Preparation of hydrido(vinyl)iridium(III) complexes from functionalized olefins by C—H activation[1]

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Abstract: The four-coordinate iridium(I) precursor *trans*-[IrCl(N_2)(PPh_3)$_2$] (**1**) reacts with functionalized olefins RCH=C(R′)C(O)R″ by displacement of the dinitrogen ligand and oxidative addition of the C—H bond to the metal center to give six-coordinate hydrido(vinyl)iridium(III) complexes [IrH(Cl){κ^2(*C*,*O*)-C(R)=C(R′)C(R″)=O}(PPh_3)$_2$] (**2**–**12**) in good to excellent yields. The reaction of [IrH(Cl){κ^2(*C*,*O*)-CH=CHC(Me)=O}(PPh_3)$_2$] (**2**) with $AgClO_4$ affords the cationic compound [IrH{κ^2(*C*,*O*)-CH=CHC(Me)=O}(PPh_3)$_2$]ClO_4 (**15**), which in solution equilibrates with the uncharged isomers [IrH($OClO_3$){κ^2(*C*,*O*)-CH=CHC(Me)=O}(PPh_3)$_2$] (**15a** and **15b**). In contrast, five-coordinate [IrH{κ^2-(*C*,*O*)-CH=CHC(Et)=O}(PPh_3)$_2$]ClO_4 (**16**), prepared from **3** and $AgClO_4$, is stable and undergoes addition reactions with CO, PPh_3, C_2H_4, $CH_3C{\equiv}CH$, MeCN, and PhCN to give the six-coordinate complexes [IrH(L){κ^2(*C*,*O*)-CH=CHC-(Et)=O}(PPh_3)$_2$]ClO_4 (**17**–**22**). The neutral hydrido(thiolato) compound [IrH(SPh){κ^2(*C*,*O*)-CH=CHC(Et)=O}(PPh_3)$_2$] (**23**) was obtained on treatment of **21** with NaSPh.

Key words: iridium, C—H activation, hydrido complexes, vinyl complexes, phosphine complexes.

Résumé : Le précurseur tétracoordiné de l'iridium(I), *trans*-[IrCl(N_2)(PPh_3)$_2$] (**1**), réagit avec les oléfines fonctionnalisées RCH=C(R′)C(O)R″ par déplacement du ligand diazote et par addition oxydante de la liaison C—H du centre métallique pour conduire à la formation des complexes hexacoordinés hydrido(vinyl)iridium(III) [IrH(Cl){κ^2(*C*,*O*)-C(R)=C(R′)C(R″)=O}(PPh_3)$_2$] (**2**–**12**) avec de bons rendements. La réaction du [IrH(Cl){κ^2(*C*,*O*)-CH=CHC(Me)=O}(PPh_3)$_2$] (**2**) avec du $AgClO_4$ conduit à la formation du composés cationique [IrH{κ^2(*C*,*O*)-CH=CHC(Me)=O}(PPh_3)$_2$]ClO_4 (**15**) qui s'équilibre en solution avec formation des isomères non chargés [IrH($OClO_3$){κ^2(*C*,*O*)-CH=CHC(Me)=O}(PPh_3)$_2$] (**15a** and **15b**). Par opposition, le composé pentacoordiné [IrH{κ^2(*C*,*O*)-CH=CHC(Et)=O}(PPh_3)$_2$]ClO_4 (**16**) qui a été préparé à partir du composé **3** et de $AgClO_4$ est stable et il donne des réactions d'additions avec le CO, le PPh_3, le C_2H_4, le $CH_3C{\equiv}CH$, le MeCn et le PhCN pour conduire à la formation de complexes hexacoordinés [IrH(L){κ^2(*C*,*O*)-CH=CHC(Et)=O}(PPh_3)$_2$]ClO_4 (**17**–**22**). Le traitement du composé **21** avec du NaSPh conduit à la formation du composé neutre [IrH(SPh){κ^2(*C*,*O*)-CH=CHC(Et)=O}(PPh_3)$_2$] (**23**).

Mots clés : iridium, activation de C—H, complexes hydrido, complexes de vinyle, complexes de phosphine.

[Traduit par la Rédaction]

Introduction

As part of our investigations on the reactivity of low-valent iridium complexes containing alkenes and alkynes as ligands, we reported (1) that upon low-temperature UV irradiation in toluene the four-coordinate ethene derivative *trans*-[IrCl(C_2H_4)(P-*i*-Pr_3)$_2$] partly rearranges to the five-coordinate hydrido(vinyl) isomer [IrH(Cl)($CH{=}CH_2$)(P-*i*-Pr_3)$_2$]. This compound is thermodynamically unstable and on warming to room temperature reconverts to the starting material. If, however, instead of the ethene complex *trans*-[IrCl(C_2H_4)(P-*i*-Pr_3)$_2$] the related methyl acrylate and dimethyl fumarate derivatives *trans*-[IrCl($CH_2{=}CHCO_2Me$)(P-*i*-Pr_3)$_2$] and *trans*-[IrCl{(*E*)-$CH(CO_2Me){=}CH(CO_2Me)$}(P-*i*-Pr_3)$_2$] are used as the precursors, UV irradiation in benzene leads to a quantitative conversion to the six-coordinate isomers [IrH(Cl){κ^2(*C*,*O*)-C(R)=CH(OMe)=O}(P-*i*-Pr_3)$_2$] in which the hydrido(vinyl)iridium moiety is stabilized by an additional linkage of one C=O group to the metal center (2).

The present paper describes a synthetic protocol for a series of neutral and cationic hydrido(vinyl)iridium(III) complexes with Ir(PPh_3)$_2$ as a building block in which the substituted vinyl group also behaves as a bidentate ligand. Due to this coordination mode, the order of thermodynamic stability [Ir](H)(CH=CHR) < [Ir](η^2-CH_2=CHR), found by Bergman (3) and Perutz (4) and their co-workers for [Ir] = (η^5-C_5Me_5)Ir(PMe_3) and (η^5-C_5H_5)Ir(C_2H_4), is reversed and the hydrido(vinyl) compounds can be isolated as stable enti-

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This paper is dedicated to Professor Arthur J. Carty, in recognition of his manifold and important contributions to organometallic chemistry.

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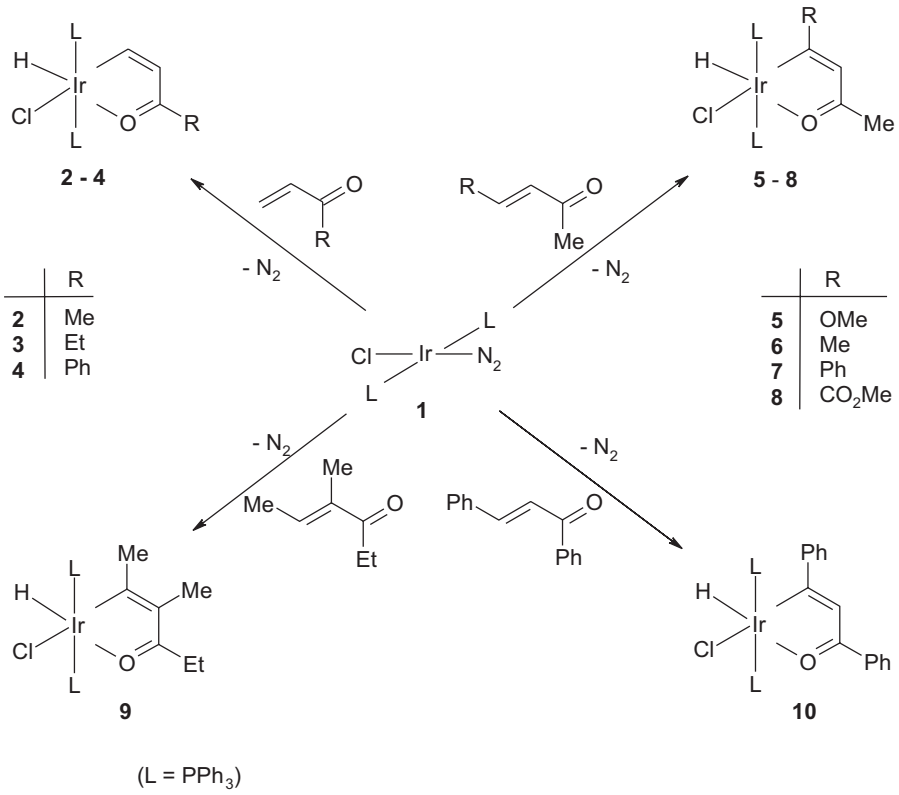
Scheme 1.



ties. Some preliminary results related to this study have already been communicated (5).

Results and discussion

The dinitrogen complex *trans*-[IrCl(N_2)(PPh_3)$_2$] (**1**), prepared by Collman and Kang (6) from *trans*-[IrCl(CO)(PPh_3)$_2$] and benzoyl azide, reacts in benzene with the Michael acceptors CH_2=CHC(O)R (R = Me, Et, Ph) to give the six-coordinate hydrido(vinyl)iridium(III) compounds **2**–**4** in about 80%–90% yield (Scheme 1). Although the displacement of the dinitrogen ligand proceeds slowly at room temperature, attempts to detect the olefin species *trans*-[IrCl{η^2-CH_2=CHC(R)=O}(PPh_3)$_2$], supposed to be generated in one of the initial steps of the reaction, by NMR spectroscopy failed. Nevertheless, we assume that these compounds are formed as intermediates but presumably are short-lived and react by intramolecular C—H activation to give the thermodynamically more stable products. In this context we note that recently Esteruelas, Oro, and co-workers (7) reported the preparation of the four-coordinate iridium(I) complex [Ir(κ^2-acac){η^2-CH_2=CHC(O)Me}(PCy_3)] from [Ir(κ^2-acac)(C_8H_{14})(PCy_3)] and methyl(vinyl) ketone, which is stable and upon heating rearranges to a mixture of two six-coordinate hydrido(vinyl)iridium(III) stereoisomers.

The hydrido(vinyl) complexes **2**–**4** are yellow or orange solids, which are not air-sensitive and readily soluble in common polar organic solvents. A characteristic feature in the IR spectra of **2**–**4** is the ν(C=O) stretching mode at 1525–1550 cm^{-1}, which is shifted by ca. 120–150 cm^{-1} to lower wavenumbers compared with the free ketones. Since this shift is consistent with a coordination of the carbonyl group to the metal center, an octahedral geometry for compounds **2**–**4** (as shown in Scheme 1) can be assumed. The ^{1}H NMR spectra of **2**–**4** display two doublets at about δ 9.60 and 6.20 (for **2** and **3**) and δ 9.97 and 6.86 (for **4**), which in agreement with results by Nesmeyanov et al. (8) and one of us (9) are assigned to the vinylic protons in α and β positions. For the hydrido ligand, there appears in the high-field region a triplet resonance at, respectively, δ –22.42 (for **2**), –22.55 (for **3**), and –21.88 (for **4**), which is split into a triplet owing to ^{1}H–^{31}P coupling. Since the chemical shift of these signals is quite similar to that of the bis(triisopropylphosphine) complex [IrH(Cl){κ^2(*C*,*O*)-$C(CO_2Me)$=CHC(OMe)=O}(P-*i*-Pr_3)$_2$], which has been characterized crystallographically (10), we assume that the hydrido ligand is trans to the oxygen and not to the carbon atom of the chelate ring. The observation of only one signal in the ^{31}P NMR spectra of **2**–**4** confirms that the phosphine ligands are trans disposed. The ^{13}C NMR spectrum of **2** displays the signals for the vinyl carbon atoms at δ 197.3 and 133.1 ppm. Due to the cis disposition of the α-C atom and the PPh_3 groups, the signal at δ 197.3 ppm is split into a triplet, while the resonance at δ 133.1 ppm appears as a singlet.

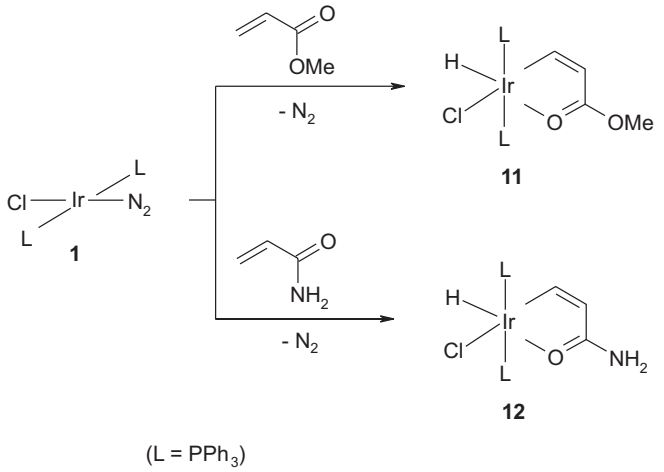
The starting material **1** not only reacts with the ketones CH_2=CHC(O)R (R = Me, Et, Ph), but also with the related derivatives RCH=CHC(O)Me (R = OMe, Me, Ph, CO_2Me), MeCH=C(Me)C(O)Et, and PhCH=CHC(O)Ph to give the corresponding hydrido(vinyl)iridium(III) complexes **5**–**10** in good to excellent yields. These reactions are considerably slower than those leading to **2**–**4**, and thus the corresponding reaction mixture has to be stirred for 18 h at 80 °C in toluene. In contrast to the conditions employed to obtain **2**–**7**, for the preparation of **8**–**10** an excess of the olefinic sub-

strate has to be used. If the dinitrogen complex **1** was treated with an equimolar amount of MeCH=C(Me)C(O)Et, the carbonyl iridium(I) compound *trans*-[IrCl(CO)(PPh_3)$_2$] (11) is generated as the dominant product. With regard to the formation of **8** from **1** and MeC(O)CH=$CHCO_2$Me, the remarkable feature is that the oxidative addition of the C—H bond adjacent to the CO_2Me functionality occurs exclusively. Moreover, it is worth mentioning that upon treatment of **1** with PhCH=CHC(O)Ph only the activation of the olefinic C—H and not that of an aromatic C—H bond is observed. The reactivity of **1** is thus different to that of the bis(triisopropylphosphine)iridium(I) derivative *trans*-[IrCl(C_8H_{14})(P-*i*-Pr_3)$_2$], which reacts with PhCH=CHC(O)Ph to give a 1:1 mixture of the two isomers [IrH(Cl){κ^2(*C*,*O*)-C(Ph)=CHC(Ph)=O}(P-*i*-Pr_3)$_2$] and [IrH(Cl){κ^2(*C*,*O*)-C_6H_4C(CH=CHPh)=O}(P-*i*-Pr_3)$_2$] (12). The ^{13}C NMR spectrum of **10** displays a triplet resonance at δ 215.0 (with ^2J(PC) = 6.1 Hz), which appears at a similar chemical shift (δ 209.4, ^2J(PC) = 5.3 Hz) as that of [IrH(Cl){κ^2(*C*,*O*)-C(Ph)=CHC(Ph)=O}(P-*i*-Pr_3)$_2$] (12) and thus supports the proposed structure.

Similarly to the Michael acceptors used for the preparation of **2**–**10**, methyl acrylate and acrylic acidamide also react with the dinitrogen compound **1** to afford the air-stable hydrido(vinyl) complexes **11** and **12** in 66% and 89% yield, respectively (Scheme 2). The IR spectrum of **12** shows the band for the ν(C=O) stretching mode at 1555 cm^{-1}, which is at nearly the same position as for **2** and **3**. In the ^{1}H NMR spectra of **11** and **12**, the hydride resonance appears at δ –25.07 (**11**) and δ –24.19 (**12**) and is significantly shifted upfield compared with **2**–**10**. We assume that this shift is due to the stronger electron-donating effect of the OMe and NH_2 functionalities compared with that of the alkyl and phenyl groups. The reaction of **1** with acrylonitrile does not lead to a stable iridium(I) or iridium(III) complex, but yields a pale yellow solid, which, according to the IR spectrum, presumably is a polymer with terminal CH_2CN and $CH(CH_3)CN$ groups (13).

To obtain a coordinatively unsaturated hydrido(vinyl)iridium(III) compound, considered to be a potential precursor for addition/insertion reactions, we attempted to eliminate the chloro ligand from **2** by using $AgPF_6$ and $AgClO_4$, respectively. The reaction of **2** with $AgPF_6$ in dichloromethane is quite rapid at room temperature and yields, after separation of AgCl and chromatographic workup of the solution, a brownish solid that owing to the ^{1}H and ^{31}P NMR spectra consists mainly (ca. 90%) of the expected compound [IrH{κ^2(*C*,*O*)-CH=CHC(Me)=O}(PPh_3)$_2$]PF_6 (**13**). Attempts to separate the by-products by fractional crystallization or repeated column chromatography failed. Typical spectroscopic data of **13** are the ^{1}H NMR resonances for the vinylic protons at δ 9.73 and 6.02 (see **2**: δ 9.58 and 6.18), the hydride signal at δ –21.38 (see **2**: δ –22.42), and the singlet in the ^{31}P NMR spectrum at δ 21.7 (see **2**: δ 14.7). Treatment of **2** with $AgPF_6$ in the presence of CO gave the cationic six-coordinate hydrido(vinyl)iridium(III) carbonyl **14** (Scheme 3) for which a correct elemental analysis was obtained. The IR spectrum of **14** (being an off-white, air-stable solid) displays a strong band for the CO ligand at 2060 cm^{-1} and a medium-to-strong absorption for the ν(C=O) stretching mode at 1580 cm^{-1}. The latter is shifted by 30 cm^{-1} to higher

Scheme 2.



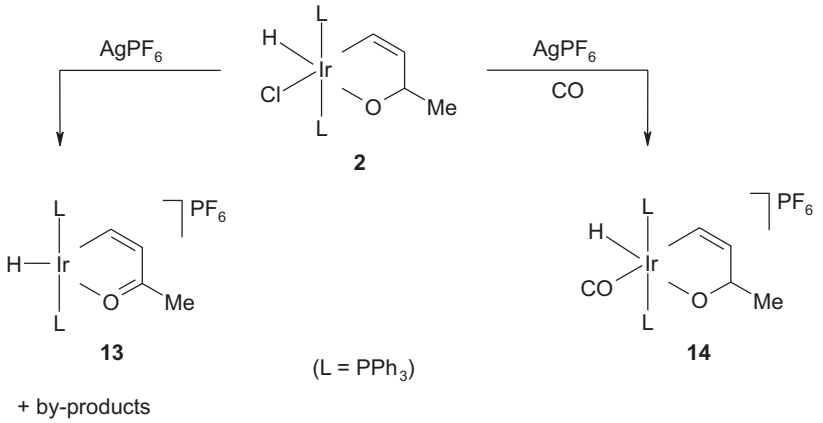
wavenumbers compared with the coordinatively unsaturated compound **13**. The hydride signal appears in the ^{1}H NMR spectrum of **14** at δ –19.09 and is thus shifted by ca. 2.3 ppm to lower fields compared with **13**.

The reaction of **2** with $AgClO_4$ was carried out under similar conditions as with $AgPF_6$ and resulted in the formation of the hydrido(vinyl) complex **15** (Scheme 4). While the poor solubility of **15** in hydrocarbons is in agreement with the formulation as an ionic compound analogous to **13**, the molar conductivity (Λ) in nitromethane (36 $cm^2\ \Omega^{-1}\ mol^{-1}$) is considerably lower than expected for a 1:1 electrolyte (see **14**: Λ = 65 $cm^2\ \Omega^{-1}\ mol^{-1}$). The ^{31}P NMR spectrum of **15** in $CDCl_3$ at room temperature shows two singlets at δ 23.1 (sharp) and δ 17.5 (broad), which after decoupling change into doublets. In CD_2Cl_2 at –80 °C three doublets appear, two of which collapse to a broadened resonance after increasing the temperature to 0 °C. Although these results have to be interpreted with caution, we assume that in solution an equilibrium between the cationic species **15** and the uncharged isomers **15a** and **15b** exists. It is well-known that not only for iridium (14), but also for various other transition metals (15), the perchlorate anion can behave as a weakly coordinated ("noninnocent") ligand that is readily replaced by better nucleophiles. It should be mentioned that the ^{1}H NMR spectrum of the product obtained from **2** and $AgClO_4$ also displays two sets of signals for the =CH, CH_3, and IrH protons, which is in agreement with the equilibrium between **15** and the nonionic species **15a** and **15b**.

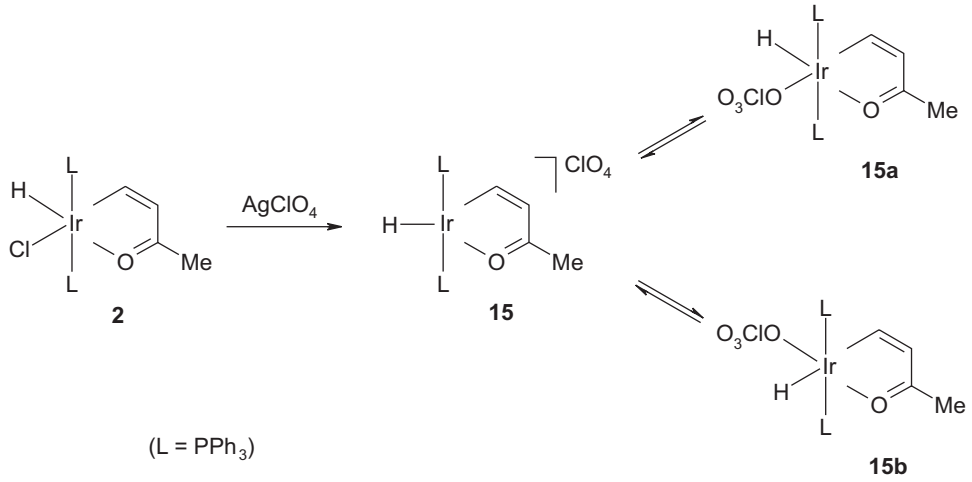
Similarly to **2**, the corresponding iridium(III) counterpart **3** reacts with $AgClO_4$ in CH_2Cl_2 to give the cationic complex **16** (Scheme 5), which, however, appears to have no tendency to coordinate the perchlorate anion. The ^{1}H as well as the ^{31}P NMR spectrum of **16** shows only one sharp resonance for the IrH proton and the phosphine ligands, respectively, and these resonances do not broaden or split into two signals by decreasing the temperature. We note that the chemical shifts of the signals observed in the ^{1}H and ^{31}P NMR spectra of **16** are nearly identical to those assigned to the cation of **15**, and thus we are convinced that the proposed structure with a five-coordinate metal center is correct.

The open coordination site in the cation of **16** can easily be occupied by CO, PPh_3, ethene, propyne, acetonitrile, and

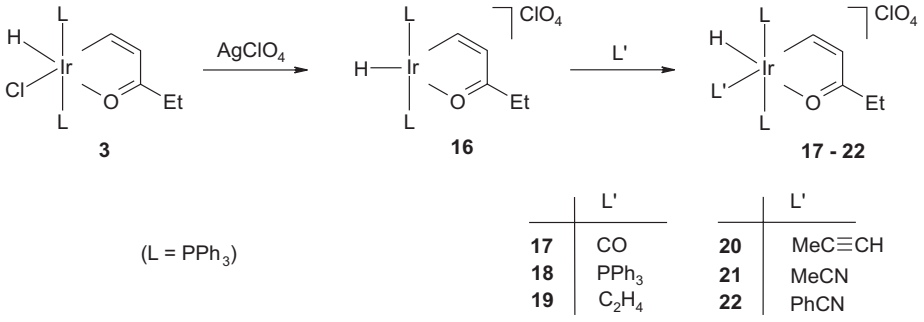
Scheme 3.



Scheme 4.



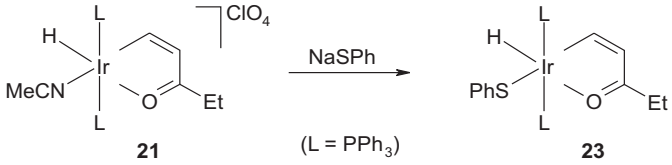
Scheme 5.



benzonitrile. With the exception of **19**, the related hydrido(vinyl)iridium(III) compounds **17**, **18**, and **20**–**22** are exceedingly stable and decompose between 112 (**20**) and 179 °C (**21**). Owing to the ionic nature, they are soluble in acetone, nitromethane, CH_2Cl_2, and $CHCl_3$, but almost insoluble in benzene and other hydrocarbons. Conductivity measurements confirm the presence of 1:1 electrolytes. The ethene complex **19** is only stable under a C_2H_4 atmosphere and has been characterized by ^1H and ^{31}P NMR spectroscopy. Typical features of **19** are the ^1H NMR signal for the ethene protons at δ 3.55 (triplet with $^3J(PH)$ = 3.1 Hz) and the singlet resonance for the ^{31}P NMR nuclei at δ 13.9, the latter being shifted upfield by 8.6 ppm compared with **16**. When we attempted to remove the volatiles and isolate compound **19**, the precursor **16** was regenerated.

In contrast to **19**, the analogous propyne complex **20** is rather inert and neither undergoes an insertion of the alkyne ligand into the Ir—H bond nor rearranges to the vinylidene isomer [IrH(=C=CHCH$_3$){κ^2(*C*,*O*)-CH=CHC(Et)=O}(PPh$_3$)$_2$]ClO$_4$ (16). However, compound **20**, as well as the nitrile iridium(III) analogues **21** and **22**, smoothly react with CO to afford the corresponding carbonyl complex **17**.

Scheme 6.



The acetonitrile ligand in **21** can not only be replaced by CO but also by thiophenolate. The reaction of **21** with NaSPh in THF proceeds slowly at room temperature and gives the neutral hydrido(thiophenolato) complex **23** in 78% yield (Scheme 6). **23** is an orange air-stable solid that has been characterized by elemental analysis and spectroscopic techniques. Attempts to also displace the acetonitrile ligand in **21** by methyl xanthogenate, K[SC(S)OMe], led to the formation of a mixture of compounds that could not be separated by fractional crystallization or column chromatography.

In summarizing, the present work has shown that, provided the olefinic substrate RCH=CHR′ possesses a substituent R′ such as C(O)R, C(O)NH_2, or C(O)OMe, the reaction of the starting material *trans*-[IrCl(N_2)(PPh_3)$_2$] (**1**) with RCH=CHR′ leads preferentially to the hydrido(vinyl)-iridium(III) complexes **2**–**12**. These compounds are remarkably stable and neither thermally nor photochemically react by intramolecular reductive elimination to give the four-coordinate olefin iridium(I) isomers *trans*-[IrCl(η^2-RCH=CHR′)(PPh_3)$_2$]. A rearrangement of this type does not occur with the cationic species [IrH(L){κ^2(*C*,*O*)-CH=CHC(R)=O}(PPh_3)$_2$]$^+$, independent of whether the ligand L is a good σ donor (MeCN, PhCN) or a destinctive π-acceptor ligand (CO, $CH_3C{\equiv}CH$). There is no doubt that the driving force for the formation of **2**–**12** from **1** and the functionalized olefin is the formation of the chelating five-membered IrC_3O ring, which remains intact even in the presence of excess CO. In this context, we note that in contrast to [IrH(Cl)(CH=CH_2)(P-*i*-Pr_3)$_2$], the related hydrido(phenyl) complex [IrH(Cl)(C_6H_5)(P-*i*-Pr_3)$_2$] is also quite stable and reacts with CO by addition and not by reductive elimination (17).

Experimental

All experiments were carried out under an atmosphere of argon by using standard Schlenk techniques. The starting material **1** was prepared as described in the literature (6). IR spectra were recorded on a PerkinElmer 1420 IR spectrometer and NMR spectra on Jeol FX 90 Q as well as Bruker AC 200 and Bruker AMX 400 instruments. Melting points (dec. temp.) were determined by DTA. Conductivity measurements were carried out in nitromethane with a Schott Konduktometer CG 851. Abbreviations used: singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m), broadened signal (br); $N = {}^1J(PC) + {}^3J(PC)$.

Preparation of [IrH(Cl){κ^2(*C*,*O*)-CH=CHC(Me)=O}(PPh_3)$_2$] (2)

A solution of **1** (94 mg, 0.12 mmol) in 6 mL of benzene was treated with methyl(vinyl)ketone (11 μL, 0.12 mmol) and stirred for 2 h at room temperature. The solvent was evaporated in vacuo, the residue was dissolved in 3 mL of benzene–hexane (1:1), and the solution chromatographed on Al_2O_3 (neutral, activity grade V, length of column 6 cm). With benzene–hexane (1:1) a yellow fraction was eluted, which was brought to dryness in vacuo. The remaining yellow, air-stable solid was washed twice with 5 mL portions of hexane (30 °C) and dried. Yield: 78 mg (80%), mp 184 °C (dec.). IR (KBr, cm^{-1}): 2190 ν(IrH), 1550 ν(C=O). ^{1}H NMR (90 MHz, $CDCl_3$) δ: 9.58 (d, 1H, *J*(HH) = 7.5 Hz, IrCH), 7.59–7.19 (m, 30H, C_6H_5), 6.18 (d, 1H, *J*(HH) = 7.5 Hz, IrCH=C*H*), 1.53 (t, 3H, *J*(PH) = 1.4 Hz, CH_3), –22.42 (t, 1H, *J*(PH) = 16.4 Hz, IrH). ^{13}C NMR (50.3 MHz, $CDCl_3$) δ: 208.0 (s, C=O), 197.3 (t, *J*(PC) = 7.0 Hz, IrCH), 133.1 (s, IrCH=*C*H), 134.3 (vt, *N* = 11.6 Hz, *ortho*-C of PC_6H_5), 131.9 (vt, *N* = 54.7 Hz, ipso-C of PC_6H_5), 129.6 (s, *para*-C of PC_6H_5), 127.7 (vt, *N* = 10.1 Hz, *meta*-C of PC_6H_5), 24.0 (s, C(O)*C*H_3). ^{31}P NMR (36.2 MHz, $CDCl_3$) δ: 14.7 (s, d in off-resonance). Anal. calcd. for $C_{40}H_{36}ClIrOP_2$: C 58.42, H 4.41; found: C 58.34, H 4.55.

Preparation of [IrH(Cl){κ^2(*C*,*O*)-CH=CHC(Et)=O}(PPh_3)$_2$] (3)

A solution of **1** (140 mg, 0.18 mmol) in 15 mL of toluene was treated with ethyl(vinyl)ketone (18 μL, 0.18 mmol) and stirred for 6 h at room temperature. The solvent was evaporated in vacuo, the remaining yellow, air-stable solid was washed twice with 5 mL portions of hexane (50 °C) and dried. Yield: 137 mg (91%), mp 178 °C (dec.). IR (KBr, cm^{-1}): 2240 ν(IrH), 1540 ν(C=O). ^{1}H NMR (90 MHz, $CDCl_3$) δ: 9.60 (d, 1H, *J*(HH) = 7.6 Hz, IrCH), 7.58–7.28 (m, 30H, C_6H_5), 6.21 (d, 1H, *J*(HH) = 7.6 Hz, IrCH=C*H*), 1.95 (q, 2H, *J*(HH) = 7.3 Hz, CH_2CH_3), 0.69 (t, 3H, *J*(HH) = 7.3 Hz, CH_2CH_3), –22.55 (t, 1H, *J*(PH) = 16.5 Hz, IrH). ^{31}P NMR (36.2 MHz, $CDCl_3$) δ: 13.6 (s, d in off-resonance). Anal. calcd. for $C_{41}H_{38}ClIrOP_2$: C 58.88, H 4.58; found: C 58.37, H 4.51.

Preparation of [IrH(Cl){κ^2(*C*,*O*)-CH=CHC(Ph)=O}(PPh_3)$_2$] (4)

A solution of **1** (140 mg, 0.18 mmol) in 15 mL of toluene was treated with phenyl(vinyl)ketone (23 μL, 0.18 mmol) and stirred for 18 h at room temperature. (Owing to the high tendency of PhC(O)CH=CH_2 to polymerize, preparation of the ketone (18) in situ from β-chloropropiophenone is recommended). The reaction mixture was worked up analogous to that described for **3**. An orange, air-stable solid was obtained. Yield: 134 mg (84%), mp 189 °C (dec.). IR (KBr, cm^{-1}): 2145 ν(IrH), 1525 ν(C=O). ^{1}H NMR (90 MHz, $CDCl_3$) δ: 9.97 (d, 1H, *J*(HH) = 7.4 Hz, IrCH), 7.72–7.17 (m, 35H, PC_6H_5 and CC_6H_5), 6.86 (d, 1H, *J*(HH) = 7.4 Hz, IrCH=C*H*), –21.88 (t, 1H, *J*(PH) = 16.5 Hz, IrH). ^{31}P NMR (36.2 MHz, $CDCl_3$) δ: 13.4 (s, d in off-resonance). Anal. calcd. for $C_{45}H_{38}ClIrOP_2$: C 61.11, H 4.33; found: C 60.74, H 4.35.

Preparation of [IrH(Cl){κ^2(*C*,*O*)-C(OMe)=CHC(Me)=O}(PPh_3)$_2$] (5)

A solution of **1** (140 mg, 0.18 mmol) in 15 mL of toluene was treated with 4-methoxybut-3-en-2-one (18 μL, 0.18 mmol) and stirred for 18 h at 80 °C. After the solution was cooled to room temperature, the solvent was evaporated

in vacuo, the remaining pale yellow, air-stable solid was washed twice with 5 mL portions of hexane (50 °C) and dried. Yield: 120 mg (78%), mp 226 °C (dec.). IR (KBr, cm^{-1}): 2175 ν(IrH), 1515 ν(C=O). ^1H NMR (90 MHz, $CDCl_3$) δ: 7.71–7.22 (m, 30H, C_6H_5), 5.17 (s, 1H, C*H*C(Me)=O), 2.54 (s, 3H, IrC(OC*H*$_3$)=CH), 1.76 (s, 3H, C(CH_3)=O), –21.92 (t, 1H, *J*(PH) = 16.0 Hz, IrH). ^{31}P NMR (36.2 MHz, $CDCl_3$) δ: 9.8 (s, d in off-resonance). Anal. calcd. for $C_{41}H_{38}ClIrO_2P_2$: C 57.77, H 4.49; found: C 57.44, H 4.67.

Preparation of [IrH(Cl){κ^2(*C*,*O*)-C(Me)=CHC(Me)=O}-(PPh_3)$_2$] (6)

The procedure was analogous to that described for **5**, using **1** (140 mg, 0.18 mmol) and pent-3-en-2-one (17 μL, 0.18 mmol) as starting materials. A yellow, air-stable solid was obtained. Yield: 125 mg (83%), mp 191 °C (dec.). IR (KBr, cm^{-1}): 2200 ν(IrH), 1535 ν(C=O). ^1H NMR (90 MHz, $CDCl_3$) δ: 7.78–7.23 (m, 30H, C_6H_5), 6.07 (s, 1H, C*H*C(Me)=O), 1.83 (s, 3H, C(CH_3)=O), 0.92 (s, 3H, IrC(C*H*$_3$)=CH), –22.67 (t, 1H, *J*(PH) = 16.4 Hz, IrH). ^{31}P NMR (36.2 MHz, $CDCl_3$) δ: 11.6 (s, d in off-resonance). Anal. calcd. for $C_{41}H_{38}ClIrOP_2$: C 58.88, H 4.58; found: C 59.37, H 4.71.

Preparation of [IrH(Cl){κ^2(*C*,*O*)-C(Ph)=CHC(Me)=O}-(PPh_3)$_2$] (7)

The procedure was analogous to that described for **5**, using **1** (140 mg, 0.18 mmol) and 4-phenylbut-3-en-2-one (25 μL, 0.18 mmol) as starting materials. An orange, air-stable solid was obtained. Yield: 133 mg (82%), mp 194 °C (dec.). IR (KBr, cm^{-1}): 2230 ν(IrH), 1540 ν(C=O). ^1H NMR (90 MHz, $CDCl_3$) δ: 7.68–7.11 (m, 30H, PC_6H_5), 7.01–6.56 (m, 5H, CC_6H_5), 1.95 (t, 3H, *J*(PH) = 1.2 Hz, C(CH_3)=O), –22.10 (t, 1H, *J*(PH) = 15.9 Hz, IrH), signal of =CH proton probably covered by signal of CC_6H_5 protons. ^{31}P NMR (36.2 MHz, $CDCl_3$) δ: 10.7 (s, d in off-resonance). Anal. calcd. for $C_{46}H_{40}ClIrOP_2$: C 61.50, H 4.49; found: C 61.43, H 4.37.

Preparation of [IrH(Cl){κ^2(*C*,*O*)-C(CO_2Me)=CHC(Me)=O}-(PPh_3)$_2$] (8)

The procedure was analogous to that described for **3**, using **1** (107 mg, 0.14 mmol) and methyl-4-oxo-2-pentenoate (24 mg, 0.28 mmol) as starting materials. An orange, air-stable solid was obtained. Yield: 97 mg (79%), mp 228 °C (dec.). IR (KBr, cm^{-1}): 2210 ν(IrH). ^1H NMR (400 MHz, $CDCl_3$) δ: 7.59–6.81 (m, 30H, PC_6H_5), 2.89 (s, 3H, CO_2CH_3), 2.03 (t, 3H, *J*(PH) = 1.2 Hz, C(CH_3)=O), –22.89 (t, 1H, *J*(PH) = 16.0 Hz, IrH), signal of =CH proton probably covered by signal of C_6H_5 protons. ^{31}P NMR (36.2 MHz, $CDCl_3$) δ: 11.5 (s, d in off-resonance). Anal. calcd. for $C_{42}H_{38}ClIrO_3P_2$: C 57.30, H 4.35; found: C 57.49, H 4.46.

Preparation of [IrH(Cl){κ^2(*C*,*O*)-C(Me)=C(Me)C(Et)=O}-(PPh_3)$_2$] (9)

The procedure was analogous to that described for **5**, using **1** (140 mg, 0.18 mmol) and 4-methylhex-4-en-3-one (69 μL, 0.54 mmol) as starting materials. A yellow, air-stable solid was obtained. Yield: 123 mg (79%), mp 218 °C (dec.). IR (KBr, cm^{-1}): 2145 ν(IrH), 1550 ν(C=O). ^1H NMR (90 MHz, $CDCl_3$) δ: 7.69–7.23 (m, 30H, PC_6H_5), 2.10 (q, 2H, *J*(HH) = 7.3 Hz, C*H*$_2$CH$_3$), 1.10 (s, 3H, IrC(CH_3)=C), 0.79 (t, 3H, *J*(HH) = 7.3 Hz, CH_2C*H*$_3$), 0.75 (s, 3H, =C(CH_3)C), –21.91 (t, 1H, *J*(PH) = 16.1 Hz, IrH). ^{31}P NMR (36.2 MHz, $CDCl_3$) δ: 11.7 (s, d in off-resonance). Anal. calcd. for $C_{43}H_{42}ClIrOP_2$: C 59.75, H 4.90; found: C 59.80, H 4.68.

Preparation of [IrH(Cl){κ^2(*C*,*O*)-C(Ph)=CHC(Ph)=O}-(PPh_3)$_2$] (10)

The procedure was analogous to that described for **5**, using **1** (140 mg, 0.18 mmol) and benzylidenacetophenone (75 mg, 0.36 mmol) as starting materials. An orange, air-stable solid was obtained. Yield: 131 mg (76%), mp 212 °C (dec.). IR (KBr, cm^{-1}): 2160 ν(IrH), 1520 ν(C=O). ^1H NMR (90 MHz, $CDCl_3$) δ: 7.96–6.62 (br m, 40H, C_6H_5), –21.43 (t, 1H, *J*(PH) = 16.4 Hz, IrH), signal of =CH proton probably covered by the broad signal of phenyl protons. ^{13}C NMR (50.3 MHz, $CDCl_3$) δ: 215.0 (t, *J*(PC) = 6.1 Hz, IrC), 199.3 (s, C=O), 144.7 (s, IrC(Ph)=*C*H), 136.9, 131.5, 131.0, 129.4, 128.5, 128.1, 126.7, 125.2 (all s, CC_6H_5), 134.7 (vt, *N* = 11.1 Hz, *ortho*-C of PC_6H_5), 131.4 (vt, *N* = 53.8 Hz, ipso-C of PC_6H_5), 129.5 (s, *para*-C of PC_6H_5), 127.3 (vt, *N* = 10.2 Hz, *meta*-C of PC_6H_5). ^{31}P NMR (36.2 MHz, $CDCl_3$) δ: 10.3 (s, d in off-resonance). Anal. calcd. for $C_{51}H_{42}ClIrOP_2$: C 63.77, H 4.41; found: C 63.39, H 4.13.

Preparation of [IrH(Cl){κ^2(*C*,*O*)-CH=CHC(OMe)=O}-(PPh_3)$_2$] (11)

A solution of **1** (94 mg, 0.12 mmol) in 6 mL of benzene was treated with methyl acrylate (11 μL, 0.12 mmol) and stirred for 2 h at 80 °C. After the solution was cooled to room temperature, it was worked up analogously to that described for **2**. A yellow, air-stable solid was obtained. Yield: 67 mg (66%), mp 159 °C (dec.). IR (KBr, cm^{-1}): 2205 ν(IrH), 1580 ν(C=O). ^1H NMR (90 MHz, $CDCl_3$) δ: 9.17 (d, 1H, *J*(HH) = 8.7 Hz, IrCH), 7.66–7.24 (m, 30H, C_6H_5), 5.77 (d, 1H, *J*(HH) = 8.7 Hz, IrCH=C*H*), 3.15 (s, 3H, OCH_3), –25.07 (t, 1H, *J*(PH) = 16.1 Hz, IrH). ^{31}P NMR (36.2 MHz, $CDCl_3$) δ: 14.7 (s, d in off-resonance). Anal. calcd. for $C_{40}H_{36}ClIrO_2P_2$: C 57.30, H 4.33; found: C 57.68, H 4.11.

Preparation of [IrH(Cl){κ^2(*C*,*O*)-CH=CHC(NH_2)=O}-(PPh_3)$_2$] (12)

A solution of **1** (94 mg, 0.12 mmol) in 6 mL of benzene was treated with methyl acrylate (9 mg, 0.12 mmol) and stirred for 3 h at room temperature. The solvent was evaporated in vacuo and the residue was recrystallized from dichloromethane–hexane (1:5) to give a white, air-stable solid. Yield: 88 mg (89%), mp 181 °C (dec.). IR (KBr, cm^{-1}): 3320, 3215 ν(NH), 2205 ν(IrH), 1555 ν(C=O). ^1H NMR (90 MHz, $CDCl_3$) δ: 8.82 (d, 1H, *J*(HH) = 7.9 Hz, IrCH), 7.53–7.16 (m, 30H, C_6H_5), 5.57 (d, 1H, *J*(HH) = 7.9 Hz, IrCH=C*H*), –24.19 (t, 1H, *J*(PH) = 16.8 Hz, IrH), signal for NH_2 protons not exactly located. ^{31}P NMR (36.2 MHz, $CDCl_3$) δ: 13.6 (s, d in off-resonance). Anal. calcd. for $C_{39}H_{35}ClIrNOP_2$: C 56.89, H 4.28, N 1.70; found: C 56.96, H 3.99, N 1.66.

Preparation of [IrH(CO){κ^2(*C*,*O*)-CH=CHC(Me)=O}-(PPh_3)$_2$]PF_6 (14)

A solution of **2** (100 mg, 0.12 mmol) in 10 mL of dichloromethane was treated with $AgPF_6$ (31 mg, 0.12 mmol)

and stirred for 15 min at room temperature in the dark under CO. After replacing the CO atmosphere for argon, the solution was filtered and the residue was washed twice with 1 mL portions of CH_2Cl_2. The filtrate was brought to dryness in vacuo, the residue was dissolved in 6 mL of hexane–CH_2Cl_2 (1:5), and the solution was chromatographed on Al_2O_3 (neutral, activity grade V, length of column 5 cm). A brownish fraction was eluted with hexane–CH_2Cl_2 (1:5) and the solvent was evaporated in vacuo. After the residue was recrystallized from CH_2Cl_2–hexane (1:5), an off-white, air-stable solid was obtained. Yield: 105 mg (91%), mp 111 °C (dec.). Conductivity (CH_3NO_2) Λ = 65 $cm^2\ \Omega^{-1}\ mol^{-1}$. IR (KBr, cm^{-1}): 2190 ν(IrH), 2060 ν(CO), 1580 ν(C=O). ^1H NMR (90 MHz, $CDCl_3$) δ: 9.47 (d, 1H, *J*(HH) = 9.2 Hz, IrCH), 7.87–7.49 (m, 30H, PC_6H_5), 6.71 (d, 1H, *J*(HH) = 9.2 Hz, IrCH=C*H*), 1.23 (s, 3H, $C(CH_3)$=O), –19.09 (t, 1H, *J*(PH) = 12.5 Hz, IrH). ^{31}P NMR (36.2 MHz, $CDCl_3$) δ: 11.7 (s, d in off-resonance). Anal. calcd. for $C_{41}H_{36}ClF_6IrO_2P_3$: C 51.30, H 3.78; found: C 51.52, H 3.67.

Preparation of [IrH{κ²(*C*,*O*)-CH=CHC(Me)=O}-(PPh₃)₂]ClO₄ (15)

A solution of **2** (140 mg, 0.17 mmol) in 15 mL of dichloromethane was treated with $AgClO_4$ (35 mg, 0.17 mmol) and stirred for 15 min at room temperature in the dark. The solution was filtered and the residue was washed twice with 1 mL portions of CH_2Cl_2. The filtrate was brought to dryness in vacuo, the remaining brown-yellow solid was washed three times with 5 mL portions of hexane and dried. Yield: 130 mg (86%), mp 131 °C (dec.). Conductivity (CH_3NO_2) Λ = 36 $cm^2\ \Omega^{-1}\ mol^{-1}$. IR (KBr, cm^{-1}): 2180 ν(IrH), 1550 ν(C=O). ^1H NMR (90 MHz, $CDCl_3$) δ: 9.72 (d, 1H, *J*(HH) = 7.4 Hz, IrCH), 7.56–7.12 (m, 30H, PC_6H_5), 5.96 (d, 1H, *J*(HH) = 7.4 Hz, IrCH=C*H*), 1.43 (s, 3H, $C(CH_3)$=O), –21.14 (t, 1H, *J*(PH) = 15.3 Hz, IrH); data for isomers **15a** and **15b** (see Scheme 3): δ: 9.59 (d, *J*(HH) = 7.4 Hz, IrCH), 6.22 (d, *J*(HH) = 7.4 Hz, IrCH=C*H*), 1.48 (s, $C(CH_3)$=O), –21.90 (br t, *J*(PH) ~ 15 Hz, IrH). ^{31}P NMR (36.2 MHz, $CDCl_3$) δ: 23.1 (s, d in off-resonance; at –80 °C in CD_2Cl_2 two doublets in off-resonance with δ 22.1 and 21.4). Anal. calcd. for $C_{40}H_{36}ClIrO_5P_2$: C 55.17, H 4.41; found: C 55.24, H 4.32.

Preparation of [IrH{κ²(*C*,*O*)-CH=CHC(Et)=O}(PPh₃)₂]-ClO₄ (16)

The procedure was analogous to that described for **15**, using **3** (140 mg, 0.17 mmol) and $AgClO_4$ (35 mg, 0.17 mmol) as starting materials. An orange, moderately air-sensitive solid was obtained. Yield: 133 mg (87%), mp 128 °C (dec.). Conductivity (CH_3NO_2) Λ = 50 $cm^2\ \Omega^{-1}\ mol^{-1}$. IR (KBr, cm^{-1}): 2185 ν(IrH), 1545 ν(C=O). ^1H NMR (90 MHz, $CDCl_3$) δ: 9.74 (d, 1H, *J*(HH) = 6.9 Hz, IrCH), 7.44–7.12 (m, 30H, PC_6H_5), 6.04 (d, 1H, *J*(HH) = 6.9 Hz, IrCH=C*H*), 1.75 (q, 2H, *J*(HH) = 7.4 Hz, CH_2CH$_3$), 0.64 (t, 3H, *J*(HH) = 7.4 Hz, CH$_2$CH_3), –21.10 (t, 1H, *J*(PH) = 15.6 Hz, IrH). ^{31}P NMR (36.2 MHz, $CDCl_3$) δ: 22.5 (s, d in off-resonance). Anal. calcd. for $C_{41}H_{38}ClIrO_5P_2$: C 54.70, H 4.25; found: C 54.51, H 4.41.

Preparation of [IrH(CO){κ²(*C*,*O*)-CH=CHC(Et)=O}-(PPh₃)₂]ClO₄ (17)

A solution of **16**, generated in situ from **3** (100 mg, 0.12 mmol) and $AgClO_4$ (25 mg, 0.12 mmol) in 10 mL of dichloromethane, was stirred for 15 min at room temperature in the dark. The solution was filtered and a slow stream of CO was passed through the filtrate for 1 min. The solvent was evaporated in vacuo, the remaining yellow solid was washed twice with 1 mL portions of CH_2Cl_2 and three times with 5 mL portions of hexane and dried. Yield: 100 mg (89%), mp 118 °C (dec.). Conductivity (CH_3NO_2) Λ = 56 $cm^2\ \Omega^{-1}\ mol^{-1}$. IR (KBr, cm^{-1}): 2195 ν(IrH), 2040 ν(CO), 1575 ν(C=O). ^1H NMR (200 MHz, $CDCl_3$) δ: 9.42 (d, 1H, *J*(HH) = 9.1 Hz, IrCH), 7.81–7.47 (m, 30H, PC_6H_5), 6.73 (dt, 1H, *J*(HH) = 6.9, *J*(PH) = 2.1 Hz, IrCH=C*H*), 1.80 (qt, 2H, *J*(HH) = 7.2, *J*(PH) = 2.4 Hz, CH_2CH$_3$), 0.53 (t, 3H, *J*(HH) = 7.2 Hz, CH$_2$CH_3), –19.20 (t, 1H, *J*(PH) = 12.4 Hz, IrH). ^{31}P NMR (36.2 MHz, $CDCl_3$) δ: 11.1 (s, d in off-resonance). Anal. calcd. for $C_{42}H_{38}ClIrO_6P_2$: C 54.34, H 4.13; found: C 54.71, H 4.25.

Preparation of [IrH{κ²(*C*,*O*)-CH=CHC(Et)=O}(PPh₃)₃]-ClO₄ (18)

A solution of **16**, generated in situ from **3** (100 mg, 0.12 mmol) and $AgClO_4$ (25 mg, 0.12 mmol) in 10 mL of dichloromethane, was treated with PPh_3 (32 mg, 0.12 mmol) and stirred for 5 min at room temperature in the dark. The solution was filtered, the filtrate was brought to dryness in vacuo, and the remaining white, air-stable solid was washed three times with 5 mL portions of toluene and twice with 5 mL portions of hexane and dried. Yield: 114 mg (82%), mp 136 °C (dec.). Conductivity (CH_3NO_2) Λ = 59 $cm^2\ \Omega^{-1}\ mol^{-1}$. IR (KBr, cm^{-1}): 2215 ν(IrH), 1550 ν(C=O). ^1H NMR (90 MHz, $CDCl_3$) δ: 8.43 (ddt, 1H, *J*(HH) = 7.3, *J*(P_{eq}H) = 7.3, *J*(P_{ax}H) = 4.2 Hz, IrCH), 7.39–6.82 (m, 30H, PC_6H_5), 6.66 (d, 1H, *J*(HH) = 7.3 Hz, IrCH=C*H*), 2.25 (m, 2H, CH_2CH$_3$), 1.11 (t, 3H, *J*(HH) = 7.1 Hz, CH$_2$CH_3), –21.47 (td, 1H, *J*(P_{ax}H) = 18.1, *J*(P_{eq}H) = 10.3 Hz, IrH). ^{31}P NMR (36.2 MHz, $CDCl_3$) δ: 2.5 (d, *J*(PP) = 17.6 Hz, dd in off-resonance, ax-PPh_3), –3.1 (d, *J*(PP) = 17.6 Hz, dt in off-resonance, eq-PPh_3). Anal. calcd. for $C_{59}H_{53}ClIrO_5P_3$: C 60.95, H 4.59; found: C 60.34, H 4.25.

Preparation of [IrH(C₂H₄){κ²(*C*,*O*)-CH=CHC(Et)=O}-(PPh₃)₂]ClO₄ (19)

A solution of **16**, generated in situ from **3** (100 mg, 0.12 mmol) and $AgClO_4$ (25 mg, 0.12 mmol) in 10 mL of $CDCl_3$, was stirred for 15 min at room temperature in the dark. The solution was filtered and a slow stream of ethene was passed through the filtrate for 5 min. The solution was concentrated to ca. 1 mL in vacuo and the product, which is only stable in an ethene atmosphere, characterized by NMR spectroscopy. ^1H NMR (90 MHz, $CDCl_3$) δ: 10.04 (d, 1H, *J*(HH) = 8.6 Hz, IrCH), 7.51–7.18 (m, 30H, PC_6H_5), 6.45 (dt, 1H, *J*(HH) = 8.6, *J*(PH) = 2.2 Hz, IrCH=C*H*), 3.55 (t, 4H, *J*(PH) = 3.1 Hz, C_2H_4), 1.97 (qt, 2H, *J*(HH) = 7.3, *J*(PH) = 2.4 Hz, CH_2CH$_3$), 0.83 (t, 3H, *J*(HH) = 7.3 Hz, CH$_2$CH_3), –20.85 (t, 1H, *J*(PH) = 14.2 Hz, IrH). ^{31}P NMR (36.2 MHz, $CDCl_3$) δ: 13.9 (s, d in off-resonance).

Preparation of [IrH(CH₃C≡CH){κ²(*C*,*O*)-CH=CHC(Et)=O}-(PPh₃)₂]ClO₄ (20)

A solution of **16**, generated in situ from **3** (100 mg, 0.12 mmol) and $AgClO_4$ (25 mg, 0.12 mmol) in 10 mL of

dichloromethane, was stirred for 15 min at room temperature in the dark. The solution was filtered and a slow stream of propyne was passed through the filtrate for 1 min. The solvent was evaporated in vacuo, the residue was dissolved in 4 mL of CH_2Cl_2–hexane (3:1) and chromatographed on Al_2O_3 (neutral, activity grade V, length of column 5 cm). With CH_2Cl_2–hexane (3:1) a brown fraction was eluted, which was concentrated to ca. 2 mL in vacuo. A brown, slightly air-sensitive solid precipitated, which was washed three times with 5 mL portions of hexane and dried. Yield: 100 mg (87%), mp 112 °C (dec.). Conductivity (CH_3NO_2) Λ = 52 $cm^2\ \Omega^{-1}\ mol^{-1}$. IR (KBr, cm^{-1}): 2185 ν(IrH), 1820 ν(C≡C), 1540 ν(C=O). ^{1}H NMR (90 MHz, $CDCl_3$) δ: 9.60 (d, 1H, *J*(HH) = 7.6 Hz, IrCH), 7.66–7.00 (m, 30H, PC_6H_5), 6.21 (d, 1H, *J*(HH) = 7.6 Hz, IrCH=C*H*), 2.55–0.61 (br m, 9H, $CH_3C{\equiv}CH$ and C_2H_5), –22.54 (t, 1H, *J*(PH) = 16.6 Hz, IrH). ^{31}P NMR (36.2 MHz, $CDCl_3$) δ: 13.7 (s, d in off-resonance). Anal. calcd. for $C_{44}H_{42}ClIrO_5P_2$: C 56.20, H 4.50; found: C 56.14, H 4.23.

Preparation of [IrH(MeCN){κ²(*C*,*O*)-CH=CHC(Et)=O}-(PPh_3)$_2$]ClO_4 (21)

A solution of **16**, generated in situ from **3** (100 mg, 0.12 mmol) and $AgClO_4$ (25 mg, 0.12 mmol) in 10 mL of dichloromethane, was added dropwise to a solution of acetonitrile (19 μL, 0.36 mmol) in 5 mL of dichloromethane. After the reaction mixture was stirred for 5 min at room temperature, the solution was filtered. The filtrate was brought to dryness in vacuo, the remaining white, air-stable solid was washed three times with 5 mL portions of hexane and dried. Yield: 101 mg (87%), mp 179 °C (dec.). Conductivity (CH_3NO_2) Λ = 61 $cm^2\ \Omega^{-1}\ mol^{-1}$. IR (KBr, cm^{-1}): 2175 ν(CN), 1565 ν(C=O). ^{1}H NMR (90 MHz, $CDCl_3$) δ: 9.77 (d, 1H, *J*(HH) = 8.3 Hz, IrCH), 7.51–7.23 (m, 30H, PC_6H_5), 6.37 (dt, 1H, *J*(HH) = 8.3, *J*(PH) = 1.7 Hz, IrCH=C*H*), 1.82 (qt, 2H, *J*(HH) = 7.6, *J*(PH) = 2.2 Hz, CH_2CH_3), 1.69 (t, 3H, *J*(PH) = 1.0 Hz, CH_3CN), 0.69 (t, 3H, *J*(HH) = 7.6 Hz, CH_2CH_3), –21.72 (t, 1H, *J*(PH) = 14.9 Hz, IrH). ^{31}P NMR (36.2 MHz, $CDCl_3$) δ: 17.3 (s, d in off-resonance). Anal. calcd. for $C_{43}H_{41}ClIrNO_5P_2$: C 54.86, H 4.39, N 1.49; found: C 54.85, H 4.88, N 1.49.

Preparation of [IrH(PhCN){κ²(*C*,*O*)-CH=CHC(Et)=O}-(PPh_3)$_2$]ClO_4 (22)

The procedure was analogous to that described for **21**, using **16** (100 mg, 0.12 mmol) and benzonitrile (37 μL, 0.36 mmol) as starting materials. A pale yellow, moderately air-sensitive solid was obtained. Yield: 108 mg (90%), mp 148 °C (dec.). Conductivity (CH_3NO_2) Λ = 59 $cm^2\ \Omega^{-1}\ mol^{-1}$. IR (KBr, cm^{-1}): 2200 ν(CN), 1555 ν(C=O). ^{1}H NMR (90 MHz, $CDCl_3$) δ: 9.75 (d, 1H, *J*(HH) = 7.3 Hz, IrCH), 7.79–7.15 (m, 35H, C_6H_5CN and PC_6H_5), 6.47 (d, 1H, *J*(HH) = 7.3 Hz, IrCH=C*H*), 1.84 (q, 2H, *J*(HH) = 7.3 Hz, CH_2CH_3), 0.65 (t, 3H, *J*(HH) = 7.3 Hz, CH_2CH_3), –21.33 (t, 1H, *J*(PH) = 15.2 Hz, IrH). ^{31}P NMR (36.2 MHz, $CDCl_3$) δ: 17.1 (s, d in off-resonance). Anal. calcd. for $C_{48}H_{43}ClIrNO_5P_2$: C 57.45, H 4.32, N 1.40; found: C 57.68, H 4.60, N 1.44.

Preparation of [IrH(SPh){κ²(*C*,*O*)-CH=CHC(Et)=O}-(PPh_3)$_2$] (23)

A suspension of **21** (120 mg, 0.13 mmol) in 15 mL of THF was treated with NaSPh (17 mg, 0.13 mmol) and stirred for 15 h at room temperature. The solvent was evaporated in vacuo, the residue was suspended in 10 mL of toluene, and the solution was filtered. The filtrate was brought to dryness in vacuo, the remaining orange, air-stable solid was washed twice with 10 mL portions of hexane and dried. Yield: 92 mg (78%), mp 157 °C (dec.). IR (KBr, cm^{-1}): 2180 ν(IrH), 1570 ν(C=O). ^{1}H NMR (90 MHz, $CDCl_3$) δ: 9.68 (d, 1H, *J*(HH) = 8.0 Hz, IrCH), 7.62–7.21 (m, 30H, PC_6H_5), 6.78–6.58 (m, 5H, SC_6H_5), 6.47 (d, 1H, *J*(HH) = 8.0 Hz, IrCH=C*H*), 1.64 (q, 2H, *J*(HH) = 7.1 Hz, CH_2CH_3), 0.35 (t, 3H, *J*(HH) = 7.1 Hz, CH_2CH_3), –22.53 (t, 1H, *J*(PH) = 15.4 Hz, IrH). ^{31}P NMR (36.2 MHz, $CDCl_3$) δ: 16.8 (s, d in off-resonance). Anal. calcd. for $C_{47}H_{43}ClIrO_5P_2S$: C 62.03, H 4.76; found: C 61.83, H 4.55.

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