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Reactions of $[IrH_2(Me_2CO)(Hpz)(PPh_3)_2]BF_4$ with alkynes: synthesis of new hydride–vinyl iridium(III) complexes

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Abstract

One of the two acetone ligands in the complex $[IrH_2(Me_2CO)_2(PPh_3)_2]BF_4$ (**1**) is displaced by pyrazole (Hpz) to give $[IrH_2(Me_2CO)(Hpz)(PPh_3)_2]BF_4$ (**2**). Treatment of **2** with methyl propiolate and acetylenedicarboxylic dimethyl ester leads to the cationic complexes $[IrH(C(COOCH_3)=CH_2)(Hpz)(PPh_3)_2]BF_4$ (**3**), $[IrH(CH=CHCOOCH_3)(Hpz)(PPh_3)_2]BF_4$ (**4**) and $[IrH(C(COOCH_3)=CH(CO_2CH_3))(Hpz)(PPh_3)_2]BF_4$ (**5**). The molecular structure of **3** has been determined by X-ray analysis. **3** crystallizes with an acetone molecule in the lattice, in the space group $P2_1/m$ with $a = 9.661(3)$ Å, $b = 22.903(3)$ Å, $c = 11.056(3)$ Å and $\beta = 99.82(1)°$. The coordination around the iridium atom is a distorted octahedron with the two phosphorus atoms of the triphenylphosphine ligands occupying *trans* positions. The equatorial plane is formed by the α-C atom, the oxygen atom of the carbonyl group of the ester, the hydride and a nitrogen atom of the pyrazole ligand. **3** reacts with $[\{Rh(\mu\text{-}OMe)(\eta^4\text{-}1,5\text{-}COD)\}_2]$ to give, via a redistribution reaction, $[IrH(CH=CHCOOCH_3)(MeOH)(PPh_3)_2]BF_4$ (**6**) and $[\{Rh(\mu\text{-}pz)(\eta^4\text{-}1,5\text{-}COD)\}_2]$. The methanol molecule of **6** is displaced by $P(OMe)_3$ and CO to yield $[IrH(CH=CHCOOCH_3)L(PPh_3)_2]BF_4$ (L = $P(OMe)_3$ (**7**) or CO (**8**)). The vinyl complexes $[IrH(C(CO_2CH_3)=CH_2)(Hpz)(P(OMe)_3)(PPh_3)_2]BF_4$ (**9**) and $[IrH(C(CO_2CH_3)=CH_2)Cl(Hpz)(PPh_3)_2]$ (**10**) were prepared by reaction of **3** with $P(OMe)_3$ and Cl^- respectively. Complex **10** reacts with $[\{Rh(\mu\text{-}OMe)(\eta^4\text{-}1,5\text{-}COD)\}_2]$ to afford the heterobimetallic compound $[H(C(CO_2CH_3)=CH_2)(PPh_3)_2Ir(\mu\text{-}pz)(\mu\text{-}Cl)Rh(\eta^4\text{-}1,5\text{-}COD)]$ (**11**).

Key words: Iridium; Hydride; Vinyl; Alkyne

1. Introduction

Complexes of formula $[IrH_2S_xL_a]^+$ (S = solvent molecule, L = other ligand, $a = 2$ or 3) have been previously prepared in coordinating solvents by treatment of complexes of the type $[Ir(\eta^4\text{-}1,5\text{-}COD)L_a]^+$ with molecular hydrogen [1] and by reaction of the pentahydrides $[IrH_5(PR_3)_2]$ with HBF_4 [2]. In the latter case, the intermediates $[IrH_2(\eta^2\text{-}H_2)_2(PR_3)_2]^+$ were detected by (NMR) spectroscopy [3].

Various catalytic studies on $[IrH_2S_xL_a]^+$ have been also carried out. It has been observed that such cations catalyse the exchange of molecular deuterium with hydrogen atoms of several organic compounds [4], silane alcoholysis [5], hydrogenation of alkenes [6], and dehydrogenation of alkenes and alkanes [7]. Since a primary step in all these catalytic reactions is substrate coordination, and because this was expected to be related to the rate of solvent exchange, rate constants and activation parameters have been also determined for solvent-exchange processes [8]. Furthermore, in connection with these catalytic studies organometallic complexes such as $[Ir(\eta^6\text{-}C_6H_5Et)(PR_3)_2]^+$ [7b], $[IrH_2(\eta^4\text{-}1,5\text{-}COD)(PR_3)_2]^+$ [9], $[Ir(\eta^5\text{-}C_5H_5)H(PR_3)_2]^+$ [7a], $[Ir(\eta^5\text{-}C_7H_9)H(PR_3)_2]^+$ [7c], $[Ir(\eta^5\text{-}C_6H_7)H(PR_3)_2]^+$ [7e], $[IrH_2(\eta^4\text{-}2,3\text{-dimethylbutadiene})(PR_3)_2]^+$, $[Ir(\eta^5\text{-indenyl})H(PR_3)_2]^+$, $[Ir(\eta^5\text{-NpEt})H(PR_3)_2]^+$ [10] (NpEt = 2-ethylnaphthalene) and $[Ir(\eta^3\text{-}2,3\text{-dimethylbuthenyl})H(PR_3)_2]^+$ [11] have been isolated or spectroscopically detected.

Although the reactivity of the iridium complexes containing solvent molecules towards alkanes, alkenes and aromatic compounds such as diiodobenzene and *o*-bromoiodobenzene have been thoroughly investi-

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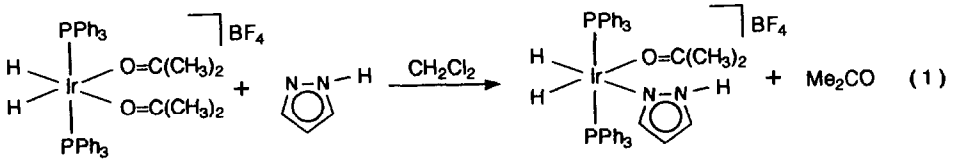


1 2

gated [7–12], to the best of our knowledge studies on the chemistry of these complexes in the presence of alkynes have not been reported. The present paper describes the synthesis and characterization of $[IrH_2(Me_2CO)(Hpz)(PPh_3)_2]^+$ and illustrates its reactivity towards alkynes. In addition, reactions of some complexes obtained in this way to give binuclear complexes are also reported.

2. Results and discussion

2.1. Synthesis of $[IrH_2(Me_2CO)(Hpz)(PPh_3)_2]BF_4$

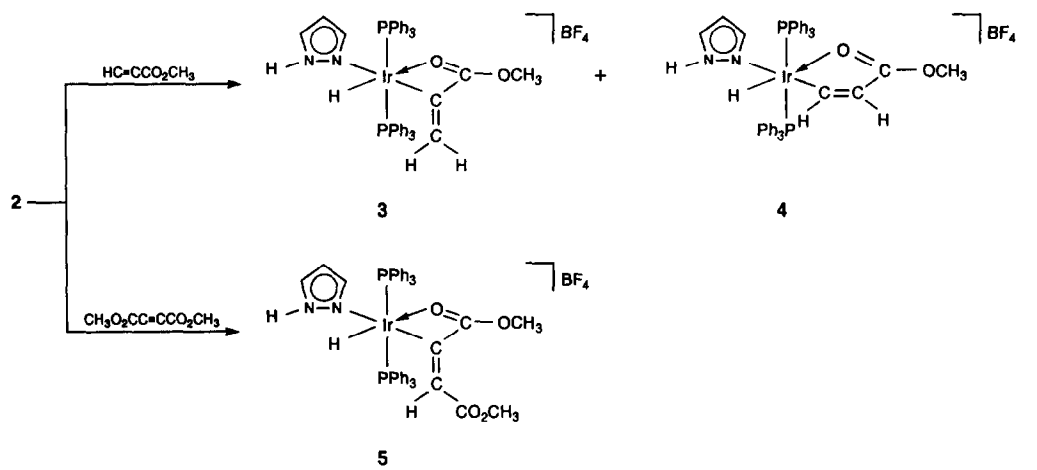
One of the two acetone molecules in the cationic complex $[IrH_2(Me_2CO)_2(PPh_3)_2]BF_4$ (**1**) can be easily and selectively displaced by pyrazole. Thus the treatment of **1** with the azole, in a 1:1 molar ratio in dichloromethane, leads to the complex $[IrH_2(Me_2CO)(Hpz)(PPh_3)_2]BF_4$ (**2**) (eqn. (1)). The substitution is certainly facilitated by the weakness of the Ir–acetone bond.

Complex **2** was fully characterized by elemental analysis, IR, and ^1H and $^{31}P\{^1H\}$ NMR spectroscopy. Consistent with the proposed structure, the ^1H NMR spectrum in chloroform-d_1 at −40°C displays two triplets of doublets in the hydride region, at −20.72 (J(PH) = 17.5 Hz, J(HH) = 7 Hz) and −27.74 (J(PH) = 16.2 Hz, J(HH) = 7 Hz) ppm. The IR spectrum in Nujol shows absorption due to $[BF_4]^-$ with T_d symmetry, together with the characteristic bands of the ligands. In particular, a band due to the carbonyl group of the acetone ligand at 1660 cm^{-1} strongly supports Ir(η^1-acetone) bonding [13].

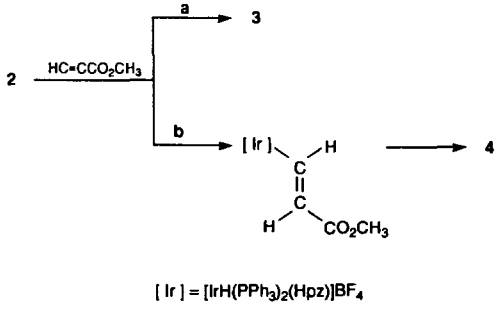
2.2. Reactions of 2 with alkynes

The acetone ligand in **2** is displaced by alkynes. Treatment of **2** with methyl propiolate in 1,2-dichloroethane for 30 min at room temperature, leads to a pale-yellow solution from which a white solid precipitates on addition of diethyl ether. According to the elemental analysis, the composition corresponds to a 1:1 adduct of the fragment $[IrH_2(Hpz)(PPh_3)_2]BF_4$ and methyl propiolate. A similar product is obtained on treatment of **2** with acetylenedicarboxylic dimethyl ester. The IR, and ^1H, $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectra of these compounds suggest that the insertion of the unsaturated substrates into one of the two Ir–H bonds of **2** has taken place. There is no doubt that the products obtained from these reactions are the complexes shown in Scheme 1.

The $^{31}P\{^1H\}$ NMR spectrum of the solid obtained from **2** and methyl propiolate shows two singlets at 11.8 and 17.9 ppm with an intensity ratio of approximately 7:1, which are assigned to the isomers **3** and **4** respectively. Characteristic signals in the ^1H NMR spectrum



Scheme 1.



Scheme 2.

are those at 6.53, 5.37 (=CH_2), and −27.84 (Ir–H) ppm for **3** and at 9.52, 5.83 (=CH) and −23.27 (Ir–H) ppm for **4**. Isomer **3** was isolated as a pure microcrystalline solid by fractional crystallization from acetone–diethyl ether. The insertion of HC≡CCO_2Me into the Ir–H bond of **2** must involve the initial displacement of the acetone ligand by the alkyne to give an alkynedihydride intermediate, followed by the migration of the hydride from the metal to the *C*H or *C*CO_2Me carbons atoms of the alkyne. Path a and path b shown in Scheme 2 correspond to the Markovnikov and the *anti*-Markovnikov types of insertion, respectively. The Markovnikov type of insertion directly leads to **3**, whereas the alternative *anti*-Markovnikov route would first give an Ir((E)CH=CHCO_2CH_3) intermediate, which subsequently isomerizes to **4**. Precedents for this process are known [14,15].

The ^{1}H NMR spectrum of **5** contains two singlets at 3.37 and 2.82 ppm, which indicate that the two $-CO_2CH_3$ groups are inequivalent. The proposal that one of the ester units coordinates to the iridium atom via the C=O oxygen atom is strongly supported by the IR spectrum which shows two C=O stretching frequencies at 1705 and 1565 cm^{-1}. For **3** the stretching frequency of the C=O group of the ester appears at 1570 cm^{-1}, suggesting that in this case the oxygen atom also coordinates. This was confirmed by a single-crystal X-ray structure analysis of **3**. A view of the molecular geometry of the cation is shown in Fig. 1. Selected bond distances and angles are listed in Table 1.

The coordination around the iridium center can be described as a distorted octahedron with the two phosphorus atoms of the triphenylphosphine ligands occupying *trans* positions (P–Ir–P = 172.2(2)°). The equatorial plane is formed by the C(1) and O(1) atoms of the chelating vinyl group (defining with the iridium atom a four-membered ring (O(1)–Ir–C(1) = 63.6(7)°)), the N(1) atom of the pyrazole group *trans* to C(1) (N(1)–Ir–C(1) = 161.8(7)°), and the hydride ligand *trans* to O(1) (O(1)–Ir–H = 162.2(5)°).

The four-membered metallacycle, the OCH_3 group and the pyrazole and hydride ligands are coplanar.

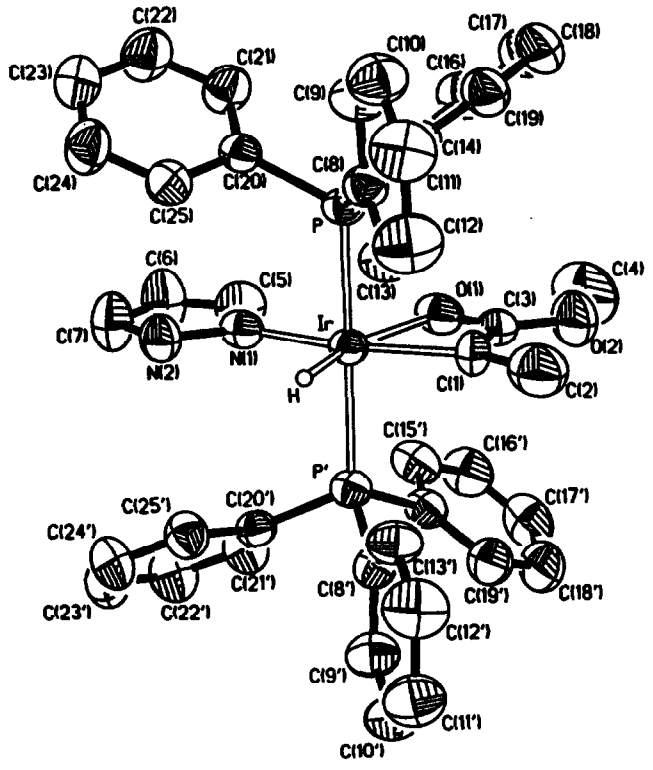


Fig. 1 ORTEP diagram of [IrH(C(COOCH$_3$)=CH$_2$)(Hpz)(PPh$_3$)$_2$]BF$_4$ (**3**).

Furthermore, the aryl groups of the phosphine ligands are mutually eclipsed. As a result of this, the equatorial plane of the octahedron is also a symmetry plane of the molecule.

The Ir–C(1) distance, 2.02(2) Å, is shorter than the Ir–C distances found in the iridium(III) complexes [IrH(CH=CH_2)Cl(CO)(η^1-^{i}$Pr_2PCH_2CH_2OCH_3$)$_2$] (2.059(6) Å) [16] and [IrH(CH=CH_2)(η^5-C_5H_5)(PMe_3)]

TABLE 1. Selected bond distances and bond angles with estimated standard deviations

Bond distances			
Ir–P	2.330(3)	O(1)–C(3)	1.25(2)
Ir–O(1)	2.28(1)	O(2)–C(3)	1.33(2)
Ir–N(1)	2.07(2)	C(1)–C(2)	1.34(3)
Ir–C(1)	2.02(2)	C(1)–C(3)	1.45(3)
Bond angles			
P–Ir–P	172.2(2)	Ir–O(1)–C(3)	88(1)
P–Ir–O(1)	93.20(9)	C(3)–O(2)–C(4)	118(2)
P–Ir–N(1)	91.7(1)	Ir–N(1)–N(2)	130(1)
P–Ir–C(1)	89.4(1)	Ir–N(1)–C(5)	126(1)
P–Ir–H	86.28(9)	N(2)–N(1)–C(5)	104(2)
O(1)–Ir–N(1)	98.2(6)	Ir–C(1)–C(2)	150(2)
O(1)–Ir–C(1)	63.6(7)	Ir–C(1)–C(3)	94(2)
O(1)–Ir–H	162.2(5)	C(2)–C(1)–C(3)	116(2)
N(1)–Ir–C(1)	161.8(7)	O(1)–C(3)–C(1)	115(2)
N(1)–Ir–H	99.6(5)	N(1)–C(5)–C(6)	111(2)
C(1)–Ir–H	98.6(6)		

(2.054(4) Å) [17], but almost identical with that of the complex $[IrH(C_6H_5)Cl(P^iPr_3)_2]$ (2.010(5) Å) [18]. The C(1)–C(2) (1.34(3) Å), C(1)–C(3) (1.45(3) Å) and C(3)–O(1) (1.25(2) Å) distances are comparable with those found for the same conformation for the vinyl ligand in related octahedral compounds [15b,19]. The Ir–O(1) distance, 2.28(1) Å, is about 9% longer than the mean of the Ir–O distances previously reported (2.088) [2,20] and about 0.05 Å longer than those found in **1** (2.220(5) and 2.235(5) Å) [2], where the oxygen atoms of the coordinated acetone are also *trans* to the hydride. The position of the hydride in **3** was not determined by the X-ray analysis, and its position was therefore calculated with the HYDEX program [21]. The Ir–P and Ir–N distances as well as the N–C and N–N distances in the pyrazole ligand are clearly in the range expected and deserve no further comments.

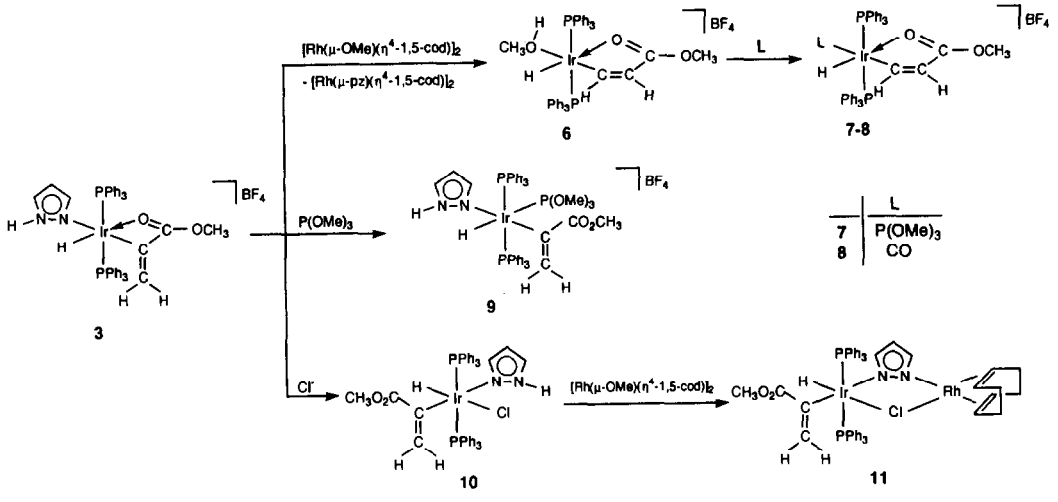
2.3. Reactions of 3

The reactivity of the hydride-vinyl derivative **3** is summarized in Scheme 3. The acidic NH group of the pyrazole ligand in this compound reacts with the methoxy-bridged $[\{Rh(\mu\text{-}OMe)(\eta^4\text{-}1,5\text{-}COD)\}_2]$ in a redistribution reaction. Treatment of **3** with the dimer $[\{Rh(\mu\text{-}OMe)(\eta^4\text{-}1,5\text{-}COD)\}_2]$, in a 2:1 molar ratio in acetone at 0°C, led to a mixture of the complexes **6** and $[\{Rh(\mu\text{-}pz)(\eta^4\text{-}1,5\text{-}COD)\}_2]$ [22], which were separated by fractional crystallization from acetone–diethyl ether. The formation of **6** from **3** also involves the isomerization of the vinyl ligand, resulting in the transformation of the four-membered ring with an exocyclic C=C double bond to a five-membered ring with an endocyclic C=C double bond. The *cis* stereochemistry of the two hydrogen atoms at the C=C double bond is supported by the H–H coupling constant for the resonances of these protons in the ^1H NMR spectrum. The value of 10 Hz is typical for this arrangement.

The methanol ligand in **6** can be readily displaced by trimethyl phosphite and carbon monoxide to yield the cationic complexes **7** and **8**, where the vinyl ligand shows the same conformation as in **6**. The proposed structures for **6–8** in Scheme 3 are supported by the spectroscopic data (see Section 3). The $^{31}P\{^1H\}$ NMR spectrum of **7** shows a characteristic AB_2 splitting pattern. In addition, the value of the P–C coupling constants of the signal assigned to the α-carbon atom of the coordinated vinyl ligand in the $^{13}C\{^1H\}$ NMR spectrum is characteristic for an arrangement of this atom *cis* to the two equivalent phosphine ligands (12 Hz) and *trans* to $P(OMe)_3$ (125 Hz). Furthermore, the IR spectra of **6–8** contain C=O stretching frequencies at about 1600 cm^{-1}, which indicate the η^1-coordination of the carbonyl ester group.

The Ir–O(1) distance in **3** indicates that the bond between the iridium atom and the carbonyl group of the ester is very weak. This group should be easily displaced from the metal by Lewis bases. In fact, **3** reacts with trimethyl phosphite and sodium chloride to give the complexes **9** and **10** respectively, in which the ester unit is not coordinated. This is substantiated by the IR spectra of these compounds, which have a ν(CO) band at about 1700 cm^{-1}. The supposition that the hydride and phosphite are *trans* in **9** is supported by the ^1H NMR spectrum in the hydride region, which shows a doublet of triplets at −8.55 ppm with P–H coupling constants of 240.9 and 15.3 Hz.

Using **10** as starting material, a new heterodinuclear compound containing a bridged $Ir(\mu\text{-}pz)(\mu\text{-}Cl)Rh$ framework can be prepared (see Scheme 3). Treatment of **10** with $[\{Rh(\mu\text{-}OMe)(\eta^4\text{-}1,5\text{-}COD)\}_2]$, in a 2:1 mo-



Scheme 3.

lar ratio in methanol, leads to **11** with a 80% yield. Although the spectroscopic data of **11** (see Section 3) are also consistent with *trans* hydride and pyrazole ligands, we assume that the arrangement of the ligands around the iridium atom is that shown in Scheme 3. We note that there is good evidence from X-ray diffraction studies on similar systems to show that during this type of reactions the stereochemistry at the metal, which binds chloride and pyrazole ligands, remains unchanged [23].

2.4. Concluding remarks

These results show that $[IrH_2(Me_2CO)(Hpz)(PPh_3)_2]BF_4$ (**2**) reacts with methyl propiolate and acetylenedicarboxylic dimethyl ester to give the hydridevinyl derivatives $[IrH(C(COOCH_3)=CH_2)(Hpz)(PPh_3)_2]BF_4$ (**3**) and $[IrH(C(COOCH_3)=CH(CO_2CH_3))(Hpz)(PPh_3)_2]BF_4$ (**5**). The acidic NH group of the pyrazole ligand in **2** reacts with the $[\{Rh(\mu\text{-OMe})(\eta^4\text{-1,5-COD})\}_2]$ to give $[IrH(CH=CHCOOCH_3)(MeOH)(PPh_3)_2]BF_4$ (**6**) and $[\{Rh(\mu\text{-pz})(\eta^4\text{-1,5-COD})\}_2]$. This reaction involves the isomerization of the vinyl ligand. Thus the four-membered ring with an exocyclic C=C double bond in **3** is transformed into a five-membered ring with an endocyclic C=C double bond.

Reactions of **3** with $P(OMe)_3$ and Cl^- afford the complexes $[IrH(C(CO_2CH_3)=CH_2)(Hpz)(P(OMe)_3)(PPh_3)_2]BF_4$ (**9**) and $[IrH(C(CO_2CH_3)=CH_2)Cl(Hpz)(PPh_3)_2]$ (**10**) respectively, and **10** with $[\{Rh(\mu\text{-OMe})(\eta^4\text{-1,5-COD})\}_2]$ gives the dinuclear compound $[H(C(CO_2CH_3)=CH_2)(PPh_3)_2Ir(\mu\text{-pz})(\mu\text{-Cl})Rh(\eta^4\text{-1,5-COD})]$ (**11**).

3. Experimental section

3.1. General considerations

All reactions were carried out under argon using Schlenk tube techniques. Solvents were dried by the usual procedures and distilled under argon prior to use. The starting materials $[IrH_2(Me_2CO)_2(PPh_3)_2]BF_4$ (**1**) [24] and $[\{Rh(\mu\text{-OMe})(\eta^4\text{-diolefin})\}_2]$ (diolefin = 1,5-COD, TFB) [25] were prepared by published methods.

3.2. Physical measurements

IR spectra were recorded on a Perkin–Elmer 783 IR spectrophotometer and NMR spectra on Varian XL 200 and Unity 300 spectrophotometers. Chemical shifts are expressed in ppm upfield from Me_4Si (^{13}C, ^1H) and 85% H_3PO_4 (^{31}P) as external references. C, H and N analyses were carried out with a Perkin–Elmer 240 C microanalyser.

3.3. Preparation of $[IrH_2(Me_2CO)(Hpz)(PPh_3)_2]BF_4$ (2)

Complex $[IrH_2(Me_2CO)_2(PPh_3)_2]BF_4$ (**1**) (46.0 mg, 0.05 mmol) was dissolved in acetone (7 ml) and the stoichiometric amount of pyrazole (3.40 mg, 0.05 mmol) was added. After concentration to about 1 ml, a microcrystalline white solid was precipitated by addition of diethyl ether. This was filtered off and washed with diethyl ether (yield, 46.6 mg (95%)). Anal. Found: C, 54.25; H, 4.60; N, 3.18. $C_{42}H_{42}BF_4IrN_2OP_2$ calc.: C, 54.15; H, 4.54; N, 3.01%. IR (Nujol): ν(NH) 3400, ν(IrH) 2310, 2300, 2240, 2210, ν(CO) 1660 cm^{-1}. ^1H NMR ($CDCl_3$, −40°C, 300 MHz): δ 11.6 (s, NH); 7.4–7.2 (PPh_3); 7.69, 6.44 and 5.59 (all br; H^3, H^5 and H^4 of Hpz); 1.48 (s, $O=C(CH_3)_2$); −20.72 (td, J(PH) = 17.5 Hz, J(HH) = 7 Hz; IrH); −27.74 (td, J(PH) = 16.2 Hz, J(HH) = 7Hz; IrH) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 80.9 MHz): δ 24.84 (s) ppm.

3.4. Preparation of $[IrH(C(COOCH_3)=CH_2)(Hpz)(PPh_3)_2]BF_4$ (3) and $[IrH(CH=CHCOOCH_3)(Hpz)(PPh_3)_2]BF_4$ (4)

A solution of **2** (93.1 mg, 0.10 mmol) in 10 ml of 1,2-dichloroethane was treated with methyl propiolate (10 μl, 0.11 mmol) and stirred for 30 min. The solution was concentrated to about 1 ml *in vacuo*. Addition of 10 ml of diethyl ether gave a white precipitate, which was washed with diethyl ether and dried *in vacuo*. A mixture of two isomers in the ratio **3**:**4** = 7:1 was obtained. The isomer **3** was isolated as a pure microcrystalline solid by fractional crystallization from acetone–diethyl ether (yield, 78 mg (82%)). Anal. Found: C, 53.70; H, 4.10; N, 2.91. $C_{43}H_{40}BF_4IrN_2O_2P_2$ calc.: C, 53.93; H, 4.21; N, 2.92%. IR (Nujol): ν(NH) 3330, ν(IrH) 2255, ν(CO) 1570 cm^{-1}. **3**: ^1H NMR ($CDCl_3$, 300 MHz): δ 11 (br, NH); 7.4–7.3 (PPh_3); 7.03, 6.87 and 5.51 (all br; H^3, H^5 and H^4 of Hpz); 6.53 and 5.37 (both d, each 1H, J(HH) = 1.8 Hz; $=CH_2$); 2.93 (s, 3H, OCH_3); −27.84 (t, J(PH) = 14.85 Hz; IrH) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.4 MHz): δ 11.8 (s) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.4 MHz): δ 179 (s, Ir–O=*C*); 143, 131 and 106 (all s; C^3, C^5 and C^4 of Hpz); 138 and 118 (both br; Ir–*C*=C and Ir–C=*C*); 134, 130 and 128 (PPh_3); 51 (s, OCH_3) ppm. **4**: ^1H NMR ($CDCl_3$, 300 MHz): δ 11.5 (br, NH); 9.52 and 5.83 (both d, each 1H, J(HH) = 8.3 Hz; –HC=CH–); 7.4–7.3 (PPh_3), −23.27 (t, J(PH) = 14.6 Hz; IrH) ppm. $^{31}P\{^1H\}$NMR ($CDCl_3$, 121.4 MHz): δ 17.9 (s) ppm.

3.5. Preparation of $[IrH(C(COOCH_3)=CH(CO_2CH_3))(Hpz)(PPh_3)_2]BF_4$ (5)

This compound was prepared as described for **3**, starting from **2** (93.1 mg, 0.10 mmol) and acetylenedicarboxylic dimethyl ester (14 μl, 0.11 mmol). A light-yellow solid was formed (yield, 81 mg (80%)). Anal.

Found: C, 53.16; H, 4.12; N, 2.73. $C_{45}H_{42}BF_4IrN_2O_4P_2$ calc.: C, 53.21; H, 4.17; N, 2.76%. IR (Nujol): ν(NH) 3370, ν(IrH) 2300, ν(CO) 1705, 1565 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 10.9 (br, NH); 7.4–7.3 (PPh_3); 7.02, 6.42 and 5.47 (all br; H^3, H^5 and H^4 of Hpz); 5.36 (s, =CHR); 3.37 and 2.82 (both s, each 3H, OCH_3); −27.26 (t, J(PH) = 14.6 Hz; IrH) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.4 MHz): δ 7.4 (s) ppm.

3.6. Preparation of $[IrH(CH=CHCOOCH_3)(MeOH)(PPh_3)_2]BF_4$ (6)

Compound **3** (95.7 mg, 0.10 mmol) was added to a suspension of $[\{Rh(\mu\text{-OMe})(\eta^4\text{-1,5-COD})\}_2]$ (48.4 mg, 0.10 mmol) in 5 ml of acetone. After stirring for 1 h at 0°C, the yellow solution was concentrated to about 1 ml. Addition of 5 ml of diethyl ether led to a white precipitate, which was washed with diethyl ether and dried *in vacuo* (yield, 55 mg (60%)) Anal. Found: C, 53.11; H, 4.64. $C_{40}H_{41}BF_4IrO_3P_2$ calc.: C, 53.43; H, 4.37%. IR (Nujol): ν(OH) 3470, ν(IrH) 2330, ν(CO) 1665 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 9.42 and 5.57 (both d, each 1H, J(HH) = 10 Hz; –HC=CH–); 7.6–7.5 (PPh_3); 3.41 (s, 3H; CH_3OH); 2.20 (s, 3H; OCH_3); −23.02 (t, J(PH) = 13.5 Hz; IrH) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.4 MHz): δ 22.8 (s) ppm.

The filtrate was taken to dryness *in vacuo* and the residue was treated with 10 ml of hexane. The resulting suspension was filtered, and the yellow filtrate was concentrated to give a yellow solid, which was filtered off and spectroscopically identified as $[\{Rh(\mu\text{-pz})(\eta^4\text{-1,5-COD})\}_2]$.

3.7. Preparation of $[IrH(CH=CHCOOCH_3)(P(OMe)_3)(PPh_3)_2]BF_4$ (7)

A solution of **6** (92.1 mg, 0.10 mmol) in 5 ml of dichloromethane was treated with a slight excess of trimethyl phosphite (13 μl, 0.11 mmol) and stirred for 2 h at room temperature. The solution obtained was concentrated to about 1 ml *in vacuo*. Addition of diethyl ether led to a white precipitate, which was washed with diethyl ether and dried *in vacuo* (yield, 86 mg (85%)). Anal. Found: C, 50.83; H, 4.67. $C_{43}H_{45}BF_4IrO_5P_3$ calc.: C, 50.95; H, 4.47%. IR (Nujol): ν(IrH) 2220, ν(CO) 1580 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 8.63 (dtd, J(HH) = 9.2 Hz; J(PH) = 2.0 Hz (P of PPh_3); J(PH) = 11.2 Hz (P of $P(OMe)_3$); –*H*C=CH–); 7.6–7.36 (PPh_3); 6.08 (dtd, J(HH) = 9.2 Hz; J(PH) = 2.3 Hz (P of PPh_3); J(PH) = 16.1 Hz (P of $P(OMe)_3$); –HC=C*H*–); 3.19 (d, J(PH) = 10.8 Hz; $POCH_3$); 2.99 (s, 3H; OCH_3), −22.95 (dt, J(PH) = 18 Hz (P of $P(OMe)_3$); J(PH) = 13.8 Hz (P of PPh_3); IrH) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.4 MHz): δ 89 (t, J(PP) = 29 Hz; $P(OMe)_3$); 14.7 (d, J(PP) = 29 Hz; PPh_3) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.4 MHz): δ 188 (dt, J(CP) = 125 Hz (P of $P(OMe)_3$); J(CP) = 12 Hz (P of PPh_3); Ir–*C*=C); 185 (d, J(CP) = 12 Hz (P of $P(OMe)_3$); Ir–C=*C*); 181 (s, Ir–O=*C*); 133, 130 and 128 (PPh_3); 53 ($P(OMe)_3$); 51 (s, OCH_3) ppm.

3.8. Preparation of $[IrH(CH=CHCOOCH_3)(CO)(PPh_3)_2]BF_4$ (8)

Complex **6** (92.1 mg, 0.10 mmol) was dissolved in dichloromethane (7 ml) and CO bubbled into the solution for 1 h. After concentration to about 1 ml, the microcrystalline white solid was precipitated by addition of diethyl ether, washed with diethyl ether and dried *in vacuo* (yield, 73 mg (80%)). Anal. Found: C, 53.14; H, 3.89. $C_{41}H_{36}BF_4IrO_3P_2$ calc.: C, 53.66; H, 3.95%. IR (CH_2Cl_2): ν(CO) 2050 cm^{-1}. IR (Nujol): ν(IrH) 2010, ν(CO) 2060, 1580 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 8.84 and 6.19 (both d, each 1H, J(HH) = 9.3 Hz; –HC=CH–); 7.4–7.1 (PPh_3); 3.15 (s, 3H; OCH_3); −20.28 (t, J(PH) = 12 Hz; IrH) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.4 MHz): δ 11.5 (s) ppm.

3.9. Preparation of $[IrH(C(CO_2CH_3)=CH_2)(Hpz)(P(OMe)_3)(PPh_3)_2]BF_4$ (9)

A solution of **3** (95.7 mg, 0.10 mmol) in 7 ml of 1,2-dichloroethane was treated with a slight excess of trimethyl phosphite (13 μl, 0.11 mmol) and stirred for 1 h at room temperature. The solution obtained was concentrated to about 1 ml *in vacuo*. Addition of hexane led to a white precipitate, which was washed with hexane and dried *in vacuo* (yield, 76 mg (70%)). Anal. Found: C, 51.47; H, 4.98; N, 2.38. $C_{46}H_{49}BF_4IrN_2O_5P_3$ calc.: C, 51.08; H, 4.56; N, 2.59%. IR (Nujol): ν(NH) 3320, ν(IrH) 2200, ν(CO) 1680 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 11.7 (br, NH); 7.4–7.2 (PPh_3); 7.60, 6.38 and 5.32 (all br; H^3, H^5 and H^4 of Hpz); 6.15 and 5.29 (both d, each 1H, J(HH) = 2 Hz; =CH_2); 3.51 (d, J(PH) = 12 Hz; $POCH_3$); 2.82 (s, 3H; OCH_3); −8.55 (dt, J(PH) = 240.9 Hz (P of $P(OMe)_3$); J(PH) = 15.3 Hz (P of PPh_3); IrH) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 80.9 MHz): δ 91 (t, J(PP) = 22 Hz; $P(OMe)_3$); 2.87 (d, J(PP) = 22 Hz; PPh_3) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 50.3 MHz): δ 174 (s, Ir–C–*C*=O); 147, 133 and 107 (all s; C^3, C^5 and C^4 of Hpz); 136 and 120 (both br; Ir–*C*=C and Ir–C=*C*); 134, 130 and 127 (PPh_3); 55 ($P(OMe)_3$); 51 (s, OCH_3) ppm.

3.10. Preparation of $[IrH(C(CO_2CH_3)=CH_2)Cl(Hpz)(PPh_3)_2]$ (10)

A solution of **3** (95.7 mg, 0.10 mmol) in 10 ml of methanol was treated with NaCl (5.8 mg, 0.10 mmol) and stirred for 2 h at room temperature. The resulting suspension was concentrated to about 1 ml and the white solid obtained was washed with methanol and dried *in vacuo* (yield, 72 mg (80%)). Anal. Found: C,

56.46; H, 4.42; N, 2.94. $C_{43}H_{40}ClIrN_2O_2P_2$ calc.: C, 56.98; H, 4.45; N, 3.09%. IR (Nujol): ν(NH) 3270, ν(IrH) 2260, ν(CO) 1705 cm^{-1}. ^1H NMR (C_6D_6, 300 MHz): δ 12 (br, NH); 8.0–7.1 (PPh_3); 6.88, 6.69 and 5.82 (all br; H^3, H^5 and H^4 of Hpz); 6.21 and 5.22 (both br, each 1H; $=CH_2$); 3.21 (s, 3H; OCH_3); −20.31 (t, J(PH) = 13.7 Hz; IrH) ppm. $^{31}P\{^1H\}$ NMR (C_6D_6, 121.4 MHz): δ 8.67 (s) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6, 75.4 MHz): δ 175 (s, Ir–C–*C*=O); 143, 133 and 107 (all s; C^3, C^5 and C^4 of Hpz); 135, 129 and 127 (PPh_3); 133 (t, J(CP) = 3 Hz; Ir–C=*C*); 132 (t, J(CP) = 25 Hz; Ir–*C*=C); 50 (s, OCH_3) ppm.

3.11. *Preparation of* $[H(C(CO_2CH_3)=CH_2)(PPh_3)_2Ir(\mu\text{-}pz)(\mu\text{-}Cl)Rh(\eta^4\text{-}1,5\text{-}COD)]$ (11)

To a suspension of $[\{Rh(\mu\text{-}OMe)(\eta^4\text{-}1,5\text{-}COD)\}_2]$ (24.2 mg, 0.05 mmol) in 10 ml of methanol was added **10** (90.6 mg, 0.10 mmol). After being stirred for 2 h, the resulting suspension was concentrated to about 1 ml and the light-yellow solid obtained was repeatedly washed with methanol and dried *in vacuo* (yield, 89 mg (80%)). Anal. Found: C, 55.10; H, 4.93; N, 2.39 $C_{51}H_{51}ClIrN_2O_2P_2Rh$ calc: C, 54.86; H, 4.60; N, 2.51%. IR (Nujol): ν(IrH) 2240, ν(CO) 1685 cm^{-1}. ^1H NMR (C_6D_6, 200 MHz): δ 7.8–7.0 (PPh_3); 7.47, 6.81 and 5.67 (all br; H^3, H^5 and H^4 of pz); 6.37 and 5.55 (both br, each 1H; $=CH_2$); 4.40 and 3.75 (both br, each 2H; –HC=CH– of C_8H_{12}); 2.24 and 1.59 (both br, each 4H; $-CH_2-$ of C_8H_{12}); 3.13 (s, 3H; OCH_3); −19.68 (t, J(PH) = 14.2 Hz; IrH) ppm. $^{31}P\{^1H\}$ NMR (C_6D_6, 121.4 MHz): δ 8.65 (s) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6, 75.4 MHz): δ 175 (s, Ir–C–*C*=O); 145, 137 and 106 (all s; C^3, C^5 and C^4 of pz); 135, 129 and 127 (PPh_3); 133 (t,

TABLE 2. Crystallographic data for **3**

Formula	$C_{43}H_{40}BF_4IrN_2O_2P_2 \cdot C_3H_6O$
Formula weight	1015.85
Crystal size (mm × mm × mm)	0.3 × 0.35 × 0.5
Crystal system	Monoclinic
Space group	$P\,2_1/m$ (No. 11)
Cell dimensions determination	23 reflections; $11° < \theta < 14°$
a (Å)	9.661(3)
b (Å)	22.903(3)
c (Å)	11.056(3)
β (°)	99.82(1)
V (Å^3)	2410(1)
Z	2
d_{calc} (g cm^{-3})	1.400
Diffractometer	Enraf–Nonius CAD4
Radiation (graphite monochromated)	Mo Kα (0.70930 Å)
Temperature (K)	293
μ (cm^{-1})	28.75
Scan method	ω–2θ
2θ (maximum) (°)	50
Total number of reflections scanned	4630
Number of unique reflections	4363
Number of observed reflections ($F_o > 3\sigma(F_o)$)	2985
Number of parameters refined	307
R	0.041
R_w	0.047
Reflection-to-parameter ratio	9.725
Residual electron density (e Å^{-3})	+2.03 to −0.81

TABLE 3. Positional parameters and estimated standard deviations

Atom	x	y	z	B_{eq} (Å^2)
Ir	0.03716(5)	0.250	0.01303(5)	2.905(8)
P	0.0494(2)	0.35153(8)	0.0052(2)	3.17(4)
O(1)	−0.2005(8)	0.250	0.0054(9)	4.3(2)
O(2)	−0.340(1)	0.250	−0.179	6.0(3)
N(1)	0.0969(9)	0.250	0.2024(9)	3.4(2)
N(2)	0.227(1)	0.250	0.2707(9)	4.2(2)
C(1)	−0.082(1)	0.250	−0.156(1)	3.4(2)
C(2)	−0.092(2)	0.250	−0.278(1)	6.6(4)
C(3)	−0.213(1)	0.250	−0.109(1)	4.0(3)
C(4)	−0.464(1)	0.250	−0.118(2)	9.1(6)
C(5)	0.011(1)	0.250	0.284(1)	5.2(3)
C(6)	0.086(1)	0.250	0.402(1)	6.1(4)
C(7)	0.225(2)	0.250	0.392(1)	5.9(4)
C(8)	0.1361(8)	0.3820(4)	−0.1141(7)	3.4(2)
C(9)	0.1581(9)	0.4416(4)	−0.1224(9)	4.5(2)
C(10)	0.221(1)	0.4637(4)	−0.2123(9)	4.9(2)
C(11)	0.269(1)	0.4293(5)	−0.2972(9)	5.4(2)
C(12)	0.251(1)	0.3697(5)	−0.2890(9)	6.0(3)
C(13)	0.1867(9)	0.3460(4)	−0.1977(8)	4.3(2)
C(14)	−0.1253(8)	0.3862(4)	−0.0167(8)	3.6(2)
C(15)	−0.2099(9)	0.3725(4)	0.0699(9)	4.7(2)
C(16)	−0.3442(9)	0.3952(5)	0.056(1)	5.5(2)
C(17)	−0.395(1)	0.4288(5)	−0.041(1)	6.2(3)
C(18)	−0.314(1)	0.4420(5)	−0.128(1)	5.9(3)
C(19)	−0.1758(9)	0.4208(4)	−0.1162(9)	4.6(2)
C(20)	0.1463(8)	0.3864(3)	0.1419(7)	3.2(2)
C(21)	0.090(1)	0.4208(4)	0.2212(8)	4.6(2)
C(22)	0.172(1)	0.4442(5)	0.3248(9)	5.5(2)
C(23)	0.313(1)	0.4336(5)	0.3494(9)	5.3(2)
C(24)	0.372(1)	0.3993(5)	0.2696(9)	5.1(2)
C(25)	0.2913(9)	0.3755(4)	0.1671(8)	4.2(2)
H	0.200	0.250	−0.030	6.0 *
F(1)	0.5086(9)	0.750	0.8152(9)	7.7(3)
F(2)	0.4615(9)	0.750	0.6104(9)	7.4(2)
F(3)	0.3210(7)	0.7017(3)	0.7165(7)	8.8(2)
B	0.402(2)	0.750	0.713(2)	5.2(4)
O(100)	0.320(1)	0.5511(4)	0.542(1)	12.2(4)
C(100)	0.275(1)	0.5942(5)	0.492(1)	7.3(3)
C(200)	0.361(1)	0.6316(7)	0.429(1)	8.9(4)
C(300)	0.130(1)	0.6141(9)	0.493(2)	12.1(6)

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $B_{eq} = (\frac{4}{3})[a^2B_{1,1} + b^2B_{2,2} + c^2B_{3,3} + ab(\cos\gamma)B_{1,2} + ac(\cos\beta)B_{1,3} + bc(\cos\alpha)B_{2,3}]$.

$J(CP) = 3$ Hz; Ir–C≡*C*); 132 (t, $J(CP) = 25$ Hz; Ir–*C*≡C); 80.6, 80.4, 76.3 and 76.1 (–HC≡CH– of C_8H_{12}); 50 (s, OCH_3); 30.9 and 30.6 ($-CH_2-$ of C_8H_{12}) ppm.

3.12. X-ray data collection

Crystals of compound **3** suitable for X-ray diffraction studies were obtained by slow diffusion of diethyl ether into a saturated acetone solution of the compound. Crystal data collection parameters are summarized in Table 2. Intensity data were corrected for Lorentz and polarization effects. An empirical absorption correction was applied (ψ scan method; minimum transmission, 92.44%). The structure was solved by direct methods (SHELXS-86) [26]. Atomic coordinates (Table 3) and anisotropic thermal parameters of all non-hydrogen atoms were refined by full-matrix least-squares (FMLS) analysis. All atoms except the PPh_3 atoms lie in the crystallographic mirror plane. So only one half of the molecule has to be calculated. The positions of the hydrogen atoms were calculated according to ideal geometry (C–H distance, 0.95 Å) and were included in the last FMLS refinement using the riding method. The position of the hydride ligand was calculated with the HYDEX program and was used only for structure factor calculation. In the last refinement cycles a weighting scheme was used with a weighting factor $w = 1/[\sigma(F_o)]^2$. The highest peaks in the last difference-fourier analysis lies in a distance of about 1.00 Å near to the iridium atom. In the crystal, one molecule of acetone is present. All calculations were performed on a Micro-VAX computer using the program package SDP [27] from Enraf–Nonius. Full details of atomic coordinates, temperature features etc. are available from the Cambridge Crystallographic Data Centre.

4. Supplementary material available

Tables of positional parameters, general displacement parameter expressions, bond lengths and bond angles (seven pages) and a listing of structure factors for **3** (22 pages) are also available.

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