Asymmetric Iridium(I)-Catalyzed Allylic Alkylation of Monosubstituted Allylic Substrates with Phosphinooxazolines as Ligands. Isolation, Characterization, and Reactivity of Chiral (Allyl)iridium(III) Complexes

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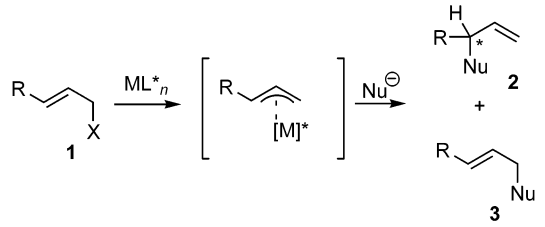
Ir^{I}-catalyzed allylic alkylations of linear aryl-substituted allylic acetates proceed with enantiomeric excess of up to 95% ee using bidentate phosphinooxazolines as chiral ligands. The chiral (π-allyl)Ir^{III} complexes **14** and **15** have been characterized by X-ray crystal structure analysis and spectroscopic data. The stoichiometric reaction between sodium dimethyl malonate and complex **14** proceeded with nucleophilic addition at the central allylic carbon as well as ligand exchange at Ir to give the iridacyclobutane complex **16**, which was fully characterized. Complex **16** was transformed into (π-allyl)Ir^{III} complexes by treatment with Lewis acid or iodine.

Introduction

Transition-metal-catalyzed allylic alkylations are important carbon−carbon bond-forming reactions with many applications in organic synthesis.[1] The regio- and enantioselectivity of these processes depend on a variety of factors: i.e. metal ion, auxiliary ligands, nucleophile, leaving group, and reaction conditions. Currently, interest is focused on allylic substitutions with terminally monosubstituted substrates leading to unsymmetrical π-allyl intermediates (Scheme 1). As a rule, palladium catalysts preferentially lead to the formation of the linear products **3**; however, a few examples have recently been found giving rise to nucleophilic addition at the higher substituted terminus.[2] In special cases, addition at the central allylic C has also been found.[3] In general, complementary results are obtained with Mo and W catalysts, which can provide successful control of regioselectivity in favor of the branched products **2** with good levels of enantioselectivity (R = Ar).[4]

In contrast, reactions catalyzed by Rh or Fe complexes generally proceed with preferential nucleophilic substitution at the carbon atom carrying the leaving group,

Scheme 1. General Scheme for the Transition-Metal-Catalyzed Allylic Alkylation of Monosubstituted Allylic Derivatives



and therefore, linear substrates give rise to achiral products. It has been proposed that these reactions proceed via σ- or π-allyl complexes, which isomerize slowly.[5] Remarkably in view of this feature, a very high degree of enantioselectivity has recently been achieved in Rh-catalyzed allylic alkylations, using chiral phosphinooxazolines as ligands, of racemic branched 2-propenyl acetates to give branched alkylation products.[6] Catalysis of allylic substitutions of linear substrates **1** with Ru complexes allows preferential production of the branched products **2**.[7]

Ir^{I} complexes prepared by combining $[IrCl(COD)]_2$ with monodentate π-acceptor ligands, for example phos-

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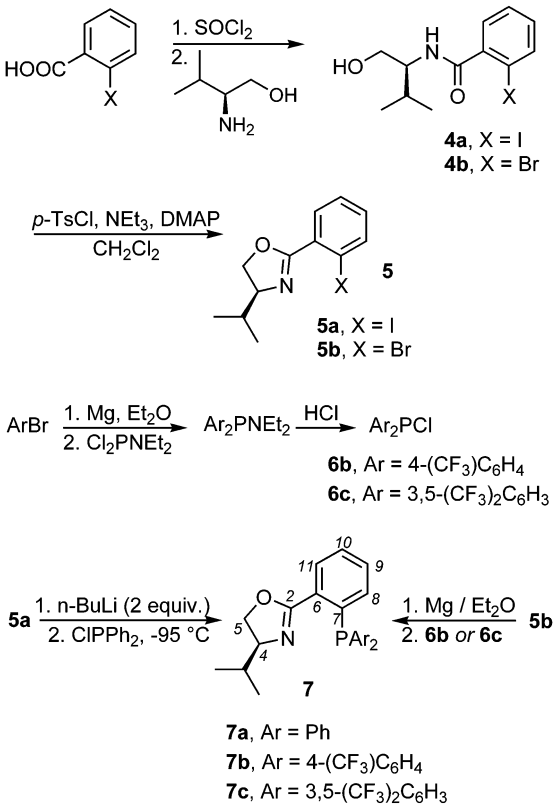
phites, also catalyze the allylic substitution of substrates **1** to give branched products **2** with a high degree of regioselectivity.[8] In 1997, this group described the first enantioselective Ir^I-catalyzed allylic substitutions of arylallyl acetates (*E*)-**1**, which gave high levels of regio- and enantioselectivity of up to 95% ee in favor of product **2** when bidentate chiral phosphinooxazolines were used as ligands.[9] In further work, allylic substitutions not only of aryl-substituted but also of alkyl-substituted substrates, using monodentate phosphorus amidites[10−12] and phosphites[13] as chiral ligands, allowed branched products **2** to be obtained with high levels of regio- and enantioselectivity.

In a recent publication, we have reported a study of the factors affecting the course of the Ir^I-catalyzed allylic substitution with monodentate ligands, as well as the isolation and characterization of (allyl)Ir^{III} complexes related to the proposed mechanism.[14] Here we present an extension of our earlier work with chiral bidentate phosphinooxazolines (PHOX) as ligands. We are now able to report preparation and full characterization of the first Ir^{III} complexes containing both an allyl and a chiral auxiliary ligand. Reactions of these species with nucleophiles have also been studied in order to better understand the mechanism of the Ir^I-catalyzed allylic substitution.

Results and Discussion

Synthesis of Phosphinooxazoline Ligands. The phosphinooxazolines have emerged as a versatile type of bidentate ligand for a variety of catalytic processes, in particular allylic alkylations.[15] Phosphinooxazolines **7** (Scheme 2) are most often prepared from 2-(2-fluorophenyl)oxazolines **5** (X = F) by nucleophilic aromatic substitution.[16] This approach is not possible for arylphosphanes, such as **7b**,**c**, with electron-withdrawing substituents. Preparation of these compounds requires polarity-reversed reaction partners, i.e., reactions of 2-(2-lithiophenyl)oxazolines **5** (X = Li) or corresponding Grignard compounds with diarylhalophosphanes. Ligands **7b**,**c** were prepared in this way in moderate overall yields (30−65%) by reaction of diarylchlorophosphanes **6b**,**c**,[17] respectively, with the Grignard reagent prepared from bromophenyloxazoline **5b**.

Scheme 2. Preparation of PHOX Ligands 7



Previously, experiments directed at preparing 2-(2-lithiophenyl)oxazolines **5** (X = Li) by direct lithiation of 2-(phenyl)oxazoline **5** (X = H) were only partially successful because of side reactions. We have now addressed this problem by using halogen metal exchange. Thus, the iodophenyloxazoline **5a** could be transformed cleanly into the lithium compound by reaction with 2 equiv of *precooled* *n*-BuLi or *t*-BuLi at −100 °C. At higher temperature addition of *n*-BuLi to the C=N group and other side reactions occurred. Quenching of the properly prepared lithium derivative with water gave pure 2-(phenyl)oxazoline **5** (X = H) in 96% isolated yield. Reaction of the lithium compound with chlorodiphenylphosphane furnished ligand **7a** in 80% isolated yield.

Allylic Substitutions. In previous studies it was found that π-acceptor ligands are required in order to obtain preparatively useful rates and selectivities in Ir^I-catalyzed allylic substitutions. Accordingly, the CF_3-substituted phosphinooxazolines **7b**,**c** were used as ligands, in addition to the standard PHOX ligand **7a** (Scheme 3).

In the first set of experiments, substrates **1a**,**b** were tested. The results, summarized in Table 1, clearly show that electronic and steric effects are very important for the course of the reaction. Thus, the CF_3-substituted ligands are superior to the parent ligand **7a**. With the ligand **7b** results are distinctly better than with the bulkier ligand **7c** (entries 3, 6, and 9). The importance of electronic effects, in particular on regioselectivity, is also apparent upon comparison of the results with arylallyl acetates **1a**,**b**. The very high degrees of regioselectivity for **1b** are due to increased stabilization of a positive charge at the arylated terminus of the allylic

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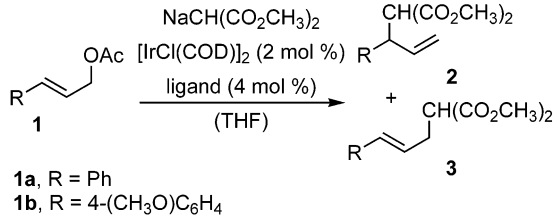
Scheme 3. Ir^{I}-Catalyzed Asymmetric Allylic Substitutions Using Phosphinooxazolines 7 as Chiral Ligands



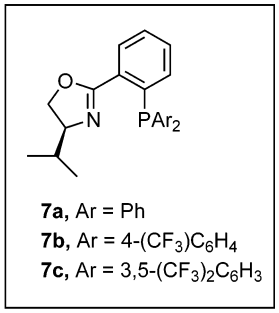


Table 1. Ir^{I}-Catalyzed Allylic Alkylations of Linear Substrates 1 Yielding Branched Product 2 and Linear Product 3[a]

entry	substrate	ligand	*T* (°C)	yield (%)	**2**:**3**[b]	ee (%)[c]
1	**1a**	**7a**	room temp	61	92:8	30
2	**1a**	**7b**	room temp	85	87:13	92
3	**1a**	**7c**	room temp	46	86:14	87
4	**1a**	**7a**	67	92	77:23	78
5	**1a**	**7b**	67	99	95:5	91
6	**1a**	**7c**	67	95	89:11	84
7	**1b**	**7a**	67	89	99:1	72
8	**1b**	**7b**	67	98	99:1	95
9	**1b**	**7c**	67	71	93:7	62

[a] Cf. Scheme 1. All reactions were carried out in THF (6 mL) using 2 mmol of **1** and 6 mmol of $NaCH(CO_2CH_3)_2$, 2 mol % of $[IrCl(COD)]_2$, and 4 mol % of the ligand; reaction time 24 h. [b] Determined by GC/MS. [c] In all cases, the *R* configuration of the major enantiomer was determined by HPLC.

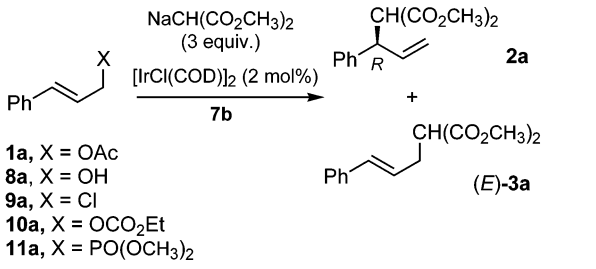
moiety.[18] An increase of temperature generally improves both enantio- and regioselectivities. This effect is probably caused by increased rates of isomerization reactions of (allyl)Ir intermediates, which are generally slow at room temperature.

Having established optimal reaction conditions and ligand, various other factors were studied: in particular, the influence of the leaving group, additives, ratio [Ir/ligand], and solvent. The results are summarized in Table 2.

As previously found for reactions catalyzed by (phosphoramidite)Ir complexes, substrates with leaving groups other than acetate reacted with markedly lower selectivity (Table 2, entries 1−5).[11,14] This observation cannot be generalized, because optimal results have been recently obtained in Ir^{I}-catalyzed aminations with allylic carbonates.[12] With LiCl as additive, the yield and enantioselectivity were almost unaffected, but a distinct decrease of regioselectivity was found (entry 6); in contrast, reactions with phosphoramidite complexes as catalysts are strongly influenced by LiCl. Use of $[IrCl(COE)_2]_2$ as the precatalyst led to a pronounced decrease of regio- and enantioselectivity (cf. entries 1 and 7). For the ligand to iridium ratio, a 1:1 ratio was optimal; however, with a 2:1 ratio the reaction also proceeded with fairly high enantio- and regioselectivity (cf. entries 1 and 8−10). Of the solvents probed, tetrahydrofuran was the most suitable (cf. entries 1 and 11−13).

(18) The allylic alkylation of alkylallyl acetates (R = Et, *i*-Pr) has been also studied using the conditions described in Table 1, but only poor yields and selectivities were obtained.

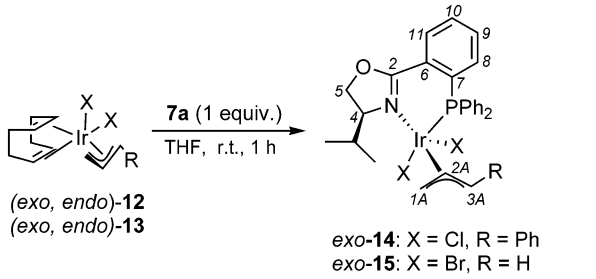
Table 2. Optimization of the Ir-Catalyzed (Ligand 7b) Allylic Alkylation of Phenyl-Substituted Substrates[a]



entry	X	solvent	Ir:**7b**	*T* (°C)	yield (%)	**2a**:**3a**[b]	ee (%)[c]
1	OAc	THF	1:1	67	99	95:5	91
2	OCO_2Et	THF	1:1	67	80	88:12	34
3	$OPO(OCH_3)_2$	THF	1:1	67	72	92:8	18
4	Cl	THF	1:1	67	80	96:4	72
5	OH	THF	1:1	67	63	73:27	81
6[d]	OAc	THF	1:1	67	95	84:16	90
7[e]	OAc	THF	1:1	67	95	63:37	86
8	OAc	THF	1:0.5	67	54	86:14	78
9	OAc	THF	1:1.5	67	90	90:10	74
10	OAc	THF	1:2	67	97	90:10	86
11	OAc	DMF	1:1	100	57	87:13	57
12	OAc	CH_3CN	1:1	100	99	81:19	47
13	OAc	dioxane	1:1	100	76	57:43	4

[a] Reaction conditions: as stated in footnote *a* of Table 1. [b] Determined by GC/MS. [c] In all cases, the *R* configuration of the major enantiomer was determined by HPLC. [d] 2 equiv of LiCl and 2 equiv of 12-crown-4 were added. [e] 2 mol % of $[IrCl(COE)_2]_2$ and 4 mol % of **7b**.

Scheme 4. Synthesis of Complexes 14 and 15



Syntheses and X-ray Crystal Structures of (π-allyl)Ir^{III} Complexes 14 and 15. In previous work with monodentate phosphoramidites as ligands, all attempts to isolate species containing both an allyl moiety and a chiral ligand were unsuccessful.[14] In contrast, reaction of the COD-containing complexes **12** (2:1 mixture of endo and exo isomers) and **13** (9:1 mixture of endo and exo isomers) with the phosphinooxazoline **7a** smoothly furnished π-allyl complexes **14** and **15**, respectively, in up to 60% yield (Scheme 4). According to $^{31}P\{^{1}H\}$ NMR of reaction mixtures, only one product was formed in each case.

Crystallization of complexes **14** and **15** from concentrated THF solutions or dichloromethane/diethyl ether

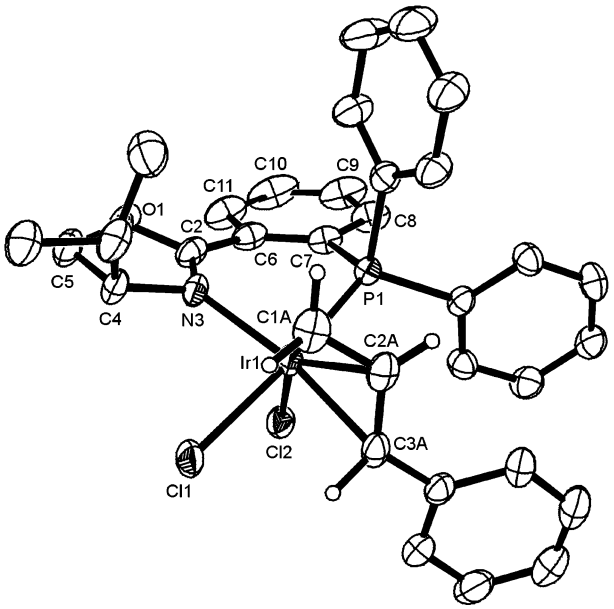


Figure 1. ORTEP view of complex **14**. Ellipsoids are drawn at the 50% probability level; most of the hydrogen atoms are omitted for the sake of clarity. Selected bond lengths (Å) with estimated standard deviations: Ir(1)−C(1A) = 2.139(3), Ir(1)−C(2A) = 2.143(2), Ir(1)−C(3A) = 2.229(3), C(1A)−C(2A) = 1.425(4), C(2A)−C(3A) = 1.412(4).

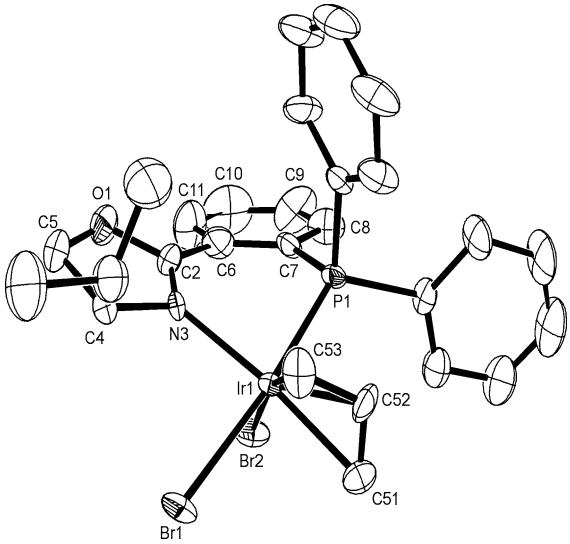


Figure 2. ORTEP view of complex **15**. Ellipsoids are drawn at the 50% probability level; hydrogen atoms are omitted for the sake of clarity.

furnished pure exo isomers (Figures 1 and 2).[19] In both complexes allyl moieties are in a cis disposition relative to phosphorus; this is the structure with minimal destabilization, due to the trans influences of carbon and phosphorus centers. In both structures the allyl ligand is found in the exo configuration. A discussion of geometric data of the allyl ligand of complex **15** is not possible because of low precision of the crystallographic data.

(19) Definition of the designations exo/endo and syn/anti in PHOX-containing allyl complexes: an exo configuration of a complex is given if 2A-H is pointing towards the phosphorus, and a syn configuration of the allyl moiety is defined by a cis disposition of the allylic substituent and 2A-H.

The syn configuration of the allyl moiety in **14** is typical for aryl−allyl ligands.[19] Lengths of the bonds $C_{1A}-C_{2A}$ (1.425(4) Å) and $C_{2A}-C_{3A}$ (1.412(4) Å) of complex **14** differ less than is typical for (π-allyl)Ir^{III} complexes.[14,20] Differences of distances $Ir-C_{1A}$ (2.139(3) Å) and $Ir-C_{3A}$ (2.229(3) Å) of complex **14**, due to the different substitution of the allylic termini, are also relatively small. It is perhaps significant that the bond to the more substituted terminus, preferentially broken in the nucleophilic substitution, is the longer one. With respect to the substitution it is also of interest to note that nucleophilic substitution with $NaCH(CO_2Me)_2$ at C_{3A} with inversion would yield the product **2a** with an *R* configuration, actually found experimentally. However, one has to be cautious concerning the significance of these observations, as long as the fastest reacting complex, among a set of isomeric complexes, has not yet been identified.

NMR Spectroscopy of (π-allyl)Ir^{III} Complexes 14 and 15. (a) Experiments at Room Temperature. (π-allyl)Ir^{III} complexes generally show slow isomerization,[20,21] compared to π-allyl complexes of the first- and second-row late transition metals. Complexes **14** and **15**, indeed, did not isomerize at room temperature, as indicated by well-defined, narrow NMR signals.

According to ^1H, $^{13}C\{^1H\}$, and ^{31}P NMR (single sharp peak at −16.0 ppm) spectra, solutions of **14**, formed by dissolving the crystalline compound, contain a single species. ^1H NMR resonances of allylic protons appear in the range 2.5−6 ppm, and the syn configuration of the allyl ligand found by X-ray diffraction is confirmed by the coupling constant $^3J_{2A,3A} = 10.9$ Hz, typical for protons in anti positions (for numbering see Scheme 4). Furthermore, there is no coupling between allylic protons and phosphorus; this confirms the relative cis disposition of the allyl ligand and the phosphorus center (cf. Figure 1). $^{13}C\{^1H\}$ NMR (room temperature) data were analyzed with the help of HMQC, HMBC, and $^{13}C\{^1H,^{31}P\}$ NMR experiments. Resonances for the allylic carbons are located in the range 32−84 ppm, as found for related (π-allyl)Ir^{III} complexes;[21b] no resonances of σ-bound allylic CH_2 groups, expected in the range 0−25 ppm,[20] were observed.

The ^1H, $^{13}C\{^1H\}$, and ^{31}P NMR (single sharp peak at 5.37 ppm) spectra of complex **15** also agree with the presence of a single species. ^1H and $^{13}C\{^1H\}$ NMR resonances for the allylic protons and carbons, respectively, appear in the expected ranges.[20,21b,c,e,22] No coupling with phosphorus was observed, which confirms for the solution structure the mutual cis disposition of the unsubstituted allyl and phosphorus ligands found in the crystal structure (cf. Figure 2).

(b) Experiments with Complex 14 at Variable Temperature. A solution of complex **14** in [D_8]toluene (Figure 3a) was heated at 90 °C for 2 h. At this

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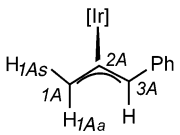
Table 3. ^{1}H NMR Resonances of Allylic Protons (ppm) for a 3:4:2 Mixture Containing 14A−C ([D$_8$]Toluene, −40 °C)



assignt	14A	14B	14C
H_{1As}	3.15 (d, ^3J(H,H) = 5.5 Hz)	3.76 (d, ^3J(H,H) = 7.0 Hz)	3.55−3.67 (m)
H_{1Aa}	3.29 (d, ^3J(H,H) = 8.8 Hz)	3.84 (d, ^3J(H,H) = 11.4 Hz)	4.16 (d, ^3J(H,H) = 10.6 Hz)
H_{2A}	4.95−5.08 (m)	6.12−6.23 (m)	6.12−6.23 (m)
H_{3A}	6.50 (d, ^3J(H,H) = 11.0 Hz)	5.69 (dd, ^3J(H,H) = 13.1, ^3J(H,P) = 8.8 Hz)	5.09 (dd, ^3J(H,H) = 12.7, ^3J(H,P) = 9.5 Hz)

temperature, a new ^{31}P{^{1}H} NMR spectrum was recorded, showing the appearance of a new sharp peak (δ −3.0 ppm) in addition to that of the starting complex (δ −15.9 ppm) (Figure 3b). The mixture was then cooled. While the signal of the starting complex **14** remained unchanged, the new signal at −3.0 ppm became broader (Figure 3c−f), splitting into two peaks (ca. −3.0 and −4.0 ppm) at lower temperatures (coalesces at 55 °C). The solution at room temperature contained three species, in the ratio 3:4:2, now designated **14A** (starting complex), **14B** (*major* isomer), and **14C** (*minor* isomer), respectively (Figure 3j).[23]

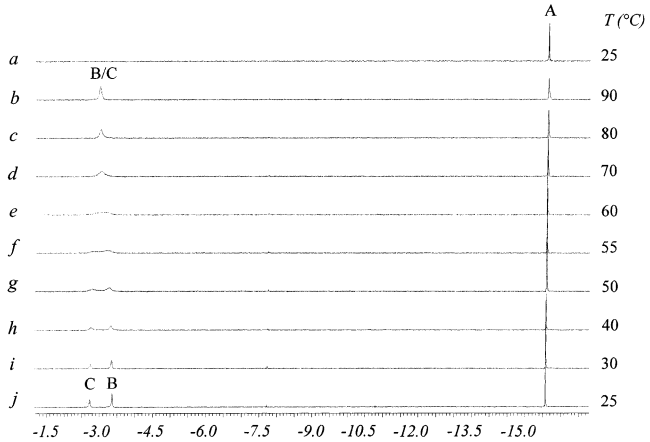


Figure 3. (a) ^{31}P{^{1}H} NMR spectrum of complex **14** at 25 °C. (b−j) ^{31}P{^{1}H} NMR spectra of the same solution after heating to 90 °C for 2 h (b) and cooling to 25 °C.

Further cooling did not alter the composition of the mixture but resulted in improved resolution of ^{1}H and ^{13}C{^{1}H} NMR spectra (Figure 4).

To further characterize complexes **14B**,**C**, ^{1}H NMR and ^{13}C{^{1}H} NMR spectra of the mixture at −40 °C were analyzed with the help of ^{1}H,^{1}H COSY, ^{1}H{^{31}P}, ^{13}C{^{31}P}, HMQC, and HMBC experiments. For all isomers, signals corresponding to the allylic protons appeared in the range 3.10−6.50 ppm (Table 3). Resonances of the syn (H_{1As}) and anti (H_{1Aa}) protons of the allylic CH_2 group of the three complexes are easily distinguished on the basis of their ^3J(H,H) coupling constants. In addition, the value of the proton coupling constant for the C*H*(Ph) terminus (^3J(H,H) = 11−13 Hz) of the allyl moiety confirmed a syn configuration of this ligand. Other than **14A**, both **14B**,**C** displayed coupling (^3J(H,P) ≈ 9 Hz) of the allylic C*H*(Ph) proton and the P atom.[24]

(23) When a solution containing isomers **14A**−**C** was stored at −40 °C, the ratio of the isomers remained unchanged (3:4:2); however, partial decomposition occurred.

Table 4. ^{13}C{^{1}H} NMR Data (ppm) of the Allylic Moiety for a 3:4:2 Mixture Containing 14A−C ([D$_8$]Toluene, −40 °C)[a]

assignt	14A	14B	14C
C_{1A}	33.8 (s)	30.2 (s)	30.5 (s)
C_{2A}	82.5 (s)	113.3 (broad s)	112.0 (broad s)
C_{3A}	65.2 (s)	83.5 (d, ^2J(C,P) = 36.7 Hz)	83.6 (d, ^2J(C,P) = 38.6 Hz)

[a] For numbering see Table 3.

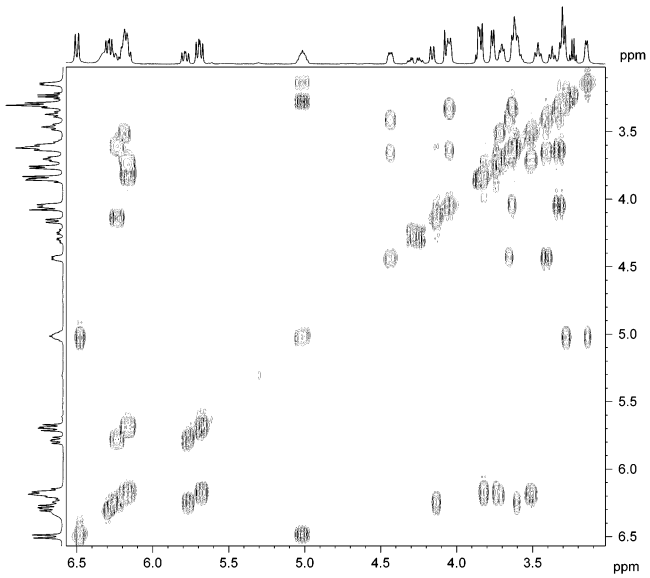


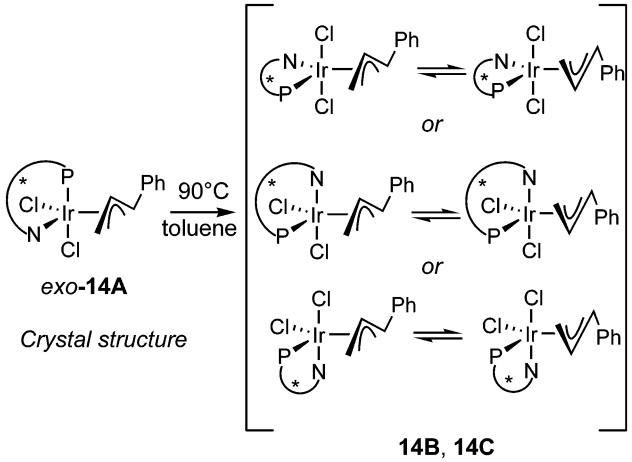
Figure 4. ^{1}H,^{1}H COSY spectrum (allylic area) of a 3:4:2 mixture of complexes **14A**−**C** in [D$_8$]toluene at −40 °C.

^{13}C{^{1}H} NMR data of the allylic moieties of **14A**−**C** are given in Table 4. Resonances of **14B**,**C** are found at 30.2 and 30.5 ppm (*C*H_2), at 113 and 112 ppm (central *C*H), and as two doublets at 83.5 and 83.6 ppm (^2J(C,P) ≈ 37 Hz) (*C*HPh termini), respectively. The data again indicate that in both isomers the allylic terminus CH(Ph) and the phosphorus center are in a trans disposition. This condition is fulfilled in the six possible isomers represented in Scheme 5. Furthermore, the downfield shifts of signals of **14B**,**C** relative to those of **14A** reflect a different electronic environment of the allyl ligands, which can be related to a stronger *asymmetry* as compared to that in **14A**.[14]

Solutions enriched in **14B**,**C** were obtained by extraction of **14A**:**14B**:**14C** mixtures with pentane/diethyl

(24) A NMR analysis of the mixture of isomers at 90 °C was also carried out. In agreement with the ^{31}P NMR data (Figure 3b), two clear 1:2 sets of signals are displayed by ^{1}H and ^{13}C NMR spectra, corresponding to **14A** and the equilibrating mixture **14B/14C**, respectively.

Scheme 5. Isomerization of the Complex *exo*-14 (14A) to a Mixture of Species 14B and 14C, Containing the Allylic Terminus CH(Ph) Trans to Phosphorus[a]



[a] For isomers **14B**,**C** the two possible arrangements of the chloro ligands are represented.

ether at −40 °C. All attempts to grow a single crystal of **14B** or **14C** from these solutions led only to crystallization of residual **14A**.

For isomers **14B**,**C** cis and trans dispositions of the chloro ligands have to be considered (cf. Scheme 5). IR measurements can give information about the relative disposition of the chloro ligands in organometallic [Ir]Cl_2 fragments. Thus, for a cis disposition two IR-active ν(IrCl) frequencies are expected in the region 400−200 cm^{-1}, while a trans disposition would display only one characteristic band.[25] IR spectra of **14A** and the 3:4:2 mixture of **14A**:**14B**:**14C** were recorded in the range 700−200 cm^{-1} (solid state, CsI pellets). Complex **14A** displayed two bands in this range, at ca. 250 and 276 cm^{-1}, as expected. However, no conclusive result could be obtained from the IR spectrum of the mixture, and therefore, the disposition of the chloro ligands in complexes **14B** and **14C** is presently unknown.

Stoichiometric Reactions of the (π-allyl)Ir^{III} Complex 14. (a) Reaction of Complex 14 with NaCH(CO_2Me)$_2$. Complexes **14** and **15** were tested as catalysts in allylic alkylations. For example, with complex **14** as catalyst, the alkylation of substrate **1a** proceeded with good yield but distinctly lower regio- (**2a**:**3a** = 61:39) and enantioselectivity (35% ee (*S*)) than the reaction catalyzed by a [IrCl(COD)]$_2$/**7a** mixture as described in Table 1. This discrepancy could be clarified in part on the basis of the following results.

The reaction of complex **14** with 2 equiv of NaCH(CO_2CH_3)$_2$ at −40 °C gave in quantitative yield a 9:1 mixture of two products, characterized by ^{31}P NMR signals at −4.6 and −12.3 ppm, respectively; only a trace of the expected substitution product **2a** could be detected by GC/MS. The major product was isolated in pure form and fully characterized (Scheme 6). Spectroscopic data and X-ray structure analysis (Figure 5) revealed the new compound as the metallacyclobutane complex **16**, resulting from nucleophilic addition at the central carbon of the allyl moiety of **14** and replacement of the chloro ligands by the bidentate dimethyl malonato ligand.

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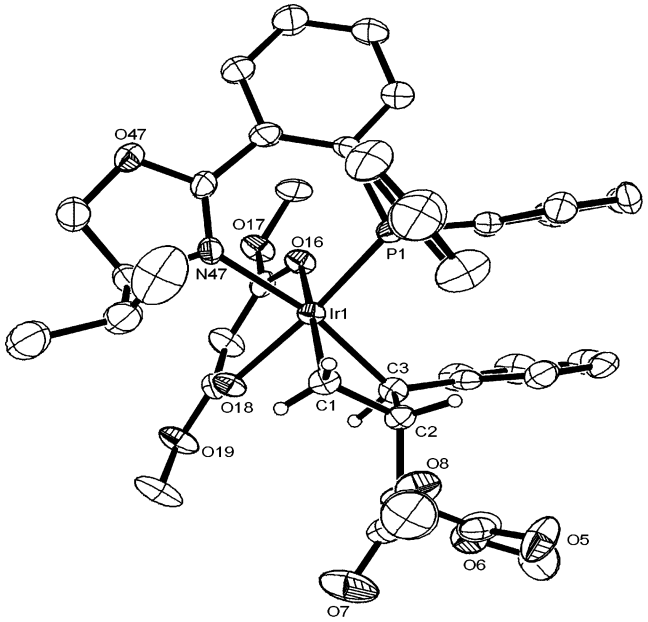
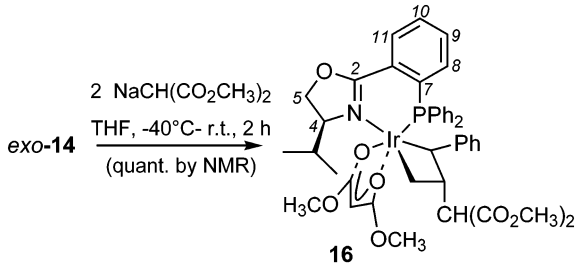


Figure 5. ORTEP view of iridacyclobutane **16**. Ellipsoids are drawn at the 50% probability level; most of the hydrogen atoms are omitted for the sake of clarity.

Scheme 6. Stoichiometric Reaction of Complex *exo*-14 with Sodium Dimethyl Malonate



Substituents Ph and CH(CO_2CH_3)$_2$ at the iridacycle are in trans disposition. The phosphorus center appears trans to an oxygen atom of the dimethyl malonate ligand; thus, destabilization because of strong trans influences of phosphorus and carbon centers is minimized.

For complex **16** in solution, the iridacyclobutane structure was confirmed by characteristic upfield resonances in both ^1H and ^{13}C NMR spectra for the Ir−CH groups. Thus, the ^1H NMR spectrum (C_6D_6, 25 °C) of complex **16** shows signals at 1.73 (dd, 1 H, ^2J(H,H) = 7.0 Hz, ^3J(H,H) = 8.4 Hz) and 1.92 ppm (ddd, 1 H, ^3J(H,P) = 4.0 Hz, ^2J(H,H) = 7.0 Hz, ^3J(H,H) = 7.0 Hz) corresponding to the diastereotopic IrCH_2 protons, one of which couples with the phosphorus center. Two singlets (2.85 and 3.31 ppm) and a doublet (3.76 ppm, ^3J(H,H) = 8.7 Hz) characterize the CH(CO_2CH_3)$_2$ substituent at the iridacyclobutane. This substituent is clearly distinguished from the bidentate ligand, for which three singlets for both CH_3 (2.88 and 3.65 ppm) and C*H* groups (5.06 ppm) are observed, respectively. The most characteristic signal of the $^{13}C\{^1H\}$ NMR spectrum (C_6D_6, 25 °C) is a doublet (^2J(C,P) = 5.2 Hz) at −16.8 ppm, corresponding to the IrCH_2 carbon of the metallacycle.

Isomers **14B**,**C** do contain an allylic terminus (CH(Ph)) trans to the phosphorus center, and therefore,

their reactivity against nucleophiles would be expected to be higher than that of **14A**. Thus, a mixture of **14A**−**C** (3:4:2) was treated with 2 equiv of $Na(CHCO_2CH_3)_2$ in THF at −40 °C followed by warming to room temperature. As in the reaction of pure **14A**, only a trace of olefin **2a**, the product of nucleophilic addition to the CHPh allylic terminus, was formed. Main reaction products were complex **16** and other nonidentified organometallic complexes.

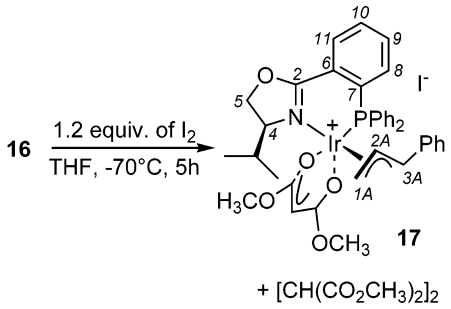
While nucleophilic addition at the central carbon is common for cationic molybdenum, tungsten, and rhodium π-allyl complexes,[26] only a few examples have been described for (allyl)Ir^{III} complexes. Thus, Bergman and co-workers reported the first iridacyclobutane complex, which was obtained by reaction of an (allyl)Ir^{III} complex with $LiEt_3BH$.[27] Further irida- and rhodacyclobutanes[21b,22a,28] and even palladacyclobutanes[3] were later obtained. In addition, a theoretical analysis of the regioselectivity of the nucleophilic addition at η^3-allyl complexes, including Ir and Rh complexes, showed complexes $CpLM(\eta^3\text{-allyl})^+$ (M = Co, Rh, Ir) to be suitable substrates for metallacyclobutane formation.[29]

Of particular relevance concerning mechanistic aspects of the allylic substitution is the work of Stryker et al., who found dichotomic behavior of $Cp(\pi\text{-allyl})Ir^{III}$ complexes: hard nucleophiles such as hydrides or enolates of cyclohexanone or propiophenone yielded metallacyclobutanes, while a soft nucleophile, malonate, gave rise to an olefin complex. For example, treatment of the complex $[(\eta^5\text{-}C_5(CH_3)_5)Ir(\eta^3\text{-}C_3H_5)(\eta^2\text{-}C_2H_2)]OTf^-$ with $KCH(CO_2CH_3)_2$ proceeded with terminal substitution rather than iridacyclobutane formation.[28c] Stryker et al. also demonstrated that metallacyclobutane complexes can be transformed into allyl complexes by treatment with Lewis acids.[28e]

(b) Reactions of Complex 16 with I_2 and BF_3. An iodinolysis experiment was carried out with complex **16**, because treatment of a metallacyclobutane complex with iodine is expected to induce liberation of a cyclopropane.[28c,e] Addition of 1.2 equiv of iodine to a solution of complex **16** in THF at −70 to −50 °C effected formation of a single, new organometallic compound (^{31}P NMR (CD_2Cl_2): δ −15.7 ppm) in high yield. The expected 1,2-disubstituted cyclopropane was not formed. Instead, $CH_2(CO_2CH_3)_2$ and its dimer $[(CO_2CH_3)_2CH]_2$ were the organic products.

The new organometallic compound is the $(\pi\text{-allyl})Ir^{III}$ complex **17** (Scheme 7), according to NMR and MS data. Thus, the ^1H NMR spectrum (−30 °C, CD_2Cl_2) shows signals of the allylic protons in the range (2.40−5.50 ppm) expected for a π-allyl ligand and three singlets (2.78, 3.58, 4.56 ppm) corresponding to the bidentate ligand $[CH(CO_2CH_3)_2]^-$. In the $^{13}C\{^1H\}$ NMR spectrum, resonances of the allylic carbons are found as singlets (31.6, 72.6, and 85.6 ppm). Absence of H,P and C,P coupling in the allylic moiety indicates a cis disposition of the allyl ligand and the phosphorus center.

Scheme 7. Conversion of the Iridacyclobutane 16 into the (π-allyl)Ir^{III} Complex 17 by Treatment with I_2



Treatment of complex **17** with 1 equiv of sodium dimethyl malonate at −30 °C effected formation of the iridacyclobutane **16**, as was anticipated. Again, products of addition at the terminal positions, **2a** and **3a**, were not formed.

In view of the results of Stryker et al. discussed above, it was of interest to treat complex **16** with Lewis acid. Thus, complex **16** was reacted with 1.5 equiv of $BF_3{\cdot}Et_2O$ in $[D_8]$THF at room temperature. Monitoring by ^1H and ^{31}P NMR showed that within 1 h a single new complex (^{31}P NMR: δ −15.7 ppm) was quantitatively formed. ^1H and $^{31}C\{^1H\}$ NMR data, along with the corresponding $^1H,^1H$ COSY, HMQC, and HMBC experiments and the HR-MS spectrum, are fully consistent with the $(\pi\text{-allyl})Ir^{III}$ complex **18** with the same cation as in complex **17** (Scheme 7).[30]

To test whether rearrangement of the metallacyclobutane to the olefinic product of a terminal nucleophilic addition can be induced, solutions of complex **16** in $[D_8]$THF were kept at 70 °C for extended periods of time. Though the reaction conditions resemble the conditions used in the catalytic process (see Table 1), only slow decomposition of **16**, not formation of olefins **2a** or **3a**, was observed.

The results described above demonstrate that formation of the iridacyclobutane is a reversible process. However, we have so far only been able to effect the backward reaction by Lewis acid. The observed oxidative dimerization of dimethyl malonate upon treatment of **16** with iodine suggests that an equilibrium between **16** and, in very low concentration, a π-allyl complex and the anion $[CH(CO_2CH_3)_2]^-$ exists. Experiments to prove this proposal by exchange of the malonate anion by another nucleophile, i.e., $[CH(CO_2Et)_2]^-$ have so far not been successful.

Conclusion

We have demonstrated that bidentate phosphinooxazolines are successful ligands for the Ir^I-catalyzed allylic alkylation of achiral arylallyl acetates, allowing high levels of both regio- and enantioselectivity in the formation of branched products. Efforts directed at the isolation of organometallic intermediates important in the catalytic cycle have led to the synthesis and char-

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(30) Despite the clarity of the structural composition of the cation **18**, the corresponding counterion, probably $[BF_4]^-$, could not yet be unequivocally identified.

acterization of the first (π-allyl)Ir^{III} complexes containing a chiral auxiliary ligand. Other than anticipated on the basis of the products of the allylic substitutions, none of the new (π-allyl)Ir^{III} complexes reacted with malonate at the terminus of the allyl ligand but at the central allylic carbon, giving rise to an iridacyclobutane species. Supplementing earlier work using hard nucleophiles, we have thus demonstrated that also with soft nucleophiles such as $NaCH(CO_2CH_3)_2$ metallacyclobutane species can be obtained. It was demonstrated that reaction of the iridacyclobutane with Lewis acid yields a π-allyl complex.

Experimental Section

General Considerations. All reactions were carried out using dry solvents under an atmosphere of dry argon. TLC: Macherey & Nagel Polygram Sil G/UV precoated sheets, treatment with I_2 or aqueous $KMnO_4$ solution for visualization of spots. Column chromatography: Fluka silica gel, grade 60 (0.04−0.063 mm). ^1H, ^{13}C, and ^{31}P NMR spectra were recorded on Bruker DRX 300 or DRX 500 instruments. ^1H NMR chemical shifts are relative to residual nondeuterated solvent in $CDCl_3$ (δ 7.26), CD_2Cl_2 (δ 5.32), C_6D_6 (δ 7.15), [D_8]THF (δ 1.72, 3.57), or [D_8]toluene (δ 2.30, 7.19). ^{13}C NMR shifts are relative to the solvents $CDCl_3$ (δ 77.0), CD_2Cl_2 (δ 53.8), C_6D_6 (δ 128.0), [D_8]THF (δ 25.20, 67.20), and [D_8]toluene (δ 20.4, 125.3, 128.0, 128.9, 137.5), and ^{31}P NMR shifts are relative to 85% H_3PO_4 (δ 0.00). MS: JEOL, JMS-700. FAB: JEOL, JMS-700; matrix 4-nitrobenzyl alcohol (NBA) or 4-nitrophenyl octyl ether (NPOE). HPLC: Hewlett-Packard HP 1090 with DAICEL Chiralcel ODH column (25 cm × 0.46 cm) in combination with DAICEL Chiralcel ODH precolumn (5 cm × 0.46 cm). Elemental analyses: Microanalytical Laboratory of the Organisch-Chemisches Institut, Universität Heidelberg. The diarylphosphinous chlorides **6b**,**c** were synthesized according to literature procedures.[17] Cinnamyl chloride, cinnamyl alcohol (**8a**), (*S*)-valinol, and $BF_3{\cdot}Et_2O$ were purchased from Aldrich-Fluka Chemicals and used as received. Alcohol **8b** was prepared according to a published procedure.[31] Allyl esters were prepared by reaction of the corresponding alcohols with acetic anhydride[14] (**1a**,**b**),[32] ethyl chloroformate (**10a**),[33] and dimethyl chlorophosphate (**11a**).[34] Compounds **2a**[2a,35] and **2b**[2a,36] were previously described and characterized. Complexes $[IrCl(COD)]_2$,[37] $[IrCl_2\{\eta^3\text{-}CH_2CHCH(C_6H_5)\}(COD)]$ (**12**),[14] and $[IrBr_2(\eta^3\text{-}C_3H_5)(COD)]$ (**13**)[14] were prepared according to published procedures.

***N*-[(1*S*)-1-(Hydroxymethyl)-2-methylpropyl]-2-iodobenzamide (4a).**[38] A suspension of *o*-iodobenzoic acid (9.92 g, 40.00 mmol) in 14.50 mL (200.00 mmol) of thionyl chloride and 0.10 mL (1.29 mmol) of DMF was heated to reflux for 3 h, and the excess thionyl chloride was removed in vacuo. A solution of the residue in CH_2Cl_2 (40 mL) was added dropwise to a cold (0 °C) solution of (*S*)-valinol (4.25 g, 42.00 mmol) and triethylamine (2.15 g, 12.00 mmol) in CH_2Cl_2 (30 mL). The mixture was allowed to reach room temperature and stirred overnight, and then water (10 mL) was added and stirring was continued for 1 h. The mixture was treated with 1 N HCl (40 mL) and extracted three times with CH_2Cl_2. The combined organic layers were washed with 1 N NaOH and water and dried over Na_2SO_4. After filtration and evaporation of the solvent, the product was purified by flash chromatography (silica gel 45 × 10 cm, petroleum ether/ethyl acetate 1:3) to give 11.29 g (84%) of **4a** as white needles. Mp: 112.5−113.5. ^1H NMR (300.13 MHz, 25 °C, $CDCl_3$): δ 0.99, 1.01 (both d, 6 H, ^3J(H,H) = 6.8 Hz, $CH(CH_3)_2$), 1.97 (m, 1 H, $CH(CH_3)_2$), 2.45 (broad s, 1 H, OH), 3.75−3.84 (m, 2 H, CH_2OH), 3.86−3.95 (m, 1 H, CHNH), 6.06 (broad d, 1 H, ^3J(H,H) = 7.9 Hz, NH), 7.06 (m, 1 H, Ar H), 7.35 (m, 2 H, Ar H), 7.81 (d, 1 H, ^3J(H,H) = 8.01 Hz, Ar H). $^{13}C\{^1H\}$ NMR (75.47 MHz, 25 °C, $CDCl_3$): δ 19.0, 19.6 (both s, $CH(CH_3)_2$), 29.0 (s, $CH(CH_3)_2$), 57.6 (s, CHNH), 63.4 (s, CH_2OH), 92.3 (s, CI), 128.2, 131.0, 139.8, 142.4 (all s, Ar CH), 170.1 (s, CO). Anal. Calcd for $C_{12}H_{16}INO_2$ (333.16): C, 43.26; H, 4.84; I, 38.09; N, 4.20. Found: C, 43.37; H, 4.86; I, 38.04; N, 4.22.

(4*S*)-2-(2-Iodophenyl)-4-isopropyl-4,5-dihydro-1,3-oxazole (5a). 4-Methylbenzenesulfonyl chloride (2.52 g, 13.20 mmol) was added to a cold (0 °C) solution of **4a** (4.00 g, 12.00 mmol), triethylamine (6.07 g, 60.00 mmol), and DMAP (0.22 g, 1.80 mmol) in CH_2Cl_2 (30 mL). The resultant mixture was warmed to room temperature and stirred overnight. The excess 4-methylbenzenesulfonyl chloride was hydrolyzed by adding water (18 mL) and heating to reflux for 30 min. Another portion of water (72 mL) was added, and the mixture was extracted three times with CH_2Cl_2. The combined organic phases were washed with saturated NaCl solution and dried over Na_2SO_4. After filtration and removal of the solvent under vacuum, the product was purified by flash chromatography (silica gel, 45 × 5 cm, petroleum ether/ethyl acetate 5:1) to give 3.38 g (89%) of **5a** as a colorless oil. ^1H NMR (300.13 MHz, $CDCl_3$): δ 0.97, 1.06 (both d, 6 H, ^3J(H,H) = 6.9 Hz, $CH(CH_3)_2$), 1.80−1.91 (m, 1 H, $CH(CH_3)_2$), 4.08−4.18 (m, 2 H, CH_2O), 4.38−4.46 (m, 1 H, CHN), 7.04−7.10 (m, 1 H, Ar H), 7.31−7.37 (m, 1 H, Ar H), 7.58−7.61 (m, 1 H, Ar H), 7.89−7.92 (m, 1 H, Ar H). $^{13}C\{^1H\}$ NMR (75.48 MHz, $CDCl_3$): δ 18.3, 18.7 (both s, $CH(CH_3)_2$), 32.6 (s, $CH(CH_3)_2$), 70.3 (s, CH_2O), 72.9 (s, CHN), 94.5 (s, C−I), 127.6, 130.4, 131.25, 133.74 (Ar CH), 140.18 (s, CC=N), 163.54 (s, C=N). Anal. Calcd for $C_{12}H_{14}INO$ (315.15): C, 45.73; H, 4.48; I, 40.47; N, 4.44. Found: C, 46.02; H, 4.54; I, 40.36; N, 4.54.

(4*S*)-2-[2-(Diphenylphosphino)phenyl]-4-isopropyl-4,5-dihydro-1,3-oxazole (7a).[16] In a *two-flask system for isothermal addition of sensitive compounds*[11] were placed a solution of the iodooxazoline **5a** (0.9 mg, 2.93 mmol) in THF (3 mL) (flask B) and a solution of diphenylphosphinous chloride (1.23 g, 5.59 mmol) in THF (6 mL) (flask A), and the system was cooled to −100 °C. *n*-BuLi (1.6 M in *n*-hexane, 3.70 mL, 5.92 mmol) was slowly added via syringe into flask B, carefully dropping the solution onto the wall of the vessel in order to ensure cooling of *n*-BuLi before it came into contact with the solution of **5a**. Then the temperature was raised to −85 °C over a period of 15 min. After the system had been cooled to −95 °C, the solution of flask A was dropwise added to flask B, and the reaction mixture was stirred for 4 h at −78 °C and then treated with deoxygenated 2 N NaOH (2 mL). The mixture was warmed to room temperature, the solvent was removed under vacuum, and the residue was purified by flash chromatography (silica gel, 48 × 3.5 cm, petroleum ether/ethyl acetate 98:2) to give 884.0 mg (80%) of **7a**.

2-Bromo-*N*-[(1*S*)-1-(hydroxymethyl)-2-methylpropyl]-benzamide (4b). A mixture of *o*-bromobenzoic acid (10.05 g, 50.00 mmol) and thionyl chloride (16.31 g, 10 mL, 137.00

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mmol) was heated to reflux for 2 h, and then the excess thionyl chloride was distilled off under vacuum. The remaining residue was then added to a cold (0 °C) stirred emulsion of 0.5 N KOH (300 mL) and a solution of valinol (5.03 g, 48.72 mmol) in diethyl ether (300 mL). A colorless compound precipitated and was dissolved by addition of ethyl acetate. After 12 h the resulting mixture was washed with NaCl solution and water and the organic phase dried over Mg_2SO_4. After evaporation of the solvent, the product was recrystallized from ethyl acetate/*n*-hexane to give 11.88 g (85%) of **4b** as colorless needles. Mp: 113−115 °C. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ 1.01 (d, 3 H, ^3J(H,H) = 7.0 Hz, CH(CH_3)$_2$), 1.02 (d, 3 H, ^3J(H,H) = 6.7 Hz, CH(CH_3)$_2$), 1.98 (m, 1 H, CH(CH$_3$)$_2$), 2.56 (t, 1 H, ^3J(H,H) = 5.5 Hz, OH), 3.71−3.83 (m, 2 H, CH_2OH), 3.89−3.97 (m, 1 H, CHNH), 6.24 (broad d, 1 H, ^3J(H,H) = 7.8 Hz, NH), 7.25 (dt, 1 H, ^4J(H,H) = 1.9, ^3J(H,H) = 7.7 Hz, Ar CH), 7.33 (dt, 1 H, ^4J(H,H) = 1.1, ^3J(H,H) = 7.5 Hz, Ar CH), 7.50 (dd, 1 H, ^4J(H,H) = 1.8, ^3J(H,H) = 7.7 Hz, Ar CH), 7.57 (dd, 1 H, ^4J(H,H) = 1.1, ^3J(H,H) = 8.1 Hz, Ar CH). ^{13}C{^{1}H} NMR (75.47 MHz, $CDCl_3$): δ 18.9, 19.6 (both s, CH(*C*H$_3$)$_2$), 29.1 (s, *C*H(CH$_3$)$_2$), 57.7 (s, *C*HNH), 63.6 (s, *C*H$_2$OH), 119.2 (s, *C*Br), 127.6 (s, Ar *C*H), 129.6 (s, Ar *C*H), 131.2 (s, Ar *C*H), 133.3 (s, Ar *C*H), 137.9 (s, *C*(CO)), 168.3 (s, *C*O). MS (EI): *m/z* = 254(24) [M − (HOCH$_2$)]$^+$. Anal. Calcd for: $C_{12}H_{16}BrNO_2$ (285.036): C, 50.52; H, 5.66; Br, 27.69; N, 4.91. Found: C, 50.46; H, 5.66; Br, 27.88; N, 4.90.

(4*S*)-2-(2-Bromophenyl)-4-isopropyl-4,5-dihydro-1,3-oxazole (5b).[16,39] A solution of **4b** (11.77 g, 41.13 mmol), triethylamine (31.50 mL, 226.00 mmol), and 4-methylbenzenesulfonyl acid chloride (8.58 g, 45.00 mmol) in CH_2Cl_2 (60 mL) was heated at reflux for 5 h in a reverse Dean−Stark apparatus. The mixture was then concentrated in vacuo and the residue subjected to flash chromatography (silica gel, 4 × 40 cm, petroleum ether/ethyl acetate 4:1) to give 9.00 g (82%) of **5b** as a colorless oil. ^{1}H NMR (300.13 MHz, 25 °C, $CDCl_3$): δ 0.97, 1.04 (2 d, 6 H, ^3J(H,H) = 6.8 Hz, CH(CH_3)$_2$), 1.89 (oct, 1 H, ^3J(H,H) = 6.7 Hz, CH(CH$_3$)$_2$), 4.10−4.19, 4.37−4.46 (2 m, 3 H, CH$_2$O, CHN), 7.25 (ddd, 1 H, ^4J(H,H) = 1.9, ^3J(H,H) = 7.5 and 9.2 Hz, Ar H), 7.32 (td, 1 H, ^4J(H,H) = 1.4, ^3J(H,H) = 7.4 Hz, Ar H), 7.61 (dd, 1 H, ^4J(H,H) = 1.3, ^3J(H,H) = 7.8 Hz, Ar H), 7.65 (dd, 1 H, ^4J(H,H) = 1.9, ^3J(H,H) = 7.6 Hz, Ar H).

(4*S*)-2-(2-{Bis[4-(trifluoromethyl)phenyl]phosphino}-phenyl)-4-isopropyl-4,5-dihydro-1,3-oxazole (7b). A suspension of Mg (243.4 mg, 10.01 mmol) in diethyl ether (5 mL) was treated with a few drops of bromoethane for activation of Mg. Then, a solution of **5b** (2.68 g, 10.01 mmol) in diethyl ether (20 mL) was added dropwise and the mixture was stirred for 30 min at room temperature. The resultant Grignard reagent was treated dropwise with a solution of bis[4-(trifluoromethyl)-phenyl]phosphinous chloride (**6b**; 3.25 g, 9.10 mmol) in diethyl ether (10 mL), and the mixture was stirred for 3 h. Then water (20 mL) was added, and the organic layer was separated and washed with saturated NH_4Cl and water and dried over Na_2SO_4. The mixture was filtered and the filtrate concentrated in vacuo. The residue was recrystallized from *n*-hexane to give 3.01 g (68%) of **7b** as colorless needles. Mp: 68−72 °C. ^{1}H NMR (300.13 MHz, $CDCl_3$; for numbering of atoms see Scheme 2): δ 0.68 (d, 3 H, ^3J(H,H) = 6.7 Hz, CH(CH_3)$_2$), 0.74 (d, 3 H, ^3J(H,H) = 6.7 Hz, CH(CH_3)$_2$), 1.48 (broad signal, 1 H, CH(CH$_3$)$_2$), 3.88−3.97 (m, 2 H, 5-H), 4.21−4.30 (m, 1 H, 4-H), 6.84 (dd, 1 H, ^3J(H,P) = 4.0, ^3J(H,H) = 7.7 Hz, 8-H), 7.26−7.71 (m, 10 H, Ar H), 7.97 (ddd, 1 H, ^4J(H,H) = 1.3, ^4J(H,P) = 3.9, ^3J(H,H) = 7.7 Hz, 11-H). ^{13}C{^{1}H} NMR (75.47 MHz, $CDCl_3$; for numbering of atoms see Scheme 2): δ 18.4, 18.6 (both s, CH(*C*H$_3$)$_2$), 32.9 (s, *C*H(CH$_3$)$_2$), 70.2 (s, C-5), 73.4 (s, C-4), 122.3 (s, Ar *C*), 125.0−125.3 (m, 2 *C*F$_3$), 125.9 (s, Ar *C*), 128.9 (s, Ar *C*H), 129.9 (d, ^2J(C,P) = 3.4 Hz, C-8), 130.8 (s, Ar *C*H), 132.0 (d, ^2J(C,P) = 20.4 Hz, C-6), 133.7 (s, Ar *C*H), 134.0 (d, ^2J(C,P) = 6.5 Hz, Ar *C*H), 134.3, (s, Ar *C*H), 136.8 (d, ^1J(C,P) = 24.8 Hz, C-7), 143.2 {2 d, ^1J(C,P) = 24.8 Hz, 2 *ipso*-[*p*-(CF$_3$)*C*$_6$H$_4$P]}, 162.1 (d, ^3J(C,P) = 2.9 Hz, C-2). ^{31}P{^{1}H} NMR (81.02 MHz, 25 °C, $CDCl_3$): δ −7.36 (s). Anal. Calcd for $C_{26}H_{22}F_6NOP$ (509.43): C, 61.30; H, 4.35; N, 2.75. Found: C, 61.14; H, 4.40; N, 2.75.

(4*S*)-2-(2-{Bis[3,5-bis(trifluoromethyl)phenyl]phosphino}phenyl)-4-isopropyl-4,5-dihydro-1,3-oxazole (7c). A few drops of bromoethane were added to a suspension of Mg (423.0 mg, 17.41 mmol) in diethyl ether (5 mL) for activation of Mg. Then a solution of **5b** (4.67 g, 17.41 mmol) in diethyl ether (20 mL) was added dropwise, and the mixture was stirred for 30 min at room temperature to form the Grignard compound. Then a solution of bis[3,5-bis(trifluoromethyl)phenyl]phosphinous chloride (**6c**; 7.14 g, 14.51 mmol) in diethyl ether (10 mL) was added dropwise and the reaction mixture stirred for 3 h. Then water (20 mL) was added and the organic layer was separated and washed with saturated NH_4Cl solution and water and dried over Na_2SO_4. After evaporation of the solvent and recrystallization of the residue from acetonitrile, 3.63 g (39%) of **7c** was obtained as colorless needles. Mp: 110−112 °C. ^{1}H NMR (300.13 MHz, 25 °C, CD_2Cl_2; for numbering of atoms see Scheme 2): δ 0.70 (d, 3 H, ^3J(H,H) = 6.8 Hz, CH(CH_3)$_2$), 0.71 (d, 3 H, ^3J(H,H) = 6.6 Hz, CH(CH_3)$_2$), 1.40−1.55 (m, 1 H, CH(CH$_3$)$_2$), 3.81−3.93 (m, 1 H, 4-H), 3.99 (dd, 1 H, ^2J(H,H) = 8.3, ^3J(H,H) = 8.5 Hz, 5-H), 4.34 (dd, 1 H, ^3J(H,H) = 8.1, ^2J(H,H) = 8.3 Hz, 5-H), 6.82 (ddd, 1 H, ^4J(H,H) = 0.9, ^3J(H,P) = 3.8, ^3J(H,H) = 7.6 Hz, 8-H), 7.41 (td, 1 H, ^4J(H,H) = 1.3, ^3J(H,H) = 7.5 Hz, 9-H), 7.52 (td, 1 H, ^4J(H,H) = 0.9, ^3J(H,H) = 7.5 Hz, 10-H), 7.69 (d, 2 H, ^3J(H,P) = 6.2 Hz, *o*-[3,5-(CF$_3$)$_2$C$_6$H$_3$]), 7.72 (d, 2 H, ^3J(H,P) = 6.2 Hz, *o*-[3,5-(CF$_3$)$_2$C$_6$H$_3$]), 7.88, 7.90 (both s, *p*-[3,5-(CF$_3$)$_2$C$_6$H$_3$]), 8.01 (ddd, 1 H, ^4J(H,H) = 1.2, ^4J(H,P) = 4.1, ^3J(H,H) = 7.6 Hz, 11-H). ^{31}P{^{1}H} NMR (81.02 MHz, 25 °C, CD_2Cl_2): δ −6.83 (s). ^{13}C{^{1}H} NMR (75.47 MHz, 25 °C, CD_2Cl_2; for numbering of atoms see Scheme 2): δ 18.4, 18.7 (both s, CH(*C*H$_3$)$_2$), 33.2 (s, *C*H(CH$_3$)$_2$), 71.0 (s, C-5), 74.0 (s, C-4), 118.2, 121.8 (both s, *C*CF$_3$), 123.0, 123.2 (both set, ^3J(C,F) = 6.0 Hz, *o*- and *p*-[3,5-(CF$_3$)$_2$*C*$_6$H$_3$]), 123.1−123.4 (m, *p*-[3,5-(CF$_3$)$_2$*C*$_6$H$_3$]), 125.4, 129.0 (both s, *C*CF$_3$), 130.0 (s, C-10), 130.1 (d, ^3J(C,P) = 2.8 Hz, C-11), 131.5 (s, C-9), 131.9 (dq, ^5J(C,P) = 6.9 Hz, ^1J(C,F) = 33.2 Hz, *C*F$_3$), 131.95 (dq, ^5J(C,P) = 6.9, ^1J(C,F) = 33.5 Hz, *C*F$_3$), 132.2 (d, ^1J(C,P) = 20.8 Hz, C-7), 133.9 (broad d, ^2J(C,P) = 32.0 Hz, *o*-[3,5-(CF$_3$)$_2$*C*$_6$H$_3$]), 134.2 (broad d, ^2J(C,P) = 32.0 Hz, *o*-[3,5-(CF$_3$)$_2$*C*$_6$H$_3$]), 134.4 (s, C-8), 135.6 (d, ^2J(C,P) = 24.9 Hz, C-6), 142.3 (d, ^1J(C,P) = 18.0 Hz, *ipso*-[3,5-(CF$_3$)$_2$C$_6$H$_3$]), 142.4 (d, ^1J(C,P) = 18.7 Hz, *ipso*-[3,5-(CF$_3$)$_2$C$_6$H$_3$]), 161.8 (d, ^3J(C,P) = 3.5 Hz, C-2). Anal. Calcd for $C_{28}H_{20}F_{12}NOP$ (645.43): C, 52.11; H, 3.12; N, 2.17. Found: C, 51.96; H, 3.13; N, 2.06.

General Procedure for the Ir-Catalyzed Allylic Alkylation. A solution of the allylic acetate (2.00 mmol), [IrCl(COD)]$_2$ (26.9 mg, 0.04 mmol), and the ligand (0.08 mmol) in THF (1 mL) was added dropwise to a 1 M solution (6 mL, 6.00 mmol) of NaCH(CO$_2$CH$_3$)$_2$ in THF. The mixture was stirred under the stated reaction conditions; then diethyl ether (2 mL) and water (4 mL) were added, and the mixture was extracted with diethyl ether (3 × 5 mL). The combined organic layers were washed with saturated NH_4Cl solution (10 mL), dried (Na_2SO_4), and concentrated in vacuo. The resultant crude product was purified by flash column chromatography (silica, 2 × 20 cm, petroleum ether/ethyl acetate 9:1) to give a mixture of substitution products **2** and **3** as a colorless oil (for analytical data see General Considerations).

Complex 14. A mixture of [IrCl$_2${η^3-CH$_2$CHCH(C$_6$H$_5$)}(COD)] (**12**; 204.0 mg, 0.42 mmol), **7a** (156.0 mg, 0.42 mmol), and tetrahydrofuran (2 mL) was stirred for 1 h at room temperature to give a clear orange-brown solution. Slow evaporation of the solvent under vacuum yielded 182.0 mg (58%) of **14** as prismatic yellow crystals, which were washed with diethyl ether and dried under vacuum. ^{1}H NMR (250.13

(39) Compound **5b** was synthesized by following a procedure slightly modified from that published.

MHz, 25 °C, CD_2Cl_2; for numbering of atoms see Scheme 4 and Table 3): δ −0.01 (d, 3 H, ^3J(H,H) = 6.8 Hz, CH(CH_3)$_2$), 0.84 (d, 3 H, ^3J(H,H) = 7.0 Hz, CH(CH_3)$_2$), 2.16−2.40 (m, 1 H, CH(CH$_3$)$_2$), 2.90 (d, 1 H, ^3J(H,H) = 9.7 Hz, 1A-Hα), 3.27 (d, 1 H, ^3J(H,H) = 6.15 Hz, 1A-H*s*), 4.42 (dd, 1 H, ^3J(H,H) = 6.6, ^2J(H,H) = 9.2 Hz, 5-H), 3.79 (dd, 1 H, ^2J(H,H) = 9.2, ^3J(H,H) = 10.0 Hz, 5-H), 5.10−5.35 (m, 1 H, 2A-H), 5.74 (d, 1 H, ^3J(H,H) = 10.9 Hz, 3A-H), 5.83−5.97 (m, 1 H, 4-H), 6.26 (dd, 1 H, J(H,P) = 8.85, J(H,H) = 10.9 Hz, Ar H), 6.75−6.90 (m, 2 H, Ar H), 6.91−7.06 (m, 4 H, Ar H), 7.07−7.28 (m, 6 H, Ar H), 7.26−7.38 (m, 1 H, Ar H), 7.40−7.63 (m, 4 H, Ar H), 8.13−8.22 (m, 1 H, 11-H). ^{31}P {^{1}H} NMR (202.46 MHz, 25 °C, CD_2Cl_2): δ −16.0 (s). ^{13}C{^{1}H} NMR (125.77 MHz, 25 °C, CD_2Cl_2): δ 13.4, 19.5 (both s, CH(CH_3)$_2$), 28.9 (s, CH(CH$_3$)$_2$), 34.4 (s, C-1A), 66.6 (s, C-3A), 68.4 (s, C-5), 72.0 (s, C-4), 83.6 (s, C-2A), 126.4 (d, ^1J(C,P) = 59.7 Hz, *ipso*-C$_6$H$_5$P), 126.9, 128.6, 128.8, (all s, allyl-bound Ar *C*H), 129.0, 129.0, 129.1 (all s, Ar *C*H PHOX), 129.6 (d, ^1J(C,P) = 55.1 Hz *ipso*-C$_6$H$_5$P), 129.9 (d, J(C,P) = 9.8 Hz, Ar *C*H PHOX), 130.7 (d, ^2J(C,P) = 28.4 Hz, C-6), 130.9 (d, ^1J(C,P) = 42.0 Hz, C-7), 131.7 (d, J(C,P) = 7.8 Hz, Ar *C*H PHOX), 131.9 (d, J(C,P) = 1.95 Hz, Ar *C*H PHOX), 132.0 (d, J(C,P) = 1.95 Hz, Ar *C*H PHOX), 133.0 (d, J(C,P) = 8.8 Hz, Ar *C*H PHOX), 133.2 (d, J(C,P) = 7.8 Hz, Ar *C*H PHOX), 133.2 (d, J(C,P) = 3.9 Hz, Ar *C*H PHOX), 140.0 (s, allylic *ipso*-C$_6$H$_5$), 164.4 (d, ^3J(C,P) = 4.9 Hz, C-2). MS (FAB): *m*/*z* 753 (10) [M]$^+$, 718 (30) [M − Cl]$^+$, 600.1 (40) {M − Cl − [CH$_2$CHCH(C$_6$H$_5$)]}$^+$. Anal. Calcd for $C_{33}H_{33}Cl_2NOPIr$: C, 52.58; H, 4.42; N, 1.86. Found: C, 52.73; H,4.70; N, 1.82.

3:4:2 Mixture of Isomers 14A−C. ^{1}H NMR (500.13 MHz, −40 °C, [D$_8$]toluene): isomer **14A**, δ −0.19 (d, 3 H, ^3J(H,H) = 6.6 Hz, CH(CH_3)$_2$), 0.58 (d, 3 H, ^3J(H,H) = 6.6 Hz, CH(CH_3)$_2$), 2.40−2.50 (m, 1 H, CH(CH$_3$)$_2$), 3.15 (d, ^3J(H,H) = 5.5 Hz, 1A-H*s*), 3.29 (d, 1 H, ^3J(H,H) = 8.8 Hz, 1A-Hα), 3.46 (dd, 1 H, ^2J(H,H) = 8.5, ^3J(H,H) = 10.2 Hz, 5-H), 3.70 (dd, 1 H, ^3J(H,H) = 6.6, ^2J(H,H) = 8.5 Hz, 5-H), 4.95−5.08 (m, 1 H, 2A-H), 6.10−6.24 (m, 1 H, 4-H), 6.28 (dd, 1 H, ^3J(H,H) = 7.7, ^3J(H,P) = 11.3 Hz, 8-H), 6.25−6.38 (m, 1 H, Ar H PHOX), 6.50 (d, 1 H, ^3J(H,H) = 11.0 Hz, 3A-H), 8.00 (dd, 1 H, ^4J(H,P) = 4.0, ^3J(H,H) = 7.7 Hz, 11-H); isomer **14B**, 0.12 (d, 3 H, ^3J(H,H) = 6.9 Hz, CH(CH_3)$_2$), 0.75 (d, 3 H, ^3J(H,H) = 6.6 Hz, CH(CH_3)$_2$), 2.68−2.79 (m, 1 H, CH(CH$_3$)$_2$), 3.26−3.34 (m, 1 H, 5-H), 3.55−3.65 (m, 1 H, 5-H), 3.76 (d, 1 H, ^3J(H,H) = 7.0 Hz, 1A-H*s*), 3.84 (d, 1 H, ^3J(H,H) = 11.4 Hz, 1A-Hα), 4.02−4.10 (m, 1 H, 4-H), 5.69 (dd, 1 H, ^3J(H,P) = 8.8, ^3J(H,H) = 13.1 Hz, 3A-H), 6.12−6.23 (m, 1 H, 2A-H), 7.90−7.97 (m, 1 H, 11-H); isomer **14C**, δ 0.17 (d, 3 H, ^3J(H,H) = 6.9 Hz, CH(CH_3)$_2$), 0.34 (d, 3 H, ^3J(H,H) = 5.9 Hz, CH(CH_3)$_2$), 2.31−2.40 (m, 1 H, CH(CH$_3$)$_2$), 3.55−3.67 (overlapped signals, 2 H, 1A-H*s* and 5-H), 4.16 (d, 1 H, ^3J(H,H) = 10.6 Hz, 1A-Hα), 4.21 (dd, 1 H, ^2J(H,H) = 9.2, ^3J(H,H) = 9.5 Hz, 5-H), 4.40−4.48 (m, 1H, 4-H), 5.09 (dd, 1 H, ^3J(H,P) = 9.5, ^3J(H,H) = 12.7 Hz, 3A-H), 6.12−6.23 (m, 1 H, 2A-H), 8.03−8.08 (m, 1 H, 11-H); aromatic protons for all isomers, 6.62−6.73, 6.74−7.18, 7.42−7.50, 7.67−7.75 (all m, 18 H). ^{31}P{^{1}H} NMR (202.46 MHz, −40 °C, [D$_8$]toluene): isomer **14A**, δ −15.9 (s); isomer **14B**, δ −3.04 (s). isomer **14C**, δ −4.01 (s). ^{13}C{^{1}H} NMR (125.77 MHz, −40 °C, [D$_8$]toluene): isomer **14A**, δ 12.3, 18.5 (both s, CH(CH_3)$_2$), 27.9 (s, CH(CH$_3$)$_2$), 33.8 (s, C-1A), 65.2 (s, C-3A), 67.2 (s, C-5), 70.9 (s, C-4), 82.5 (s, C-2A), 139.1 (s, allylic *ipso*-C$_6$H$_5$), 161.6 (d, ^3J(C,P) = 4.7 Hz, C-2); isomer **14B**, δ 14.0, 17.5 (both s, CH(CH_3)$_2$), 27.5 (s, CH(CH$_3$)$_2$), 30.2 (s, C-1A), 67.7 (s, C-5), 73.8 (s, C-4), 83.5 (d, ^2J(C,P) = 36.7 Hz, C-3A), 113.3 (broad s, C-2A), 142.7 (d, ^3J(C,P) = 4.7 Hz, allyl-bound *ipso*-C$_6$H$_5$), 162.2 (d, ^3J(C,P) = 2.8 Hz, C-2); isomer **14C**, δ 13.7, 18.0 (both s, CH(CH_3)$_2$), 27.0 (s, CH(CH$_3$)$_2$), 30.5 (s, C-1A), 67.4 (s, C-5), 74.9 (s, C-4), 83.6 (d, ^2J(C,P) = 38.6 Hz C-3A), 112.0 (broad s, C-2A), 142.5 (d, ^3J(C,P) = 5.4 Hz, allyl-bound *ipso*-C$_6$H$_5$), 163.0 (d, ^3J(C,P) = 3.7 Hz, C-2); aromatic carbons for all isomers, 124.6, 127.5, 128.2, 128.3, 128.4, 129.1, 130.4, 130.7, 130.9, 131.2, 132.3, 134.7 (d, J(C,P) = 9.4 Hz), 134.8, 134.9(d, J(C,P) = 9.5 Hz); other signals overlapped with those of the solvent.

Complex 15. A mixture of [IrBr$_2$(η^3-C$_3$H$_5$)(COD)] (**13**; 204.0 mg, 0.42 mmol), **7a** (156.0 mg, 0.42 mmol), and THF (2 mL) was stirred for 1 h at room temperature, at which point a clear orange-brown solution was obtained. After removal of the solvent under vacuum, crystallization of the residue from CH_2Cl_2/diethyl ether yielded yellow crystals of the title complex, which were washed twice with diethyl ether and dried. Yield: 182.0 mg (58%). ^{1}H NMR (500 MHz, 25 °C, C_6D_6; numbering of atoms see Scheme 4 and Table 3): δ 0.22 (d, 3 H, ^3J(H,H) = 7.4 Hz, CH(CH_3)$_2$), 0.54 (d, 3 H, ^3J(H,H) = 7.35 Hz, CH(CH_3)$_2$), 2.45 (dqq, 1 H, ^3J(H,H) = 3.35, ^3J(H,H) = 7.0, ^3J(H,H) = 7.0 Hz, CH(CH$_3$)$_2$), 3.24 (d, 1 H, ^3J(H,H) = 6.7 Hz, 1A-H*s*), 3.54 (d, 1 H, ^3J(H,H) = 7.4 Hz, 1A-H*s*), 3.58 (dd, 1 H, ^2J(H,H) = 8.7, ^3J(H,H) = 10.7 Hz, anti 5-H), 3.67 (d, 1 H, ^3J(H,H) = 10.0 Hz, 1A-Hα), 3.74 (dd, 1 H, ^3J(H,H) = 6.7, ^2J(H,H) = 8.7 Hz, syn 5-H), 3.93 (m, 1 H, 2A-H), 4.20 (d, 1 H, ^3J(H,H) = 10.7 Hz, allylic 1A-Hα), 6.23 (ddd, 1 H, ^3J(H,H) = 3.35, ^3J(H,H) = 6.7, ^3J(H,H) = 10.7 Hz, 3-H), 6.48 (dd, 1 H, ^3J(H,H) = 8.7, ^3J(H,P) = 11.7 Hz, 8-H), 6.70 (dd, 2 H, ^3J(H,H) = 7.7, ^3J(H,P) = 9.7 Hz, *o*-C$_6$H$_5$), 6.75 (tt, 1 H, ^4J(H,P) = 1.0, ^3J(H,H) = 7.7 Hz, 9-H), 6.80 (ddd, 2 H, ^4J(H,P) = 2.35, ^3J(H,H) = 7.7, ^3J(H,H) = 8.0 Hz, *m*-C$_6$H$_5$), 6.89 (tt, 1 H, ^5J(H,P) = 1.35, ^3J(H,H) = 6.7 Hz, *p*-C$_6$H$_5$), 6.92−7.08 (m, 6 H, 4-H, *o*-, *m*-, and *p*-C$_6$H$_5$), 8.00 (dd, 1 H, ^4J(H,P) = 4.0, ^3J(H,H) = 8.0 Hz, 11-H). ^{31}P{^{1}H} NMR (202.45 MHz, 25 °C, C_6D_6): δ 5.37 (s). ^{13}C{^{1}H} NMR (125.77 MHz, 25 °C, C_6D_6): δ 12.6 (s, CH(CH_3)$_2$), 18.7 (s, CH(CH_3)$_2$), 28.2 (s, CH(CH$_3$)$_2$), 40.0, 41.7 (both s, C-1A), 67.7 (s, C-5), 73.3 (s, C-4), 84.6 (s, C-2A), 128.0 (d, ^1J(C,P) = 24.4 Hz, *ipso*-C$_6$H$_5$P), 128.2 (d, ^1J(C,P) = 32.9 Hz, *ipso*-C$_6$H$_5$P), 129.1, 129.2 (both s, Ar *C*H), 130.4 (d, J(C,P) = 9.4 Hz, Ar *C*), 130.5 (d, ^1J(C,P) = 27.3 Hz, C-7), 131.1 (d, J(C,P) = 2.9 Hz, Ar *C*H), 131.2 (d, J(C,P) = 8.4 Hz, Ar *C*H), 131.3 (d, J(C,P) = 1.9 Hz, Ar *C*H), 131.7 (d, J(C,P) = 2.8 Hz, Ar *C*H), 132.2 (d, J(C,P) = 9.4 Hz, Ar *C*H), 132.3 (d, J(C,P) = 2.8 Hz, Ar *C*H), 132.5 (d, J(C,P) = 8.5 Hz, Ar *C*H), 163.7 (d, ^3J(C,P) = 5.7 Hz, C-2). Anal. Calcd for $C_{27}H_{29}Br_2NOPIr$: C, 42.35; H, 3.82; N, 1.83. Found: C, 42.72; H, 3.89; N, 1.87. HR-MS (FAB): calcd for [M]$^+$ ($C_{27}H_{29}ON[^{79}Br][^{81}Br]P[^{191}Ir]$) 764.9939, found 764.9946; calcd for [M]$^+$ ($C_{27}H_{29}[^{81}Br]_2NOP[^{191}Ir]$) 766.9919, found 766.9918; calcd for [M − Br]$^+$ ($C_{27}H_{29}[^{81}Br]NOP[^{191}Ir]$) 686.0756, found 686.0761.

Complex 16. A 0.5 M solution of NaCH(CO$_2$CH$_3$)$_2$ (0.08 mmol) in THF (0.16 mL) was added to a solution of the complex *exo*-**14** (30.2 mg, 40.00 mmol) in THF (1 mL) at −30 °C. The reaction mixture was stirred and allowed to reach room temperature within 4 h and then left to stand overnight at −5 °C. The mixture was filtered and the filtrate concentrated in vacuo. The residue crystallized upon treatment with diethyl ether/pentane as a yellow powder (9:1 mixture of two isomers). Yield: 23.5 mg (62%). For the numbering of the atoms of the PHOX ligand, see Scheme 6. Major isomer: ^{1}H NMR (500.13 MHz, 25 °C, C_6D_6) δ 0.11 (d, 3 H, ^3J(H,H) = 6.7 Hz, CH(CH_3)$_2$), 0.35 (d, 3 H, ^3J(H,H) = 7.0 Hz, CH(CH_3)$_2$), 1.73 (dd, 1 H, ^2J(H,H) = 7.0, ^3J(H,H) = 8.4 Hz, IrCH_2), 1.92 (ddd, 1 H, ^3J(H,P) = 4.0, ^2J(H,H) = 7.0, ^3J(H,H) = 7.0 Hz, IrCH_2), 2.25−2.32 (m, 1 H, CH(CH$_3$)$_2$), 2.85 (s, 3 H, CH[CH(CO$_2$CH_3)$_2$]), 2.88 (s, 3 H, Ir[CH(CO$_2$CH_3)$_2$]), 3.31 (s, 3 H, CH[CH(CO$_2$CH_3)$_2$]), 3,45 (dd, 1 H, ^2J(H,H) = 9.2, ^3J(H,H) = 9.7 Hz, 5-H), 3.63 (dd, 1 H, ^3J(H,H) = 5.3, ^2J(H,H) = 9.2 Hz, 5-H), 3.65 (s, 3 H, Ir[CH(CO$_2$CH_3)$_2$]), 3.76 (d, 1 H, ^3J(H,H) = 8.7 Hz, CH[CH(CO$_2$CH$_3$)$_2$]), 3.92−4.01 (m, 2 H, CH[CH(CO$_2$CH$_3$)$_2$] and IrCH(C$_6$H$_5$)), 4.29 (ddd, 1 H, ^3J(H,H) = 3.35, ^3J(H,H) = 5.35, ^3J(H,H) = 9.7 Hz, 4-H), 5.06 (s, 1 H, Ir[CH(CO$_2$CH$_3$)$_2$]), 6.51 (dd, 1 H, ^3J(H,H) = 8.0, ^3J(H,P) = 10.0 Hz, 8-H), 6.58 (dd, 1 H, ^3J(H,H) = 7.7, ^3J(H,H) = 8.0 Hz, 9-H), 6.63 (ddd, 2 H, ^4J(H,P) = 2.3, ^3J(H,H) = 7.65, ^3J(H,H) = 7.65 Hz, *m*-C$_6$H$_5$ PHOX), 6.65−6.73 (m, 2 H, *o*- or *m*-C$_6$H$_5$ of IrCH(C$_6$H$_5$)), 6.76 (t, 1 H, ^3J(H,H) = 7.0 Hz, *p*-C$_6$H$_5$ of IrCH(C$_6$H$_5$)), 6.78 (ddd, 1 H, ^5J(H,P) = 1.0, ^3J(H,H) = 8.0, ^3J(H,H) = 8.0 Hz, 10-H), 6.85−7.05 (m, 2 H, *o*- or *m*-C$_6$H$_5$ of IrCH(C$_6$H$_5$)), 6.86 (td, 1 H, ^5J(H,P) = 1.3, ^3J(H,H) = 7.4 Hz, *p*-C$_6$H$_5$ PHOX), 7.05−7.12 (m, 3 H, signals over-

lapped with those of the solvent, *p*- and *o*-C_6H_5 PHOX), 7.26 (td, 2 H, ^4J(H,P) = 2.0, ^3J(H,H) = 7.7 Hz, *m*-C_6H_5 PHOX), 7.52 (dd, 2 H, ^3J(H,H) = 7.7, ^3J(H,P) = 8.8 Hz, *o*-C_6H_5 PHOX), 7.94 (ddd, 1 H, ^4J(H,H) = 1.0, ^4J(H,P) = 3.7, ^3J(H,H) = 8.0 Hz, 11-H); $^{31}P\{^1H\}$ NMR (202.46 MHz, 25 °C, C_6D_6) δ −4.6 (s); $^{13}C\{^1H\}$ NMR (125.76 MHz, 25 °C, C_6D_6) δ −16.8 (d, ^2J(C,P) = 5.2 Hz, Ir*C*H$_2$), 3.9 (d, ^2J(C,P) = 3.4 Hz, Ir*C*H(C_6H_5)), 13.1 (s, CH(*C*H$_3$)$_2$), 18.8 (s, CH(*C*H$_3$)$_2$), 28.5 (s, *C*H(CH$_3$)$_2$), 50.2, 51.15 (both s, Ir[CH(CO$_2$*C*H$_3$)$_2$]), 51.25, 51.3 (s, CH[CH(CO$_2$*C*H$_3$)$_2$]), 52.2 (s, *C*H[CH(CO$_2$CH$_3$)$_2$]), 64.6 (s, CH[*C*H(CO$_2$CH$_3$)$_2$]), 66.5 (s, Ir[*C*H(CO$_2$CH$_3$)$_2$]), 66.7 (s, C-5), 71.3 (s, C-4), 121.1 (s, *p*-*C*$_6$H$_5$ of IrCH(C_6H_5)), 127.6 (d, ^3J(C,P) = 11.1 Hz, *m*-*C*$_6$H$_5$ PHOX), 127.9, 128.3 (both s, *o*- and *m*-*C*$_6$H$_5$ of IrCH(C_6H_5)), 128.5 (d, ^3J(C,P) = 10.3 Hz, *m*-*C*$_6$H$_5$ PHOX), 129.3 (d, ^3J(C,P) = 3.0 Hz, *p*-*C*$_6$H$_5$ PHOX), 129.8 (d, ^4J(C,P) = 7.8 Hz, C-11), 130.0 (d, ^4J(C,P) = 6.8 Hz C-10 and *p*-*C*$_6$H$_5$ PHOX), 130.3 (d, ^1J(C,P) = 26.7 Hz, *ipso*-*C*$_6$H$_5$P), 130.6 (d, ^1J(C,P) = 21.5 Hz, *ipso*-*C*$_6$H$_5$P), 131.6 (d, ^3J(C,P) = 7.8 Hz, C-9), 132.9 (d, ^1J(C,P) = 50.8 Hz, C-7), 133.3 (d, ^2J(C,P) = 7.5 Hz, *o*-*C*$_6$H$_5$ PHOX), 133.3 (d, ^2J(C,P) = 12.4 Hz, C-6), 134.8 (d, ^2J(C,P) = 3.46 Hz, C-8), 151.6 (s, *ipso*-*C*$_6$H$_5$ of IrCH(C_6H_5)), 160.5 (d, ^3J(C,P) = 2.8 Hz, C-2), 168.1, 169.0 (both s, CH[CH(*C*O$_2$CH$_3$)$_2$]), 173.4 (d, ^3J(C,P) = 3.5 Hz, Ir[CH(*C*O$_2$CH$_3$)$_2$]), 173.7 (s, Ir[CH(*C*O$_2$CH$_3$)$_2$]); MS (FAB) *m/z* 945.2 (0.5) $[M]^+$, 814.2 (50) $\{[M] - [CH(CO_2Me)_2]\}^+$. Anal. Calcd for $C_{43}H_{47}NO_9PIr$: C, 54.59; H, 5.01; N, 1.48. Found: C, 54.86; H,5.14; N, 1.57.

Complex 17. A 0.55 M solution of I_2 in THF (0.45 mL, 0.25 mmol of I_2) was added to a cold (−78 °C) solution of complex **16** (234.0 mg, 0.25 mmol) in THF (3.50 mL). The resultant mixture was stirred at −70 to −50 °C for 3 h, and the progress of the reaction was monitored by $^{31}P\{^1H\}$ NMR, showing incomplete conversion; full conversion was reached upon further addition of 0.07 mmol of I_2 and 2 h of reaction at −70 °C. The solvent was removed under vacuum at room temperature, and diethyl ether (2 mL) was added at −60 °C to precipitate an orange-yellow powder. The tetraester $[(CO_2CH_3)_2CH]_2$ was extracted from the precipitate by repeated washing with cold (−20 °C) diethyl ether (monitoring by TLC: petroleum ether/ethyl acetate 4:1, visualization of spots with $KMnO_4$). $[(CO_2CH_3)_2CH]_2$ was further purified by flash chromatography (petroleum ether/ethyl acetate 4:1) and isolated as white crystals (26.5 mg, 80%). The residual orange-yellow powder was identified as complex **17**, yield 90.0 mg (39%). ^1H NMR (500.13 MHz, −30 °C, CD_2Cl_2; numbering of atoms see Scheme 7 and Table 3): δ −0.03 (d, 3 H, ^3J(H,H) = 6.7 Hz, CH(C*H*$_3$)$_2$), 0.79 (d, 3 H, ^3J(H,H) = 7.4 Hz, CH(C*H*$_3$)$_2$), 2.08−2.21 (m, 1 H, C*H*(CH$_3$)$_2$), 2.42 (broad d, 1 H, ^3J(H,H) = 8.7 Hz, 1A-H*a*), 2.78 (s, 3 H, OC*H*$_3$), 3.58 (broad signal, 4 H, OC*H*$_3$ and 1A-H*s*), 4.37 (d, 1 H, ^3J(H,H) = 11.4 Hz, 3A-H), 4.41−4.80 (m, 2 H, 5-H and 4-H), 4.56 (s, 1 H, C*H*(CO$_2$Me)$_2$), 4.67 (dd, 1 H, ^2J(H,H) = 9.35, ^3J(H,H) = 10.05 Hz, 5-H), 5.35−5.46 (m, 1 H, 2A-H), 6.36 (dd, 1 H, ^3J(H,H) = 7.3, ^3J(H,P) = 12.0 Hz, 8-H), 6.50−7.15 (m, 10 H, Ar H), 7.23 (t, 1 H, ^3J(H,H) = 7.3 Hz, Ar H), 7.30 (t, 1 H, ^3J(H,H) = 7.3 Hz, Ar H), 7.43 (dd, 1 H, ^3J(H,H) = 7.3, ^3J(H,H) = 8.0 Hz, 9-H), 7.55 (dd, 2 H, ^3J(H,H) = 6.0, ^3J(H,H) = 6.7 Hz, Ar H), 7.62 (dd, 1 H, ^3J(H,H) = 7.3 Hz, Ar H), 7.71 (dd, 1 H, ^3J(H,H) = 7.3, ^3J(H,H) = 8.0 Hz, 10-H), 8.19 (dd, ^4J(H,P) = 3.7, ^3J(H,H) = 7.7 Hz, 11-H). $^{31}P\{^1H\}$ NMR (202.46 MHz, −30 °C, CD_2Cl_2): δ −15.7 (s). $^{13}C\{^1H\}$ NMR (125.77 MHz, −30 °C, CD_2Cl_2; numbering of atoms see Scheme 7 and Table 3): δ 11.7, 18.7 (both s, CH(*C*H$_3$)$_2$), 28.4 (s, *C*H(CH$_3$)$_2$), 31.6 (s, C-1A), 51.5, 52.5 (both s, CH(CO$_2$*C*H$_3$)$_2$), 67.4 (s, *C*H(CO$_2$CH$_3$)$_2$), 68.5 (s, C-5), 69.4 (s, C-4), 72.6 (s, C-3A), 85.6 (s, C-2A), 122.5 (d, ^1J(C,P) = 65.8 Hz, *ipso*-*C*$_6$H$_5$P), 123.8 (d, ^1J(C,P) = 65.8 Hz, *ipso*-*C*$_6$H$_5$P), 125.7 (d, ^1J(C,P) = 61.3 Hz, C-7), 127.4, (s, allylic Ar *C*H), 127.8 (d, ^2J(C,P) = 9.0 Hz, C-6), 128.5 (d, J(C,P) = 12.0 Hz, Ar *C*H PHOX), 129.0 (s, allylic Ar *C*H), 129.9 (d, J(C,P) = 10.5 Hz, Ar *C*H PHOX), 131.5 (d, ^3J(C,P) = 7.5 Hz, C-11), 131.8 (d, J(C,P) = 9.0 Hz, Ar *C*H PHOX), 131.9 (s, allylic Ar *C*H), 132.0 (d, J(C,P) = 12.7 Hz, Ar *C*H PHOX), 132.6 (d, J(C,P) = 3.0 Hz, Ar *C*H PHOX), 132.7 (s, C-10), 133.6 (d, ^3J(C,P) = 4.5 Hz, C-9), 134.0 (d, ^2J(C,P) = 9.0 Hz, C-8), 136.4 (s, allylic *ipso*-C_6H_5), 164.4 (d, ^3J(C,P) = 4.5 Hz, C-2), 172.2, 173.9 (both s, CH(*C*O$_2$CH$_3$)$_2$). MS (FAB): *m/z* 814.3 (100) ($[M]^+$), 697.3 (15) $\{[M] - C_3H_4(C_6H_5)\}^+$. HR-MS (FAB): calcd for $[M]^+$ ($C_{38}H_{40}NO_5PIr$) 814.2283, found 814.2231; calcd for $[(MI) - H]^+$ ($C_{38}H_{39}NO_5PIIr$) 940.1241, found 940.1235.[40]

Complex 18. $BF_3{\cdot}Et_2O$ (4 μL, 0.03 mmol) was added to a solution of complex **16** (20.0 mg, 0.02 mmol) in $[D_8]$THF (0.60 mL) at room temperature. After 60 min both ^1H and $^{31}P\{^1H\}$ NMR spectra showed a complete, clean reaction, yielding a mixture of **18** and $CH_2(CO_2CH_3)_2$ (ratio 2:1, respectively). Removal of the solvent under vacuum followed by addition of diethyl ether caused the precipitation of 8.0 mg of complex **18** as a yellow powder. ^1H NMR (500.13 MHz, 25 °C, $[D_8]$THF): δ 0.10 (d, 3 H, ^3J(H,H) = 7.4 Hz, CH(C*H*$_3$)$_2$), 0.87 (d, 3 H, ^3J(H,H) = 6.7 Hz, CH(C*H*$_3$)$_2$), 2.18−2.27 (m, 1 H, C*H*(CH$_3$)$_2$), 2.51 (dd, 1 H, ^2J(H,H) = 2.0, ^3J(H,H) = 10.0 Hz, 1A-H*a*), 2.84, 3.64 (both s, 3 H, OC*H*$_3$), 3.71 (dd, 1 H, ^2J(H,H) = 2.0, ^3J(H,H) = 6.05 Hz, 1A-H*s*), 4.41 (d, 1 H, ^3J(H,H) = 11.4 Hz, 3A-H), 4.56 (s, 1 H, C*H*(CO$_2$CH$_3$)$_2$), 4.56−4.62 (m, 1 H, 4-H), 4.67 (dd, 1 H, ^3J(H,H) = 9.35, ^2J(H,H) = 10.05 Hz, 5-H), 4.75 (dd, 1 H, ^3J(H,H) = 10.0, ^2J(H,H) = 10.05 Hz, 5-H), 5.83−5.94 (m, 1 H, 2A-H), 6.47 (dd, 1 H, ^3J(H,H) = 7.7, ^3J(H,P) = 12.0 Hz, 8-H), 6.86−6.99 (m, 4 H, Ar H), 6.96 (dd, 2 H, ^3J(H,H) = 7.5, ^3J(H,H) = 8.0 Hz, allylic *m*-C_6H_5), 7.03 (d, 2 H, ^3J(H,H) = 8.0 Hz, allylic *o*-C_6H_5), 7.18 (t, 1 H, ^3J(H,H) = 7.5 Hz, allylic *p*-C_6H_5), 7.25−7.35 (m, 3 H, Ar H), 7.52 (t, 1 H, ^3J(H,H) = 7.7 Hz, 9-H), 7.57−7.67 (m, 3 H, Ar H), 7.80 (t, 1 H, ^3J(H,H) = 7.7 Hz, 10-H), 8.30 (ddd, ^4J(H,H) = 1.35, ^4J(H,P) = 4.0, ^3J(H,H) = 7.7 Hz, 11-H) ppm. $^{31}P\{^1H\}$ NMR (202.46 MHz, 25 °C, $[D_8]$THF): δ −15.7 (s) ppm. $^{13}C\{^1H\}$ NMR (125.77 MHz, 25 °C, $[D_8]$THF): δ 12.8, 18.9 (both s, CH(*C*H$_3$)$_2$), 29.6 (s, *C*H(CH$_3$)$_2$), 31.6 (s, C-1A), 51.6, 52.6 (both s, CH(CO$_2$*C*H$_3$)$_2$), 67.8 (s, *C*H(CO$_2$CH$_3$)$_2$), 69.8 (s, C-5), 70.9 (s, C-4), 73.7 (s, C-3A), 87.8 (s, C-2A), 124.6 (d, ^1J(C,P) = 65.8 Hz, *ipso*-*C*$_6$H$_5$P), 125.5 (d, ^1J(C,P) = 65.8 Hz, *ipso*-*C*$_6$H$_5$P), 127.8 (d, ^1J(C,P) = 60.8 Hz, C-7), 127.8, (s, allylic *p*-C_6H_5), 128.0 (s, allylic *o*-C_6H_5), 129.3 (d, J(C,P) = 11.0 Hz, Ar *C*H), 129.4 (d, ^3J(C,P) = 9.0 Hz, C-6), 129.6 (s, allylic *m*-C_6H_5), 130.8 (d, J(C,P) = 6.0 Hz, C-11), 132.5 (s, Ar *C*H), 133.2 (d, J(C,P) = 3.0 Hz, Ar *C*H), 133.3 (d, J(C,P) = 11.0 Hz, Ar *C*H), 133.5 (d, J(C,P) = 10.0 Hz, Ar *C*H), 133.7 (s, C-10), 134.6 (d, ^3J(C,P) = 4.0 Hz, C-9), 134.8 (d, ^2J(C,P) = 8.0 Hz, C-8), 138.3 (s, allylic *ipso*-C_6H_5), 165.9 (d, ^3J(C,P) = 5.0 Hz, C-2), 173.8, 175.3 [both s, CH(*C*O$_2$CH$_3$)$_2$]. MS (FAB): *m/z* 814.3 (100) ($[M]^+$), 697.3 (16) $\{[M] - C_3H_4(C_6H_5)\}^+$. HR-MS (FAB): calcd for $[M]^+$ $C_{38}H_{40}NO_5PIr$ 814.2273, found 814.2278.[41]

X-ray Crystal Structure Analyses. Crystals of compound **14** were obtained as yellow prisms by slow evaporation of solvent from a saturated solution in THF. Single crystals of complex **15** were grown as yellow needles by slow diffusion of diethyl ether into a saturated solution of **15** in CH_2Cl_2. Single crystals of complex **16** were grown at −40 °C as yellow needles from concentrated mixtures of diethyl ether and pentane.

All crystallographic measurements were carried out on a Bruker Smart CCD diffractometer with graphite-monochromated Mo Kα radiation at 200(2) K. Data covering a complete sphere in reciprocal space were collected using series of 0.3° ω scans in each case. Intensities were corrected for Lorentz and polarization effects, and an empirical absorption correction was applied using SADABS[42] on the basis of the Laue symmetry of the reciprocal space. All structures were solved by direct methods and refined against F^2 with a full-matrix least-squares algorithm using the SHELXTL-PLUS (5.10)

(40) All attempts to isolate complex **17** completely free of tetraester $[CH(CO_2CH_3)_2]_2$ and I_2 were unsuccessful, and therefore, a correct elemental analysis of this compound could not be obtained.

(41) Attempts to isolate complex **18** sufficiently pure for elemental analysis were unsuccessful and led to decomposition of the compound.

(42) Sheldrick, G. M. Unpublished work, 1996. Based on the method described in: Blessing, R. H. *Acta Crystallogr., Sect. A* **1995**, *51*, 33.

Table 5. Crystal Data and Details of the Structure Refinement for Compounds 14−16

	14	15	16
empirical formula	$C_{37}H_{41}Cl_2IrNO_2P$	$C_{27}H_{29}Br_2IrNOP$	$C_{43}H_{47}IrNO_9P$
cryst shape	polyhedron	polyhedron	polyhedron
a (Å)	21.7131(1)	14.4894(2)	11.0776(1)
b (Å)	11.4932(2)	10.6987(1)	18.9168(3)
c (Å)	14.0906(2)	26.2240(1)	19.2024(3)
β (deg)	90	96.521(1)	90
space group	$P2_12_12$	$P2_1$	$P2_12_12_1$
Z	4	6	4
cryst size (mm^3)	0.30 × 0.21 × 0.18	0.30 × 0.19 × 0.16	0.21 × 0.14 × 0.09
μ (mm^{-1})	4.03	8.01	3.41
transmissn	0.54−0.45	0.36−0.21	0.78−0.63
θ range (deg)	1.5−27.5	0.8−27.5	2.1−27.5
no. of rflns collected	36 658	42 184	42 095
no. of indep rflns	8058	18 349	9239
R(int)	0.0297	0.0435	0.0683
R1 ($I > 2\sigma(I)$)	0.017	0.050	0.031
wR2 ($I > 2\sigma(I)$)	0.039	0.105	0.048
Flack param	−0.008(3)	−0.021(9)	−0.018(5)

software package.[43] The allylic hydrogen atoms were refined isotropically in the case of complex **14** but not taken into account in the case of **15**. Hydrogen atoms in the iridacyclobutane unit were refined isotropically in the case of complex **16**. All other hydrogen atoms in were treated using appropriate riding models.

The files CCDC 210168−210170 contain the supplementary crystallographic data for these structures. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K.; fax +44 1223 336033; e-mail deposit@ccdc.cam.ac.uk). Crystal data and details of the structure refinement are given in Table 5.

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Supporting Information Available: Tables and figures giving X-ray analysis data for complexes **14**−**16**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0401105

(43) Sheldrick, G. M. Bruker Analytical X-ray Division, Madison, WI, 1997.