. T.; Lai, C. L.; Hu, C. H.; Lee, H. M. *Chem.—Eur. J.* **2007**, 582.
(57) Nanchen, S.; Pfaltz, A. *Helv. Chim. Acta* **2006**, *89*, 1559.
(58) Seo, H.; Park, H.; Kim, B. Y.; Lee, J. H.; Son, S. U.; Chung, Y. K. *Organometallics* **2003**, *22*, 618.
(59) Song, G.; Wang, X.; Li, Y.; Li, X. *Organometallics* **2008**, *27*, 1187.
(60) Stylianides, N.; Danopoulos, A. A.; Tsoureas, N. *J. Organomet. Chem.* **2005**, *690*, 5948.
(61) Tsoureas, N.; Danopoulos, A. A.; Tulloch, A. A. D.; Light, M. E. *Organometallics* **2003**, *22*, 4750.
(62) Waetzig, J. D.; Swift, E. C.; Jarvo, E. R. *Tetrahedron* **2009**, *65*, 3197.
(63) Wang, A. E.; Xie, J. H.; Wang, L. X.; Zhou, Q. L. *Tetrahedron* **2005**, *61*, 259.
(64) Wang, A. E.; Zhong, J.; Xie, J. H.; Li, K.; Zhou, Q. L. *Adv. Synth. Catal.* **2004**, *346*, 595.
(65) Wolf, J.; Labande, A.; Daran, J.-C.; Poli, R. *Eur. J. Inorg. Chem.* **2008**, *2008*, 3024.
(66) Wolf, J.; Labande, A.; Daran, J. C.; Poli, R. *J. Organomet. Chem.* **2006**, *691*, 433.
(67) Zhong, J.; Xie, J. H.; Wang, A. E.; Zhang, W.; Zhou, Q. L. *Synlett* **2006**, 1193.
(68) Gischig, S.; Togni, A. *Organometallics* **2004**, *23*, 2479.
(69) Lee, H. M.; Chiu, P. L.; Zeng, J. Y. *Inorg. Chim. Acta* **2004**, *357*, 4313.
(70) Miranda-Soto, V.; Grotjahn, D. B.; DiPasquale, A. G.; Rheingold, A. L. *J. Am. Chem. Soc.* **2008**, *130*, 13200.
(71) Blase, V.; Pape, T.; Hahn, F. E. *J. Organomet. Chem.* **2011**, *696*, 3337.
(72) Chiu, P. L.; Lee, H. M. *Organometallics* **2005**, *24*, 1692.
(73) Flores-Figueroa, A.; Kaufhold, O.; Hepp, A.; Fröhlich, R.; Hahn, F. E. *Organometallics* **2009**, *28*, 6362.
(74) Hahn, F. E.; Jahnke, M. C.; Pape, T. *Organometallics* **2006**, *25*, 5927.
(75) Kaufhold, O.; Stasch, A.; Edwards, P. G.; Hahn, F. E. *Chem. Commun.* **2007**, 1822.
(76) Kaufhold, O.; Stasch, A.; Pape, T.; Hepp, A.; Edwards, P. G.; Newman, P. D.; Hahn, F. E. *J. Am. Chem. Soc.* **2008**, *131*, 306.
(77) Steinke, T.; Shaw, B. K.; Jong, H.; Patrick, B. O.; Fryzuk, M. D. *Organometallics* **2009**, *28*, 2830.
(78) Flores-Figueroa, A.; Pape, T.; Feldmann, K.-O.; Hahn, F. E. *Chem. Commun.* **2010**, *46*, 324.
(79) Lin, J. C. Y.; Huang, R. T. W.; Lee, C. S.; Bhattacharyya, A.; Hwang, W. S.; Lin, I. J. B. *Chem. Rev.* **2009**, *109*, 3561.
(80) Lee, H. M.; Zeng, J. Y.; Hu, C.-H.; Lee, M.-T. *Inorg. Chem.* **2004**, *43*, 6822.
(81) Zeng, J. Y.; Hsieh, M. H.; Lee, H. M. *J. Organomet. Chem.* **2005**, *690*, 5662.
(82) Crabtree, R. *Acc. Chem. Res.* **1979**, *12*, 331.
(83) Choi, J.; MacArthur, A. H. R.; Brookhart, M.; Goldman, A. S. *Chem. Rev.* **2011**, *111*, 1761.
(84) Crabtree, R. H. *Chem. Rev.* **2010**, *110*, 575.
(85) Suzuki, T. *Chem. Rev.* **2011**, *111*, 1825.
(86) Vazquez-Serrano, L. D.; Owens, B. T.; Buriak, J. M. *Chem. Commun.* **2002**, 2518.
(87) Dobereiner, G. E.; Nova, A.; Schley, N. D.; Hazari, N.; Miller, S. J.; Eisenstein, O.; Crabtree, R. H. *J. Am. Chem. Soc.* **2011**, *133*, 7547.
(88) Weinberg, D. R.; Hazari, N.; Labinger, J. A.; Bercaw, J. E. *Organometallics* **2010**, *29*, 89.
(89) Dobereiner, G. E.; Chamberlin, C. A.; Schley, N. D.; Crabtree, R. H. *Organometallics* **2010**, *29*, 5728.
(90) Metallinos, C.; Du, X. *Organometallics* **2009**, *28*, 1233.
(91) Fu, C. F.; Chang, Y. H.; Liu, Y. H.; Peng, S. M.; Elsevier, C. J.; Chen, J. T.; Liu, S. T. *Dalton Trans.* **2009**, 6991.
(92) Chang, Y. H.; Fu, C. F.; Liu, Y. H.; Peng, S. M.; Chen, J. T.; Liu, S. T. *Dalton Trans.* **2009**, 861.
(93) Brown, J. A.; Irvine, S.; Kennedy, A. R.; Kerr, W. J.; Andersson, S.; Nilsson, G. N. *Chem. Commun.* **2008**, 1115.

(94) Gruendemann, S.; Kovacevic, A.; Albrecht, M.; Faller, J. W.; Crabtree, R. H. *J. Am. Chem. Soc.* **2002**, *124*, 10473.
(95) Stylianides, N.; Danopoulos, A. A.; Tsoureas, N. *J. Organomet. Chem.* **2005**, *690*, 5948.
(96) Miranda-Soto, V.; Grotjahn, D. B.; Cooksy, A. L.; Golen, J. A.; Moore, C. E.; Rheingold, A. L. *Angew. Chem., Int. Ed.* **2011**, *50*, 631.
(97) Passays, J.; Ayad, T.; Ratovelomanana-Vidal, V.; Gaumont, A.-C.; Jubault, P.; Leclerc, E. *Tetrahedron: Asymmetry* **2011**, *22*, 562.
(98) Gong, X.; Zhang, H.; Li, X. *Tetrahedron Lett.* **2011**, *52*, 5596.
(99) Caruso, F.; Camalli, M.; Rimml, H.; Venanzi, L. M. *Inorg. Chem.* **1995**, *34*, 673.
(100) Chen, W.; Wu, B.; Matsumoto, K. *J. Organomet. Chem.* **2002**, *654*, 233.
(101) Liu, X.; Pattacini, R.; Deglmann, P.; Braunstein, P. *Organometallics* **2011**, *30*, 3302.
(102) Garrison, J. C.; Youngs, W. J. *Chem. Rev.* **2005**, *105*, 3978.
(103) Lin, I. J. B.; Vasam, C. S. *Coord. Chem. Rev.* **2007**, *251*, 642.
(104) Appelhans, L. N.; Zuccaccia, D.; Kovacevic, A.; Chianese, A. R.; Miecznikowski, J. R.; Macchioni, A.; Clot, E.; Eisenstein, O.; Crabtree, R. H. *J. Am. Chem. Soc.* **2005**, *127*, 16299.
(105) Liu, X. H.; Lacour, J.; Braunstein, P. *Dalton Trans.* **2012**, *41*, 138.
(106) Raynal, M.; Liu, X. H.; Pattacini, R.; Vallée, C.; Olivier-Bourbigou, H.; Braunstein, P. *Dalton Trans.* **2009**, 7288.
(107) Sculfort, S.; Braunstein, P. *Chem. Soc. Rev.* **2011**, *40*, 2741.
(108) Teo, B.-K.; Calabrese, J. C. *J. Am. Chem. Soc.* **1975**, *97*, 1256.
(109) Teo, B.-K.; Calabrese, J. C. *Inorg. Chem.* **1976**, *15*, 2474.
(110) Huang, Z.; White, P. S.; Brookhart, M. *Nature* **2010**, *465*, 598.
(111) Arunachalampillai, A.; Olsson, D.; Wendt, O. F. *Dalton Trans.* **2009**, 8626.
(112) Zhu, K.; Achord, P. D.; Zhang, X.; Krogh-Jespersen, K.; Goldman, A. S. *J. Am. Chem. Soc.* **2004**, *126*, 13044.
(113) Grimm, J. C.; Nachtigal, C.; Mack, H. G.; Kaska, W. C.; Mayer, H. A. *Inorg. Chem. Commun.* **2000**, *3*, 511.
(114) Gischig, S.; Togni, A. *Organometallics* **2004**, *24*, 203.
(115) Knishevitsky, A. V.; Korotkikh, N. I.; Cowley, A. H.; Moore, J. A.; Pekhtereva, T. M.; Shvaika, O. P.; Reeske, G. *J. Organomet. Chem.* **2008**, *693*, 1405.
(116) Goll, J. M.; Fillion, E. *Organometallics* **2008**, *27*, 3622.
(117) Shishkov, I. V.; Rominger, F.; Hofmann, P. *Dalton Trans.* **2009**, 1428.
(118) Simonovic, S.; Whitwood, A. C.; Clegg, W.; Harrington, R. W.; Hursthouse, M. B.; Male, L.; Douthwaite, R. E. *Eur. J. Inorg. Chem.* **2009**, *2009*, 1786.
(119) Al Thagfi, J.; Dastgir, S.; Lough, A. J.; Lavoie, G. G. *Organometallics* **2010**, *29*, 3133.
(120) Bellemin-Laponnaz, S. *Polyhedron* **2010**, *29*, 30.
(121) Bessel, M.; Rominger, F.; Straub, B. F. *Synthesis* **2010**, *2010*, 1459.
(122) Diez-Gonzalez, S.; Escudero-Adan, E. C.; Benet-Buchholz, J.; Stevens, E. D.; Slawin, A. M. Z.; Nolan, S. P. *Dalton Trans.* **2010**, *39*, 7595.
(123) Han, X.; Koh, L.-L.; Liu, Z.-P.; Weng, Z.; Hor, T. S. A. *Organometallics* **2010**, *29*, 2403.
(124) Liu, Q.-X.; Shi, M.-C.; Wang, Z.-Q.; Liu, S.-W.; Ge, S.-S.; Zang, Y.; Wang, X.-G.; Guo, J.-H. *Polyhedron* **2010**, *29*, 2121.
(125) Hohloch, S.; Su, C.-Y.; Sarkar, B. *Eur. J. Inorg. Chem.* **2011**, *2011*, 3067.
(126) Liu, Q.-X.; Chen, A.-H.; Zhao, X.-J.; Zang, Y.; Wu, X.-M.; Wang, X.-G.; Guo, J.-H. *CrystEngComm* **2011**, *13*, 293.
(127) Themed issue: Selective Functionalization of C-H Bonds. *Chem. Rev.* **2010**; *110*, 575−1211.
(128) Goldman, A. S.; Roy, A. H.; Huang, Z.; Ahuja, R.; Schinski, W.; Brookhart, M. *Science* **2006**, *312*, 257.
(129) Choi, J.; Wang, D. Y.; Kundu, S.; Choliy, Y.; Emge, T. J.; Krogh-Jespersen, K.; Goldman, A. S. *Science* **2011**, *332*, 1545.
(130) Gupta, M.; Hagen, C.; Flesher, R. J.; Kaska, W. C.; Jensen, C. M. *Chem. Commun.* **1996**, 2083.
(131) Gupta, M.; Hagen, C.; Kaska, W. C.; Cramer, R. E.; Jensen, C. M. *J. Am. Chem. Soc.* **1997**, *119*, 840.
(132) Göttker-Schnetmann, I.; White, P.; Brookhart, M. *J. Am. Chem. Soc.* **2004**, *126*, 1804.
(133) Morales-Morales, D.; Redon, R.; Yung, C.; Jensen, C. M. *Inorg. Chim. Acta* **2004**, *357*, 2953.
(134) Ahuja, R.; Kundu, S.; Goldman, A. S.; Brookhart, M.; Vicente, B. C.; Scott, S. L. *Chem. Commun.* **2008**, 253.
(135) Albrecht, M. *Chem. Rev.* **2009**, *110*, 576.
(136) Dobereiner, G. E.; Crabtree, R. H. *Chem. Rev.* **2010**, *110*, 681.
(137) Esswein, M. J.; Nocera, D. G. *Chem. Rev.* **2007**, *107*, 4022.
(138) Göttker-Schnetmann, I.; Brookhart, M. *J. Am. Chem. Soc.* **2004**, *126*, 9330.
(139) Hermann, D.; Gandelman, M.; Rozenberg, H.; Shimon, L. J. W.; Milstein, D. *Organometallics* **2002**, *21*, 812.
(140) Huang, Z.; Brookhart, M.; Goldman, A. S.; Kundu, S.; Ray, A.; Scott, S. L.; Vicente, B. C. *Adv. Synth. Catal.* **2009**, *351*, 188.
(141) Jensen, C. M. *Chem. Commun.* **1999**, 2443.
(142) Kanzelberger, M.; Singh, B.; Czerw, M.; Krogh-Jespersen, K.; Goldman, A. S. *J. Am. Chem. Soc.* **2000**, *122*, 11017.
(143) Krogh-Jespersen, K.; Czerw, M.; Summa, N.; Renkema, K. B.; Achord, P. D.; Goldman, A. S. *J. Am. Chem. Soc.* **2002**, *124*, 11404.
(144) Kuklin, S. A.; Sheloumov, A. M.; Dolgushin, F. M.; Ezernitskaya, M. G.; Peregudov, A. S.; Petrovskii, P. V.; Koridze, A. A. *Organometallics* **2006**, *25*, 5466.
(145) Punji, B.; Emge, T. J.; Goldman, A. S. *Organometallics* **2010**, *29*, 2702.
(146) Renkema, K. B.; Kissin, Y. V.; Goldman, A. S. *J. Am. Chem. Soc.* **2003**, *125*, 7770.
(147) M. Jensen, C. *Chem. Commun.* **1999**, 2443.
(148) *Kappa CCD Reference Manual*; Bruker-Nonius BV: Delft, The Netherlands, 1998.
(149) Sheldrick, M. *SHELXL-97, Program for crystal structure refinement*; University of Göttingen: Göttingen, Germany, 1997.