Substitution and Migratory Insertion Reactions of Square-Planar Allenylidene Iridium Complexes†

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A series of (allenylidene)iridium(I) complexes of general composition *trans*-[IrX{=C=C=C(Ph)R}(P*i*Pr$_3$)$_2$] [X = Br (**5**), I (**6**), NCO (**7**, **8**), NCS (**9**, **10**), OH (**11**, **12**), N_3 (**13**, **14**)] was prepared from the corresponding chloro derivatives *trans*-[IrCl{=C=C=C(Ph)R}(P*i*Pr$_3$)$_2$] (**3**, **4**) by salt metathesis. An X-ray crystal structure analysis of **4** (R = Ph) confirmed the almost linear arrangement of the Ir−C−C−C chain. The azido compounds **13** (R = Ph) and **14** (R = *t*Bu) react with CO by migratory insertion of the allenylidene ligand into the Ir−N_3 bond. While the product *trans*-[Ir{C≡C−CR(Ph)N_3}(CO)(P*i*Pr$_3$)$_2$] with R = *t*Bu (**16**) is thermally stable, the related complex with R = Ph (**15**) rearranges slowly in benzene to the metalated acrylonitrile derivative *trans*-[Ir{C(CN)=CPh$_2$}(CO)(P*i*Pr$_3$)$_2$] (**17**) by elimination of N_2. Treatment of the phenolato compound *trans*-[Ir(OPh){=C=C=C(Ph)*t*Bu}(P*i*Pr$_3$)$_2$] (**19**), obtained from the analogous hydroxo derivative **12** and phenol, with CO also proceeds by migratory insertion and affords the functionalized (alkynyl)iridium(I) complex *trans*-[Ir{C≡C−C*t*Bu(Ph)OPh}(CO)(P*i*Pr$_3$)$_2$] (**20**) in excellent yield. The Lewis basicity of the hydroxo compounds **11** and **12** was also illustrated by the reactions with CF_3CO_2H, NEt_3·3HF, and [pyH]BF_4, which gave the substitution products *trans*-[Ir(κ^1-O_2CCF_3){=C=C=C(Ph)*t*Bu}(P*i*Pr$_3$)$_2$] (**21**), *trans*-[IrF(=C=C=CPh$_2$)(P*i*Pr$_3$)$_2$] (**22**), and *trans*-[Ir{=C=C=C(Ph)*t*Bu}(py)(P*i*Pr$_3$)$_2$]BF_4 (**23**), respectively. In methanol solution, both **11** and **12** react by complete fragmentation of 1 equiv of CH_3OH to afford the octahedral (allenyl)dihydridoiridium(III) complexes [IrH_2(CH=C=C(Ph)R}(CO)(P*i*Pr$_3$)$_2$] (**24**, **25**). An unprecedented type of insertion reaction occurs by treating the hydroxo derivatives **11** and **12** with an excess of 1-alkynes R′C≡CH (R′ = Ph, CO_2Me), which leads to the formation of the novel five-coordinate iridium(III) compounds [Ir(C≡CR′)$_2$(η^1-(*E*)-CH=CR′−CH=C=C(Ph)R}(P*i*Pr$_3$)$_2$] (**26**−**29**). From **26**, **27** (R′ = Ph), and CO, the octahedral 1:1 adducts **30** and **31** are formed. The molecular structures of **22** and **26** have been determined by X-ray crystallography.

Introduction

In the search for analogues of the square-planar rhodium complexes *trans*-[RhCl(=C=C=CRR′)(P*i*Pr$_3$)$_2$],[1] we recently reported that the iridium counterpart *trans*-[IrCl(=C=C=CPh$_2$)(P*i*Pr$_3$)$_2$] can be obtained from the dihydrido compound [IrH_2Cl(P*i*Pr$_3$)$_2$] and HC≡CCPh$_2$OH via [IrHCl(C≡CCPh$_2$OH)(P*i*Pr$_3$)$_2$] or the isomer *trans*-[IrCl(=C=CHCPh$_2$OH)(P*i*Pr$_3$)$_2$] as the intermediate.[2] Since allenylidenes such as vinylidenes and the more carbon-rich cumulenylidenes C(=C)$_n$=CRR′ (n = 2, 3)[3] are predicted to be good π-acceptor ligands,[4] it could be anticipated that in square-planar (allenylidene)iridium(I) complexes of the general composition *trans*-[IrCl(=C=C=CRR′)(P*i*Pr$_3$)$_2$] the C_3RR′ unit would exert a strong influence on the ligand in the *trans* position. Hence, we started to study the substitution reactions of the chloro derivatives with the particular aim to replace the chloride not only by other halides but also by pseudohalides such as OCN^- or N_3^- and by hydroxide. It was only recently that we observed that the vinylidene iridium(I) compounds *trans*-[IrX(=C=CRR′)(P*i*Pr$_3$)$_2$] with X = OH and N_3 are useful starting materials for the synthesis of a variety of iridium(I) complexes which are not (or hardly) accessible on other routes.[5]

In this paper we describe our investigations on the reactivity of iridium allenylidenes *trans*-[IrCl{=C=C=C(Ph)R}(P*i*Pr$_3$)$_2$] toward various anionic nucleophiles. Moreover, we illustrate that in the presence of CO the C_3RR′ unit undergoes migratory insertion reactions into both Ir−N and Ir−O bonds, thus generating new functionalized alkynyl groups coordinated to iridium(I). A rather unusual insertion process takes place upon treatment of the hydroxo complexes *trans*-[Ir(OH){=C=C=C(Ph)R}(P*i*Pr$_3$)$_2$] with terminal alkynes, which leads

† Dedicated to Professor R. G. Bergman on the occasion of his 60th birthday.

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(2) Werner, H.; Lass, R. W.; Gevert, O.; Wolf, J. *Organometallics* **1997**, *16*, 4077−4088.

(3) For iridium complexes with carbon-rich cumulenylidenes as ligands see: (a) Lass, R. W.; Steinert, P.; Wolf, J.; Werner, H. *Chem. Eur. J.* **1996**, *2*, 19−23. (b) Ilg, K.; Werner, H. *Angew. Chem.* **2000**, *112*, 1691−1693; *Angew. Chem., Int. Ed.* **2000**, *39*, 1632−1634.

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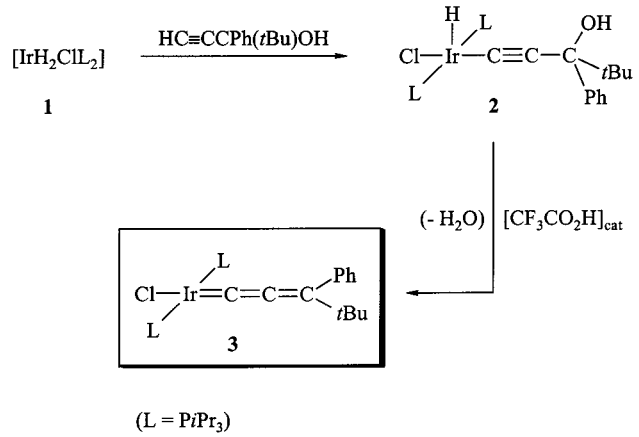
Table 1. Crystallographic Data for 4, 22, and 26

formula	$C_{33}H_{52}ClIrP_2$	$C_{33}H_{52}FIrP_2$	$C_{57}H_{69}IrP_2$
fw	738.34	721.89	1008.26
cryst size, mm^3	0.19 × 0.16 × 0.15	0.19 × 0.14 × 0.11	0.21 × 0.18 × 0.16
cryst syst	monoclinic	monoclinic	triclinic
space group	$P2_1$ (No. 5)	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)
cell dimens determn	25 reflns, $10° < \theta < 15°$	24 reflns,$5° < \theta < 15°$	24 reflns,$5° < \theta < 15°$
a, Å	11.9916(10)	8.6057(13)	13.600(4)
b, Å	11.1053(10)	34.735(3)	13.634(4)
c, Å	12.7777(10)	10.8860(15)	14.994(4)
α, deg			83.92(2)
β, deg	98.658(10)	95.737	66.63(3)
γ, deg			87.23(2)
V, $Å^3$	1682.2(2)	3237.7(7)	2537.8(13)
Z	2	4	2
d_{calc}, $g·cm^{-3}$	1.458	1.481	1.319
temp, K	193(2)	173(2)	193(2)
μ, mm^{-1}	4.162	4.248	2.728
scan method	*ω*/*θ*	*ω*/*θ*	*ω*/*θ*
2*θ*(max), deg	46	47	45
tot. no. of reflns	3704	5131	6946
no. of unique reflns	3534 [*R*(int) = 0.0404]	4604 [*R*(int) = 0.0657]	6598 [*R*(int) = 0.0483]
no. of obsd reflns [$I > 2\sigma(I)$]	3338	2743	5794
no. of reflns used for refinement	3534	4597	6598
no. of params refined	347	346	598
final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0332$, $wR_2 = 0.0833^a$	$R_1 = 0.0661$, $wR_2 = 0.1386^a$	$R_1 = 0.0370$ $wR_2 = 0.0672^a$
R indices (all data)	$R_1 = 0.0368$, $wR_2 = 0.0866^a$	$R_1 = 0.1363$, $wR_2 = 0.1702^a$	$R_1 = 0.0464$, $wR_2 = 0.0718^a$
absolute structure param	0.317(14)		
resid electron density, e $Å^{-3}$	0.624/−0.712	1.173/−1.682	0.620/−1.097

[a] $w^{-1} = 1/[\sigma^2F_o^2 + (0.0636P)^2 + 0.0000P]$ (**4**), $1/[\sigma^2F_o^2 + (0.0750P)^2 + 0.0000P]$ (**22**), $1/[\sigma^2F_o^2 + (0.0160P)^2 + 5.7281P]$ (**26**), where $P = [F_o^2 + 2F_c^2]/3$.

Scheme 1



to the formation of a highly unsaturated C_5 ligand. A few of these results have already been communicated.[6]

Results and Discussion

Preparation of Allenylidene Iridium Complexes by Salt Metathesis. In addition to the previously described chloro compound *trans*-[IrCl(=C=C=CPh_2)-($PiPr_3$)$_2$] (**4**),[2] the structurally related complex **3**, containing one phenyl and one *tert*-butyl group as substituents at the *γ*-carbon atom of the IrC_3 chain, was also prepared (Scheme 1). The procedure to obtain **3** followed the methodology that we had developed for the diphenyl analogue **4**. Treatment of the dihydrido complex **1** with the propargylic alcohol HC≡CCPh(*t*Bu)OH in hexane at −20 °C led to the formation of the iridium(III) derivative **2**, which was isolated as a red solid in 84% yield. Typical features of **2** are the hydride resonance at *δ* −42.44 (i.e., at remarkably high field) in the ^{1}H NMR spectrum and the OH, Ir−H, and C≡C stretching modes at, respectively, 3481, 2300, and 2092 cm^{-1} in the IR spectrum. Similar data have been observed for related five-coordinate hydrido(alkynyl)- and hydrido(diyndiyl)iridium(III) complexes.[2] Since only one signal appears in the ^{31}P NMR spectrum of **2**, we conclude that the two phosphine ligands are *trans* disposed in the basal plane of a square pyramid.

If a solution of **2** in ether is stirred for 3 h at room temperature in the presence of small amounts of trifluoroacetic acid, a quantitative conversion to the allenylidene compound **3** occurs by elimination of water. The IR and NMR spectroscopic data of **3** (which is a red-violet, only moderately air-sensitive solid) are similar to those of **4** and of the analogous rhodium(I) complex *trans*-[RhCl{=C=C=C(Ph)*t*Bu}($PiPr_3$)$_2$].[7] Since in each of the ^{1}H, ^{13}C, and ^{31}P NMR spectra of **4** only one set of signals for the phosphorus, hydrogen, and carbon atoms of the $PiPr_3$ ligands has been observed, we assume that the barrier for rotation around the Ir−C bond is quite small on the NMR time scale.

Attempts to replace the chloro ligand of **3** or **4** by methyl, vinyl, or phenyl using the corresponding organo lithium compound as a substrate failed. If instead of RLi the analogous Grignard reagent RMgX (X = Br or I) reacted with the chloro derivative, a mixture of products was formed, among which the bromo or iodo complexes *trans*-[IrX{=C=C=C(Ph)R}($PiPr_3$)$_2$] (X = Br, I) were the major components. These compounds (illustrated by using **4** as the starting material) are more conveniently prepared by salt metathesis from the

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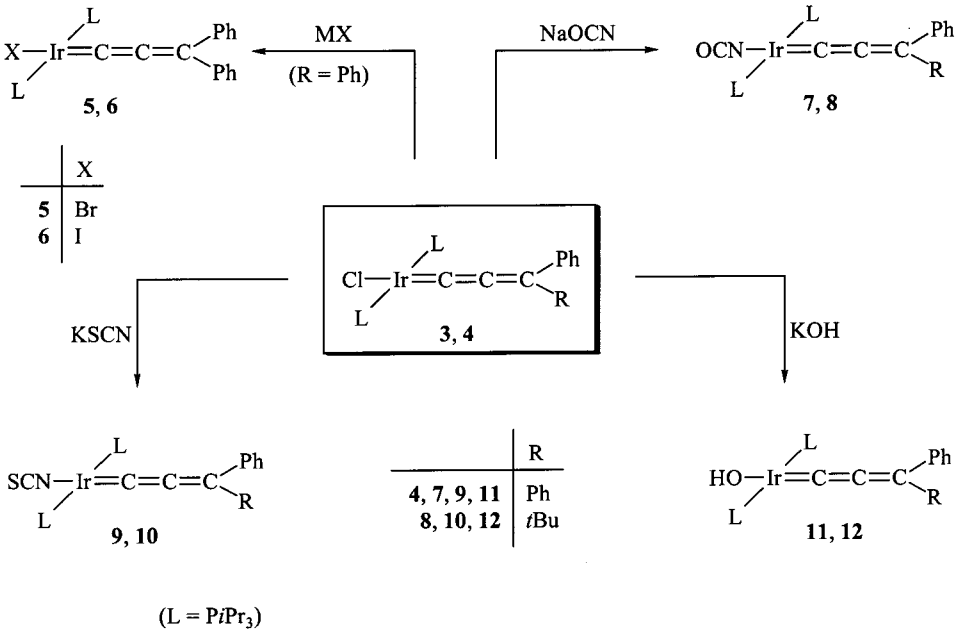
Scheme 2



chloro complex and NaBr or KI, respectively. Both **5** and **6** (see Scheme 2) are deeply colored solids which have been characterized by elemental analyses and IR and NMR spectroscopy. In solution, **5** and even more **6** are less stable than **4**, which is probably due to the weakening of the allenylidene−metal bond by reducing the π-donor capability of the ligand X in *trans* disposition.

Compounds **3** and **4** react not only with alkalimetal halides but also with excess NaOCN and KSCN in acetone at room temperature to give the isocyanato and isothiocyanato complexes **7**−**10** as red or dark red, almost air-stable solids in 86−95% isolated yield. The IR spectra of **7** and **8** display two strong absorptions at around 2230 and 1450 cm^{-1}, which are assigned to the asymmetrical and symmetrical NCO stretching modes. Since it has been established that the symmetrical stretch for *O*-bonded isocyanates appears below 1200 cm^{-1} and that for *N*-bonded NCO ligands in the region between 1300 and 1500 cm^{-1},[8] we conclude that in **7** and **8** an Ir−NCO linkage exists. A similar criterion can be applied regarding the coordination of the NCS ligand in compounds **9** and **10**. Since for *S*-bonded isothiocyanates the asymmetrical NCS stretching mode should be observed at around 2120 cm^{-1} and for the *N*-bonded analogues at around 2070 cm^{-1},[9] the appearance of an infrared band at 2077 cm^{-1} for **9** and at 2080 cm^{-1} for **10** indicates that in both cases the isothiocyanate is linked via the nitrogen atom to iridium(I). In this context we note that the IR spectrum of the Vaska-type complex *trans*-[Ir(NCS)(CO)(PPh_3)$_2$] also indicates an *N*-coordination of the NCS unit.[10]

In contrast to the hydroxorhodium(I) compounds *trans*-[Rh(OH)(=C=C=CRR′)(P*i*Pr$_3$)$_2$], which were prepared by treatment of the corresponding chloro derivatives with KO*t*Bu in a mixture of benzene and *tert*-butyl alcohol,[11] the iridium(I) counterparts **11** and **12** (Scheme 2) were obtained from **3** or **4** and excess KOH in acetone as orange and green microcrystalline solids. The presence of the hydroxo ligand is indicated both by the strong absorption at 3643 cm^{-1} (**11**) or 3648 cm^{-1} (**12**) in the IR and by the broadened singlet at δ 4.25 (**11**) or 3.80 (**12**) in the ^{1}H NMR spectrum. The chemical shifts for the resonances of the allenylidene carbon atoms in the ^{13}C NMR spectrum of **12** are quite similar to those of **3**, which supports the assumption that the *trans* influence of the chloro and the hydroxo ligands is of comparable magnitude.

The synthesis of the azido complexes **13** and **14** follows the route that we have used to obtain the isocyanato and isothiocyanato analogues **7**−**10**. This procedure is equally similar to that for the preparation of the rhodium(I) compounds *trans*-[RhN_3(=C=C=CRR′)(P*i*Pr$_3$)$_2$],[7] *trans*-[RhN_3(CO)(PR_3)$_2$] (R = Ph, Cy),[12] and [$RhN_3(PPh_3)_3$].[13] The most typical spectroscopic data of **13** and **14** are the two low-field signals (both triplets) in the ^{13}C NMR spectra between δ 250 and 205 for the α- and β-carbon atoms of the IrC_3 chain and the intense $\nu(N_3)$ mode in the IR spectra at 2066 cm^{-1} (**13**) and 2078 cm^{-1} (**14**), respectively.

Migratory Insertions of Allenylidene Units into Ir−N and Ir−O Bonds. In acetone, the azido complexes **13** and **14** react quite rapidly with carbon monoxide to afford yellow microcrystalline solids **15** and **16** in 83% and 90% isolated yield. The analytical composition of both **15** and **16** corresponds to that of 1:1 adducts between the corresponding starting material and CO. While in the IR spectra of the products two

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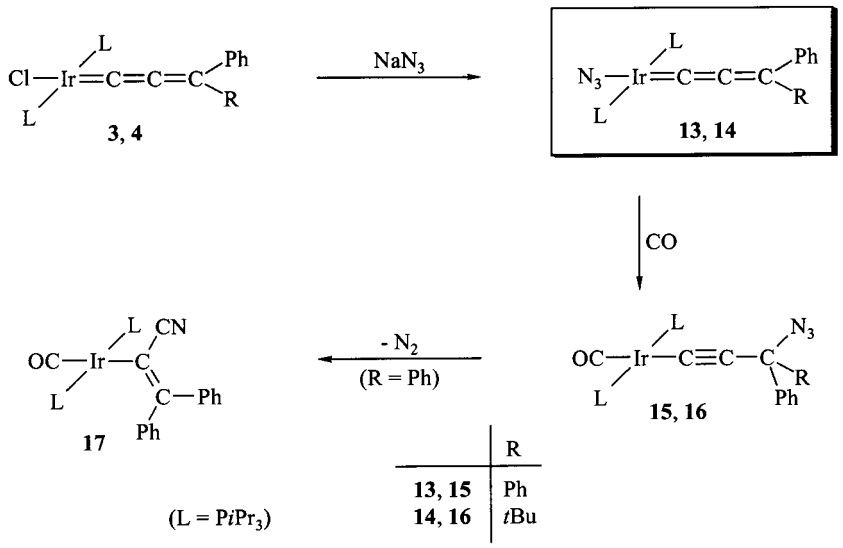
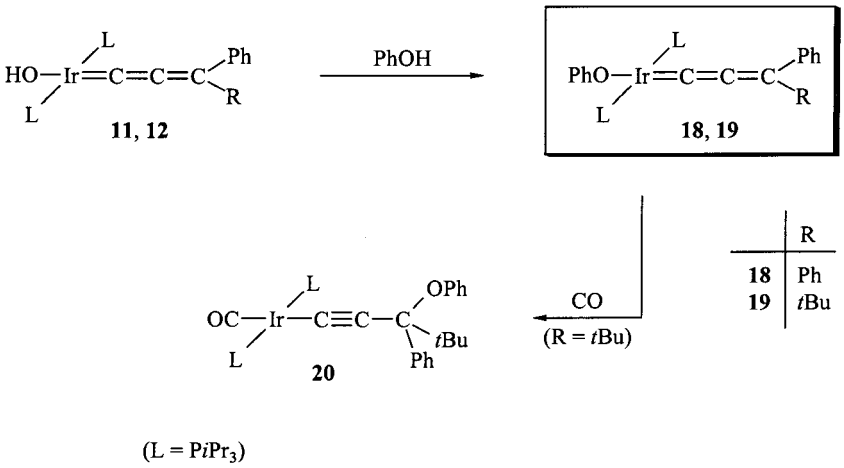
Scheme 3



Scheme 4

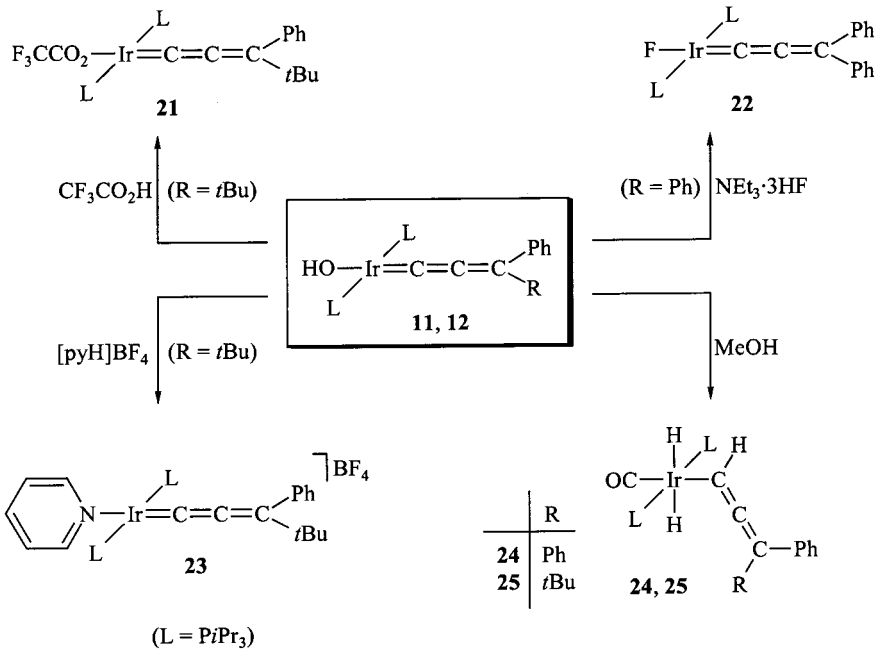


strong absorptions at, respectively, 2098 and 1933 cm^{-1} for **15** and 2104 and 1932 cm^{-1} for **16** are observed, assigned to N_3 and CO stretching modes, the ^{13}C NMR spectra exhibit a triplet resonance at around δ 125−127 and a singlet resonance at around δ 115 for the carbon atoms of an alkynyl group. From these data we conclude (see Scheme 3) that treatment of the azido complexes with CO results in a migration of the N_3^- ligand to the allenylidene unit and that the intact azido group is linked to the γ-carbon atom of the C_3 chain.

The thermal stability of compounds **15** and **16** is remarkably different. While solutions of **16** in benzene can be stirred for 24 h at room temperature without any decomposition or rearrangement, the corresponding diphenyl derivative **15** is more labile and, under the same conditions, slowly reacts to give first an (nonisolated) intermediate and then a new product. According to the IR spectra, taken after 4−6 h, the intermediate contains besides the carbonyl ligand [ν(CO) = 1909 cm^{-1}] an azido group [$\nu(N_3)$ = 2076 cm^{-1}] and a cumulene fragment [ν(C=C=C) = 1862 cm^{-1}]. We therefore assume that in the first step of the thermal reaction of **15** the allenyl complex *trans*-[Ir{C(N_3)=C=CPh_2}(CO)($PiPr_3$)$_2$] is generated by migration of the N_3 unit from the γ-carbon to the α-carbon atom of the C_3 chain. Stirring the benzene solution for 24 h leads to the disappearance of the IR bands of the intermediate and, after evaporation of the solvent and recrystallization from acetone at −78 °C, to the isolation of a yellow solid with the analytical composition of **17** in 90% yield. The IR spectrum of **17** displays instead of three (as for the intermediate) *two* strong absorptions at 2159 and 1937 cm^{-1}, which we assign to CN and CO stretching modes. Since the ^{13}C NMR spectrum exhibits *three* resonances in the region between δ 161 and 126, which all show P,C couplings, we assume that the new product is a four-coordinate carbonyl(vinyl)iridium(I) derivative. We note that a related rhodium(I) complex (with *p*-anisyl instead of phenyl substituents at the β-carbon atom of the vinylic ligand) is known and has been characterized by X-ray crystallography.[7]

In the presence of CO, the phenolato compound **19** behaves similarly to the azido analogue **14**. For the preparation of both **18** and **19**, instead of a salt metathesis of the chloro derivatives **3**, **4**, and NaOR[14] the more convenient method consists in the acid−base reaction of **11** and **12** with phenol (Scheme 4). The reactions are carried out in benzene at room temperature and afford the phenolates **18** and **19** as dark red or brown solids in excellent yield. Under the conditions used for the synthesis, there is no attack of PhOH at the allenylidene unit. The reaction of **19**[15] with CO takes

Scheme 5



place in pentane and gives the insertion product **20** as a yellow, moderately air-sensitive solid in 83% yield. The presence of the functionalized alkynyl ligand is indicated in the ^{13}C NMR spectrum by the appearance of two signals at δ 125.4 (triplet for C_α) and 115.2 (singlet for C_β). Moreover, the elemental analysis and the mass spectrum confirm the supposed composition. The (trifluoroacetato)iridium(I) complex **21**, prepared from the hydroxo compound **12** and CF_3CO_2H in benzene, also reacts with CO, but, in contrast to the analogous reaction of **12** with phenol, in this case no analytically pure product could be isolated.

Reactions of the (Allenylidene)hydroxo Iridium Complexes with Other Acidic Substrates. The ability of the hydroxo compounds **11** and **12** to behave as organometallic Brönsted bases is illustrated not only by the reactions with PhOH and CF_3CO_2H but also by those with NEt_3·3HF and $[pyH]BF_4$ (see Scheme 5). We have recently shown that triethylamine-tris(hydrogen fluoride), which has been used for the first time by Grushin et al. as a versatile fluorinating agent in the chemistry of late transition metals,[16] can be successfully applied for the preparation of rhodium(I) as well as iridium(I) complexes with metal−fluorine bonds.[5,17] Treatment of **11** with NEt_3·3HF in benzene affords, after recrystallization from acetone, the fluoro compound **22** as a red solid in 88% yield. The single

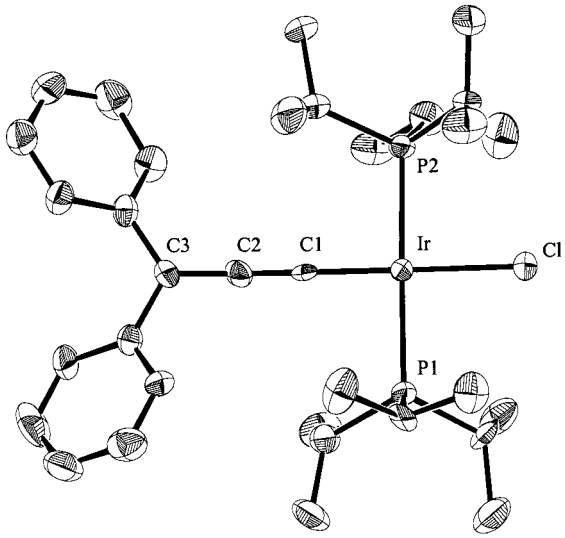


Figure 1. Molecular diagram of compound **4**. Selected bond distances (Å) and angles (deg): Ir−Cl = 2.3649(19), Ir−P1 = 2.344(3), Ir−P2 = 2.340(3), Ir−C1 = 1.862(7), C1−C2 = 1.247(11), C2−C3 = 1.360(11); Cl−Ir−P1 = 89.55-(15), Cl−Ir−P2 = 89.27(15), Cl−Ir−C1 = 178.1(5), P1−Ir−P2 = 178.42(9), P1−Ir−C1 = 90.6(6), P2−Ir−C1 = 90.5(6), Ir−C1−C2 = 178.5(14), C1−C2−C3 = 176.7(14).

resonances in the ^{19}F and ^{31}P NMR spectra of **22** are split into a triplet and a doublet, both due to P,F couplings.

The molecular structure of **22** and, for comparison, also that of the chloro analogue **4** has been determined by X-ray crystallography. The molecular diagrams in Figures 1 and 2 reveal that in both cases the iridium is coordinated in an almost perfect square-planar fashion. The two phosphine ligands are *trans* to each other with an eclipsed conformation along the P−Ir−P axis. The Ir−C1 distance of 1.85(2) Å for **4** and 1.862(7) Å for **22** is slightly shorter than in the carbene complex *trans*-$[IrCl(=CPh_2)(PiPr_3)_2]$ (1.887(5) Å)[18] but somewhat longer than in the corresponding vinylidene derivative *trans*-

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(15) Compound **18** behaves similarly toward CO, but this reaction has not been studied in detail.

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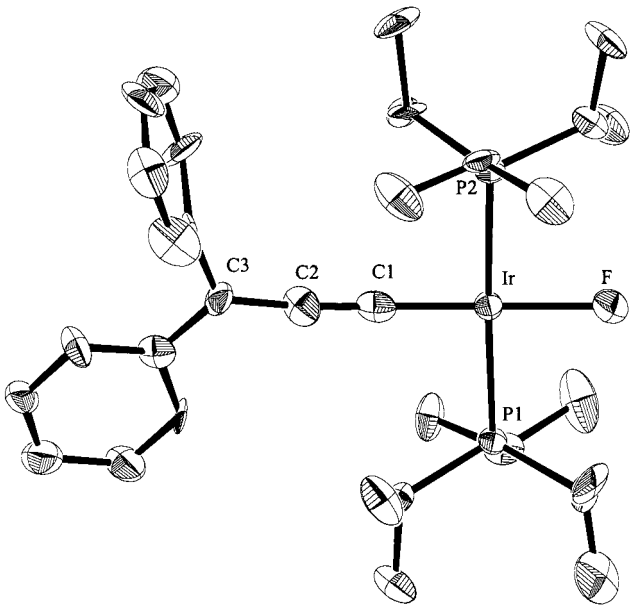

Figure 2. Molecular diagram of compound **22**. Selected bond distances (Å) and angles (deg): Ir−F = 2.015(10), Ir−P1 = 2.317(4), Ir−P2 = 2.326(4), Ir−C1 = 1.85(2), C1−C2 = 1.22(2), C2−C3 = 1.37(2); F−Ir−P1 = 88.5(3), F−Ir−P2 = 89.0(3), F−Ir−C1 = 179.3(6), P1−Ir−P2 = 177.51(16), P1−Ir−C1 = 91.0(5), P2−Ir−C1 = 91.5(5), Ir−C1−C2 = 177.1(17), C1−C2−C3 = 173(2).

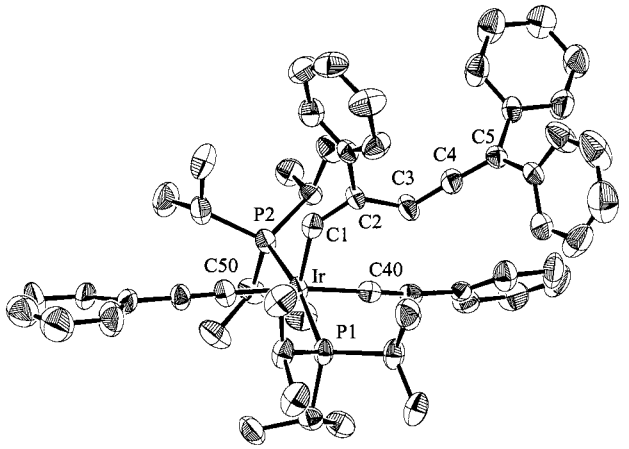

Figure 3. Molecular diagram of compound **26**. Selected bond distances (Å) and angles (deg): Ir−C1 = 1.998(6), Ir−C40 = 2.020(6), Ir−C50 = 2.018(6), Ir−P1 = 2.359(2), Ir−P2 = 2.371(2), C1−C2 = 1.35(1), C2−C3 = 1.46(1), C3−C4 = 1.32(1), C4−C5 = 1.31(1); C1−Ir−C40 = 98.0(2), C1−Ir−C50 = 89.5(2), C1−Ir−P1 = 95.1(2), C1−Ir−P2 = 96.7(2), C40−Ir−C50 = 172.4(3), C40−Ir−P1 = 92.2(2), C40−Ir−P2 = 89.3(2), C50−Ir−P1 = 87.7(2), C50−Ir−P2 = 89.3(2), P1−Ir−P2 = 167.77(6), Ir−C1−C2 = 135.8(5), C1−C2−C3 = 125.0(6), C2−C3−C4 = 127.9(6), C3−C4−C5 = 175.1(6), Ir−C40−C41 = 176.9(5), Ir−C50−C51 = 177.9(6).

[IrCl(=C=CHCO$_2$Me)(P*i*Pr$_3$)$_2$] (1.764(6) Å).[19] This order of bond lengths is in agreement with that found in the chloro rhodium counterparts. The two carbon−carbon distances in the IrC$_3$ chain differ by 0.12−0.15 Å, which indicates that besides the usual bonding description Ir=C=C=C a second zwitterionic resonance structure has to be taken into consideration.[20] The IrC$_3$ chain is nearly linear with only a slight bending at C2 in the case of **22**. We note that the *ipso*-carbon atoms C30 and C40 of the two phenyl groups do not lie in the same plane as the ligand atoms around iridium, the dihedral angle between the best planes [X−Ir−C1−P1−P2] and [C3−C30−C40] being 14(1)° for **4** and 19(2)° for **22**, respectively. There is a small difference in the Ir−P bond distances in **4** and **22**, which we explain by the different electronic influence of the chloro and fluoro ligands.

Under acidic conditions, the OH group of the Brönsted bases *trans*-[Ir(OH){=C=C=C(Ph)R}(P*i*Pr$_3$)$_2$] can also be replaced by neutral ligands. This is exemplified by the preparation of the cationic complex **23** from **12** and [pyH]BF$_4$ (see Scheme 5). The composition of **23**, which was isolated as a red-violet, thermally rather labile solid, was substantiated not only by elemental analysis but also by conductivity measurements and spectroscopic data. The ^{13}C NMR spectrum of **23** exhibits, in contrast to the spectra **4** and **22**, the resonance of the α-carbon atom of the IrC$_3$ unit at significantly lower field than that of the *β*-carbon atom. The acetone derivative *trans*-[Ir(O=CMe$_2$){=C=C=C(Ph)*t*Bu}(P*i*Pr$_3$)$_2$]BF$_4$ seems to be more labile than the pyridine compound **23** since we observed that upon treatment of **12** with HBF$_4$ in acetone, even at −78 °C, only decomposition of the starting material occurs.

Attempts to perform substitution reactions of the hydroxo complexes **11** and **12** in *methanol* as the solvent led to a noteworthy result. After dissolving **11** or **12** in CH$_3$OH at room temperature, in a relatively short period of time a change of color from orange or green to pale brown took place, and, after removal of the solvent and crystallization of the residue from pentane, the carbonyl(dihydro)iridium(III) compounds **24** and **25** (see Scheme 5) were isolated in, respectively, 88% and 91% yield. Apart from the strong *ν*(CO) stretching mode at 1978 cm^{-1} (**24**) and 1972 cm^{-1} (**25**) in the IR spectra, the most typical spectroscopic features of the octahedral complexes are both the hydride resonance at *δ* −9.27 (**24**) and −9.47 (**25**) and the signal for the CH=C=C proton at *δ* 6.53 (**24**) and 6.31 (**25**) in the ^{1}H NMR spectra. The chemical shift of the latter is in good agreement with that of other allenyl transition-metal complexes.[21] Since the NMR spectra display only one single resonance for the Ir−H protons, which is split into a sharp doublet of triplets due to P,H and H,H couplings, and only one signal for the two phosphorus atoms, there is no doubt that the two hydrides as well as the two P*i*Pr$_3$ ligands are in *trans* disposition.

If the reaction of **11** is carried out in CD$_3$OD instead of CH$_3$OH, the tris(deuterio) compound [IrD$_2$(CD=C=CPh$_2$)(CO)(P*i*Pr$_3$)$_2$] **(24-*d*$_3$)** is formed, the ^{1}H NMR spectrum of which does not exhibit a signal around *δ*

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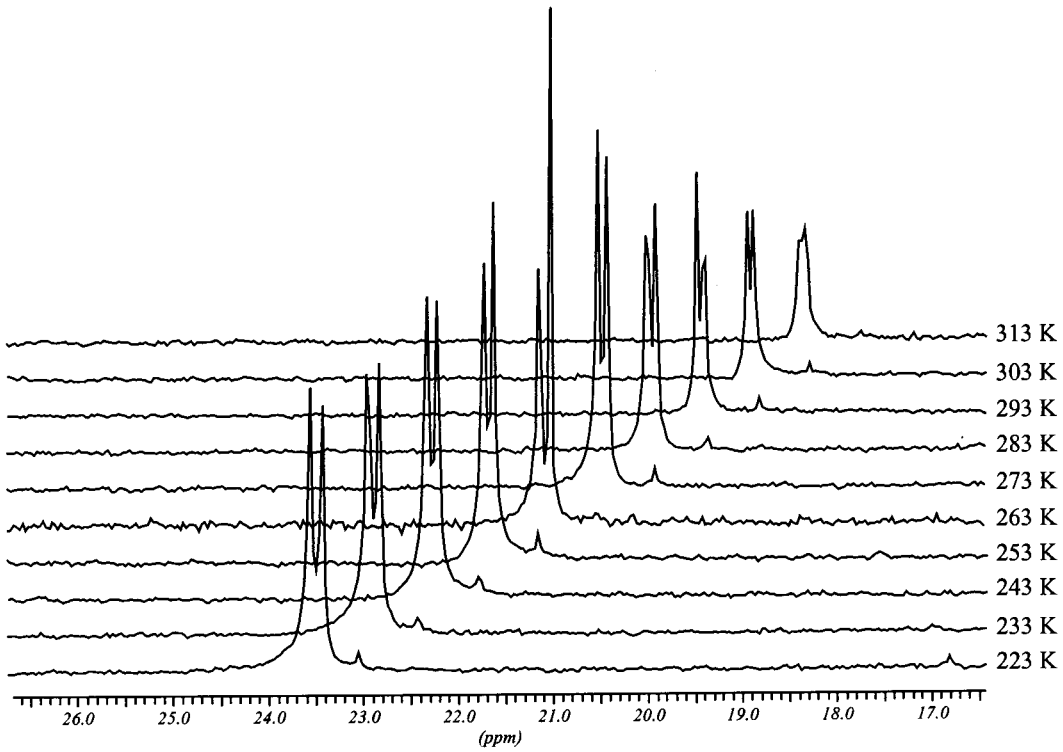
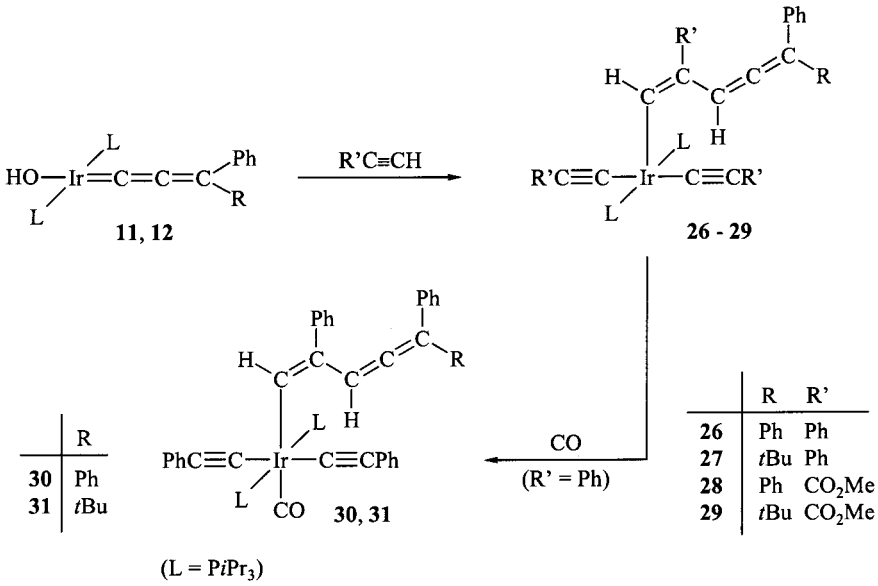


Figure 4. VT ^{31}P NMR spectrum of compound **27** (in toluene-d_8).

Scheme 6



6.5 or in the high-field region. It should be mentioned that there is ample precedence for the generation of a (carbonyl)hydrido complex from a chloro, bromo, or iodo metal precursor and a primary alcohol (or its anion) and that it is generally assumed that (aldehyde)(hydrido)-metal intermediates are involved in this fragmentation process.[22,23] The nearest analogy to the formation of **24** and **25** from **11** and **12**, we are aware of, is the preparation of $[IrH_2(CO)(CH{=}CHPh)(P\mathit{i}Pr_3)_2]$ from *trans*-$[IrCl(=C{=}CHPh)(P\mathit{i}Pr_3)_2]$ and $NaOCH_3$, which affords the vinyl compound in excellent yield.[24]

A New Type of Alkyne Insertion into a Carbon−Iridium Bond. The observation that the (hydroxo)-vinylidene complex *trans*-$[Ir(OH)(=C{=}CHPh)(P\mathit{i}Pr_3)_2]$ reacts with phenylacetylene and methylpropiolate by elimination of water to give the alkynyl derivatives *trans*-$[Ir(C{\equiv}CR)(=C{=}CHPh)(P\mathit{i}Pr_3)_2]$[5] prompted us to study also the reactivity of **11** and **12** toward terminal alkynes. Stirring a solution of **11** or **12** in benzene with a 10-fold excess of the alkyne for 30 min at room temperature leads to a change of color from orange to violet or red and, after chromatographic workup and

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recrystallization from pentane, affords the novel iridium(III) complexes **26**−**29** in 87−92% isolated yield (Scheme 6). The elemental analyses as well as the spectroscopic data of the compounds indicated that not only a substitution of the OH group for a C≡CR unit but also the coordination of a second alkynyl ligand plus the generation of a highly unsaturated C_5 moiety had taken place.

The supposed stereochemistry of the products formed by alkyne insertion has been substantiated by the X-ray crystal structure analysis of **26** (Figure 3). The coordination geometry around the metal center is square-pyramidal with two *trans*-disposed alkynyls and two *trans*-disposed phosphines in the basal plane and the σ-bonded allenylvinyl unit in the apical position. The bond angles of the two axes, P1−Ir−P2 (167.77(6)°) and C40−Ir−C50 (172.4(3)°), deviate somewhat from the ideal value of 180°, which is possibly due to the steric requirements of the C_5 ligand. The Ir−C1 bond lies not exactly perpendicular to the basal plane of the pyramide but is slightly bent toward the carbon atom C50. The distance Ir−C1 (1.998(6) Å) is marginally shorter than the Ir−C40 and Ir−C50 bond lengths (2.020(6) and 2.018(6) Å) but virtually identical to the Ir−C distance in the six-coordinate (vinyl)iridium(III) complex [IrHCl(CH=CH_2)(NCMe)(P*i*Pr_3)$_2$] (1.99(2) Å).[25] The carbon−carbon bond lengths C1−C2, C3−C4, and C4−C5 (1.35(1), 1.32(1), and 1.31(1) Å) are significantly shorter than the distance C2−C3 (1.46(1) Å), which confirms the presence of an allenylvinyl ligand.

The ^{31}P NMR data of compounds **26**−**29** deserve some comment. While the spectra of **26**, **28**, and **29** display at room temperature the expected single resonance, indicating the equivalence of the two phosphine ligands, the spectrum of **27** shows two slightly broadened singlets in close proximity. They probably represent the two central lines of an AB system. At lower temperatures, the two signals sharpen (Figure 4), whereas by increasing the temperature from 293 to 313 K (when decomposition begins to occur) the lines broaden and would presumably coalesce at around 320−330 K. Although we have not done a reliable VT NMR study for **29** (and therefore cannot make any conclusion about the nonrigidity of this compound), we assume that the observed temperature dependence of the ^{31}P NMR spectrum of **27** is due to the linkage of two different substituents at the terminal carbon atom of the C_5 chain. Provided that the rotation around the C−C single bond of the allenylvinyl ligand is slow on the NMR time scale, the two phosphines are stereochemically nonequivalent and thus two separate signals should appear. In contrast to **26**, the ^{1}H and ^{13}C NMR spectra of **27** also display *two* resonances for the PC*H* and the P*C*H nuclei of the isopropyl groups, which supports our assumption about the different environment at the sites of the P*i*Pr_3 ligands.

With regard to the mechanism of formation of the complexes **26**−**29**, the most remarkable feature is that despite the strength of the metal−carbon double bond in the starting materials **11** and **12** a coupling of an alkyne molecule with the C_3 fragment occurs under exceedingly mild conditions. It is conceivable that the insertion reaction is preceded first by the substitution of OH for C≡CR′ followed by the generation of the (hydrido)iridium(III) intermediate [IrH(C≡CR′)$_2${=C=C=C(Ph)R}(P*i*Pr_3)$_2$], which then rearranges to an allenyl unit that undergoes the C−C coupling process. It should be mentioned that in contrast to **11** the related compound *trans*-[RhCl(=C=C=CPh_2)(P*i*Pr_3)$_2$] reacts with phenylacetylene to give, via coupling of the C_3 moiety with the alkyne *and* one of the phosphines, a rhodium(I) complex containing the unusual Wittig-type ylide *i*Pr_3P=CH−C(Ph)=C=C=CPh_2 as a neutral π-bonded ligand.[26] The reaction of **11** with PhC≡CD affords the bis(deuterio) derivative **26**-d_2, the ^{1}H NMR spectrum of which does not exhibit a signal for the IrC*H* or the C*H*=C=CPh_2 proton. From this we conclude that the OH unit (or the eliminated water molecule) is not involved in the formation of the allenylvinyl ligand.

In the presence of carbon monoxide, compounds **26** and **27** do not react by insertion of CO into the Ir−CH bond. Instead, addition of CO to the metal center occurs, and the octahedral (carbonyl)iridium(III) complexes **30** and **31** are formed in excellent yields. Both compounds are significantly more stable in solution than the coordinatively unsaturated precursors **26** and **27**. In complete analogy with **27**, the ^{31}P NMR spectrum of **31** (but not that of **30**) displays two signals at δ −4.0 and −4.2, which confirms that the two phosphine ligands are stereochemically not exactly equivalent. Moreover, the ^{13}C NMR spectrum of **31** exhibits two resonances for the Ir−*C*≡C carbon atoms at δ 86.5 and 80.9, indicating that in contrast to **27** also the two alkynyl groups are different. We assume that due to the increase of the coordination number from five to six the rotation around the metal−vinyl bond is somewhat hindered, and thus a different stereochemical environment of the ligands lying in the basal plane of the octahedron results.

Conclusions

The work presented in this paper illustrates that the (allenylidene)iridium(I) complexes of general composition *trans*-[IrCl{=C=C=C(Ph)R}(P*i*Pr_3)$_2$] (**3**, **4**) offer a rich chemistry indeed. The chloro ligand can be substituted not only by other halides but also by relatives thereof such as OCN^-, SCN^-, or N_3^- and even by OH^-. The noteworthy message is that besides **3** and **4** the corresponding hydroxo compounds *trans*-[Ir(OH){=C=C=C(Ph)R}(P*i*Pr_3)$_2$] (**11**, **12**) can equally be used as starting materials to incorporate anionic *O*-donor, *N*-donor, and *C*-donor ligands into the coordination sphere of iridium. The azido (**13**, **14**) and phenolato (**19**) complexes react with carbon monoxide by migratory insertion of the allenylidene unit into the Ir−N and Ir−O bonds, thus generating functionalized alkynyl ligands. While the insertion product *trans*-[Ir{C≡CCPh(N$_3$)R}(CO)(P*i*Pr_3)$_2$] with R = *t*Bu (**16**) is quite inert, the analogous compound with R = Ph (**15**) reacts under mild conditions by elimination of N_2 to afford the cyano-substituted (vinyl)iridium(I) complex **17**. The hydroxo derivatives **11** and **12** not only undergo acid−base reactions with PhOH, CF_3CO_2H, NEt_3·3HF, and [pyH]-

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BF_4 but also react with methanol by complete fragmentation of the OCH_3 moiety to give the six-coordinate (allenyl)(carbonyl)dihydridoiridium(III) compounds **24** and **25**. An unusual insertion process, for which to the best of our knowledge there is no precedence, takes place upon treatment of the hydroxo complexes **11** and **12** with phenylacetylene and methylpropiolate leading via C−C coupling to a novel σ-bonded C_5 unit. Although some mechanistic details of the reactions of **11** and **12** with various substrates are still unresolved, the results summarized in Schemes 4, 5, and 6 supplement recent discoveries by Milstein[27] and Bergman,[28] which showed that both (hydroxo)- and (alkoxo)iridium(III)—not iridium(I)—compounds are valuable starting materials for carrying out substitution, elimination, and insertion reaction.

Experimental Section

All reactions were carried out under an atmosphere of argon by Schlenk techniques. The starting materials **1**,[29] **4**,[2] and HC≡CCPh(*t*Bu)OH[30] were prepared as described in the literature. NMR spectra were recorded on Bruker AC 200 and Bruker AMX 400 instruments at room temperature. IR spectra were recorded on a Bruker IFS 25 FT-IR and mass spectra on a Finnigan MAT 90 (70 eV) or on a Hewlett-Packard G 1800 GCD instrument. Melting points were measured by DTA. The term vt indicates a virtual triplet, and $N = {}^3J(P,H) + {}^5J(P,H)$ or ${}^1J(P,C) + {}^3J(P,C)$.

Preparation of [IrHCl{C≡CCPh(*t*Bu)OH}(P*i*Pr$_3$)$_2$] (2). A solution of **1** (170 mg, 0.31 mmol) in 20 mL of hexane was treated at −20 °C with HC≡CCPh(*t*Bu)OH (58 mg, 0.31 mmol), which led to a rapid evolution of gas (H_2) and to a change of color from orange-yellow to red. After the reaction mixture was warmed to room temperature, it was stirred for 10 min and then concentrated to ca. 5 mL in vacuo. A red solid precipitated, the crystallization of which was completed by storing the solution at −78 °C. The solid was separated from the mother liquor, washed with small amounts of pentane (0 °C), and dried in vacuo: yield 192 mg (84%); mp 42 °C. Anal. Calcd for $C_{31}H_{58}ClIrOP_2$: C, 50.56; H, 7.94. Found: C, 50.10; H, 7.81. IR (C_6H_6): ν(OH) 3481, ν(IrH) 2300, ν(C≡C) 2092 cm^{-1}. ^{1}H NMR (C_6D_6, 200 MHz): δ 7.90, 7.24 (both m, 5 H, C_6H_5), 3.11 (m, 6 H, PC*H*CH$_3$), 1.20 [br m, 45 H, PCHC*H*$_3$ and C(CH$_3$)$_3$], −42.44 [t, J(P,H) = 11.6 Hz, 1 H, Ir−H]. ^{13}C NMR (C_6D_6, 50.3 MHz): δ 146.2 (s, *ipso*-C of C_6H_5), 128.5, 128.3, 126.6, 126.4 (all s, C_6H_5), 115.6 (s, Ir−C≡*C*), 80.7 [t, J(P,C) = 16.3 Hz, Ir−*C*≡C], 74.0 (s, COH), 39.9 [s, *C*(CH$_3$)$_3$], 26.3 [s, C(*C*H$_3$)$_3$], 25.4 (vt, N = 26.4 Hz, P*C*HCH$_3$), 20.5 (s, PCH*C*H$_3$). ^{31}P NMR (C_6D_6, 162.0 MHz): δ 37.8 (s).

Preparation of *trans*-[IrCl{=C=C=C(Ph)*t*Bu}(P*i*Pr$_3$)$_2$] (3). A solution of **2** (200 mg, 0.27 mmol) in 10 mL of ether was treated with 4 μL of CF_3CO_2H and stirred for 3 h at room temperature. The solvent was evaporated in vacuo, the residue was dissolved in 3 mL of acetone, and the solution was stored for 18 h at −78 °C. A red-violet solid precipitated, which was separated from the mother liquor, washed with small amounts of pentane (0 °C), and dried in vacuo: yield 178 mg (91%); mp 154 °C. Anal. Calcd for $C_{31}H_{56}ClIrP_2$: C, 51.83; H, 7.86. Found: C, 51.99; H, 7.73. MS (70 eV): m/z 718 (M$^+$ for ^{193}Ir). IR (C_6H_6): ν(C=C=C) 1890 cm^{-1}. ^{1}H NMR (C_6D_6, 200 MHz): δ 7.16, 7.04, 6.83 (all m, 5 H, C_6H_5), 2.88 (m, 6 H, PC*H*CH$_3$), 1.27 [dvt, N = 13.5, J(H,H) = 7.3 Hz, 36 H, PCHC*H*$_3$], 1.06 [s, 9 H, C(CH$_3$)$_3$]. ^{13}C NMR (C_6D_6, 100.6 MHz): δ 237.8 [t, J(P,C) = 3.7 Hz, Ir=C=*C*=C], 215.6 [t, J(P,C) = 13.4 Hz, Ir=*C*=C=C], 162.7 (s, *ipso*-C of C_6H_5), 152.8 (s, Ir=C=C=*C*), 126.5, 126.2, 115.6 (all s, C_6H_5), 57.2 [s, *C*(CH$_3$)$_3$], 22.9 (vt, N = 26.9 Hz, P*C*HCH$_3$), 22.5 [s, C(*C*H$_3$)$_3$], 20.0 (s, PCH*C*H$_3$). ^{31}P NMR (C_6D_6, 162.0 MHz): δ 22.4 (s).

Preparation of *trans*-[IrBr(=C=C=CPh$_2$)P*i*Pr$_3$)$_2$] (5). A solution of **4** (52 mg, 0.07 mmol) in 15 mL of acetone was treated with NaBr (35 mg, 0.35 mmol) and stirred for 6 h at room temperature. The solvent was evaporated, the residue was extracted with 30 mL of benzene/pentane (1:5), and the extract was brought to dryness in vacuo. The residue was dissolved in 3 mL of acetone, and the solution was stored for 12 h at −78 °C. Dark red crystals precipitated, which were separated from the mother liquor, washed twice with 1 mL of pentane (0 °C), and dried: yield 46 mg (83%); mp 152 °C dec. Anal. Calcd for $C_{33}H_{52}BrIrP_2$: C, 50.63; H, 6.70. Found: C, 50.51; H, 6.71. IR (C_6H_6): ν(C=C=C) 1866 cm^{-1}. ^{1}H NMR (C_6D_6, 200 MHz): δ 7.99, 7.59, 6.71 (all s, 10 H, C_6H_5), 3.13 (m, 6 H, PC*H*CH$_3$), 1.33 [dvt, N = 13.4, J(H,H) = 7.3 Hz, 36 H, PCHC*H*$_3$]. ^{13}C NMR (C_6D_6, 50.3 MHz): δ 249.8 [t, J(P,C) = 3.8 Hz, Ir=C=*C*=C], 193.9 [t, J(P,C) = 14.0 Hz, Ir=*C*=C=C], 162.8 [t, J(P,C) = 1.9 Hz, *ipso*-C of C_6H_5], 140.0 [t, J(P,C) = 1.9 Hz, Ir=C=C=*C*], 130.0, 126.6, 121.1 (all s, C_6H_5), 23.7 (vt, N = 26.8 Hz, P*C*HCH$_3$), 20.3 (s, PCH*C*H$_3$). ^{31}P NMR (C_6D_6, 81.0 MHz): δ 16.4 (s).

Preparation of *trans*-[IrI(=C=C=CPh$_2$)(P*i*Pr$_3$)$_2$] (6). A solution of **4** (65 mg, 0.09 mmol) in 15 mL of acetone was treated with KI (150 mg, 0.90 mmol) and stirred for 3 h at room temperature. The solvent was evaporated, the residue was extracted with 50 mL of pentane, and the extract was brought to dryness in vacuo. The residue was dissolved in 2 mL of acetone, and the solution was stored for 12 h at −78 °C. Violet crystals precipitated, which were separated from the mother liquor, washed twice with 1 mL of pentane (0 °C), and dried: yield 64 mg (88%); mp 78 °C dec. Anal. Calcd for $C_{33}H_{52}IIrP_2$: C, 47.77; H, 6.32. Found: C, 47.42; H, 6.21. IR (KBr): ν(C=C=C) 1879 cm^{-1}. ^{1}H NMR (C_6D_6, 200 MHz): δ 8.02, 7.59, 6.70 (all s, 10 H, C_6H_5), 3.27 (m, 6 H, PC*H*CH$_3$), 1.33 [dvt, N = 13.5, J(H,H) = 6.7 Hz, 36 H, PCHC*H*$_3$]. ^{13}C NMR (C_6D_6, 50.3 MHz): δ 248.1 [t, J(P,C) = 4.2 Hz, Ir=C=*C*=C], 186.2 [t, J(P,C) = 14.0 Hz, Ir=*C*=C=C], 163.3 (s, *ipso*-C of C_6H_5), 141.4 [t, J(P,C) = 2.4 Hz, Ir=C=C=*C*], 130.1, 126.6, 120.7 (all s, C_6H_5), 24.8 (vt, N = 26.8 Hz, P*C*HCH$_3$), 20.5 (s, PCH*C*H$_3$). ^{31}P NMR (C_6D_6, 81.0 MHz): δ 13.1 (s).

Preparation of *trans*-[Ir(NCO)(=C=C=CPh$_2$)(P*i*Pr$_3$)$_2$] (7). This compound was prepared as described for **6** from **4** (60 mg, 0.08 mmol) and NaOCN (55 mg, 0.80 mmol) in 15 mL of acetone. Dark red solid: yield 53 mg (88%); mp 147 °C dec. Anal. Calcd for $C_{34}H_{52}IrONP_2$: C, 54.82; H, 7.04; N, 1.88. Found: 54.61; H, 6.93; N, 1.77. IR (KBr): $\nu(OCN)_{as}$ 2228, ν(C=C=C) 1882, $\nu(OCN)_{sym}$ 1448 cm^{-1}. ^{1}H NMR (C_6D_6, 400 MHz): δ 7.96, 7.58, 6.71 (all s, 10 H, C_6H_5), 2.76 (m, 6 H, PC*H*CH$_3$), 1.23 [dvt, N = 13.8, J(H,H) = 7.3 Hz, 36 H, PCHC*H*$_3$]. ^{13}C NMR (C_6D_6, 100.6 MHz): δ 250.5 [t, J(P,C) = 3.1 Hz, Ir=C=*C*=C], 212.5 [t, J(P,C) = 14.1 Hz, Ir=*C*=C=C], 162.1 (s, *ipso*-C of C_6H_5), 147.0 (m, NCO), 137.8 [t, J(P,C) = 2.0 Hz, Ir=C=C=*C*], 130.1, 130.0, 126.6 (all s, C_6H_5), 23.8 (vt, N = 25.4 Hz, P*C*HCH$_3$), 20.0 (s, PCH*C*H$_3$). ^{31}P NMR (C_6D_6, 162.0 MHz): δ 20.7 (s).

Preparation of *trans*-[Ir(NCO){=C=C=C(Ph)*t*Bu}(P*i*Pr$_3$)$_2$] (8). This compound was prepared as described for **6** from **3** (64 mg, 0.09 mmol) and NaOCN (59 mg, 0.09 mmol) in 15 mL of acetone. Dark red solid: yield 62 mg (95%); mp 147 °C dec. Anal. Calcd for $C_{32}H_{56}IrNOP_2$: C, 53.02; H, 7.79; N, 1.93. Found: C, 53.32; H, 7.58; N, 1.81. IR (CH_2Cl_2): $\nu(OCN)_{as}$ 2229, ν(C=C=C) 1895, $\nu(OCN)_{sym}$ 1458 cm^{-1}. ^{1}H NMR (C_6D_6,

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200 MHz): δ 7.11, 7.03, 6.81 (all m, 5 H, C_6H_5), 2.58 (m, 6 H, PC*H*CH_3), 1.18 [dvt, N = 14.0 Hz, J(H,H) = 7.0 Hz, 36 H, PCHC*H*$_3$], 1.03 [s, 9 H, C(CH_3)]. ^{13}C NMR (C_6D_6, 50.3 MHz): δ 237.7 [t, J(P,C) = 3.7 Hz, Ir=C=*C*=C], 228.9 [t, J(P,C) = 14.0 Hz, Ir=*C*=C=C], 162.4 (s, *ipso*-C of C_6H_5), 152.3 [t, J(P,C) = 2.4 Hz, Ir=C=C=*C*], 145.5 (m, NCO), 126.6, 126.2, 115.8 (all s, C_6H_5), 56.6 [s, *C*(CH_3)$_3$], 23.5 (vt, N = 26.8 Hz, P*C*HCH$_3$), 22.6 [s, C(*C*H$_3$)$_3$], 19.8 (s, PCH*C*H$_3$). ^{31}P NMR (C_6D_6, 81.0 MHz): δ 24.5 (s).

Preparation of *trans*-[Ir(NCS)(=C=C=CPh$_2$)(P*i*Pr$_3$)$_2$] (9). This compound was prepared as described for **6** from **4** (74 mg, 0.10 mmol) and KSCN (97 mg, 1.00 mmol) in 15 mL of acetone. Dark red solid: yield 65 mg (86%); mp 84 °C. Anal. Calcd for $C_{34}H_{52}IrNP_2S$: C, 53.66; H, 6.89; N, 1.85; S, 4.21. Found: C, 53.40; H, 6.80; N, 1.76; S, 4.00. IR (CH_2Cl_2): ν(SCN)$_{as}$ 2077, ν(C=C=C) 1886, ν(SCN)$_{sym}$ 1463 cm^{-1}. ^{1}H NMR (C_6D_6, 400 MHz): δ 7.94, 7.57, 6.90 (all m, 10 H, C_6H_5), 2.74 (m, 6 H, PC*H*CH_3), 1.23 [dvt, N = 13.8, J(H,H) = 7.0 Hz, 36 H, PCHC*H*$_3$]. ^{13}C NMR (C_6D_6, 100.6 MHz): δ 246.3 [t, J(P,C) = 3.6 Hz, Ir=C=*C*=C], 217.6 [t, J(P,C) = 13.2 Hz, Ir=*C*=C=C], 163.2 (s, NCS), 163.1 (s, *ipso*-C of C_6H_5), 140.5 [t, J(P,C) = 2.5 Hz, Ir=C=C=*C*], 130.1, 127.0, 122.0 (all s, C_6H_5), 24.1 (vt, N = 26.7 Hz, P*C*HCH$_3$), 20.0 (s, PCH*C*H$_3$). ^{31}P NMR (C_6D_6, 162.0 MHz): δ 22.3 (s).

Preparation of *trans*-[Ir(NCS){=C=C=C(Ph)*t*Bu}(P*i*Pr$_3$)$_2$] (10). This compound was prepared as described for **6** from **3** (61 mg, 0.08 mmol) and KSCN (78 mg, 0.80 mmol) in 15 mL of acetone; reaction time 4 h. Red solid: yield 56 mg (90%); mp 151 °C dec. Anal. Calcd for $C_{32}H_{56}IrNP_2S$: C, 51.87; H, 7.62; N, 1.89; S, 4.33. Found: C, 52.02; H, 7.48; N, 1.77; S, 4.43. IR (CH_2Cl_2): ν(SCN)$_{as}$ 2080, ν(C=C=C) 1901, ν(SCN)$_{sym}$ 1462 cm^{-1}. ^{1}H NMR (C_6D_6, 200 MHz): δ 7.06, 6.78 (both m, 5 H, C_6H_5), 2.54 (m, 6 H, PC*H*CH_3), 1.17 [dvt, N = 13.5, J(H,H) = 6.8 Hz, 36 H, PCHC*H*$_3$], 1.00 [s, 9 H, C(CH_3)$_3$]. ^{13}C NMR (C_6D_6, 100.6 MHz): δ 235.0 [t, J(P,C) = 3.0 Hz, Ir=C=*C*=C], 234.6 [t, J(P,C) = 12.2 Hz, Ir=*C*=C=C], 161.7 [t, J(P,C) = 2.4 Hz, Ir=C=C=*C*], 161.9 (s, *ipso*-C of C_6H_5), 156.0 (s, SCN), 126.7, 126.4, 115.9 (all s, C_6H_5), 56.5 [s, *C*(CH_3)$_3$], 23.9 (vt, N = 25.6 Hz, P*C*HCH$_3$), 22.7 [s, *C*(CH_3)$_3$], 19.8 (s, PCH*C*H$_3$). ^{31}P NMR (C_6D_6, 81.0 MHz): δ 25.3 (s).

Preparation of *trans*-[Ir(OH)(=C=C=CPh$_2$)(P*i*Pr$_3$)$_2$] (11). A solution of **4** (70 mg, 0.09 mmol) in 20 mL of acetone was treated with KOH (34 mg, 0.60 mmol) and stirred for 2 h at room temperature. A change of color from red to orange was observed. The solvent was evaporated in vacuo, the residue was extracted with 50 mL of pentane, and the solution was concentrated to ca. 3 mL in vacuo. After the solution was stored for 12 h at −78 °C, orange crystals precipitated, which were separated from the mother liquor, washed with small amounts of pentane (0 °C), and dried: yield 54 mg (84%); mp 104 °C dec. Anal. Calcd for $C_{33}H_{53}IrOP_2$: C, 55.05; H, 7.42. Found: C, 55.53; H, 7.57. IR (C_6H_6): ν(OH) 3643 ν(C=C=C) 1857 cm^{-1}. ^{1}H NMR (C_6D_6, 400 MHz): δ 8.10, 7.60, 6.79 (all m, 10 H, C_6H_5), 4.25 (br s, 1 H, OH), 2.80 (m, 6 H, P*C*HCH$_3$), 1.31 [dvt, N = 13.5, J(H,H) = 7.3 Hz, 36 H, PCHC*H*$_3$]. ^{13}C NMR (C_6D_6, 100.6 MHz): δ 252.8 [t, J(P,C) = 3.1 Hz, Ir=C=*C*=C], 202.7 [t, J(P,C) = 12.7 Hz, Ir=*C*=C=C], 161.9 [t, J(P,C) = 2.5 Hz, *ipso*-C of C_6H_5], 129.8, 125.5, 121.8 (all s, C_6H_5), 22.6 (vt, N = 24.4 Hz, P*C*HCH$_3$), 20.0 (s, PCH*C*H$_3$); signal of Ir=C=C=*C* not exactly located. ^{31}P NMR (C_6D_6, 162.0 MHz): δ 23.5 (s).

Preparation of *trans*-[Ir(OH){=C=C=C(Ph)*t*Bu}(P*i*Pr$_3$)$_2$] (12). This compound was prepared as described for **11** from **3** (80 mg, 0.11 mmol) and KOH (34 mg, 0.60 mmol) in 20 mL of acetone; reaction time 3 h. Green solid: yield 58 mg (75%); mp 63 °C dec. Anal. Calcd for $C_{31}H_{57}IrOP_2$: C, 53.19; H, 8.21. Found: C, 53.12; H, 8.27. IR (C_6H_6): ν(OH) 3480, ν(C=C=C) 1869 cm^{-1}. ^{1}H NMR (C_6D_6, 200 MHz): δ 7.25, 7.02, 6.88 (all m, 5 H, C_6H_5), 3.80 (br s, 1 H, OH), 2.62 (m, 6 H, PC*H*CH_3), 1.26 [dvt, N = 13.5, J(H,H) = 6.8 Hz, 36 H, PCHC*H*$_3$], 1.13 [s, 9 H, C(CH_3)]. ^{13}C NMR (C_6D_6, 50.3 MHz): δ 239.1 [t, J(P,C) = 3.7 Hz, Ir=C=*C*=C], 217.4 [t, J(P,C) = 12.8 Hz, Ir=*C*=C=C], 162.0 (s, *ipso*-C of C_6H_5), 138.7 [t, J(P,C) = 2.4 Hz, Ir=C=C=*C*], 126.5, 125.6, 117.0 (all s, C_6H_5), 54.9 [s, *C*(CH_3)$_3$], 23.1 [s, C(*C*H$_3$)$_3$], 22.2 (vt, N = 25.6 Hz, P*C*HCH$_3$), 19.9 (s, PCH*C*H$_3$). ^{31}P NMR (C_6D_6, 81.0 MHz): δ 27.1 (s).

Preparation of *trans*-[Ir(N$_3$)(=C=C=CPh$_2$)(P*i*Pr$_3$)$_2$] (13). This compound was prepared as described for **6** from **4** (74 mg, 0.10 mmol) and NaN_3 (33 mg, 0.50 mmol) in 15 mL of acetone. Deep red solid: yield 68 mg (91%); mp 114 °C dec. Anal. Calcd for $C_{33}H_{52}IrN_3P_2$: C, 53.21; H, 7.04; N, 5.64. Found: C, 52.93; H, 6.71; N, 5.48. MS (70 eV): m/z 745 (M^+ for ^{193}Ir), 717 [$M^+ - N_2$], 703 [$M^+ - N_3$]. IR (hexane): ν(N_3) 2066, ν(C=C=C) 1870 cm^{-1}. ^{1}H NMR (C_6D_6, 400 MHz): δ 7.97, 7.57, 6.72 (all m, 10 H, C_6H_5), 2.78 (m, 6 H, PC*H*CH_3), 1.26 [dvt, N = 13.5, J(H,H) = 7.0 Hz, 36 H, PCHC*H*$_3$]. ^{13}C NMR (C_6D_6, 100.6 MHz): δ 248.3 [t, J(P,C) = 3.1 Hz, Ir=C=*C*=C], 206.4 [t, J(P,C) = 13.7 Hz, Ir=*C*=C=C], 161.9 (br s, *ipso*-C of C_6H_5), 136.0 (br s, Ir=C=C=*C*), 130.0, 126.5, 121.7 (all s, C_6H_5), 24.0 (vt, N = 25.8 Hz, P*C*HCH$_3$), 19.9 (s, PCH*C*H$_3$). ^{31}P NMR (C_6D_6, 162.0 MHz): δ 23.5 (s).

Preparation of *trans*-[Ir(N$_3$){=C=C=C(Ph)*t*Bu}(P*i*Pr$_3$)$_2$] (14). This compound was prepared as described for **6** from **3** (45 mg, 0.06 mmol) and NaN_3 (40 mg, 0.60 mmol) in 15 mL of acetone; reaction time 1.5 h. Orange solid: yield 43 mg (95%); mp 98 °C dec. Anal. Calcd for $C_{31}H_{56}IrN_3P_2$: C, 51.34; H, 7.79; N, 5.80. Found: C, 51.71; H, 7.61; N, 5.93. IR (CH_2Cl_2): ν(N_3) 2078, ν(C=C=C) 1895 cm^{-1}. ^{1}H NMR (C_6D_6, 200 MHz): δ 7.02, 6.82 (both m, 5 H, C_6H_5), 2.61 (m, 6 H, PC*H*CH_3), 1.21 [dvt, N = 13.5, J(H,H) = 6.8 Hz, 36 H, PCHC*H*$_3$], 1.05 [s, 9 H, C(CH_3)$_3$]. ^{13}C NMR (C_6D_6, 50.3 MHz): δ 235.8 [t, J(P,C) = 4.9 Hz, Ir=C=*C*=C], 222.8 [t, J(P,C) = 14.0 Hz, Ir=*C*=C=C], 162.1 (s, *ipso*-C of C_6H_5), 150.8 (s, Ir=C=C=*C*), 126.6, 126.2, 116.0 (all s, C_6H_5), 52.6 [s, *C*(CH_3)$_3$], 23.7 (vt, N = 25.6 Hz, P*C*HCH$_3$), 22.7 [s, C(*C*H$_3$)$_3$], 19.7 (s, PCH*C*H$_3$). ^{31}P NMR (C_6D_6, 81.0 MHz): δ 27.0 (s).

Preparation of *trans*-[Ir{C≡CC(N$_3$)Ph$_2$}(CO)(P*i*Pr$_3$)$_2$] (15). A slow stream of CO was passed through a solution of **13** (72 mg, 0.10 mmol) in 10 mL of acetone for 15 s at −78 °C. When the solution was warmed to room temperature, a change of color from deep red to orange-yellow occurred. The solution was stirred for 5 min at 20 °C, concentrated to ca. 2 mL in vacuo, and then stored for 24 h at −78 °C. Yellow crystals precipitated, which were separated from the mother liquor, washed with small amounts of acetone (−20 °C), and dried: yield 62 mg (83%); mp 86 °C dec. Anal. Calcd for $C_{34}H_{52}IrN_3OP_2$: C, 52.83; H, 6.78; N, 5.44. Found: C, 52.38; H, 7.00; N, 5.29. IR (hexane): ν(N_3) 2098, ν(CO) 1933 cm^{-1}. ^{1}H NMR (C_6D_6, 400 MHz): δ 7.67, 7.16, 7.06 (all m, 10 H, C_6H_5), 2.59 (m, 6 H, PC*H*CH_3), 1.24 [dvt, N = 13.5, J(H,H) = 7.0 Hz, 36 H, PCHC*H*$_3$]. ^{13}C NMR (C_6D_6, 100.6 MHz): δ 188.0 [t, J(P,C) = 10.2 Hz, Ir−CO], 144.4 (s, *ipso*-C of C_6H_5), 130.8, 128.7, 127.8 (all s, C_6H_5), 127.4 [t, J(P,C) = 4.1 Hz, Ir−*C*≡C−C], 115.0 (br s, Ir−C≡*C*−C), 71.7 (s, Ir−C≡C−*C*), 25.6 (vt, N = 27.7 Hz, P*C*HCH$_3$), 19.8 (s, PCH*C*H$_3$). ^{31}P NMR (C_6D_6, 162.0 MHz): δ 42.4 (s).

Preparation of *trans*-[Ir{C≡CCPh(N$_3$)*t*Bu}(CO)(P*i*Pr$_3$)$_2$] (16). This compound was prepared as described for **15** from **14** (40 mg, 0.06 mmol) and CO in 10 mL of acetone. Yellow solid: yield 39 mg (90%); mp 76 °C dec. Anal. Calcd for $C_{32}H_{56}IrN_3OP_2$: C, 51.04; H, 5.70; N, 5.58. Found: C, 50.78; H, 5.40; N, 5.76. IR (C_6H_6): ν(N_3) 2104, ν(C≡C) 2050, ν(CO) 1932 cm^{-1}. ^{1}H NMR (C_6D_6, 200 MHz): δ 7.72, 7.11 (both m, 5 H, C_6H_5), 2.70 (m, 6 H, PC*H*CH_3), 1.29 [dvt, N = 13.9, J(H,H) = 7.3 Hz, 18 H, PCHC*H*$_3$], 1.27 [dvt, N = 13.2, J(H,H) = 6.6 Hz, 18 H, PCHC*H*$_3$], 1.11 [s, 9 H, C(CH_3)$_3$]. ^{13}C NMR (C_6D_6, 50.3 MHz): δ 187.0 [t, J(P,C) = 11.0 Hz, Ir−CO], 141.1 (s, *ipso*-C of C_6H_5), 129.0, 128.3, 127.1 (all s, C_6H_5), 124.4 [t, J(P,C) = 15.8 Hz, Ir−*C*≡C], 114.9 (s, Ir−C≡*C*), 77.5 (s, Ir−C≡C−*C*), 41.0 [s, *C*(CH_3)$_3$], 26.3 [s, C(*C*H$_3$)$_3$], 26.0 (vt, N = 26.9 Hz, P*C*HCH$_3$), 20.1, 20.0 (both s, PCH*C*H$_3$). ^{31}P NMR (C_6D_6, 81.0 MHz): δ 42.3 (s).

Preparation of *trans*-[Ir{η^1-C(CN)=CPh$_2$}(CO)(P*i*Pr$_3$)$_2$] (17). A solution of **15** (50 mg, 0.06 mmol) in 1 mL of benzene was stirred for 24 h at room temperature. The solvent was evaporated in vacuo, the residue was dissolved in 2 mL of acetone, and the solution was stored for 15 h at −78 °C. Yellow crystals precipitated, which were separated from the mother liquor, washed with small amounts of acetone (0 °C), and dried: yield 43 mg (90%); mp 161 °C dec. Anal. Calcd for $C_{34}H_{52}IrNOP_2$: C,54.82; H, 7.04; N, 1.88. Found: C, 54.71; H, 7.14; N, 1.75. IR (C_6H_6): ν(CN) 2159, ν(CO) 1937 cm^{-1}. ^{1}H NMR (C_6D_6, 400 MHz): δ 8.64, 7.40, 7.35, 7.13 (all m, 10 H, C_6H_5), 2.42 (m, 6 H, PC*H*CH$_3$), 1.30 [dvt, *N* = 14.2, *J*(H,H) = 7.3 Hz, 18 H, PCHC*H*$_3$], 1.03 [dvt, *N* = 13.5, *J*(H,H) = 7.0 Hz, 18 H, PCHC*H*$_3$]. ^{13}C NMR (C_6D_6, 100 MHz): δ 186.0 [t, *J*(P,C) = 11.1 Hz, Ir−CO], 161.3 [t, *J*(P,C) = 5.1 Hz, Ir−C(CN)=*C*], 146.3, 143.4 (both s, *ipso*-C of C_6H_5), 142.4 [t, *J*(P,C) = 12.7 Hz, Ir−*C*(CN)=C], 130.8, 129.3, 128.7, 128.3, 127.4, 127.1 (all s, C_6H_5), 125.9 [t, *J*(P,C) = 2.0 Hz, Ir−C(*C*N)=C], 26.5 (vt, *N* = 27.5 Hz, P*C*HCH$_3$), 20.5, 19.5 (both s, PCH*C*H$_3$). ^{31}P NMR (C_6D_6, 162.0 MHz): δ 32.7 (s).

Preparation of *trans*-[Ir(OPh)(=C=C=CPh$_2$)(P*i*Pr$_3$)$_2$] (18). A solution of **11** (57 mg, 0.08 mmol) in 10 mL of benzene was treated with phenol (7.5 mg, 0.08 mmol) and stirred for 5 min at room temperature. A rapid change of color from orange to red occurred. The solvent was evaporated in vacuo, and the residue extracted with 25 mL of acetone. After the extract was concentrated to ca. 2 mL and then stored for 20 h at −78 °C, dark red crystals precipitated. They were separated from the mother liquor, washed twice with small quantities of pentane (−20 °C), and dried: yield 49 mg (82%); mp 86 °C dec. Anal. Calcd for $C_{39}H_{57}IrOP_2$: C, 58.84; H, 7.22. Found: C, 58.63; H, 7.45. IR (C_6H_6): ν(C=C=C) 1868 cm^{-1}. ^{1}H NMR (C_6D_6, 100.6 MHz): δ 7.98, 7.57, 7.28, 6.78, 6.65, 6.43 (all m, 15 H, C_6H_5), 2.60 (m, 6 H, PC*H*CH$_3$), 1.25 [dvt, *N* = 13.2, *J*(H,H) = 7.0 Hz, 36 H, PCHC*H*$_3$]. ^{13}C NMR (C_6D_6, 100.6 MHz): δ 255.7 [t, *J*(P,C) = 3.6 Hz, Ir=C=*C*=C], 203.6 [t, *J*(P,C) = 13.7 Hz, Ir=*C*=C=C], 169.3 (s, *ipso*-C of OC_6H_5), 162.7 [t, *J*(P,C) = 2.0 Hz, *ipso*-C of C_6H_5), 131.8 [t, *J*(P,C) = 3.1 Hz, Ir=C=C=*C*], 129.7, 128.9, 126.2, 121.8, 121.7, 115.4 (all s, C_6H_5), 23.8 (vt, *N* = 25.8 Hz, P*C*HCH$_3$), 20.2 (s, PCH*C*H$_3$). ^{31}P NMR (C_6D_6, 162.0 MHz): δ 23.3 (s).

Preparation of *trans*-[Ir(OPh){=C=C=C(Ph)*t*Bu}(P*i*Pr$_3$)$_2$] (19). This compound was prepared as described for **18** from **12** (40 mg, 0.06 mmol) and phenol (5.4 mg, 0.06 mmol) in 10 mL of benzene. Brown solid: yield 41 mg (89%); mp 131 °C. Anal. Calcd for $C_{37}H_{61}IrOP_2$: C, 57.26; H, 7.92. Found: C, 57.43; H, 7.80. IR (C_6H_6): ν(C=C=C) 1875 cm^{-1}. ^{1}H NMR (C_6D_6, 200 MHz): δ 7.26, 7.17, 7.03, 6.86, 6.65, 6.48 (all m, 10 H, C_6H_5), 2.44 (m, 6 H, PC*H*CH$_3$), 1.20 [dvt, *N* = 13.4, *J*(H,H) = 6.7 Hz, 36 H, PCHC*H*$_3$], 1.10 [s, 9 H, C(CH$_3$)$_3$]. ^{13}C NMR (C_6D_6, 50.3 MHz): δ 240.8 [t, *J*(P,C) = 3.7 Hz, Ir=C=*C*=C], 219.3 [t, *J*(P,C) = 13.4 Hz, Ir=*C*=C=C], 169.1 (s, *ipso*-C of OC_6H_5), 163.0 [t, *J*(P,C) = 2.4 Hz, Ir=C=C=*C*], 146.5 (s, *ipso*-C of C_6H_5), 129.7, 126.5, 126.0, 121.3, 116.5, 115.0 (all s, C_6H_5), 56.4 [s, *C*(CH$_3$)$_3$], 23.4 (vt, *N* = 24.4 Hz, P*C*HCH$_3$), 23.0 [s, C(*C*H$_3$)$_3$], 20.0 (s, PCH*C*H$_3$). ^{31}P NMR (C_6D_6, 162.0 MHz): δ 27.2 (s).

Preparation of *trans*-[Ir{C≡CCPh(OPh)*t*Bu}(CO)(P*i*Pr$_3$)$_2$] (20). A slow stream of CO was passed through a solution of **19** (45 mg, 0.06 mmol) in 10 mL of pentane for 30 s at −78 °C. After the solution was warmed to room temperature, the solvent was evaporated in vacuo, the residue was dissolved in 2 mL of acetone, and the solution was stored for 18 h at −78 °C. Yellow crystals precipitated, which were separated from the mother liquor, washed with small quantities of pentane (−20 °C), and dried: yield 39 mg (83%); mp 157 °C. Anal. Calcd for $C_{38}H_{61}IrO_2P_2$: C, 56.76; H, 7.65. Found: C, 56.51; H, 7.69. MS (70 eV): *m*/*z* 804 (M^+ for ^{193}Ir), 711 ($M^+ - OC_6H_5$). IR (C_6H_6): ν(CO) 1930 cm^{-1}. ^{1}H NMR (C_6D_6, 400 MHz): δ 7.65, 7.10, 7.05, 6.96, 6.67 (all m, 10 H, C_6H_5), 2.67 (m, 6 H, PC*H*CH$_3$), 1.30 [s, 9 H, C(CH$_3$)$_3$], 1.27, 1.22 [both dvt, *N* = 13.8, *J*(H,H) = 6.8 Hz, 18 H each, PCHC*H*$_3$]. ^{13}C NMR (C_6D_6, 100.6 MHz): δ 186.8 [t, *J*(P,C) = 11.2 Hz, Ir−CO], 157.1 (s, *ipso*-C of C_6H_5), 141.0 (s, *ipso*-C of OC_6H_5), 129.5, 128.6, 128.3, 126.9, 119.6, 118.6 (all s, C_6H_5), 125.4 [t, *J*(P,C) = 15.7 Hz, Ir−*C*≡C], 115.2 (s, Ir−C≡*C*), 86.6 (s, Ir−C≡C−*C*), 41.8 [s, *C*(CH$_3$)$_3$], 26.5 [s, C(*C*H$_3$)$_3$], 26.2 (vt, *N* = 27.5 Hz, P*C*HCH$_3$), 20.3, 20.2 (both s, PCH*C*H$_3$). ^{31}P NMR (C_6D_6, 162.0 MHz): δ 42.1 (s).

Preparation of *trans*-[Ir(κ^1-O$_2$CCF$_3$){=C=C=C(Ph)*t*Bu}(P*i*Pr$_3$)$_2$] (21). A solution of **12** (60 mg, 0.08 mmol) in 10 mL of benzene was treated dropwise with a solution of CF_3CO_2H (6.6 μL, 0.08 mmol) in 1 mL of benzene at room temperature. A rapid change of color from green to red-violet occurred. After the solution was stirred for 5 min at 20 °C and then for 20 min at 40 °C, the solvent was evaporated in vacuo. The oily residue was dissolved in 2 mL of acetone, and the solution was stored for 12 h at −78 °C. Red-violet crystals precipitated, which were separated from the mother liquor, washed with small amounts of pentane (0 °C), and dried: yield 62 mg (91%); mp 106 °C. Anal. Calcd for $C_{33}H_{56}IrO_3P_2$: C, 49.80; H, 7.09. Found: C, 49.49; H, 6.90. IR (KBr): ν(C=C=C) 1902, $\nu(OCO)_{as}$ 1709, $\nu(OCO)_{sym}$ 1457 cm^{-1}. ^{1}H NMR (C_6D_6, 200 MHz): δ 7.04, 6.79 (both m, 5 H, C_6H_5), 2.45 (m, 6 H, PC*H*CH$_3$), 1.21 [dvt, *N* = 13.5, *J*(H,H) = 6.8 Hz, 36 H, PCHC*H*$_3$], 1.01 [s, 9 H, C(CH$_3$)$_3$]. ^{13}C NMR (C_6D_6, 50.3 MHz): δ 235.8 [t, *J*(P,C) = 3.7 Hz, Ir=C=*C*=C], 224.9 [t, *J*(P,C) = 13.4 Hz, Ir=*C*=C=C], 161.8 [t, *J*(P,C) = 2.4 Hz, Ir=C=C=*C*], 160.0 [q, *J*(P,C) = 36.0 Hz, *C*O$_2$CF$_3$], 156.1 (br s, *ipso*-C of C_6H_5), 128.3, 126.6, 116.0 (all s, C_6H_5), 117.7 [q, *J*(F,C) = 291.1 Hz, CO$_2$*C*F$_3$], 56.7 [s, *C*(CH$_3$)$_3$], 23.7 (vt, *N* = 25.6 Hz, P*C*HCH$_3$), 22.8 [s, C(*C*H$_3$)$_3$], 19.9 (s, PCHC*H*$_3$). ^{19}F NMR (C_6D_6, 188.0 MHz): δ −74.5 (s). ^{31}P NMR (C_6D_6, 81.0 MHz): δ 26.8 (s).

Preparation of *trans*-[IrF(=C=C=CPh$_2$)(P*i*Pr$_3$)$_2$] (22). A solution of **11** (69 mg, 0.10 mmol) in 10 mL of benzene was treated with NEt$_3$·3HF (5.2 μL, 0.10 mmol) and stirred for 3 min at room temperature. The solvent was evaporated in vacuo, and the residue was extracted with 50 mL of pentane. The extract was brought to dryness in vacuo, the residue was dissolved in 3 mL of acetone, and the solution was stored for 24 h at −78 °C. Red crystals precipitated, which were separated from the mother liquor, washed with small amounts of pentane (0 °C), and dried: yield 61 mg (88%); mp 89 °C dec. Anal. Calcd for $C_{33}H_{52}FIrP_2$: C, 54.90; H, 7.26. Found: C, 55.09; H, 7.11. IR (CH_2Cl_2): ν(C=C=C) 1872 cm^{-1}. ^{1}H NMR (C_6D_6, 400 MHz): δ 8.03. 7.60, 6.76 (all m, 10 H, C_6H_5), 2.81 (m, 6 H, PC*H*CH$_3$), 1.33 [dvt, *N* = 13.5, *J*(H,H) = 7.0 Hz, 36 H, PCHC*H*$_3$]. ^{13}C NMR (C_6D_6, 100.6 MHz): δ 259.1 (m, Ir=C=*C*=C), 210.0 (m, Ir=*C*=C=C), 163.0 (s, *ipso*-C of C_6H_5), 129.9, 126.1, 122.0 (all s, C_6H_5), 127.3 (m, Ir=C=C=*C*), 23.1 (vt, *N* = 25.4 Hz, P*C*HCH$_3$), 20.1 (s, PCH*C*H$_3$). ^{19}F NMR (C_6D_6, 188.0 MHz): δ −145.3 [t, *J*(P,F) = 20.0 Hz]. ^{31}P NMR (C_6D_6, 162.0 MHz): δ 26.2 [d, *J*(F,P) = 20.3 Hz].

Preparation of *trans*-[Ir(py){=C=C=C(Ph)*t*Bu}(P*i*Pr$_3$)$_2$]BF$_4$ (23). A solution of **12** (70 mg, 0.10 mmol) in 10 mL of acetone was treated at −78 °C with [pyH]BF_4 (17 mg, 0.10 mmol), which led to a change of color from green to red-violet. After the solution was warmed to room temperature, the solvent was evaporated in vacuo, and the residue was suspended in 30 mL of pentane. The suspension was irradiated in an ultrasonic bath for 10 min, which led to the formation of a red-violet solid. This was separated from the mother liquor and dried: yield 79 mg (93%); mp 38 °C dec. Anal. Calcd for $C_{36}H_{61}BF_4IrNP_2$: C, 50.94; H, 7.24; N, 1.65. Found: C, 51.21; H, 7.01; N, 1.58. $\Lambda(CH_3NO_2)$: 64 cm^2 Ω^{-1} mol^{-1}. IR (CH_2Cl_2): ν(C=C=C) 1909 cm^{-1}. ^{1}H NMR (acetone-d_6, 200 MHz): δ 8.21, 8.04, 7.88 (all m, 5 H, NC_5H_5), 7.44−7.23 (m, 5 H, C_6H_5), 2.18 (m, 6 H, PC*H*CH$_3$), 1.20 [dvt, *N* = 14.6, *J*(H,H) = 7.3 Hz, 36 H, PCHC*H*$_3$]. ^{13}C NMR (acetone-d_6, 100.6 MHz): δ 248.4 [t, *J*(P,C) = 14.0 Hz, Ir=*C*=C=C], 228.6 [t, *J*(P,C) = 3.7 Hz, Ir=C=*C*=C], 159.5 (s, *ipso*-C of C_6H_5), 127.8, 127.1, 126.9, 117.0, 116.7 (all s, C_6H_5 and NC_5H_5), 116.8 [t, *J*(P,C) = 3.0 Hz, Ir=

C═C═*C*], 56.7 [s, *C*(CH$_3$)$_3$], 24.7 (vt, N = 26.9 Hz, P*C*HCH$_3$), 23.1 [s, C(*C*H$_3$)$_3$], 19.6 (s, PCH*C*H$_3$). ^{31}P NMR (acetone-d_6, 81.0 MHz): δ 21.6 (s). ^{19}F NMR (acetone-d_6, 188.0 MHz): δ −150.7 (s).

Preparation of [IrH$_2$(CH═C═CPh$_2$)(CO)(P*i*Pr$_3$)$_2$] (24). A solution of **11** (55 mg, 0.08 mmol) in 10 mL of methanol was stirred for 30 min at room temperature. The solvent was evaporated in vacuo, and the residue was suspended in 40 mL of pentane. After the suspension was irradiated for 10 min in an ultrasonic bath, a pale yellow solid was formed, which was separated from the mother liquor and dried: yield 51 mg (88%); mp 28 °C dec. Anal. Calcd for $C_{34}H_{54}IrOP_2$: C, 55.67; H, 7.42. Found: C, 55.89; H. 7.38. IR (KBr): ν(IrH) 2209, ν(CO) 1978, ν(C═C═C) 1885 cm^{-1}. ^{1}H NMR (C_6D_6, 200 MHz): δ 7.53, 7.13 (both m, 10 H, C_6H_5), 6.54 (m, 1 H, HC═C═C), 2.14 (m, 6 H, PC*H*CH$_3$), 1.13 [dvt, N = 13.5, J(H,H) = 6.8 Hz, 36 H, PCHC*H*$_3$], −9.27 [dt, J(P,H) = 13.6, J(H,H) = 3.4 Hz, 2 H, Ir−H]. ^{13}C NMR (C_6D_6, 50.3 MHz): δ 208.1 [t, J(P,C) = 3.0 Hz, HC═*C*═C], 176.1 [t, J(P,C) = 9.7 Hz, Ir−CO], 141.3, 132.1 (both s, *ipso*-C of C_6H_5), 130.1, 129.9, 129.3, 126.6, 125.4, 121.5 (all s, C_6H_5), 98.9 (s, HC═C═*C*), 63.4 [t, J(P,C) = 11.0 Hz, H*C*═C═C], 24.5 (vt, N = 29.3 Hz, P*C*HCH$_3$), 19.0 (s, PCH*C*H$_3$). ^{31}P NMR (C_6D_6, 81.0 MHz): δ 32.8 (s).

Preparation of [IrD$_2$(CD═C═CPh$_2$)(CO)(P*i*Pr$_3$)$_2$] (24-*d*$_3$). This compound was prepared as described for **24** (50 mg, 0.07 mmol) from **11** and 5 mL of CD$_3$OD. Pale yellow solid: yield 44 mg (86%). ^{1}H NMR (C_6D_6, 200 MHz): δ 7.68, 7.52, 7.09 (all m, 10 H, C_6H_5), 2.12 (m, 6 H, PC*H*CH$_3$), 1.13 [dvt, N = 13.1, J(H,H) = 7.3 Hz, 36 H, PCHC*H*$_3$]. ^{31}P NMR (C_6D_6, 81.0 MHz): δ 32.8 (s).

Preparation of [IrH$_2${CH═C═C(Ph)*t*Bu}(CO)(P*i*Pr$_3$)$_2$] (25). This compound was prepared as described for **24** from **12** (80 mg, 0.11 mmol) and 10 mL of methanol. Pale yellow solid: yield 75 mg (91%): mp 72 °C dec. Anal. Calcd for $C_{32}H_{59}IrOP_2$: C, 53.83; H, 8.33. Found: C, 54.08; H, 8.11. IR (KBr): ν(IrH) 2053, ν(CO) 1972, ν(C═C═C) 1764 cm^{-1}. ^{1}H NMR (C_6D_6, 400 MHz): δ 7.27, 7.12, 7.02 (all m, 5 H, C_6H_5), 6.31 (m, 1 H, HC═C═C), 2.16 (m, 6 H, PC*H*CH$_3$), 1.30 [s, 9 H, C(CH$_3$)$_3$], 1.18, 1.09 [both dvt, N = 13.7, J(H,H) = 7.6 Hz, 18 H, PCHC*H*$_3$], −9.47 [dt, J(P,H) = 13.8, J(H,H) = 4.6 Hz, 2 H, Ir−H]. ^{13}C NMR (C_6D_6, 100.6 MHz): δ 207.5 [t, J(P,C) = 3.0 Hz, HC═*C*═C], 176.5 [t, J(P,C) = 9.2 Hz, Ir−CO], 142.0 (s, *ipso*-C of C_6H_5), 130.4, 127.6, 125.0 (all s, C_6H_5), 102.7 (s, HC═C═*C*), 63.3 [t, J(P,C) = 11.2 Hz, H*C*═C═C], 50.8 [s, *C*(CH$_3$)$_3$], 31.7 [s, C(*C*H$_3$)$_3$], 24.5 (vt, N = 29.3 Hz, P*C*HCH$_3$), 19.0 (s, PCH*C*H$_3$). ^{31}P NMR (C_6D_6, 81.0 MHz): δ 33.0 (s).

Preparation of [Ir(C≡CPh)$_2${η^1-(*E*)-CH═CPhCH═C═CPh$_2$}(P*i*Pr$_3$)$_2$] (26). A solution of **11** (55 mg, 0.08 mmol) in 10 mL of benzene was treated with an excess of phenylacetylene (81 μL, 0.80 mmol) and stirred for 30 min at room temperature. A change of color from orange to deep violet occurred. The solvent was evaporated in vacuo, the residue was dissolved in 1 mL of benzene, and the solution was chromatographed on Al_2O_3 (neutral, acitivity grade V, height of column 5 cm). With pentane, a violet fraction was eluted, which was brought to dryness in vacuo. Recrystallization from pentane at −78 °C gave violet crystals, which were separated from the mother liquor and dried: yield 70 mg (87%); mp 53 °C. Anal. Calcd for $C_{57}H_{69}IrP_2$: C, 67.90; H, 6.90. Found: C, 68.01; H, 7.04. IR (C_6H_6): ν(C≡C) 2078, 2076 cm^{-1}. ^{1}H NMR (C_6D_6, 400 MHz): δ 9.36 (s, 1 H, HC═C═C), 7.93 (br s, 1 H, IrCH), 7.63, 7.46, 7.34, 7.23, 7.15−6.93, 6.74 (all m, 25 H, C_6H_5), 3.27 (m, 6 H, PC*H*CH$_3$), 1.32 [dvt, N = 13.2, J(H,H) = 6.6 Hz, 18 H, PCHC*H*$_3$], 1.27 [dvt, N = 13.2, J(H,H) = 7.0 Hz, 18 H, PCHC*H*$_3$]. ^{13}C NMR (C_6D_6, 100.6 MHz): δ 211.6 (s, HC═*C*═C), 177.3 [t, J(P,C) = 4.0 Hz, Ir−CH═*C*], 153.3, 148.5, 143.5, 138.4 (all s, *ipso*-C of C_6H_5), 132.9, 132.6, 131.3, 130.4, 128.8, 128.6, 128.4, 128.3, 127.9, 127.6, 126.8, 126.1 (all s, C_6H_5), 119.3 [t, J(P,C) = 12.2 Hz, Ir−*C*≡CPh], 115.3 [t, J(P,C) = 4.1 Hz, Ir−C≡*C*Ph], 111.4 (s, HC═C═*C*), 104.5 [t, J(P,C) = 8.1 Hz, IrCH], 100.9 (s, H*C*═C═C), 24.6 (vt, N = 26.4 Hz, P*C*HCH$_3$), 20.4, 20.2 (both s, PCH*C*H$_3$). ^{31}P NMR (C_6D_6, 162.0 MHz): δ 13.0 (s).

Preparation of [Ir(C≡CPh)$_2${η^1-(*E*)-CD═CPhCD═C═CPh$_2$}(P*i*Pr$_3$)$_2$] (26-*d*$_2$). This compound was prepared as described for **26** from **11** (42 mg, 0.06 mmol) and excess PhC≡CD (60 μL, 0.60 mmol). Violet solid: yield 51 mg (85%). ^{1}H NMR (C_6D_6, 200 MHz): δ 7.70, (all m, 25 H, C_6H_5), 3.26 (m, 6 H, PC*H*CH$_3$), 1.29 (m, 36 H, PCHC*H*$_3$). ^{31}P NMR (C_6D_6, 81.0 MHz): δ 13.5 (s).

Preparation of [Ir(C≡CPh)$_2${η^1-(*E*)-CH═CPhCH═C═C(Ph)*t*Bu}(P*i*Pr$_3$)$_2$] (27). This compound was prepared as described for **26** from **12** (38 mg, 0.05 mmol) and excess phenylacetylene (50 μL, 0.50 mmol). Violet solid: yield 48 mg (91%); mp 121 °C dec. Anal. Calcd for $C_{55}H_{73}IrP_2$: C, 66.84; H, 7.44. Found: C, 66.59; H, 7.54. IR (KBr): ν(C≡C) 2084, 2071, ν(C═C═C) 1874 cm^{-1}. ^{1}H NMR (C_6D_6, 200 MHz): δ 8.80 (s, 1 H, HC═C═C), 7.52 (br s, 1 H, IrCH), 7.66, 7.44, 7.21, 7.05 (all m, 2 OH, C_6H_5), 3.26, 3.17 (both m, 3 H each, PC*H*CH$_3$), 1.31, 1.17 (both m, 18 H each, PCHC*H*$_3$), 1.09 [s, 9 H, C(CH$_3$)$_3$]. ^{13}C NMR (C_6D_6, 100.6 MHz): δ 211.8 (s, HC═*C*═C), 144.9, 139.4 (both s, *ipso*-C of C_6H_5), 133.9 [t, J(P,C) = 4.1 Hz, Ir−CH═*C*], 128. 3, 128.0, 127.8, 127.1, 125.9, 125.1, 122.6 (all s, C_6H_5), 115.8 (s, Ir−C≡*C*), 101.1 [t, J(P,C) = 8.1 Hz, IrCH], 99.3 (s, H*C*═C═C), 97.4 (s, HC═C═*C*), 53.3 [s, *C*(CH$_3$)$_3$], 30.1 [s, C(*C*H$_3$)$_3$], 24.3, 22.6 (both m, P*C*HCH$_3$), 20.0, 19.8 (both s, PCH*C*H$_3$), signal of Ir*C*≡C not exactly located. ^{31}P NMR (C_6D_6, 81.0 MHz): δ 13.0, 12.9 (both s).

Preparation of [Ir(C≡CCO$_2$Me)$_2${η^1-(*E*)-CH═C(CO$_2$Me)-CH═CPh$_2$}(P*i*Pr$_3$)$_2$] (28). This compound was prepared as described for **26** from **10** (57 mg, 0.08 mmol) and excess methylpropiolate (50 μL, 0.80 mmol). Red-orange solid: yield 71 mg (89%); mp 62 °C dec. Anal. Calcd for $C_{45}H_{63}IrO_6P_2$: C, 56.65; H, 6.66. Found: C, 56.95; H, 6.51. IR (C_6H_6): ν(C≡C) 2084, ν(OCO)$_{as}$ = 1686, ν(OCO)$_{sym}$ = 1431 cm^{-1}. ^{1}H NMR (C_6D_6, 400 MHz): δ 9.40 (s, 1 H, HC═C═C), 8.63 (br s, 1 H, IrCH), 7.80, 7.24, 7.11 (all m, 10 H, C_6H_5), 3.41 (s, 6 H, CO$_2$CH$_3$), 3.33 (s, 3 H, CO$_2$CH$_3$), 3.11 (m, 6 H, PC*H*CH$_3$), 1.13 [dvt, N = 14.0, J(H,H) = 7.1 Hz, 36 H, PCHC*H*$_3$]. ^{13}C NMR (C_6D_6, 100.6 MHz): δ 211.4 (s, HC═*C*═C), 162.8, 154.5 (both s, CO$_2$CH$_3$), 138.7 (s, *ipso*-C of C_6H_5), 129.5, 128.5, 126.8 (all s, C_6H_5), 126.4 [t, J(P,C) = 4.1 Hz, Ir−C≡*C*], 123.5 [t, J(P,C) = 7.1 Hz, Ir−*C*H═C], 111.4 (s, HC═C═*C*), 94.2 (s, H*C*═C═C), 51.4, 51.3 (both s, CO$_2$CH$_3$), 25.1 (vt, N = 27.3 Hz, P*C*HCH$_3$), 19.9 (s, PCH*C*H$_3$), signals for Ir−CH═*C* and Ir−*C*≡C not exactly located. ^{31}P NMR (C_6D_6, 162.0 MHz): δ 16.9 (s).

Preparation of [Ir(C≡CCO$_2$Me)$_2${η^1-(*E*)-CH═C(CO$_2$Me)-CH═C═C(Ph)*t*Bu}(P*i*Pr$_3$)$_2$] (29). This compound was prepared as described for **26** from **12** (34 mg, 0.05 mmol) and excess methylpropiolate (60 μL, 0.67 mmol). Red-orange solid: yield 42 mg (92%); mp 98 °C. Anal. Calcd for $C_{43}H_{67}IrO_6P_2$: C, 55.29; H, 7.23. Found: C, 54.97; H, 7.21. IR (KBr): ν(C≡C) 2081, ν(OCO)$_{as}$ = 1684, ν(OCO)$_{sym}$ = 1457 cm^{-1}. ^{1}H NMR (C_6D_6, 400 MHz): δ 9.02 (s, 1 H, HC═C═C), 8.11 (br s, 1 H, IrCH), 7.57, 7.22, 7.13 (all m, 5 H, C_6H_5), 3.43 (br s, 9 H, CO$_2$CH$_3$), 3.08 (m, 6 H, PC*H*CH$_3$), 1.39 [s, 9 H, C(CH$_3$)$_3$], 1.13 (m, 36 H, PCHC*H*$_3$). ^{13}C NMR (CD_2Cl_2, 50.3 MHz): δ 206.2 (s, HC═*C*═C), 163.6, 154.6 (both s, CO$_2$CH$_3$), 138.9 (s, *ipso*-C of C_6H_5), 129.7, 128.6, 127.7 (all s, C_6H_5), 126.7 [t, J(P,C) = 3.7 Hz, Ir-*C*H═C], 126.1 (br s, Ir−CH═*C*), 121.6 [t, J(P,C) = 4.2 Hz, Ir−*C*≡C], 119.9 (br s, Ir−C≡*C*), 114.3 (s, HC═C═C), 91.8 (s, HC═C═*C*), 66.4 [s, *C*(CH$_3$)$_3$], 51.9, 51.4 (both s, CO$_2$CH$_3$), 30.1 [s, C(*C*H$_3$)$_3$], 25.0 (vt, N = 26.8 Hz, PCH*C*H$_3$), 19.9, 19.8 (both s, PCH*C*H$_3$). ^{31}P NMR (C_6D_6, 162.0 MHz): δ 16.3 (s).

Preparation of [Ir(C≡CPh)$_2${η^1-(*E*)-CH═CPhCH═C═CPh$_2$}(CO)(P*i*Pr$_3$)$_2$] (30). A slow stream of CO was passed through a solution of **26** (30 mg, 0.03 mmol) in 5 mL of benzene for 15 s at room temperature. A change of color from violet to light yellow occurred. After the solution was stirred for 5 min, the solvent was evaporated in vacuo. The oily residue was dissolved in 1 mL of pentane and the solution stored for 6 h at −78 °C. A pale yellow solid precipitated, which was

separated from the mother liquor and dried: yield 28 mg (93%); mp 136 °C dec. Anal. Calcd for $C_{58}H_{69}IrOP_2$: C, 67.22; H, 6.71. Found: C, 67.53; H, 6.66. IR (CH_2Cl_2): ν(C≡C) 2114, ν(CO) 2031, ν(C=C=C) 1936 cm^{-1}. ^1H NMR (C_6D_6, 200 MHz): δ 9.51 (s, 1 H, HC=C=C), 8.15 [t, J(P,H) = 3.5 Hz, 1 H, IrCH], 7.65, 7.42, 7.0 (all m, 25 H, C_6H_5), 2.89 (m, 6 H, PC*H*CH_3), 1.42 [dvt, N = 14.3, J(H,H) = 6.0 Hz, 18 H, PCHC*H*$_3$], 1.27 [dvt, N = 13.5, J(H,H) = 6.6 Hz, 18 H, PCHC*H*$_3$]. ^{13}C NMR (C_6D_6, 50.3 MHz): δ 210.6 (s, HC=*C*=C), 172.0 [t, J(P,C) = 12.7 Hz, Ir−CO], 147.7 (s, *ipso*-C of C_6H_5), 142.7 [t, J(P,C) = 3.6 Hz, Ir−CH=*C*], 135.4 [t, J(P,C) = 12 Hz, Ir−*C*H=C], 132.0, 131.1, 131.0, 129.5, 129.4, 126.7, 125.9, 125.6, 125.5 (all s, C_6H_5), 112.6 (s, Ir−C≡*C*), 110.9 (s, H*C*=C=C), 107.4 (s, Ir−C≡*C*), 101.9 (s, HC=C=*C*), 86.4 [t, J(P,C) = 12.2 Hz, Ir−*C*≡C], 80.4 [t, J(P,C) = 11.0 Hz, Ir−*C*≡C], 24.9 (vt, N = 28.0 Hz, P*C*HCH$_3$), 20.2, 19.6 (both s, PCH*C*H$_3$). ^{31}P NMR (C_6D_6, 81.0 MHz): δ −3.8 (s).

Preparation of [Ir(C≡CPh)$_2$\{η^1-(*E*)-CH=CPhCH=C=C-(Ph)*t*Bu\}(CO)(P*i*Pr$_3$)$_2$] (31). This compound was prepared as described for **30** from **27** (50 mg, 0.05 mmol) and CO in 10 mL of benzene/pentane (1:1). Pale yellow solid: yield 47 mg (92%); mp 136 °C dec. Anal. Calcd for $C_{56}H_{73}IrOP_2$: C, 66.81; H, 7.24. Found: C, 67.53; H, 6.66. MS (70 eV): m/z 1017 (M^+). IR (CH_2Cl_2): ν(C≡C) 2115, ν(CO) 2027, ν(C=C=C) 1928 cm^{-1}. ^1H NMR (C_6D_6, 200 MHz): δ 8.97 (s, 1 H, HC=C=C), 7.78 [t, J(P,H) = 2.9 Hz, IrCH], 7.64, 7.50, 7.39−7.19, 7.10−6.94 (all m, 20 H, C_6H_5), 2.94, 2.74 (both m, 3 H each, PC*H*CH_3), 1.30 [dvt, N = 13.5, J(H,H) = 6.6 Hz, 36 H, PCHC*H*$_3$], 1.13 [s, 9 H, C(CH$_3$)$_3$]. ^{13}C NMR (C_6D_6, 50.3 MHz): δ 205.0 (s, HC=*C*=C), 171.8 [t, J(P,C) = 7.3 Hz, Ir−CO], 148.7 (s, *ipso*-C of C_6H_5), 143.9 [t, J(P,C) = 3.7 Hz, Ir−CH=*C*], 131.1, 131.0, 130.0, 129.6, 126.4, 125.7, 125.5, 125.4 (all s, C_6H_5), 115.5 (s, H*C*=C=C), 112.4, 107.3, 100.3 (all s, Ir−C≡*C* and HC=C=*C*), 86.5 [t, J(P,C) = 12.2 Hz, Ir−*C*≡C], 80.9 [t, J(P,C) = 11.0 Hz, Ir−*C*≡C], 67.9 [s, *C*(CH$_3$)$_3$], 34.8 [s, C(*C*H$_3$)$_3$], 24.9 (m, PCHCH$_3$), 20.3, 20.2 (both s, PCH*C*H$_3$). ^{31}P NMR (C_6D_6, 81.0 MHz): δ −4.0, −4.2 (both s).

X-ray Structural Determination of Compounds 4, 22, and 26. Single crystals of **4** were grown by cooling a solution in ether to −60 °C, those of **22** by cooling a solution in acetone to −60 °C, and those of **26** by cooling a solution in ether to 5 °C. The data were collected on an Enraf-Nonius CAD4 diffractometer using monochromated Mo Kα radiation (λ = 0.71073 Å). Crystal data were corrected by Lorentz and polarization effects, and empirical absorption corrections were applied (Ψ-scan method, minimum transmission 61.25% (**4**), 90% (**22**), 84.03% (**26**)). The structures were solved by direct methods (SHELXS-97).[31] Atomic coordinates and anisotropic thermal parameters of non-hydrogen atoms were refined by full-matrix least squares on F^2 (SHELXL-97).[32] The positions of all hydrogen atoms were calculated according to ideal geometry and refined using the riding method.

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Supporting Information Available: Tables of crystal data and refinement parameters, bond lengths and angles, and positional and thermal parameters for **4**, **22**, and **26**. This material is available free of charge via the Internet at http://pubs.acs.org.

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