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Reactivity of Allylphosphines with Iridium Complexes: Diallylphosphines as New Bidentate Ligands

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ABSTRACT

Addition of four equivalents of t-butyldiallylphosphine **1a** *to a solution of one equivalent of* $[(COE)_2IrCl]_2$ *in* $CHCl_3$ *at low temperature produced two isomers of the complex* $[t\text{-}Bu(C_3H_5)PCH_2CH{=}CH)]IrHCl(COE)\text{-}[PtBu(C_3H_5)_2]$ (**2a**), *which evolve at 40°C to* $[t\text{-}Bu(C_3H_5)PCH_2CH{=}CH)]IrCl(C_8H_{15})[PtBu(C_3H_5)_2]$ (**3a**), *by a hydride transfer from iridium to the cyclooctene (COE) ligand. It is reasonable that the unsaturation at the iridium center is fulfilled by interactions with the allyl moieties of the phosphine that are not metalated. This has been demonstrated by bubbling CO into a solution of* **3a** *in* $CHCl_3$ *at room temperature to obtain the carbonyl complex* $[t\text{-}Bu(C_3H_5)\text{-}PCH_2CH{=}CH)]Ir(CO)Cl(C_8H_{15})[PtBu(C_3H_5)_2]$ (**4a**). *Under the same conditions, the reaction of diisopropylamindiallylphosphine* **1b** *and anisyldiallylphosphine* **1c** *afforded a mixture of isomers* **3b** *and* **3c**, *respectively. These results show that diallylphosphines can be considered to be a new family of bidentate ligands. Finally, the reaction of these phosphines with* $[(COD)IrCl]_2$ *(COD = 1,5 cyclooctadiene) shows the formation of tetracoordinated iridium (I) complexes IrCl(COD)(PR3), which are thermally stable.* © 1998 John Wiley & Sons, Inc. Heteroatom Chem 9:253–259, 1998

INTRODUCTION

Polyphosphines [1] and phosphines with various functional groups as substituents [2] have attracted the attention of chemists. Since the early seventies, after the publication of the preparation of nickel catalysts of phosphinoenolate ligands and their use in the selective polymerization and oligomerization of ethylene [3,4], they have played an important role in homogeneous catalysis. These ligands are expected to exert more control of the coordination sphere of the metal with the possible consequence of providing new catalytic properties of the resulting complexes [5,6]. Ligands containing phosphorus and oxygen as donor atoms have attracted even more interest [7]. This is because the phosphorus atom is strongly bonded to the metal, with the oxygen atom forming only a weak bond. This can be reversibly broken to create a vacant coordination site on the metal center, inducing catalytic activity [8] and increasing its electronic density that facilitates the oxidative addition of a substrate [9].

We have reported on the thermal decomposition of allyl and diallylphosphines as a novel way to generate phosphalkene derivatives, via a retroene type of propene elimination involving a six-center transition state [10–14].

We are now developing new methods for the synthesis of heterofunctional allyl phosphines, and we are also studying their reactivity. As a part of this work, we have started to evaluate their potential as polydentate ligands, the main consideration being that the C–C double bond of the allyl moiety, if it is coordinated, can act as a labile function that could

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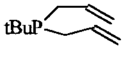
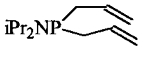
enhance the reactivity of the metal center and facilitate the catalytic transformations of substrates within the coordination sphere. Thus, we report here our first results on the study of the reactivity of different diallylphosphines toward chloro-bridged bis(cyclooctene) and cyclooctadiene iridium dimers.

RESULTS AND DISCUSSION

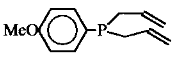
Four allylphosphines have been chosen for this study, in order to evaluate the influence of the substitution of the phosphorus atom on the reactivity.



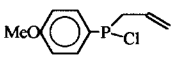
1a



1b



1c



1d

Starting from the easily available diisopropylaminodichlorophosphine, allyl(4-methoxyphenyl)-chlorophosphine **1d** was directly obtained in better than 60% yield by successive substitution of the chlorine atoms by the 4-methoxyphenyl and allyl groups, followed by HCl bubbling, without isolation of the intermediates (Figure 1).

Addition of a second equivalent of allylmagnesium bromide permits the obtainment of the 4-methoxyphenyldiallylphosphine **1c** (Figure 1).

Reactions with $[(COE)_2IrCl]_2$

Addition of four equivalents of *t*-butyldiallylphosphine **1a** to a solution of one equivalent of $[(COE)_2IrCl]_2$ (COE = cyclooctene) in $CHCl_3$ at −50°C produced an intense red solution that immediately changed to clear yellow and then became dark at room temperature. ^{31}P NMR analysis of the clear yellow solution showed the clean formation of two AB systems ($\delta_{P1} = 50.9$, $\delta_{P2} = -76.9$, $J_{PP} = 327.5$ and $\delta_{P1} = 48.3$, $\delta_{P2} = -82.3$, $J_{PP} = 324.5$) in about a 90:10 ratio, the large coupling constant indicating the *trans* configuration of the phosphines. The ^1H NMR spectrum shows two doublets for the *t*-butyl protons ($\delta = 1.07$, $^3J_{PH} = 12.0$ and $\delta = 1.22$, $^3J_{PH} = 14.5$), a pseudo-triplet in the zone of hydride resonance ($\delta = -21.6$, $J_{PH} = 11.6$), and a doublet of doublets at low field ($\delta = 7.64$, $^3J_{HH} = 8.5$, $^3J_{PH} = 17.0$), in addition to a complex resonance pattern for allylic protons ($\delta = 4.8$–6.2). The presence of a hydride substituent coupled with two *cis* nonequivalent phosphines and the doublet of doublets at low field prompt us to propose a metallization of one of the allyl moieties, forming a six-coordinated Iridium (III) derivative incorporating a five-membered metallacycle (Figure 2). These spectroscopic data were consistent with the formation of two isomers of the metalated complex $[t\text{-Bu}(C_3H_5)PCH_2CH{=}CH)]$-$IrHCl(COE)[PtBu(C_3H_5)_2]$ (**2a**).

This result can be compared with the reported reaction of di-*t*-butylallylphosphine [15,16] with the same iridium dimer in which the two cyclooctene ligands are displaced and the sixth coordination site is taken by another coordinating agent from the reaction medium (Figure 3A). When the reaction is carried out without another coordinating agent present, a five-coordinated metalated species is formed (Figure 3B) [15]. These results are certainly due to the steric hindrance of the two *t*-butyl groups.

In our case, only one cyclooctene ligand is displaced from the metal, and this can be explained by the lesser steric hindrance of the diallyl phosphine.

The presence of the cyclotene ligand on **2a** is confirmed by the clean isomerization, even at low temperature, of **2a**, by a hydride migration to the double bond of the cyclotene (Figure 4), that results

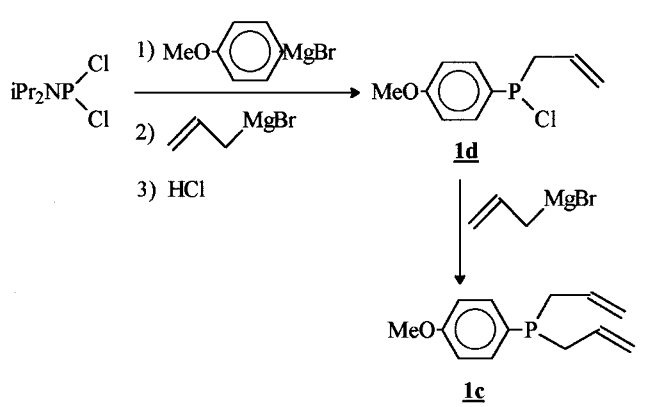


FIGURE 1

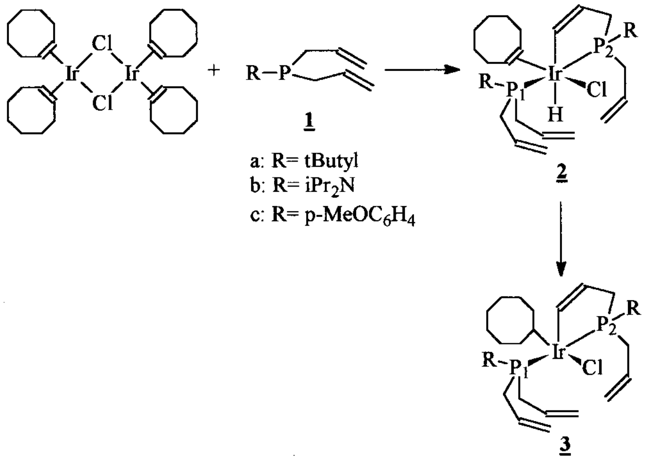


FIGURE 2

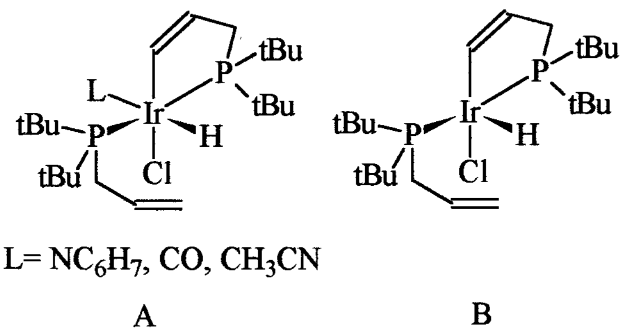


FIGURE 3

in the formation of the unsaturated $[t\text{-Bu}(C_3H_5)P(CH_2CH=CH)]IrCl(C_8H_{15})[PtBu(C_3H_5)_2]$ (3a) complex. This product showed in its ^{31}P NMR spectrum an AB pattern (δ = 27.3, δ = −46.4, J_{PP} = 314.3), the large coupling constant indicating the *trans* configuration of the two coordinated phosphines. The ^{1}H NMR spectrum shows the disappearance of the hydride substituent and the displacement of the signal due to the proton of the metalated double bond that brought about a pseudo-triplet signal (δ = 7.79, $^3J_{HH}$ = 8.5, $^3J_{PH}$ = 8.5). Interesting aspects are shown by the analysis of the ^{13}C NMR spectra of 3a in the region of the allyl resonances, showing three types of allyl fragments (δ = 116.2, $^2J_{PC}$ = 8.9, δ = 131.84, $^3J_{PC}$ = 6.9; δ = 117.3, $^2J_{PC}$ = 9.7, δ = 133.2, $^3J_{PC}$ = 8.22; and δ = 117.5, $^2J_{PC}$ = 8.5, δ = 133.7, $^3J_{PC}$ = 5.9), the last two being slightly less intense than the first. It seems reasonable to think that the unsaturation at the iridium center is fulfilled by interactions with the allyl moieties, meaning that the diallylphosphine is acting as a bidentate ligand. This observation has not been reported in the case of the unsaturated iridium derivative obtained with di-*t*-butylallylphosphine (Figure 3B) [15].

Unsaturated iridium derivatives have been reported to be able to activate a large variety of organic molecules by coordination of the organic substrate to the unsaturated iridium center, as, for example, in the recent synthesis of iridapyrrole complexes by reaction of the bisethylene complex $Tp^*Ir(C_2H_4)_2$ with acetonitrile [17 and references therein]. In our case, it is of interest that the complex is possibly stabilized by an intramolecular interaction.

Despite our best efforts, we did not obtain a single crystal suitable for an X-ray study of 2a or 3a in order to establish the stereochemistry of the reaction and to see how close the allyl double bonds are to the metal center.

The lability of 3a has been demonstrated by bubbling CO into a solution of this complex in $CHCl_3$ at room temperature. A new AB system is observed in the ^{31}P NMR spectrum (δ = 43.3, δ = 33.3, J_{PP} = 261.4), and no other signals are observed. The ^{1}H NMR spectrum shows the displacement of the signal corresponding to the proton on the metalated carbon as a pseudo triplet (δ = 7.13, J_{HH} = 5.9, J_{PH} = 5.9).

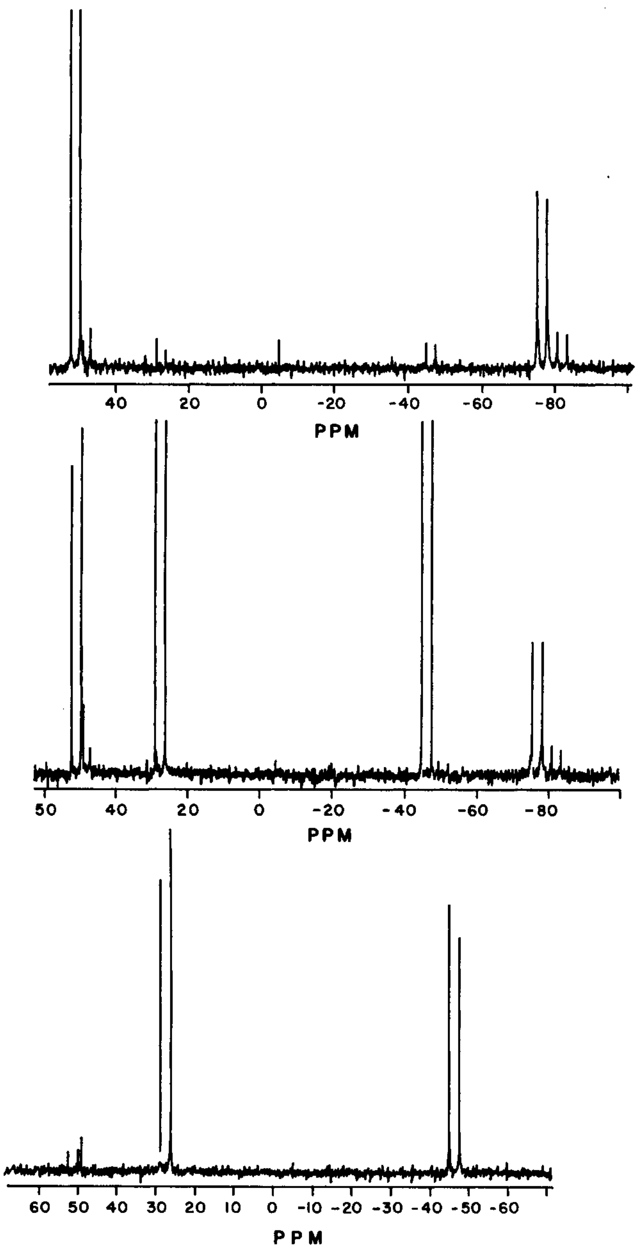


FIGURE 4 ^{31}P {^{1}H} NMR (CDCl$_3$) evolution of **2a** to **3a:** (*top*) spectrum at 0°C, (*middle*) after 10 minutes at 40 °C, (*bottom*) after 30 minutes at 40 °C.

The ^{13}C NMR spectrum shows more significant changes; besides the signals corresponding to the metalated carbon and its neighboring groups (δ =

127.5, $^3J_{PC}$ = 3.6, $^3J_{PC}$ = 11.6 and δ = 123.2, $^2J_{PC}$ = 4.8, respectively), signals corresponding to two types of allyl fragments (δ = 118.1, $^2J_{PC}$ = 8.9; δ = 133.4, $^3J_{PC}$ = 5.9; and δ = 118.3, $^2J_{PC}$ = 10.3; δ = 132.3, $^3J_{PC}$ = 7.54) are apparent. The appearance of only two types of allyl groups clearly demonstrates that there is no other interaction with the metal center, the unsaturation now being filled by the CO ligand. These spectroscopic data are consistent with the formulation [*t*-Bu(C_3H_5)P($CH_2CH=CH$)]Ir(CO)Cl(C_8H_{15})-[PtBu(C_3H_5)$_2$] (**4a**) (Figure 5).

Under the same working conditions, the reaction of diisopropylaminodiallylphosphine **1b** and 4-methoxyphenyldiallylphosphine **1c** with (COE)$_2$-IrCl]$_2$ immediately affords a mixture of isomers of **3b** and **3c,** respectively (Table 1, Figure 2); no hydride intermediate complex was observed, probably due to the fact that these more electron-rich phosphines favor the stabilization of the unsaturated iridium complexes. In the two cases, the analysis made by ^{1}H and ^{13}C NMR spectroscopy showed a more complicated spectrum that is difficult to interpret. Nevertheless, the values of the ^{31}P NMR chemical shift and the coupling constants indicated that they are analogous to those observed in **3a.**

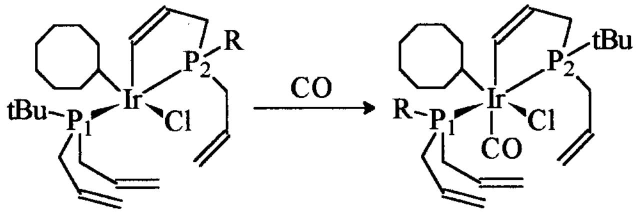
Low-temperature NMR experiments, performed in order to derive greater insight into the reaction mechanism, were unfruitful because the evolution of the reaction was different in the NMR tube than in the schlenk procedure, producing a mixture of starting material, intermediates, and the final unsaturated product.

Reaction of the allyl(4-methoxyphenyl)-chlorophosphine **1d,** under the same conditions, did not lead to the formation of the metalated product and resulted instead in the formation of a complex mixture of polyphosphorated complexes. We think that, in this case, the lesser steric hindrance of the phosphine favored the coordination of more than two phosphines, and the reaction could not be controlled under our working conditions.

Reactions with [(COD)IrCl]$_2$

Under the same conditions mentioned previously, [(COD)IrCl]$_2$ (COD = 1,5 cyclooctadiene) shows a different reactivity toward the allyl phosphines **1a–d.** In all cases, the clean formation of the tetracoordinated iridium (I) complexes were observed (Figure 6). The structures were established by the analysis of the ^{1}H, ^{13}C, and ^{31}P NMR spectra.

Heating a solution of **4a–d** at 100°C in toluene for 4 hours did not produce either a displacement of the cyclooctadiene or a C–H activation (Figure 7), and the complex remained unchanged. This may be explained in terms of a greater lability of the COE ligand than that of the COD one. Prolonged times of heating only caused decomposition of the complexes.



3a **4a**

FIGURE 5

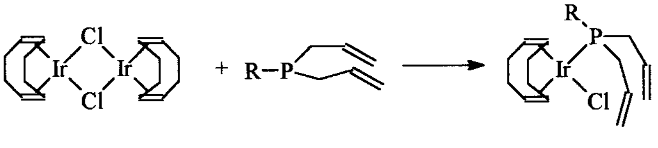


FIGURE 6

TABLE 1 ^{31}P{^{1}H} NMR Data for Complexes **2** and **3** (δ in ppm and J_{pp} in Hz)

		2			3	
	δ_{P1}	δ_{P2}	J_{PP}	δ_{P1}	δ_{P2}	J_{PP}
a	50.9	−76.9	327.5	27.3	−46.4	314.3
	48.3	−82.3	324.5			
b				35.2	−46.2	374.0
				broad	broad	
c				13.4	−39.9	325.0
				13.3	−40.1	320.3

a, **b**, **c**, P$_1$, and P$_2$ relative to starting phosphine, as in Figure 2.

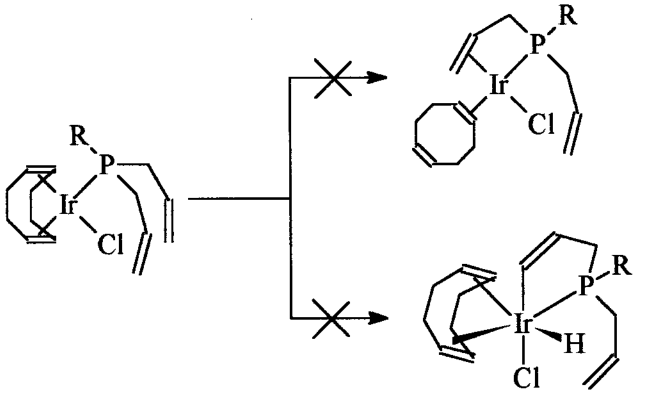


FIGURE 7

Having obtained an allylchlorophosphine complex, such as **4d,** it was tempting to try to obtain the stabilized phosphabutadiene by the abstraction of HCl. Treatment of a THF solution of **4a** with Et_3N led only to the recovery of the unchanged allylchlorophosphine complex (Figure 8). The use of stronger bases, such as DBU, *t*-BuOK, or lithium bistrimethylsilylamide, resulted in the formation of insoluble products that we were not able to characterize.

This preliminary work shows the different reactivity of diallylphosphines toward $[COE_2IrCl]_2$ and $[CODIrCl]_2$. In the reaction of diallylphosphines with $[COE_2IrCl]_2$, a C–H activation is observed with the subsequent insertion of the cyclooctene ligand into the Ir–H bond, affording an unsaturated complex of iridium intramolecularly stabilized by the allyl substituents on the phosphine ligand. This shows that diallylphosphines can act as bidentate ligands and that diallylphosphines can reasonably be considered to function as a new family of bidentate ligands. Reactions of diallylphosphines with $[CODIrCl]_2$ showed the formation of tetracoordinated iridium (I) complexes that are thermally stable.

Further work is being carried out to elucidate the stereochemistry of **3a** and to test its reactivity toward organic molecules such as nitriles, alkenes, and other unsaturated substrates.

EXPERIMENTAL

All of the reactions and manipulations were carried out under an argon atmosphere in schlenk-type glassware. Solvents of analytical grade were distilled from appropriate drying agents under N_2 prior to use. Iridium (III) trichloride hydrate was purchased from Aldrich. NMR spectra (usually in $CDCl_3$) were obtained by use of a Brucker AM-300 instrument. Published preparations were used for $[(COE)_2IrCl]_2$ [18], $[(COD)IrCl]_2$ [19], *t*-butyldiallylphosphine [10], and diisopropylamino-diallylphosphine [14].

Allyl(4-methoxyphenyl)chlorophosphine (**1d**). A filtered solution of 0.54 mole of (4-methoxyphenyl)magnesium bromide was added dropwise to a solution of 100 g (0.50 mole) of diisopropylaminodichlorophosphine in 300 mL of anhydrous THF cooled to −78°C.

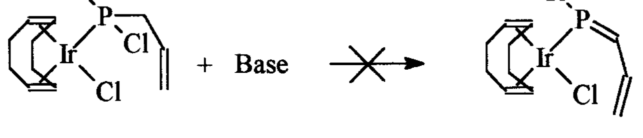


FIGURE 8

When the addition was finished, the reaction mixture was warmed to room temperature for 1 hour. The mixture was recooled to −78°C, and a solution of 0.54 mole of allylmagnesium bromide was added dropwise. When the addition was finished, the reaction mixture was warmed to room temperature, allowed to stand for 2 hours, and then filtered. Hydrogen chloride was then bubbled into the filtered solution at 0°C. The solution was evaporated, and allylchloro(4-methoxyphenyl)phosphine distilled under reduced pressure to produce 71 g (68% yield) of liquid of $bp_{0.5}$ 84–87°C.

$^{31}P\{^1H\}$ NMR $\delta = 81.5$. ^1H NMR: 2.9 (t, $^3J_{HH} = 8$ Hz, 2H, PCH_2), 3.8 (s, 3H, CH_3O), 5.09 (m, 2H, $C{=}CH_2$), 5.66 (m, 1H, $CH{=}C$), 6.96 (d, $^3J_{HH} = 9$ Hz, 2H, m-CH), 7.65 (dd, $^3J_{HH} = 9$ Hz, $^3J_{PH} = 9$ Hz, 2H, o-CH). ^{13}C NMR: 41.5 (d, $^1J_{PC} = 14$ Hz, $P\underline{C}H_2$), 55.4 (s, CH_3O), 114.3 (d, $^3J_{PC} = 9$ Hz, $C{=}\underline{C}H_2$), 119.4 (d, $^2J_{PC} = 10$ Hz, 0-C), 125.8 (d, $^1J_{PC} = 10$ Hz, i-C) 130.3 (d, $^3J_{PC} = 8$ Hz, m-C), 133.5 (d, $^2J_{PC} = 27$ Hz, $\underline{C}H{=}C$), 162 (s, p-C).

(4-Methoxyphenyl)diallylphosphine (**1c**). A filtered solution of 0.3 mole of allylmagnesium bromide in THF was added dropwise to a cooled solution of 0.256 mole (55g) of **1d.** When the addition was finished, the mixture was warmed to room temperature and maintained at this temperature for 2 hours,then filtered, and the solvent evaporated. Compound **1c** was distilled under reduced pressure. $Bp_{0.5} = 82–86$°C (32.5 g, 61% yield).

$^{31}P\{^1H\}$ NMR $\delta = -29.5$. ^1H NMR: 2.36 (t, $^3J_{HH} = 4$ Hz, 2H, PCH_2), 3.77 (s, 3H, CH_3O), 4.96 (m, 4H, $C{=}C\underline{H}_2$), 5.71 (m, 2H, $C\underline{H}{=}C$), 6.89 (d, $^3J_{HH} = 8$ Hz, 2H, m-CH), 7.42 (dd, $^3J_{HH} = 3$ Hz, $^3J_{PH} = 3$ Hz 2H, o-CH). ^{13}C NMR: 32.6 (d, $^1J_{PC} = 15$ Hz, $P\underline{C}H_2$), 55.11 (s, CH_3O), 113.9 (d, $^3J_{PC} = 8$ Hz, $C{=}\underline{C}H_2$), 116.8 (d, $^2J_{PC} = 9$ Hz, o-C), 127.5 (d, $^1J_{PC} = 15$ Hz, i-C), 133.2 (d, $^3J_{PC} = 7$ Hz, m-C), 133.97 (d, $^2J_{PC} = 20$ Hz, $\underline{C}H{=}C$), 160 (s, p-C).

Reaction of $t\text{-}BuP(CH_2CH{=}CH_2)_2$ (**1a**) *with* $[(COE)_2IrCl]_2$. An amount of 121 mg (7.2×10^{-4} mole) of **1a** was added dropwise to a solution of 160 mg (1.79×10^{-4} mole) of $[(COE)_2IrCl]_2$ in 10 mL of freshly distilled and degassed $CHCl_3$ cooled at −60°C. After completion of the addition, the mixture was kept at this temperature for 15 minutes and then allowed to reach 0°C. After concentration of the solvent, addition of *n*-pentane to the residual liquid produced **2a** as an unstable, cream-colored powder after collection by filtration.

The heating at 40°C of a solution of **2a** yielded **3a** quantitatively after 1 hour. After the evaporation of the solvent, the crude product remained as an orange oil. ^{31}P {^{1}H} NMR: $\delta_{P1} = 27.3$, $\delta_{P2} = -46.4$ (dd, $^2J_{PP} = 314.3$ Hz). ^{1}H NMR: 1.28 [d, $^3J_{PH} = 12.3$, $(C\underline{H}_3)_3C$], 1.37 [d, $^3J_{PH} = 14.7$, $(C\underline{H}_3)_3C$], 2.1 (m, $PC\underline{H}_2$), 3.6 (m, CH_2, C_8H_{15}), 4.25 (m, IrCH, C_8H_{15}), 5.13 (m, $C{=}C\underline{H}_2$), 5.8 (m, $C\underline{H}{=}C$, $IrC{=}C\underline{H}$), 7.79 (pt, $^3J_{HH} = 8.5$, $^3J_{PH} = 8.5$, $IrC\underline{H}{=}C$). ^{13}C NMR: 26.7 [bs, $PC(\underline{C}H_3)_3$], 28.7 [bs, $PC(\underline{C}H_3)_3$], 30.3, 32.9 (m, PCH_2), 74.3 (bd, $^2J_{PC} = 8.3$, $Ir\underline{C}H$, C_8H_{15}), 116.2 (d, $^2J_{PC} = 8.9$, $\underline{C}H{=}C$), 117.3 (d, $^2J_{PC} = 9.7$, $\underline{C}H{=}C$), 117.5 (d, $^2J_{PC} = 8.5$, $\underline{C}H{=}C$), 124.15 (dd, $^2J_{PC} = 13.6$, $^3J_{PC} = 4.8$, $Ir\underline{C}{=}C$), 128.5 (d, $^2J_{PC} = 5.5$, $IrC{=}\underline{C}$), 131.8 (d, $^3J_{PC} = 6.9$, $C{=}\underline{C}H_2$), 133.2 (d, $^3J_{PC} = 8.2$, $C{=}\underline{C}H_2$), 133.7 (d, $^3J_{PC} = 5.9$, $C{=}\underline{C}H_2$).

Reaction of **3a** *with CO.* CO was bubbled into a solution of **3a** in $CHCl_3$ at room temperature for 5 minutes. The solution was concentrated and *n*-pentane was added until complete precipitation of product had occurred. After filtration, a pale yellow solid, **4a**, was obtained.

^{31}P {^{1}H} NMR: $\delta_{P1} = 43.3$, $\delta_{P2} = 33.3$ (dd, $^2J_{PP} = 261.4$ Hz). ^{1}H NMR: 1.28 [d, $^3J_{PH} = 13.8$, $(C\underline{H}_3)_3C$], 1.33 [d, $^3J_{PH} = 13.1$ $(C\underline{H}_3)_3C$], 2.1–3.8 (series of multiplets, $PC\underline{H}_2$, CH_2 C_8H_{15}), 5.2 (m, $C{=}C\underline{H}_2$), 6.0 (m, $C\underline{H}{=}C$, $IrC{=}C\underline{H}$), 7.13 (pt, $^3J_{HH} = 5.9$, $^3J_{PH} = 5.9$, $IrC\underline{H}{=}C$). ^{13}C NMR: 27.4 [bs, $PC(\underline{C}H_3)_3$], 28.4 [bs, $PC(\underline{C}H_3)_3$], 31.7–35.1 [series of multiplets, $P\underline{C}(CH_3)_3$, PCH_2], 67.9 (s, $Ir\underline{C}H$, C_8H_{15}), 118.1 (d, $^2J_{PC} = 8.9$, $\underline{C}H{=}C$), 118.3 (d, $^2J_{PC} = 10.3$, $\underline{C}H{=}C$), 123.2 (d, $^2J_{PC} = 4.8$, $IrC{=}\underline{C}$), 127.5 (dd, $^2J_{PC} = 11.6$, $^3J_{PC} = 3.6$, $Ir\underline{C}{=}C$), 132.3 (d, $^3J_{PC} = 7.5$, $C{=}\underline{C}H_2$), 133.4 (d, $^3J_{PC} = 5.9$, $C{=}\underline{C}H_2$), 174.0 (s, $Ir\underline{C}O$).

Analogous reactions of $[(COE)_2IrCl]_2$ with diallyldiisopropylaminophosphine **1b,** (4-methoxyphenyl)diallylphosphine **1c,** and allyl(4-methoxyphenyl)chlorophosphine **1d** were carried out using the same method.

Reaction of t-BuP(CH$_2$CH=CH$_2$)$_2$ (**1a**) *with [(COD)IrCl]$_2$.* To a solution of 120 mg (1.78×10^{-4} moles) of $[(COD)IrCl]_2$ in 10 mL of freshly distilled and degassed $CHCl_3$, cooled to −60°C, was added dropwise 61 mg (3.57×10^{-4} mole) of *t*-butyldiallylphosphine **1a.** When the addition had been completed, the mixture was warmed to room temperature and stirred for an additional hour. The solvent was then evaporated, giving **5a** as a deep orange oil.

^{31}P {^{1}H} NMR: $\delta = 9.5$ (s). ^{1}H NMR: 1.28 [d, $^3J_{PH} = 13.6$, $PC(C\underline{H}_3)_3$], 1.6, 2.57, 2.8, and 3.3 (series of multiplets, C_8H_{12}), 2.1 (m, PCH_2), 4.9 (m, $CH{=}CH$, C_8H_{12}), 5.1 (m, $C{=}CH_2$), 5.9 (m, $CH{=}C$). ^{13}C NMR: 24.7 [d, $^2J_{PC} = 25$, $PC(\underline{C}H_3)_3$], 29.0 (d, $^1J_{PC} = 18$, PCH_2), 29.1 (s, CH_2, C_8H_{12}), 33.8 (d, $^3J_{PC} = 3$), 35.0 (d, $^2J_{PC} = 24$), 91.6 (d, $^3J_{PC} = 14$, $C{=}C$, C_8H_{12}), 118.6 (d, $^2J_{PC} = 10$, $\underline{C}H{=}C$), 132.0 (d, $^3J_{PC} = 5$, $C{=}\underline{C}H_2$).

Analogous iridium complexes of diallyldiisopropylaminophosphine (**5b**), (4-methoxyphenyl)diallylphosphine (**5c**), and allyl(4-methoxyphenyl)chlorophosphine (**5d**) were prepared using the same method.

5b: ^{31}P {^{1}H}NMR: $\delta = 52.2$ (s). ^{1}H NMR: 1.3 [d, $^3J_{PH} = 7.1$, $PNCH(C\underline{H}_3)_2$], 1.6, 2.7, 3.1, and 3.3 (series of multiplets, C_8H_{12}), 2.2 (m, PCH_2), 3.9 [m, $PNC\underline{H}(CH_3)_2$], 5.1 (m, $CH{=}CH$ C_8H_{12}), 5.2 (m, $CH{=}C$), 6.2 (m, $C{=}CH_2$). ^{13}C NMR: 25.2 [d, $^2J_{PC} = 2$, $PNCH(\underline{C}H_3)_2$], 32.2 (d, $^2J_{PC} = 29$, PCH_2), 52.3 (d, $^3J_{PC} = 3$), 91.6 (d, $^3J_{PC} = 14$, $C{=}C$, C_8H_{12}), 118.2 (d, $^2J_{PC} = 10$, $\underline{C}H{=}C$), 132.0 (d, $^3J_{PC} = 2$, $C{=}\underline{C}H_2$).

5c: ^{31}P {^{1}H}NMR: $\delta = -1.4$ (s). ^{1}H NMR: 1.7 (m, C_8H_{12}), 2.1 (m, PCH_2), 2.9 (m, C_8H_{12}), 5.1 (m, $CH{=}CH$, C_8H_{12}, $CH{=}C$), 5.8 (m, $C{=}CH_2$), 6.9 (d, $^3J_{HH} = 7.4$, m-CH), 7.5 (pt, $^3J_{HH} = {^3J_{PH}} = 8.9$, o-CH). ^{13}C NMR: 28.3 (d, $^1J_{PC} = 29.8$, PCH_2), 52.5 (s, OCH_3), 92.9 (d, $^2J_{PC} = 14$, $CH{=}CH$, C_8H_{12}), 113.7 (d, $^2J_{PC} = 11.7$, $\underline{C}H{=}C$), 118.9 (d, $^2J_{PC} = 10$, o-CH), 120.5 (d, $^1J_{PC} = 49$, i-C), 130.8 (d, $^3J_{PC} = 4$, m-CH), 133.4 (d, $^3J_{PC} = 10$, $C{=}\underline{C}H_2$), 160.9 (d, $^3J_{PC} = 1.7$, OCH_3).

5d: ^{31}P {^{1}H}NMR: $\delta_{P1} = 95.1$ (s). ^{1}H NMR: 1.9, 2.4, 3.3, and 3.5 (series of multiplets, C_8H_{12}), 2.3 (m, PCH_2), 5.2–5.3 (m, $CH{=}CH$, C_8H_{12}, $CH{=}C$), 6.0 (m, $C{=}CH_2$), 6.9 (dd, $^3J_{HH} = 8.8$, $^4J_{PH} = 2$, m-CH), 8.0 (dd, $^3J_{HH} = 8.7$, $^3J_{PH} = 11$, o-CH). ^{13}C NMR: 40.9 (d, $^1J_{PC} = 24$, PCH_2), 55.3 (s, OCH_3), 98.8 (d, $^2J_{PC} = 6.3$, $CH{=}CH$, C_8H_{12}), 99.0 (d, $^2J_{PC} = 5.5$, $CH{=}CH$, C_8H_{12}), 114.0 (d, $^2J_{PC} = 12$, $\underline{C}H{=}C$), 120.6 (d, $^2J_{PC} = 13$, o-CH), 125.7 (d, $^1J_{PC} = 44$, i-C), 128.9 (d, $^3J_{PC} = 6$, m-CH), 132.5 (d, $^4J_{PC} = 14$, p-C), 134.7 (d, $^3J_{PC} = 16$, $C{=}\underline{C}H_2$), 162.4 (d, $^3J_{PC} = 2$, OCH_3).

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REFERENCES

[1] M. Peuckert, W. Keim, *Organometalics, 2,* 1983, 594.

[2] W. Levason: Phosphine complexes of transition metals, in F. R. Hartley (ed): S. Patai Series: The Chemistry of Fonctinal Groups: *The Chemistry of Organophosphorus Compounds,* Interscience, New York, pp. 567–641 (1990).

[3] P. W. Glockner, W. Keim, R. F. Mason, U.S. Pat 3 647 914, 1971 (*Chem. Abstr.,* 1971. 75, 88072 g).

[4] W. Keim, F. H. Kowald, R. Goddard, C. Krüger, *Angew. Chem. Int. Ed. Engl., 17,* 1978, 466.

[5] See, for example, D. Matt, N. Sutter-Beydoun, J. P. Brunette, F. Balegroune, D. Grandjean, *Inorg. Chem., 32,* 1993, 3488, and references therein.

[6] D. W. Meek, T. J. Mazanec, *Acc. Chem. Res., 14,* 1981, 266.

[7] F. A. Cotton, B. Hong, *Prog. Inorg. Chem., 40,* 1992, 266.

[8] A. Bader, E. Lindner, *Coord. Chem. Rev., 108,* 1991, 27.

[9] E. M. Miller, B. L. Shaw, *J. Chem. Soc. Dalton Trans.,* 1974, 480.

[10] G. Martín, E. Ocando-Mavarez, A. Osorio, M. Laya, M. Canestrari, *Heteroatom Chem., 3,* 1992, 395.

[11] G. Martín, E. Ocando-Mavarez, *Heteroatom Chem., 2,* 1991, 651.

[12] G. Martin, E. Ocando-Mavarez, A. Andrade, *Phosphorus, Sulfur and Silicon, 77,* 1993, 148.

[13] E. Ocando-Mavarez, G. Martin, A. Andrade, *Heteroatom Chem., 8,* 1997, 91.

[14] E. Ocando-Mavarez, G. Martin, L. Rodriguez, W. Muñoz, *Heteroatom Chem., 8,* 1997, 97.

[15] S. Hietkamp, D. J. Stufkens, K. Vrieze, *J. Organometal. Chem., 122,* 1976, 419.

[16] S. Hietkamp, D. J. Stufkens, K. Vrieze, *J. Organometal. Chem., 134,* 1977, 95.

[17] Y. Alvarado, P. J. Daff, P. J. Perez, M. L. Poveda, R. Sanchez-Delgado, E. Carmona, *Organometallics, 15,* 1996, 2192.

[18] J. L. Herde, J. C. Lambert, C. V. Senoff, *Inorg. Synth., 15,* 1974, 18.

[19] L. M. Haines, E. Singleton, *J. Chem. Soc. Dalton Trans.,* 1972, 1891.