Synthesis and Structural Characterization of a Series of Novel Polyaromatic Ligands Containing Pyrene and Related Biscyclometalated Iridium(III) Complexes†

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A series of novel polyaromatic ligands containing pyrene with different types of substitution around the central pyridine ring were synthesized via Suzuki cross-coupling reactions. The series consists of 4-methyl-2-pyren-1-ylpyridine (**5**), in which the pyrene ring is attached to the 2-position of pyridine; 2-(3,5-bis(trifluoromethyl)phenyl)-5-pyren-1-ylpyridine (**16**), in which the pyrene ring is attached to the 5-position of pyridine; and 4-methyl-2-(3-pyren-1-ylphenyl)pyridine (**30**), in which the pyrene ring is attached to the 3-position of the 2-phenylpyridine moiety. The novel, sterically bulky di-*tert*-butyl(pyren-1-yl)phosphine (**25**) was used for the first time as a ligand in the Suzuki coupling reaction. The palladium complexes **6**, **7**, and **31** were also isolated as catalyst degradation products from the corresponding Suzuki reactions. Some of the largest cyclometalated systems to date have been synthesized by the biscycloiridation of the above three types of pyrene-containing phenylpyridine ligands in trimethyl phosphate. The systems include complexes **10** and **12**, in which the pyrene ring is cyclometalated by iridium; complex **19**, in which the pyrene ring is attached to a pyridine moiety; and complex **32**, in which the pyrene is attached to a cyclometalated phenyl moiety. In the solid state, complexes **12** and **19** exhibit π-stacking arrangements through the large aromatic systems of the pyrene rings. The plane-to-plane distances of the $\pi-\pi$ stacked complexes **12** and **19** vary from 3.40 to 3.53 Å. The π-stacking distance can be affected by the size of the solvent molecules incorporated in the cavities formed by the pyrene rings. Complex **32** does not have π-stacked aromatic rings.

Introduction

Polycyclic aromatic hydrocarbons (PAH) have been a focus of research for a long time starting from geology, where PAH occur naturally with other sources of carbon;[1] to molecular biology, where fluorescent properties of PAH were exploited for good purposes[2] and the carcinogenic properties of PAH were subjects of the preventive measures;[3] and to interstellar exploration, where PAH were identified among the most stable compounds in the cosmos.[4]

The large delocalization of π-electrons in PAH such as pyrene, perylene, chrysene, and coronene offers distinctive material properties and unique bonding modes. For example, aromatic−aromatic or $\pi-\pi$ stackings are known to be important noncovalent intermolecular forces in PAH.[5] Adducts of PAH[6] and more recently chromium[7] and iron[8] organometallic derivatives of PAH with classical electron-transfer organic counterparts, such as tetracyanoethylene and thiourea, have attracted substantial interest in chemistry and physics.

Metal derivatives of PAH are gaining interest because the presence of the metal atom may substantially affect magnetic and optical properties of these materials.[9] Metal−PAH complexes are also important models for catalysis and surface science, particularly that of carbon surfaces.[10] Increasing interest in metal−PAH systems has motivated many groups to synthesize these species by different methods. Gas-phase experiments using FT-ICR mass spectrometry were first applied to observe metal−PAH ion complexes.[11] Laser vaporization of film-coated metal samples in molecular beam cluster sources was widely used to produce a variety of metal−PAH complexes.[12]

Our focus of research in metal−PAH complexes lies in bis N^C cyclometalated derivatives with direct σ-bonds between the metal, e.g., iridium or platinum, and PAH of varying sizes. However, the cyclometalation of pyridine-substituted pyrene ligands, which are model compounds for N^C cyclometalation, is a challenging task: it was found that these ligands undergo cyclometalation reactions reluctantly.[13] We have discovered that

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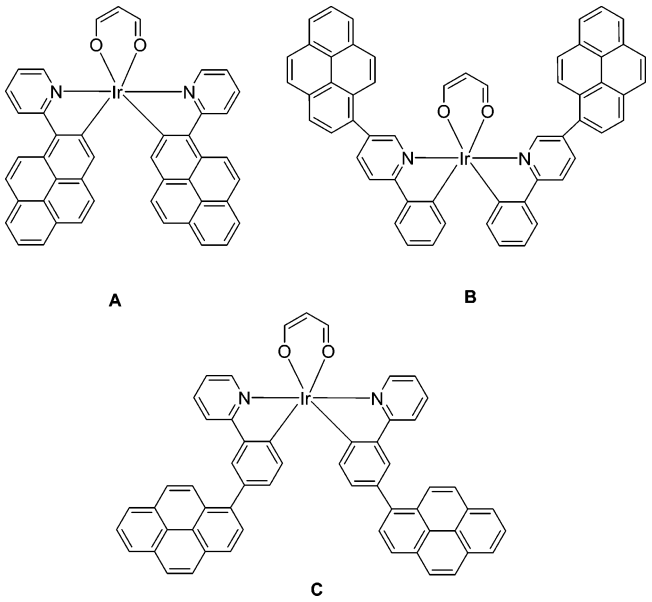
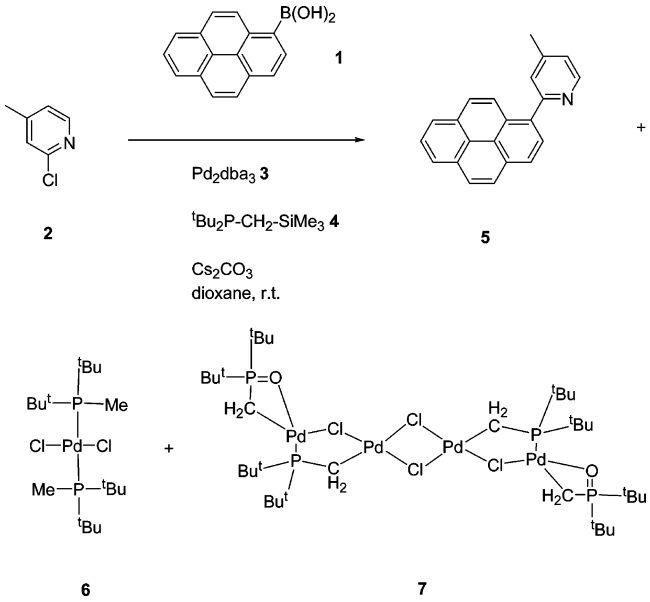
Scheme 1



Scheme 2



the use of trimethyl phosphate as a medium for the cyclometalation of simple phenylpyridine ligands with iridium and platinum has a clear advantage over the widely used procedure of cyclometalation in 2-ethoxyethanol.[14] Cyclometalation in trimethyl phosphate takes place at lower temperatures, and the purification step is simplified because the resultant metal-bridged chloride dimers precipitate out of the reaction mixture, while the starting metal chlorides and ligands are soluble in trimethyl phosphate. Electrophilic reactions, e.g., cyclometalation, take place in trimethyl phosphate in many difficult cases.[15] This is due in part to trimethyl phoshate's ability to react with hydrogen halides formed *in situ*, thus shifting the reaction equilibrium toward cyclometalation.

The present work expands the methodology of cycloiridation in trimethyl phosphate to pyrene-containing ligands. The purpose of this is to develop practical methods of synthesis of these complexes in quantities sufficient enough to facilitate further studies of their properties.[16]

The synthesis of a series of novel pyrene-containing ligands by the Suzuki cross-coupling reaction is also reported in this study. There are several bonding types that show how the pyrene can be incorporated into the cyclometalated iridium complexes. Here we report three generic types: type **A**, in which the pyrene ring is cyclometalated by iridium; type **B**, in which the pyrene ring is attached to a pyridine moiety; and type **C**, in which the pyrene is attached to a cyclometalated phenyl moiety (Scheme 1).

Results and Discussion

Synthesis of Pyrene Cycloiridiated Complexes, in which the Pyrene Ring Is Cyclometalated by Iridium. The pyrene ring was attached to the 2-position of pyridine by means of a Suzuki coupling reaction. The reaction between pyrene-1-boronic acid (**1**) and 2-chloro-4-methylpyridine (**2**) catalyzed by Pd_2dba_3 **3**/*tert*-Bu_2P-CH_2-$SiMe_3$ (**4**)[17] resulted in the isolation of 4-methyl-2-pyren-1-ylpyridine (**5**) (Scheme 2).

Compound **5** was purified by chromatography on silica gel under aerobic conditions. Two palladium-containing complexes, **6** and **7**, were also isolated from this reaction (Scheme 2).

The mononuclear complex **6** has been described previously in the literature particularly in terms of its conformational interconversions.[18] Tetranuclear complex **7** has tight four-membered (C−P−O−Pd) chelating rings with transannular nonbonding phosphorus−palladium distances of 2.6931(6) Å (Figure 1). A Cambridge Structural Database (CSD) search was performed using the QUEST3D routine to evaluate transannular phosphorus−palladium distances in a four-membered ring. While there are no data on (C−P−O−Pd) chelating rings, the distances for other four-membered chelating rings with oxygen or carbon atoms vary from 2.58 to 2.88 Å.[19] Thus, the distance of 2.6931(6) Å appears to be typical for this kind of transannular interaction.

Consistent with X-ray study, the ^{31}P NMR spectrum of tetranuclear complex **7** consists of two broad singlets at δ 117.06

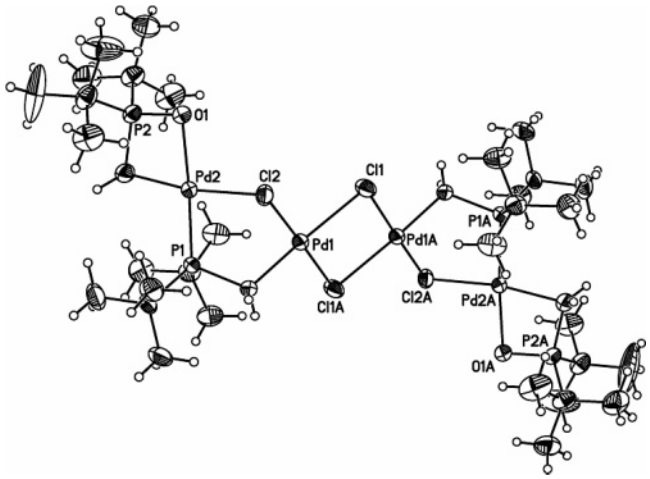


Figure 1. ORTEP drawing of tetranuclear complex **7**. The bonding Pd2−P1 distance is 2.2404(6) Å. The nonbonding transannular Pd2−P2 distance is 2.6931(6) Å.

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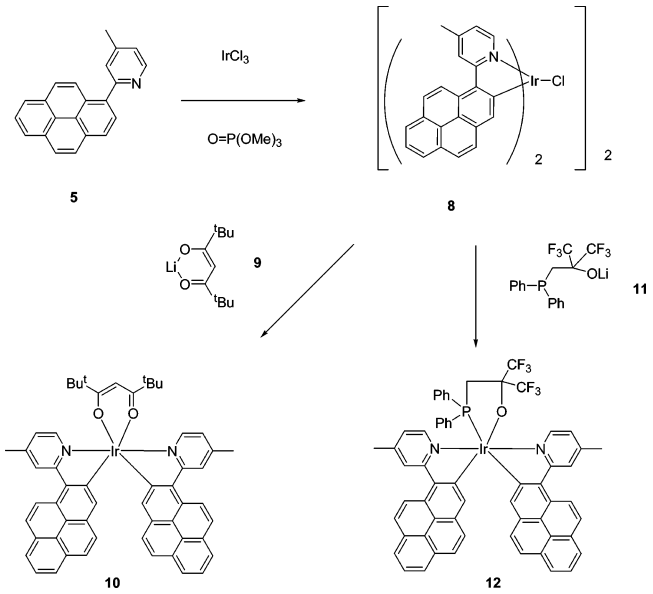
(phosphoryl group) and 86.65 (phosphino group). The tentative assignment of the downfield signal to the phosphoryl group and upfield signal to the phosphino group was done on the basis of earlier studies of the mixed phosphine oxide/phosphine complexes of palladium and cyclometalated complexes with a di-*tert*-butylphosphino moiety.[20]

Compounds **6** and **7** are lacking trimethylsilyl groups and apparently resulted from two different well-documented processes in organophosphorus chemistry involving the species from the Suzuki catalytic cycle.[21] The loss of trimethylsilyl groups in complex **7** likely resulted from the desilylation, which is known to take place in the triad (P−C−Si), even in the presence of a very weak acid such as methanol.[22] The boronic acid and chloroboronic acid $ClB(OH)_2$ are likely intermediates in the Suzuki catalytic cycle.[21] The compounds with the triad (P−C−Si) are known to react with various chlorides of general formula E−Cl with the formation of a (P−C−E) moiety and with elimination of chlorotrimethylsilane.[23] This is what likely happens when this kind of trimethylsilyl chloride elimination takes place with palladium chloride species formed in the Suzuki catalytic cycle. Further studies of the mechanism of the formation of **6** and **7** have not been pursued at this point.

As noted above, the pyridine-substituted pyrene ligands are known to undergo cyclometalation reactions reluctantly.[13] Therefore, we carried out the cycloiridation of 4-methyl-2-pyren-1-ylpyridine (**5**) in trimethyl phosphate. The cycloiridation of **5** took place, and the Ir(III)-bridged dichloride dimer **8** precipitated from the trimethyl phosphate solution, simplifying the purification step. The dichloride dimer **8** was practically insoluble in commonly used solvents, making spectroscopic characterization difficult. While low solubility of iridium dichloride dimers has been noted before,[24] the introduction of pyrene moieties evidently deteriorates the solubility further. To enhance the solubility, Cl/O^O and Cl/P^O ligand exchange reactions with ligands containing tertiary butyl groups and trifluoromethyl groups were undertaken to obtain the mononuclear cyclometalated complexes. Thus, the reaction of lithium 2,2,6,6-tetramethylheptane-3,5-dionate (**9**) with complex **8** led to O^O complex **10** of type **A**. The reaction between lithium 2-[(diphenylphosphanyl)methyl]-1,1,1,3,3,3-hexafluoropropan-2-olate (**11**) and complex **8** afforded P^O complex **12** of type **A** (Scheme 3).

In principle, cyclometalation of 4-methyl-2-pyren-1-ylpyridine (**5**) could occur at two positions of the pyrene moiety: at the 2-position with the formation of a five-membered cyclometalated ring, as in **10** and **12**, or at the 10-position of the pyrene moiety with formation of a six-membered cyclometalated ring. Crystals of **12** were grown from methylene chloride and analyzed by X-ray crystallography to confirm the mode of cyclometalation (Figure 2).

Scheme 3



According to X-ray analysis, the cyclometalation reaction takes place with the formation of a five-membered ring. The ^{31}P NMR spectra of pure complex **12** and its reaction mixture indicate that the cyclometalation is selective: only a resonance at δ 9.54 was detected in both cases. The ^{1}H NMR spectrum of complex **10** shows a singlet for the two tertiary butyl groups of the 2,2,6,6-tetramethylheptane-3,5-dionate ligand at δ 1.05 and a singlet for the two methyl groups of the pyridine moieties at δ 2.85, suggesting a symmetrical cyclometalated ligand environment in complex **10**, which is typically found for *trans-N,N*-cyclometalated geometries in O^O octahedral iridium complexes. The same *trans-N,N*-cyclometalated geometry was established by X-ray analysis for the analogous P^O complex **12**.

Synthesis of a Pyrene Cycloiridiated Complex in Which the Pyrene Ring Is Attached to a Pyridine Moiety. Two selective Suzuki cross-coupling reactions were used to assemble a ligand of type **B** (Scheme 4). The methodology of preferential coupling first at an aryl−iodide bond (instead of an aryl−chloride) was utilized for the synthesis of the target ligand. Pyrene-1-boronic acid (**1**) reacts with 2-chloro-5-iodopyridine (**13**) selectively with replacement of iodide first to form 2-chloro-5-pyren-1-ylpyridine (**14**). A second Suzuki coupling of **14** and 3,5-bis(trifluoromethyl)phenylboronic acid (**15**) resulted in the formation of target ligand **16** for the cyclometalation step. The same catalytic protocol for palladium cross-coupling reactions for **14** and **16** of type **B** was used as for the preparation of the compound **5** of type **A**.

The ^{19}F NMR spectrum of **16** exhibits a singlet at δ −63.60 ppm, suggesting that there is free rotation of the 3,5-bis-(trifluoromethyl)phenyl group around the pyridine moiety in the solution of methylene chloride.

X-ray analysis of **16** confirmed the substitution of the pyrene moiety at the 5-position of the central pyridine ring and the substitution of the 3,5-bis(trifluoromethyl)phenyl moiety at the 2-position of the central pyridine ring (see Supporting Information). Cyclometalation of **16** by iridium(III) chloride was carried out using trimethyl phosphate as the solvent, resulting in the

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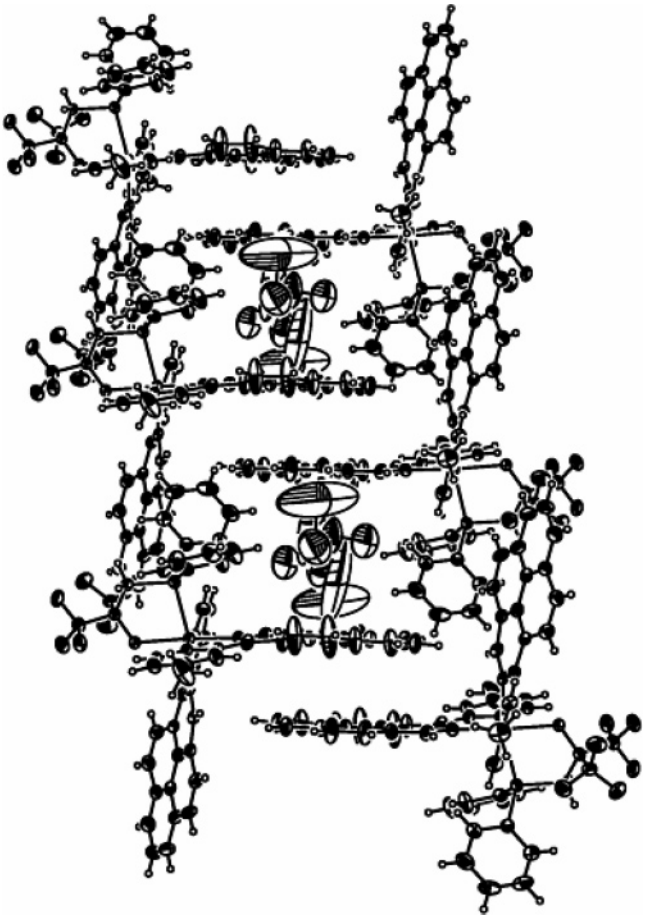
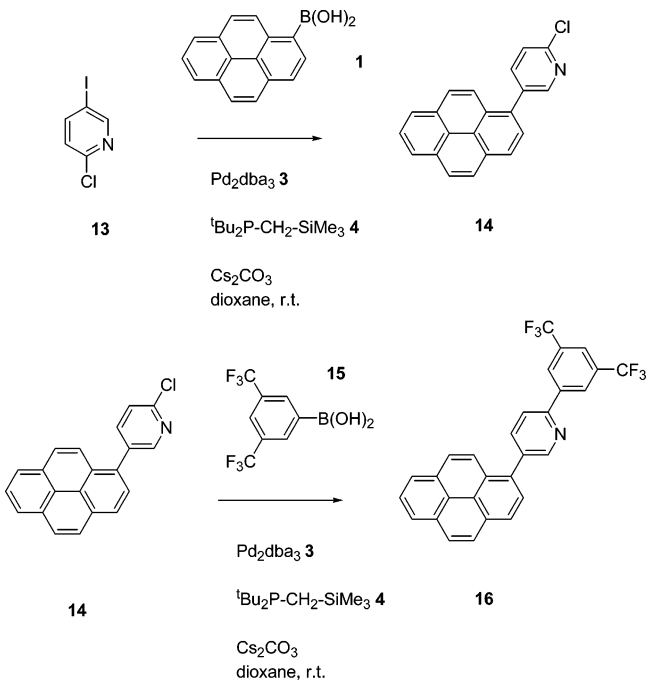


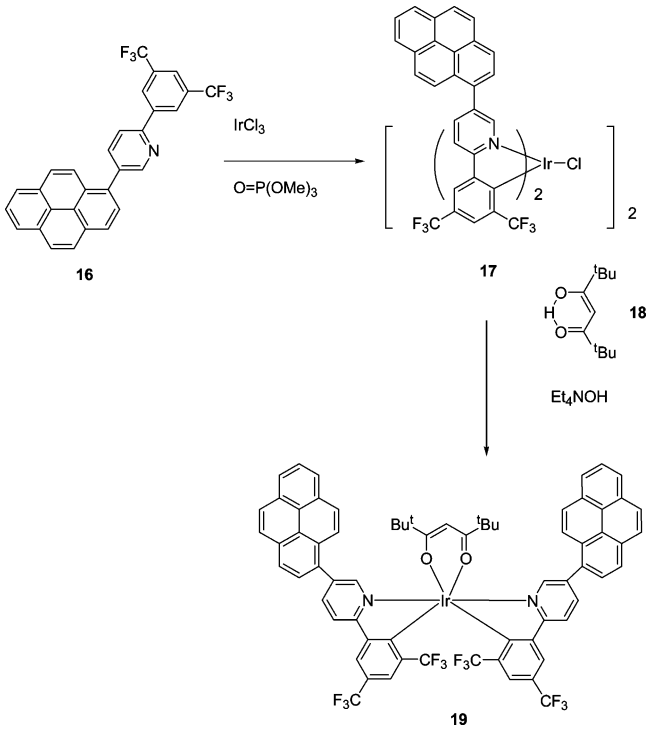
Figure 2. Packing diagram of iridium, bis[1-(4-methyl-2-pyridinyl-κN)-2-pyrenyl-κC], [3-(di-phenylphosphino)-1,1,1-trifluoro-2-(trifluoromethyl)-2-propanolato-κO,-κP]-. (**12**). The methylene chloride takes available space in cavities created by pyrene rings. The plane-to-plane distance of π-stacked pyrene rings is 3.46 Å. Complex **12** is a *trans-N,N*-isomer.

Scheme 4



formation of the Ir(III)-bridged dichloride dimer **17**. The reaction between 2,2,6,6-tetramethylheptane-3,5-dione (**18**), complex **17**, and tetraethylammonium hydroxide led to complex **19** of type **B** (Scheme 5).

Scheme 5



Complex **19** was characterized crystallographically (Figure 4) to prove the C^N cyclometalated mode of coordination of the five-membered ring (as shown in Scheme 5). An alternative bonding mode, namely, remote cyclometalation of the pyrene moiety of **16** instead of the phenyl moiety with formation of a very strained seven-membered ring, was not observed. The ^{1}H NMR spectroscopy suggests that complex **19** exists as one isomer only in solution: a singlet at δ 0.65 for two tertiary butyl groups of the 2,2,6,6-tetramethylheptane-3,5-dionate ligand is observed. The ^{19}F NMR spectrum of **19** exhibits two singlets at δ −59.37 and − 62.04, and not a simple singlet as for starting ligand **16**, because the cyclometalation reaction fixes the free rotation of the 3,5-bis(trifluoromethyl)phenyl moiety around the pyridine moiety.

Synthesis of Pyrene Cycloiridiated Complex in Which the Pyrene Is Attached to a Cyclometalated Phenyl Moiety. Two sequential palladium-catalyzed cross-coupling reactions were used to prepare a ligand of type **C** for the cyclometalation step. The first reaction was the Suzuki cross-coupling reaction between 2-bromo-5-methylpyridine (**20**) and 3-chlorophenylboronic acid (**21**) or 3-bromophenylboronic acid (**22**), which afforded 2-(3-chlorophenyl)-4-methylpyridine (**23**) and 2-(3-bromophenyl)-4-methylpyridine (**24**), respectively.

The catalytic protocol was different in this case, because the combination of Pd_2dba_3 **3**/*tert*-Bu_2P-CH_2-$SiMe_3$ (**4**) as the catalyst in this reaction did not result in the formation of product **23** or **24**. Unreacted 2-bromo-5-methylpyridine (**20**) was recovered from these attempts. To effect the desired coupling reactions, di-*tert*-butyl(pyren-1-yl)phosphine (**25**) was successfully employed as a novel ligand for Suzuki catalysis. The steric bulk in phosphine **25** is derived from the tertiary butyl group and from the large, flat pyrene group. Compound **25** was synthesized by the following sequence. The low-temperature reaction between *n*-butyllithium and 1-bromopyrene (**26**) in THF was carried out, resulting in two processes: Li/Br exchange and Bu/Br substitution. Refluxing of almost equimolar amounts

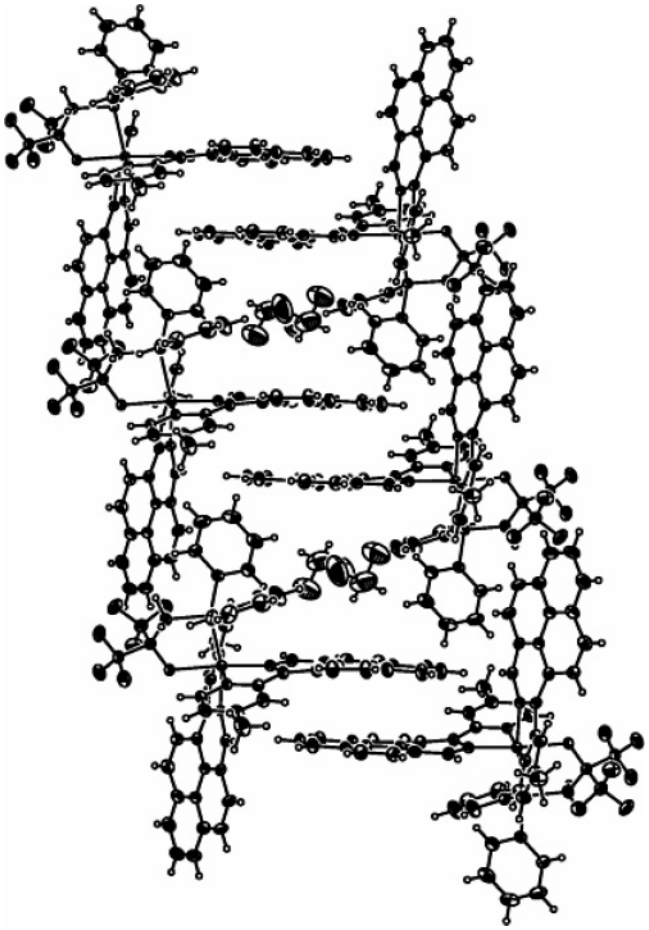


Figure 3. Packing diagram of iridium, bis[1-(4-methyl-2-pyridinyl-κN)-2-pyrenyl-κC], [3-(di-phenylphosphino)-1,1,1-trifluoro-2-(trifluoromethyl)-2-propanolato-κO, -κP]-, (**12**). The acetone takes available space in cavities created by pyrene rings. The plane-to-plane distance of π-stacked pyrene rings is 3.53 Å. Complex **12** is a *trans-N,N*-isomer.

of di-*tert*-butylchlorophosphine (**27**) with the above reaction mixture afforded di-*tert*-butyl(pyren-1-yl)phosphine (**25**). The phosphine **25** was separated from 1-butylpyrene[25] (**28**) by recrystallization at −30 °C and an additional distillation (Scheme 6). The ^{31}P NMR spectrum of **25** has a singlet at δ +25.63, which is a typical value for di-*tert*-butyl-substituted tertiary phosphines.[26a] A crystal structure of **25** was undertaken in order to shed light on the long standing issue in organophoshorus chemistry of possible conjugation of the lone pair of electrons of the phosphorus atom and the aromatic system of the pyrene ring.[26b] A crystal of **25** suitable for X-ray analysis was grown from pentane (Figure 5). Two *tert*-butyl groups are oriented above and below the pyrene plane in **25**, suggesting that the lone pair of electrons at phosphorus is orthogonal to the pyrene and therefore cannot participate in the conjugation.

The bridged cyclometalated palladium complex **29** was isolated as the only product of catalyst degradation from this Suzuki coupling (Scheme 6). The structure of **29** with the C^P five-membered cyclopalladiated moiety was confirmed by X-ray analysis (Figure 6). These C^P cyclopalladinations take place very easily in many cases and do not even require the presence of a base.[27] Many efficient palladacyclic precatalysts, such as complex **29**, for cross-coupling reactions have been reported in the past few years. A comparison of the catalytic properties of **29** with other previously reported palladacyclic precatalysts is beyond the scope of this paper.

A second Suzuki reaction between 2-(3-bromo-phenyl)-4-methylpyridine (**24**) and pyrene-1-boronic acid (**1**) was used to complete the synthesis of ligands of type **C**, affording 4-methyl-2-(3-pyren-1-ylphenyl)pyridine (**30**). The same catalytic protocol was used as for the preparation of ligands **5**, **14**, and **16** of types **A** and **B** (Scheme 6).

The structure of compound **30** was analyzed by X-ray analysis to confirm the substitution pattern of the central pyridine ring (see Supporting Information).

The cycloiridation of **30** by iridium(III) chloride was carried out in trimethyl phosphate as the solvent. The thus formed Ir(III)-bridged dichloride dimer **31** precipitated from the reaction mixture. The reaction between 2,2,6,6-tetramethylheptane-3,5-dione (**18**), complex **31**, and tetraethylammonium hydroxide afforded complex **32** of type **C** (Scheme 7). The structure of **32** was analyzed by X-ray analysis and confirmed that ortho-cyclometalation occurred at the phenyl moiety with the formation of a five-membered ring. The remote cyclometalation of the pyrene ring with formation of a nine-membered ring did not take place. A crystal of **32** suitable for X-ray analysis was grown from pentane (Figure 7). Analysis of the ^{1}H NMR spectrum of the bulk of complex **32** confirms the selectivity of the above cyclometalation. There is only one isomer exhibiting a singlet at δ 1.05 for the two tertiary butyl groups of the 2,2,6,6-tetramethylheptane-3,5-dionate ligand and a singlet for the two methyl groups of the pyridine moieties at δ 2.63. The aromatic protons of the pyrene, pyridine, and phenyl moieties appear as very complex multiplets in a typical region for aromatic protons from 6.60 to 8.50 ppm with the correct ratio to methyl protons discussed above.

Solid-State Structures of Biscyclometalated Ir(III) Complexes Containing Pyrene and Its Starting Ligands. $\pi-\pi$ Stacking is an important attribute of PAH containing large arenes, e.g., pyrenes, which can affect different properties of the materials made from these compounds.[5] Thus special attention was paid to analyze these noncovalent $\pi-\pi$ interactions in the prepared ligands and their complexes.

Two ligands, **16** and **30**, which were analyzed by X-ray in this study, do not exhibit $\pi-\pi$ stacking in the solid state (see Supporting Information). Apparently, the presence of even one bulky substituent, e.g., phenylpyridine groups in **16** and **30**, is sufficient to push the pyrene rings further apart and disrupt the $\pi-\pi$ stacking.

π-Stacking arrangements in the cyclometalated derivatives **14**, **19**, and **32** are not so straightforward. For example, X-ray analysis reveals that there is an intramolecular π-stacking of pyrene rings in complex **14** of type **A** (Figure 2). The plane-to-plane distance is 3.46 Å, which is typical for aromatic−aromatic $\pi-\pi$ interactions.[14a,28] Molecules of the solvent, such as methylene chloride in Figure 2, can be trapped in the cavities created by the π-stacking of large pyrene moieties. To separate the π-stacking even further and in the hopes of breaking the π-stacking, a slightly larger molecule, acetone, was used to push the pyrene planes further apart. A crystal of compound **14** was grown from acetone and analyzed by X-ray (Figure 3). The experiments with acetone did not break the π-stacking of the

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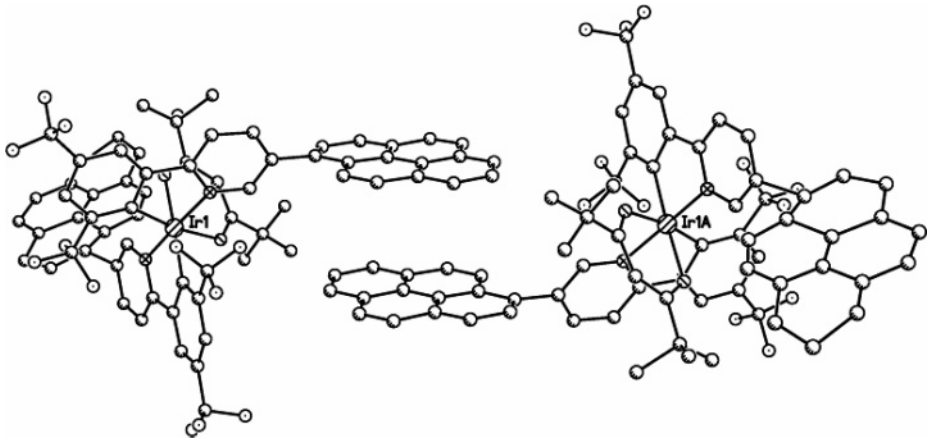
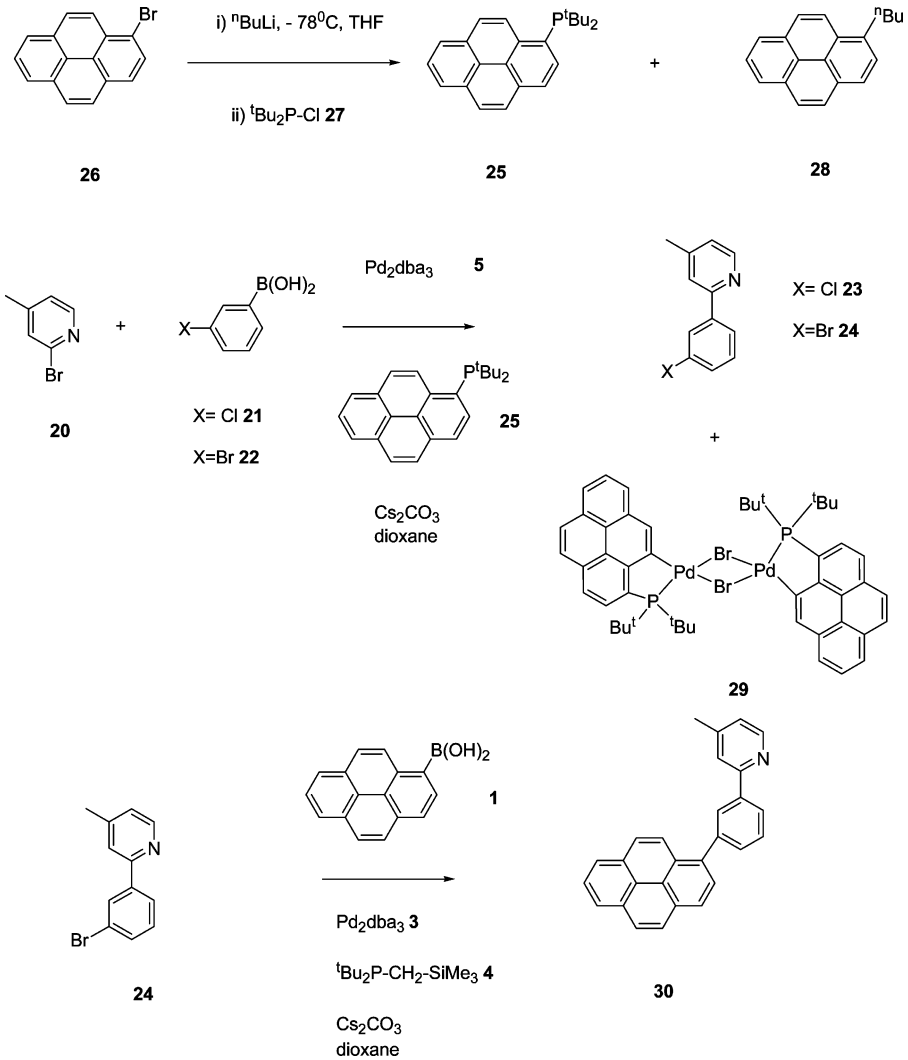


Figure 4. Packing diagram of iridium, bis[4,6-bis(trifluoromethyl)-2-(5-pyren-1-yl-2-pyridinyl-κN)-phenyl-κC], (2,2,6,6-tetramethyl-3,5-heptanedionato-κO,κO′)-, **19**. The plane-to-plane distance of π-stacked pyrene rings is 3.40 Å. Complex **19** is a *trans-N,N*-isomer.

Scheme 6



pyrene moieties, although it was slightly larger, at 3.53 Å. Evidently, bulkier molecules are needed to break the π-stacking in this case. Complex **19** of type **B** has a typical π-stacking arrangement of two pyrene rings from two different molecules with a plane-to-plane distance of 3.40 Å (Figure 4). However, the X-ray analysis of complex **32** of type **C** has shown that there are no $\pi-\pi$-stackings between any aromatic rings. The plane-to-planes distances of the $\pi-\pi$ stacked complexes **12** and **19** vary from 3.40 to 3.53 Å. These values tend to be on the short side of the usual range of 3.3−3.9 Å for these phenomena.[14a,28]

It thus appears that the bis-cycloiridation of phenylpyridine ligands with pyrene moieties increases the tendency to π-stack.

All analyzed complexes **14**, **19**, and **32** were found to be *trans-N,N*-isomers (Table 1).

The cyclometalated bonds between iridium and carbon in **14**, **19**, and **32** (from 1.99 to 2.04 Å) were found to be within the range for other similar cyclometalated Ir−C bond lengths for

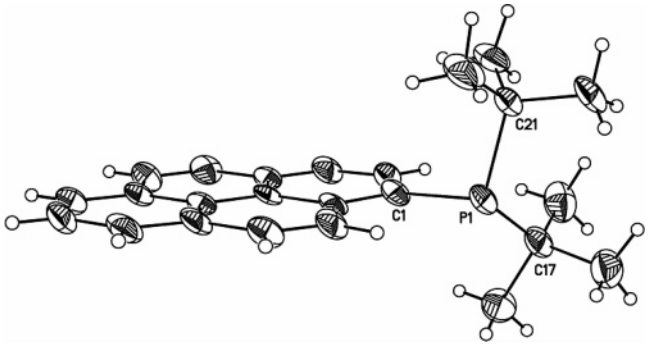


Figure 5. ORTEP drawing of di-*tert*-butyl(pyren-1-yl)phosphine (**25**).

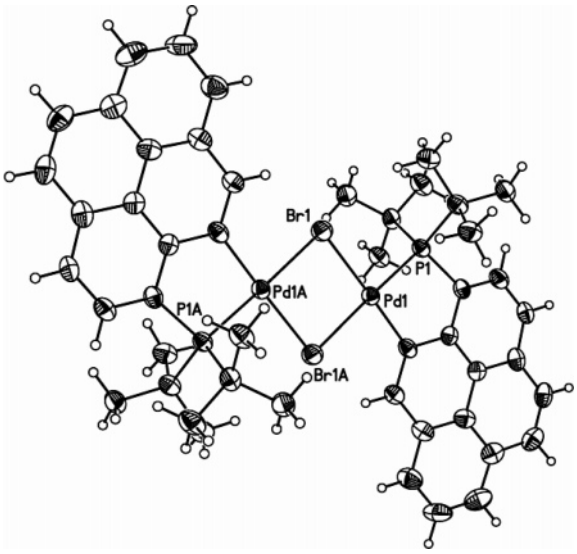
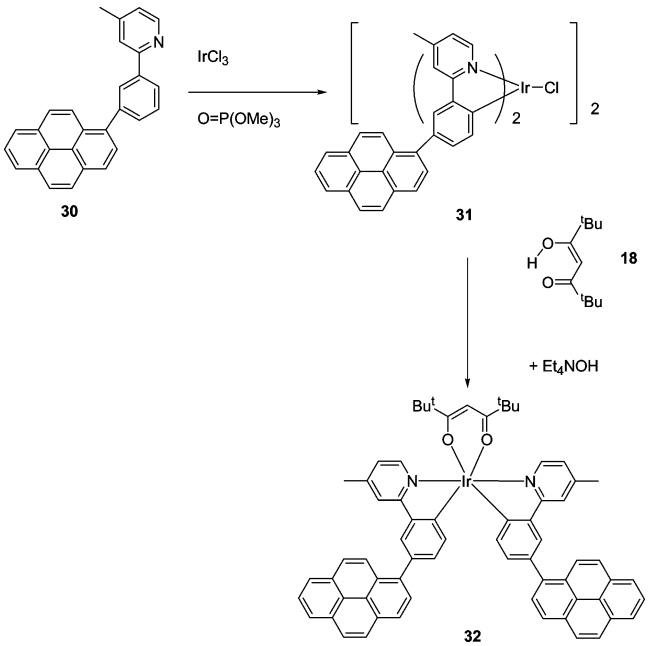


Figure 6. ORTEP drawing of the bridged cyclometalated palladium complex **29**.

Scheme 7



phenylpyridine ligands.[29] The bond lengths between iridium and nitrogen atoms in **14**, **19**, and **32** are again within the normal range from 2.03 to 2.07 Å.[29] Normal bond lengths were found in **14**, **19**, and **32** between iridium and oxygen (from 2.11 to 2.16 Å) and iridium and phosphorus atoms (2.36 Å).[29]

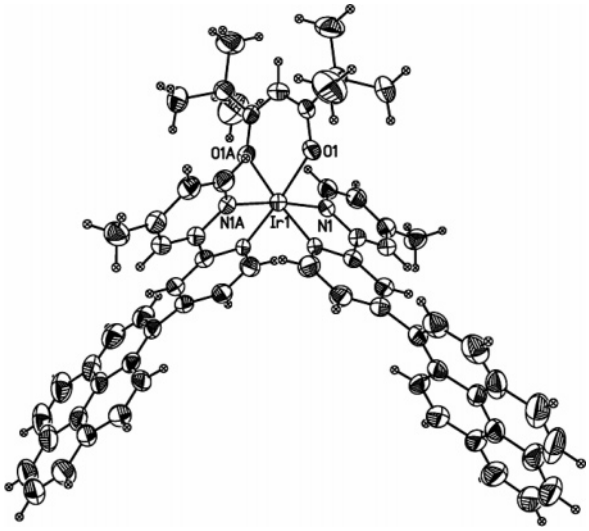


Figure 7. ORTEP drawing of iridium, bis[4-(pyren-1-yl)-2-(4-methyl-2-pyridinyl-κN)phenyl-κC],(2,2,6,6-tetramethyl-3,5-heptanedionato-κO,κO), (**32**). Complex **32** is a *trans-N,N*-isomer. There are no $\pi-\pi$-stackings between any aromatic rings.

Summary

A series of novel polyaromatic ligands containing pyrene with different types of substitution around the central pyridine ring were synthesized by Suzuki cross-coupling reactions. Among them are 4-methyl-2-pyren-1-ylpyridine (**5**), in which the pyrene ring is attached to the 2-position of pyridine; 2-(3,5-bis-(trifluoromethyl)phenyl)-5-pyren-1-ylpyridine (**16**), in which the pyrene ring is attached to the 5-position of pyridine; and 4-methyl-2-(3-pyren-1-ylphenyl)pyridine (**30**), in which the pyrene ring is attached to the 3-position of the 2-phenylpyridine moiety. The sterically bulky di-*tert*-butyl(pyren-1-yl)phosphine ligand **25** was utilized for the first time as a ligand in the Suzuki cross-coupling reaction. The palladium complexes **6**, **7**, and **31** were also isolated from the Suzuki cross-coupling reactions.

The cyclometalation of pyrene ligands **5**, **16**, and **30** by $IrCl_3$ in trimethyl phosphate was found to be a reliable procedure leading to the synthesis of bulky organometallic complexes **14**, **19**, and **32**. The five-membered C^N cycloiridiated ring was selectively formed in all cases, in preference to larger rings. The complexes **14**, **19**, and **32** were investigated by X-ray analysis. Complex **14** of type **A**, in which the pyrene ring is cyclometalated by iridium, and complex **19** of type **B**, in which the pyrene ring is attached to a pyridine moiety, exhibit intermolecular π-stacking arrangements through the large aromatic systems of the pyrene rings. The complex **32** of type **C**, in which the pyrene is attached to a cyclometalated phenyl moiety, does not have π-stacked aromatic rings.

Studies of different physical properties of the above pyrene compounds are under way and will be reported in due course.

Experimental Section

General Procedures. All air-sensitive compounds were prepared and handled under a N_2/Ar atmosphere using standard Schlenk and inert-atmosphere box techniques. Anhydrous solvents were used in the reactions. Solvents were distilled from drying agents or passed through columns under an argon or nitrogen atmosphere. Pyrene-

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Table 1. Plane-to-planes Distances of the $\pi-\pi$ Stacked Complexes and Selected Bond Lengths in 14, 19, and 32

	14 as an adduct with methylene chloride	**14** as an adduct with acetone	**19**	**32**
plane-to-planes distances, Å	3.46	3.53	3.40	N/A
isomer by N, N orientation	*trans-N,N*	*trans-N,N*	*trans-N,N*	*trans-N,N*
Ir−C bond length, Å	2.012(4)	1.999(4)	2.024(7)	1.988(4)
Ir−C bond length, Å	2.038(4)	2.034(4)	2.038(6)	1.988(4)
Ir−N bond length, Å	2.035(3)	2.034(3)	2.028(5)	2.038(3)
Ir−N bond length, Å	2.070(3)	2.062(3)	2.036(6)	2.038(3)
Ir−O or P bond length, Å	2.3643(10)	2.3615(12)	2.090(5)	2.128(2)
	Ir−P	Ir−P	Ir−O	Ir−O
Ir−O bond length, Å	2.161(3)	2.164(3)	2.108(5)	2.128(2)

1-boronic acid, 3,5-bis(trifluoromethyl)phenylboronic acid, 2-chloro-5-iodopyridine, cesium carbonate, tris(dibenzylideneacetone)-dipalladium(0), trimethyl phosphate, 2,2,6,6-tetramethylheptane-3,5-dione, and tetrabutylammonium hydroxide as 55−60% solution in water were purchased from Aldrich. Iridium (+3) chloride trihydrate was purchased from Alfa Aesar. 2-Chloro-4-methyl-pyridine was purchased from Matrix Scientific.

4-Methyl-2-pyren-1-ylpyridine (5). 2-Chloro-4-methylpyridine (**2**) (6.99 g, 0.0548 mol), 15.00 g (0.0610 mol) of pyrene-1-boronic acid (**1**), 1.39 g (0.0015 mol) of tris(dibenzylideneacetone)-dipalladium(0) (**3**), 0.85 g (0.0037 mol) of di-*tert*-butyl(trimethyl-silylmethyl)phosphane (**4**), 19.86 g (0.0610 mol) of cesium carbonate, and 100 mL of 1,4-dioxane were stirred for 7 days at ambient temperature. The resulting mixture was poured into 200 mL of water and extracted twice by 200 mL of methylene chloride. The organic phase was dried over magnesium sulfate overnight and filtered. The solvent was removed in a rotovapor, and the residue was purified by chromatography on silica gel with an eluent of petroleum ether/ethyl ether at 10/0.5. Yield of 4-methyl-2-pyren-1-ylpyridine (**5**) was 4.20 g (26%) as a yellow solid. ^{1}H NMR (CD_2Cl_2): δ 2.63 (s, 6H, Me), 7.10−9.15 (m, 12H, arom-H). Anal. Calcd for $C_{22}H_{15}N$ (mol wt: 293.36): C, 90.07; H, 5.15; N, 4.77. Found: C, 89.88; H, 5.30; N, 4.72. GC/MS (direct probe): exact mass calculated for $C_{22}H_{15}N$ 293.12, found 293.12. Complex **6** was isolated in 25% yield on Pd_2dba_3 (0.38 g) as yellow crystals with data identical to published.[5a] Complex **7** was isolated as deep golden crystals with no mp until 250 °C. It was the last compound to elute from the column. Yield of **7** was 0.36 g (19% on Pd_2dba_3). ^{1}H NMR (500 MHz, CD_2Cl_2, TMS): δ 0.45 (s, 4H, Pd-CH_2), 1.20 (d, $^3J_{PH}$ = 13.7 Hz, 36H, Me_3C), 1.36 (d, $^3J_{PH}$ = 13.8 Hz, 36H, Me_3C), 2.00 (s, 4H, Pd-CH_2). ^{31}P NMR (500 MHz, CD_2Cl_2): δ 117.06 (s, 1P), 86.65 (s, 1P). Anal. Calcd for $C_{36}H_{80}Cl_4O_2P_4Pd_4$ (mol wt: 1236.41): C, 34.97; H, 6.52. Found: C, 35.16; H, 6.59.

Iridium, Di-μ-chlorotetrakis[1-(4-methyl-2-pyridinyl-κN)-2-pyrenyl-κC], (8). 4-Methyl-2-pyren-1-ylpyridine (**7**) (3.90 g, 0.0133 mol), 1.64 g (0.0047 mol) of iridium(III) chloride trihydrate, and 30 mL of trimethyl phosphate were stirred at 90 °C for 48 h under the flow of nitrogen. The formed precipitate was filtered and dried under 1.0 mm vacuum. The yield of the dimer **8** was 4.97 g (92%) as a green powder. Complex **8** is practically insoluble in commonly used solvents. This is why the crude chloro-bridged dimer **8** was used without further purification in the next steps according to established practice in cyclometalation research.[24]

Iridium, bis[1-(4-methyl-2-pyridinyl-κN)-2-pyrenyl-κC],-(2,2,6,6-tetramethyl-3,5-heptanedionato-κO,κO′)-, (10). Iridium, di-μ-chlorotetrakis[1-(4-methyl-2-pyridinyl-κN)-2-pyrenyl-κC], (**8**) (2.68 g, 0.0017 mol), 2.45 g (0.0129 mol) of lithium 2,2,6,6-tetramethylheptane-3,5-dionate **9**, 1.0 g of 40% solution of sodium hydroxide in water, and 20 mL of THF were refluxed for 2 h under an argon atmosphere. The reaction mixture was poured into 200 mL of water and extracted with 200 mL of diethyl ether twice. The extracts were dried over magnesium sulfate overnight and filtered. The solvent was removed in a rotavapor, and the residue was purified by chromatography on silica gel with an eluent of petroleum ether/ethyl ether at 10/0.5. Yield of iridium, bis[1-(4-methyl-2-pyridinyl-κN)-2-pyrenyl-κC], (2,2,6,6-tetramethyl-3,5-heptanedionato-κO,κO′)-, (**10**) was 0.73 g (23%) as a brown solid with no mp until 200 °C. ^{1}H NMR (CD_2Cl_2): δ 1.05 (s, 18H, t-Bu), 2.85 (s, 6H, Me), 5.75 (s, 1H, H-C═), 7.20−9.10 (m, 22H, arom-H). ^{13}C NMR (CD_2Cl_2) (selected signals): δ 195.5 (s, C═O). GC/MS (direct probe): exact mass calculated for $C_{55}H_{47}IrN_2O_2$ 960.33, found 960.33. Anal. Calcd for $C_{55}H_{47}IrN_2O_2$ (mol wt: 960.19): C, 68.80; H, 4.93; N, 2.92. Found: C, 69.07; H, 5.18; N, 3.16.

Iridium, bis[1-(4-methyl-2-pyridinyl-κN)-2-pyrenyl-κC], [3-(diphenylphosphino)-1,1,1-trifluoro-2-(trifluoromethyl)-2-propanolato-κO, -κP]-, (12) and Lithium 2-[(diphenylphosphanyl)-methyl]-1,1,1,3,3,3-hexafluoropropan-2-olate (11). Lithium diphenylphosphide (0.93 g, 0.0048 mol) was dissolved in 20 mL of THF and cooled to −35 °C. 2,2-Bis(trifluoromethyl)oxirane (0.99 g, 0.0055 mol) was added at the same temperature in one portion. After 1 h the reaction mixture contained only one chemical shift in the ^{31}P NMR spectrum, at −27.17 ppm, which is consistent with the structure. The solution was used "as is" in the next step. Iridium, di-μ-chlorotetrakis[1-(4-methyl-2-pyridinyl-κN)-2-pyrenyl-κC], (**8**) (2.62 g, 0.0016 mol) and 0.0048 mol of lithium 2-[(diphenylphosphanyl)methyl]-1,1,1,3,3,3-hexafluoropropan-2-olate (**11**) in 20 mL of THF were stirred at room temperature for 24 h. The reaction mixture was purified by chromatography on silica gel with an eluent of petroleum ether/ethyl acetate at 10/0.5. Yield of iridium, bis[1-(4-methyl-2-pyridinyl-κN)-2-pyrenyl-κC], ([3-(diphenylphosphino)-1,1,1-trifluoro-2-(trifluoromethyl)-2-propanolato-κO, -κP])-, (**12**) was 1.37 g (37%) as a yellow solid with no mp until 200 °C. ^{1}H NMR (CD_2Cl_2): δ 2.60 (b, 6H, Me), 3.05−3.10 (m, 1H, CH2-CF3), 3.50−3.60 (m, 1H, CH2−CF3), 6.40−9.10 (m, 32H, arom-H). ^{19}F NMR (CD_2Cl_2): δ −75.46 (m, 3F, CF3), −78.39 (m, 3F, CF3). ^{31}P NMR (CD_2Cl_2): δ 9.54 (s, 1P). Anal. Calcd for $C_{60}H_{40}F_6IrN_2OP$ (exact mass: 1142.15): C, 63.10; H, 3.53; N, 2.45. Found: C, 63.38; H, 3.60; N, 2.64. Structure was proven by X-ray analysis.

2-Chloro-5-pyren-1-ylpyridine (14). 2-Chloro-5-iodopyridine (**13**) (12.00 g, 0.0512 mol), 10.0 g (0.0406 mol) of pyrene-1-boronic acid (**1**), 0.74 g (0.0008 mol) of tris(dibenzylideneacetone)-dipalladium(0) (**3**), 0.45 g (0.0019 mol) of di-*tert*-butyl(trimethyl-silylmethyl)phosphane (**4**), 9.43 g (0.0289 mol) of cesium carbonate, and 100 mL of 1,4-dioxane were stirred for 7 days at ambient temperature. The resulting mixture was poured into 200 mL of water and extracted twice with 200 mL of methylene chloride. The organic phase was dried over magnesium sulfate overnight and filtered. The solvent was removed in a rotovapor, and the residue was purified by chromatography on silica gel with an eluent of petroleum ether/ethyl ether at 10/0.5. Yield of 2-chloro-5-pyren-1-ylpyridine (**14**) was 9.47 g (59%) as a yellow solid. ^{1}H NMR (CD_2Cl_2): δ 6.83−9.20 (m, 21H, arom-H). Anal. Calcd for $C_{21}H_{12}ClN$ (mol wt: 313.78): C, 80.38; H, 3.85; N, 4.46. Found: C, 80.53; H, 3.89; N, 4.52. GC/MS (direct probe): exact mass calculated for $C_{21}H_{12}ClN$ 313.07, found 313.07.

2-(3,5-Bis(trifluoromethyl)phenyl)-5-pyren-1-ylpyridine (16). 2-Chloro-5-pyren-1-ylpyridine (**14**) (6.30 g, 0.0200 mol), 6.73 g (0.0261 mol) of 3,5-bis(trifluoromethyl)phenylboronic acid (**15**), 0.47 g (0.0005 mol) of tris(dibenzylideneacetone)dipalladium(0) (**3**), 0.29 g (0.0013 mol) of di-*tert*-butyl(trimethylsilylmethyl)-phosphane (**4**), 8.50 g (0.0261 mol) of cesium carbonate, and 100

mL of 1,4-dioxane were stirred for 7 days at ambient temperature. The resulting mixture was poured into 200 mL of water and extracted twice with 200 mL of methylene chloride. The organic phase was dried over magnesium sulfate overnight and filtered. The solvent was removed in a rotovapor, and the residue was purified by chromatography on silica gel with an eluent of petroleum ether/ethyl ether at 10/0.5. Yield of 2-(3,5-bis(trifluoromethyl)-phenyl)-5-pyren-1-ylpyridine (**16**) was 5.70 g (58%) as a yellow solid. ^{1}H NMR (CD_2Cl_2): δ 7.10−9.05 (m, 29H, arom-H). ^{19}F NMR (CD_2Cl_2): δ −63.60 (s, 6F, CF3). Anal. Calcd for $C_{29}H_{15}F_6N$ (mol wt: 491.43): C, 70.88; H, 3.08; N, 2.85. Found: C, 71.04; H, 3.16; N, 3.10. GC/MS (direct probe): exact mass calculated for $C_{29}H_{15}F_6N$ 491.11, found 491.11. The structure was proven by X-ray analysis.

Iridium, di-μ-chlorotetrakis[4,6-bis(trifluoromethyl)-2-(5-pyren-1-yl-2-pyridinyl-κN)phenyl-κC], (17). 2-(3,5-Bis(trifluoromethyl)phenyl)-5-pyren-1-ylpyridine (**16**) (4.00 g, 0.0081 mol), 1.36 g (0.0039 mol) of iridium(III) chloride trihydrate, and 60 mL of trimethyl phosphate were stirred at 90 °C for 48 h under a flow of nitrogen. The formed precipitate was filtered and dried under 1.0 mm vacuum. The yield of the dimer **17** was 4.50 g (92%) as a green powder. Complex **17** is practically insoluble in commonly used solvents. This is why the crude chloro-bridged dimer **17** was used without further purification in the next steps according to established practice in cyclometalation research.[24]

Iridium, bis[4,6-bis(trifluoromethyl)-2-(5-pyren-1-yl-2-pyridinyl-κN)phenyl-κC], (2,2,6,6-tetramethyl-3,5-heptanedionato-κO,κO′)-, (19). Iridium, di-μ-chlorotetrakis[4,6-bis(trifluoromethyl)-2-(5-pyren-1-yl-2-pyridinyl-κN)phenyl-κC] (**17**) (2.0 g, 0.0008 mol), 0.91 g (0.0049) of 2,2,6,6-tetramethylheptane-3,5-dione (**18**), 1.83 g of a 40% solution of tetraethylammonium hydroxide in water, and 20 mL of THF were refluxed for 2 h under an argon atmosphere. The reaction mixture was poured into 200 mL of water and extracted with 200 mL of diethyl ether twice. The extracts were dried over magnesium sulfate overnight and filtered. The solvent was removed in a rotavapor, and the residue was purified by chromatography on silica gel with an eluent of petroleum ether/ethyl ether at 10/0.5. Yield of iridium, bis[4,6-bis-(trifluoromethyl)-2-(5-pyren-1-yl-2-pyridinyl-κN)phenyl-κC], (2,2,6,6-tetramethyl-3,5-heptanediona-to-κO,κO′)-, (**19**) was 1.14 g (51%) as a brown solid with no mp until 200 °C. ^{1}H NMR (CD_2Cl_2): δ 0.65 (s, 18H, t-Bu), 5.75 (s, 1H, H-C═O), 7.10−8.60 (m, 28H, arom-H). ^{13}C NMR (CD_2Cl_2) (selected signals): δ 195.7 (s, C═O). ^{19}F NMR (CD_2Cl_2): δ −59.37 (s, 3F, CF3), −62.04 (s, 3F, CF3). Anal. Calcd for $C_{69}H_{47}F_{12}IrN_2O_2$ (mol wt: 1356.32): C, 61.10; H, 3.49; N, 2.07. Found: C, 61.49; H, 3.53; N, 2.32. Structure was proven by X-ray analysis.

Di-*tert*-butyl(pyren-1-yl)phosphine (25). 1-Bromopyrene (**26**) (24.00 g, 0.0854 mol) was dissolved in 240 mL of THF and cooled to −78 °C. A 64 mL portion of a 1.6 M solution of *n*-butyllithium in hexane was added to the reaction mixture dropwise. Then, 18.50 g (0.1020 mol) of di-*tert*-butylchlorophosphine (**27**) was added to the reaction mixture at −78 °C. The reaction mixture was allowed to warm to RT, and an aqueous solution of ammonium chloride was added slowly, followed by 200 mL of pentane. The organic phase was separated, dried with magnesium sulfate, and filtered. The cooling of the resulting solution to −35 °C afforded a white solid, which after recrystallization from ethanol yielded 11.25 g (51% of yield) of 1-butylpyrene (**28**) with mp 67 °C.[11] ^{1}H NMR (500 MHz, C_6D_6, TMS): δ 0.95 (d, t, $^3J_{HH}$ = 8.4 Hz, 3H, Me), 1.49 (m, 2H, CH_2), 1.80 (m, 2H, CH_2), 3.30 (m, 2H, CH_2), 7.70−9.00 (m, 9H, pyrene-H). Anal. Calcd for $C_{20}H_{18}$ (mol wt: 258.36): C, 92.98; H, 7.02. Found: C, 92.82; H, 7.24. The residue from the recrystallization was purified by vacuum distillation. The yield of di-*tert*-butyl(pyren-1-yl)phosphine (**25**) was 10.05 g (34%) with bp 187 °C/0.001 mm and mp 97.07 °C. ^{31}P NMR (500 MHz, C_6D_6): δ +25.63 ppm. ^{1}H NMR (500 MHz, C_6D_6, TMS): δ 1.45 (d, $^3J_{PH}$ = 11.8 Hz, 18H, Me_3C), 7.60−9.10 (m, 9H, pyrene-H). Anal. Calcd for $C_{24}H_{27}P$ (mol wt: 346.44): C, 83.20; H, 7.86; P, 8.94. Found: C, 82.95; H, 8.01; P, 9.20. The structure was proven by X-ray analysis.

2-(3-Chlorophenyl)-4-methylpyridine (23). 3-Chlorophenylboronic acid (**21**) (10.00 g, 0.0640 mol), 13.20 g (0.0770 mol) of 2-bromo-5-methylpyridine (**20**), 20.84 g (0.0640 mol) of cesium carbonate, 1.47 g (0.0016 mol) of tris(dibenzylideneacetone)-dipalladium(0) (**3**), 1.33 g (0.0038 mol) of di-*tert*-butyl(pyren-1-yl)phosphine (**25**), and 100 mL of dioxane were refluxed for 12 h. The reaction mixture was filtered, and the solvent was removed under vacuum. The resulting mixture was purified by vacuum distillation. Yield of 2-(3-chlorophenyl)-4-methylpyridine (**23**) was 7.09 g (45%) with bp at 114 °C/0.1 mm. The sample solidified upon standing at ambient temperature. ^{1}H NMR (CD_2Cl_2): δ 2.56 (s, 3H, Me) 7.40−8.80 (m, 7H, arom-H). Anal. Calcd for $C_{12}H_{10}$-ClN (mol wt: 203.67): C, 70.77; H, 4.95; N, 6.88. Found: C, 70.93; H, 5.14; N, 6.95. The structure has been confirmed by X-ray analysis.

The residue from the distillation was recrystallized from methylene chloride, yielding 0.56 g of Pd complex **29** as a yellow solid with no mp until 200.00 °C. ^{31}P NMR (500 MHz, CD_2Cl_2): δ +60.27 ppm. ^{1}H NMR (500 MHz, CD_2Cl_2, TMS): δ 1.30 (s, 36H, Me_3C), 6.50−9.00 (m, 16H, pyrene-H). Anal. Calcd for $C_{48}H_{52}$-$Br_2P_2Pd_2$ (mol wt: 1063.52): C, 54.21; H, 4.93. Found: 54.38; H, 5.21. The structure was proven by X-ray analysis.

2-(3-Bromophenyl)-4-methylpyridine (24). 3-Bromophenylboronic acid (**22**) (10.00 g, 0.0500 mol), 10.00 g (0.0580 mol) of 2-bromo-5-methylpyridine (**20**), 16.22 g (0.0500 mol) of cesium carbonate, 1.14 g (0.0012 mol) of tris(dibenzylideneacetone)-dipalladium(0) (**3**), 1.04 g (0.0030 mol) of di-*tert*-butyl(pyren-1-yl)phosphine (**25**), and 100 mL of dioxane were refluxed for 12 h. The reaction mixture was filtered, and the solvent was removed under vacuum. The resulting mixture was purified by vacuum distillation. Yield of 2-(3-bromophenyl)-4-methylpyridine (**24**) was 3.43 g (45%) with bp at 121 °C/0.1 mm. The sample solidified upon standing at ambient temperature. ^{1}H NMR (C_6D_6): δ 1.95 (s, 3H, Me) 6.50−8.40 (m, 7H, arom-H). Anal. Calcd for $C_{12}H_{10}$-BrN (mol wt: 248.12): C, 58.09; H, 4.06; N, 5.65. Found: C, 58.26; H, 4.29; N, 5.68.

4-Methyl-2-(3-pyren-1-ylphenyl)pyridine (30). 2-(3-Bromophenyl)-4-methylpyridine (**24**) (3.43 g, 0.0138 mol), 5.00 g (0.0203 mol) of pyrene-1-boronic acid (**1**), 0.47 g (0.0005 mol) of tris-(dibenzylideneacetone)dipalladium(0) (**3**), 0.26 g (0.0011 mol) of di-*tert*-butyl(trimethylsilylmethyl)phosphane (**4**), 6.62 g (0.0203 mol) of cesium carbonate, and 100 mL of 1,4-dioxane were stirred for 7 days at ambient temperature. The resulting mixture was poured into 200 mL of water and extracted twice with 200 mL of methylene chloride. The organic phase was dried over magnesium sulfate overnight and filtered. The solvent was removed in a rotovapor, and the residue was purified by chromatography on silica gel with an eluent of petroleum ether/ethyl ether at 10/0.5. Yield of 4-methyl-2-(3-pyren-1-ylphenyl)pyridine (**30**) was 4.20 g (26%) as a white solid. ^{1}H NMR (THF-d_8): δ 2.23 (s, 3H, Me) 7.00−8.55 (m, 16H, arom-H). Anal. Calcd for $C_{28}H_{19}N$ (mol wt: 369.46): C, 91.03; H, 5.18; N, 3.79. Found: C, 91.05; H, 5.24; N, 3.91. The structure was proven by X-ray analysis.

Iridium, di-μ-chlorotetrakis[4-(pyren-1-yl)-2-(4-methylpyridinyl-κN)-phenyl-κC], (31). 4-Methyl-2-(3-pyren-1-yl-phenyl)-pyridine (**30**) (2.13 g, 0.0058 mol), 1.00 g (0.0028 mol) of iridium-(III) chloride trihydrate, and 100 mL of trimethyl phosphate were stirred at 90 °C for 3 days under a flow of nitrogen. The resulting yellow precipitate was filtered, washed by 100 mL of pentane, and dried under 1.0 mm vacuum. The yield of the dimer **31** was 2.59 g (93%) as a yellow powder. Complex **31** is practically insoluble in commonly used solvents. This is why the crude chloro-bridged

Table 2. Summary of Crystal Data, Data Collection, and Structural Refinement Parameters for 7, 12, 16, and 19

	7	**12** (CH_2Cl_2)	**12** (acetone)	**16**	**19**
empirical formula	$C_{18}H_{40}Cl_2OP_2Pd_2$	$C_{62}H_{44}Cl_4F_6Ir\ N_2OP$	$C_{66}H_{50}F_6IrN_2\ O_3P$	$C_{29}H_{15}F_6N$	$C_{80}H_{73}F_{12}IrN2O_2$
fw	618.14	1311.96	1256.25	491.42	1514.6
cryst color, form	gold, irreg block	gold, triangular prism	gold, prism	colorless, plate	yellow, irreg block
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic	triclinic
space group	*P*2(1)/*n*	*P*2/*c*	*P*2/*c*	*P*2(1)/*c*	$P\bar{1}$
a (Å)	15.4000(15)	20.4653(19)	20.579(3)	17.850(3)	11.2969(12)
b (Å)	11.3999(11)	12.1974(11)	12.2266(19)	15.742(3)	11.3209(11)
c (Å)	15.4278(15)	22.708(2)	22.819(4)	7.7547(15)	25.322(3)
α (deg)	90	90	90	90	87.237(2)
β (deg)	110.881(2)	112.026(2)	113.766(3)	95.164(5)	87.976(2)
γ (deg)	90	90	90	90	80.299(2)
V (Å^3)	2530.6(4)	5254.8(8)	5254.6(14)	2170.2(7)	3187.2(6)
Z	4	4	4	4	2
density (g/cm3)	1.622	1.658	1.588	1.504	1.578
abs *μ* (mm^{-1})	1.764	2.843	2.645	0.124	2.183
F(000)	1248	2608	2520	1000	1536
cryst size (mm)	0.48 × 0.22 × 0.22	0.25 × 0.25 × 0.16	0.24 × 0.22 × 0.20	0.26 × 0.25 × 0.03	0.21 × 0.17 × 0.13
temp (°C)	−100	−100	−100	−100	−100
scan mode	*ω*	*ω*	*ω*	*ω*	*ω*
detector	Bruker-CCD	Bruker-CCD	Bruker-CCD	Bruker-CCD	Bruker-CCD
θ_{max} (deg)	28.28	28.29	28.29	28.28	28.32
no. obsd reflns	11 782	27 531	33 923	9698	21 300
no. uniq reflns	5936	12 015	12 505	4858	14 512
R_{merge}	0.016	0.030	0.043	0.221	0.037
no. params	238	696	716	325	785
S[a]	1.043	1.041	1.027	0.93	0.852
R indices [$I > 2\sigma(I)$][b]	wR2 = 0.064, R1 = 0.025	wR2 = 0.081, R1 = 0.034	wR2 = 0.090, R1 = 0.039	wR2 = 0.215, R1 = 0.112	wR2 = 0.143, R1 = 0.062
R indices (all data)[b]	wR2 = 0.068, R1 = 0.030	wR2 = 0.090, R1 = 0.051	wR2 = 0.104, R1 = 0.067	wR2 = 0.319, R1 = 0.379	wR2 = 0.171, R1 = 0.121
max. diff peak, hole (e/Å^3)	0.901, −0.410	1.841, −1.438	2.266, −1.196	0.401, −0.325	1.450, −0.706

[a] GooF = $S = \{\sum[w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$, where *n* is the number of reflections, and *p* is the total number of refined parameters. [b] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$, $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$ (sometimes denoted as R_w^2).

Table 3. Summary of Crystal Data, Data Collection, and Structural Refinement Parameters for 23, 25, 29, 30, and 32

	23	**25**	**29**	**30**	**32**
empirical formula	$C_{12}H_{10}ClN$	$C_{24}H_{27}P$	$C_{24}H_{26}BrPPd$	$C_{28}H_{19}N$	$C_{67}H_{55}IrN_2O_2$
fw	203.66	346.43	531.73	369.44	1112.33
cryst color, form	colorless, wedge	colorless, plate	colorless, irreg block	colorless, rect plate	orange, prism
cryst syst	orthorhombic	monoclinic	monoclinic	monoclinic	tetragonal
space group	*Pca*2(1)	*P*2(1)/*c*	*P*2(1)	*P*2(1)/*c*	*P*4/*ncc*
a (Å)	7.4452(10)	16.865(10)	12.327(3)	9.345(4)	25.909(3)
b (Å)	10.9266(15)	8.172(5)	12.964(3)	7.429(3)	25.909(3)
c (Å)	12.0699(16)	14.598(9)	16.075(2)	27.666(11)	18.352(4)
α (deg)	90	90	90	90	90
β (deg)	90	103.052(12)	108.464(13)	107.310(15)	90
γ (deg)	90	90	90	90	90
V (Å^3)	981.9(2)	1960(2)	2436.7(9)	1833.7(13)	12319(3)
Z	4	4	4	4	8
density (g/cm3)	1.378	1.174	1.449	1.338	1.199
abs *μ* (mm^{-1})	0.343	0.143	2.473	0.077	2.209
F(000)	424	744	1064	776	4512
cryst size (mm)	0.36 × 0.14 × 0.06	0.52 × 0.40 × 0.05	0.24 × 0.24 × 0.12	0.33 × 0.21 × 0.02	0.34 × 0.08 × 0.08
temp (°C)	−100	−100	−100	−100	−100
scan mode	*ω*	*ω*	*ω*	*ω*	*ω*
detector	Bruker-CCD	Bruker-CCD	Bruker-CCD	Bruker-CCD	Bruker-CCD
θ_{max} (deg)	29.12	24.25	30.56	23.81	27.69
no. obsd reflns	7915	9388	18 540	8964	120 248
no. uniq reflns	2596	3108	6888	2798	7216
R_{merge}	0.0421	0.1032	0.0732	0.1126	0.0965
no. params	128	232	250	263	330
S[a]	1.043	0.806	0.88	0.956	1.081
R indices [$I > 2\sigma(I)$][b]	wR2 = 0.106, R1 = 0.042	wR2 = 0.138, R1 = 0.063	wR2 = 0.108, R1 = 0.050	wR2 = 0.148, R1 = 0.068	wR2 = 0.086, R1 = 0.040
R indices (all data)[b]	wR2 = 0.115, R1 = 0.061	wR2 = 0.152, R1 = 0.130	wR2 = 0.120, R1 = 0.093	wR2 = 0.194, R1 = 0.167	wR2 = 0.100, R1 = 0.096
max. diff peak, hole (e/Å^3)	0.230, −0.335	0.423, −0.505	1.173, −1.530	0.240, −0.222	0.966, −0.545

[a] GooF = $S = \{\sum[w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$, where *n* is the number of reflections, and *p* is the total number of refined parameters. [b] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$, $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$ (sometimes denoted as R_w^2).

dimer **31** was used without further purification in the next steps according to established practice in cyclometalation research.[24]

Iridium, bis[4-(pyren-1-yl)-2-(4-methyl-2-pyridinyl-κN)-phenyl-κC],(2,2,6,6-tetramethyl-3,5-heptanedionato-κO,κO), (32).

Iridium, di-μ-chlorotetrakis[4-(pyren-1-yl)-2-(4-methyl-2-pyridinyl-κN)phenyl-κC], (**31**) (1.80 g, 0.0019 mol), 0.70 g (0.0038 mol) of 2,2,6,6-tetramethylheptane-3,5-dione (**18**), 1.38 g of a 40% solution of tetraethylammonium hydroxide in water, and 60 mL of THF were refluxed for 12 h under an argon atmosphere. The solvent was removed in a rotavapor, and the residue was purified by chromatography on silica gel with an eluent of petroleum ether/ethyl ether at 10/2. Yield of iridium, bis[4-(pyren-1-yl)-2-(4-methyl-2-pyridinyl-κN)phenyl-κC], (2,2,6,6-tetramethyl-3,5-heptanedionato-κO,κO), (**32**) was 0.35 g (30%) as a yellow solid with no mp until 200 °C. ^{1}H NMR (CD_2Cl_2): δ 1.05 (s, 18H, Me), 2.63 (s, 6H, Me), 5.67 (s, 1H, H-C═), 6.60 (m, 1H, arom-H), 7.12 (m, 2H, arom-H), 7.90−8.50 (m, 25H, arom-H). Anal. Calcd for $C_{67}H_{55}IrN_2O_2$ (mol wt: 1112.38): C, 72.34; H, 4.98. Found: C, 72.38; H, 5.20. The structure was proven by X-ray analysis.

X-ray Diffraction Studies. Data for all structures were collected using a Bruker CCD system at −100 °C. Structure solution and refinement were performed using the SHELXTL[30] set of programs. The Platon-Squeeze[31] program was used to correct the data where the solvent molecules could not be correctly modeled (compounds **29** and **30**). This led to cif errors for the formula, as the atom list differed from the correct formula. The high *r*-factors for compound **16** were due to nonmerohedral twinning that could not be modeled using the program Gemini for this poorly formed data crystal. The structural parameters are reported in Tables 2 and 3.

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Supporting Information Available: Crystallographic information files (CIF) of compounds **7**, **12**, **16**, **19**, **25**, **29**, **30**, and **32** are available free of charge via the Internet at http://pubs.acs.org.

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