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Synthesis and Characterization of New Hydridoiridium Complexes Containing Carboxylate Ligands

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The complexes $IrH_2(\eta^2\text{-}O_2CR)(PPh_3)_2$ (R = (*S*)-CH(NaphOMe)Me (**2**), (*R*)-CH(OMe)Ph (**3**), (*R*)-$C(CF_3)$(OMe)Ph (**4**), (*S*)-$\overline{\mathrm{CHOC({=}O)CH_2CH_2}}$ (**5**)) have been prepared by reaction of $IrH_5(PPh_3)_2$ (**1**) with the corresponding carboxylic acid RCO_2H. The reactivity of these compounds toward acetylenedicarboxylic dimethyl ester and HBF_4 has been studied. **2–5** react with acetylenedicarboxylic dimethyl ester to afford the hydrido-vinyl complexes $IrH\{C(CO_2Me){=}CH(CO_2Me)\}(\eta^2\text{-}O_2CR)(PPh_3)_2$ (R = (*S*)-CH(NaphOMe)Me (**6**), (*R*)-CH(OMe)Ph (**7**), (*R*)-$C(CF_3)$(OMe)Ph (**8**), (*S*)-$\overline{\mathrm{CHOC({=}O)CH_2CH_2}}$ (**9**)) by insertion of the alkyne into one of the two Ir–H bonds of the starting complexes. Reactions of **2** and **3** with HBF_4 in diethyl ether lead to the hydrido-bridged dinuclear complexes $[Ir_2H_2(PPh_3)_4(\mu\text{-}H)_2(\mu\text{-}\eta^2\text{-}O_2CR)]BF_4$ (R = (*S*)-CH(NaphOMe)Me (**10**), (*R*)-CH(OMe)Ph (**11**)). The molecular structure of **11** was determined by an X-ray investigation. Compound **11** crystallizes in the orthorhombic system, space group $P2_12_12_1$, with cell dimensions $a = 14.082(1)$ Å, $b = 23.169(2)$ Å, and $c = 25.291(3)$ Å, and $Z = 4$. The structure was refined to the following R and R_w values: 0.0414 and 0.0389 for 8343 observed reflections. The cation of **11** can be described as a dinuclear species of 32 valence electrons. Electron counting, to satisfy the 18-electron rule, suggests the presence of an iridium-iridium double bond which is consistent with the observed iridium-iridium distance (2.6592(6) Å). EHT-MO calculations on the model $[Ir_2H_2(PH_3)_4(\mu\text{-}H)_2(\mu\text{-}\eta^2\text{-}O_2CH)]^+$ suggests the existence of a "partial" double bond between the metal atoms. However, the interaction between metals is not based on the direct overlap of the iridium orbitals, but on the three center bonds formed by the bridging system.

Introduction

The chemistry of hydride complexes of transition metals has received increasing attention in recent years, owing to the possibilities offered by these compounds for the design of homogeneous catalysts[1] and the preparation of other types of complexes.[2] The study of the nature of the metal–hydrogen and hydrogen–hydrogen interactions[3] has been another relevant factor in the development of this field, mainly since the first report by Kubas *et al.* on the coordination of molecular hydrogen to a transition metal.[4]

Mononuclear hydridoiridium complexes have proved to be active catalysts[5] and useful starting materials for the synthesis of hydride-bridged bimetallic compounds.[6] Well-studied systems of this type include the simple phosphine complexes $IrH_5(PR_3)_2$[7] and $IrH_3(PR_3)_3$,[8] the mixed carbonyl phosphine compounds $IrH(CO)_2(PR_3)_2$,[9] and the cationic solvates $[IrH_2S_2(PR_3)_2]^+$ [10] (S = solvent). With the notable exception of the Crabtree's work[11] on alkane dehydrogenation, comparatively little is known about the chemistry of dihydride complexes of formula $IrH_2(\eta^2\text{-}O_2CR)(PR_3)_2$.

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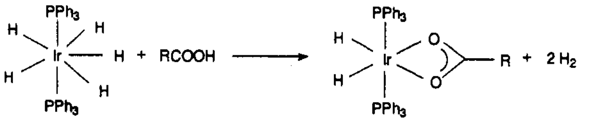
For several years we have been exploring the reactivity and catalytic potential of hydrido-iridium complexes of the types $IrH(diolefin)L_2$[12] [diolefin = 1,5-cyclooctadiene (COD), tetrafluorobenzobarrelene (TFB); L = PPh_3, $AsPh_3$; L_2 = $Ph_2P(CH_2)_nPPh_2$], $IrH_2SiR_3(diolefin)L$[13] (diolefin = COD, TFB; L = $AsPh_3$, PR_3), $IrH_2Cl(PiPr_3)_2$[14] and $IrH_2(pz)(Hpz)(PPh_3)_2$[15] (Hpz = pyrazole). Continuing our work in this field, we now report the synthesis and reactivity of new $IrH_2(\eta^2\text{-}O_2CR)(PPh_3)_2$ compounds. In the course of this research the hydrido-bridged dinuclear cation $[Ir_2H_2(PPh_3)_4(\mu\text{-}H)_2(\mu\text{-}\eta^2\text{-}O_2C\{(R)\text{-}CH(OMe)Ph\})]^+$ has been isolated as its BF_4^- salt and characterized by a single-crystal X-ray structural analysis. EHT-MO calculations on the model $[Ir_2H_2(PH_3)_4(\mu\text{-}H)_2(\mu\text{-}\eta^2\text{-}O_2CH)]^+$ cation have been also carried out.

In addition, it should be noted that the hydrido-bridged dinuclear complexes of iridium previously reported and characterized by single-crystal X-ray analysis have in the core of their structures some of the following units: $Ir_2H_4(\mu\text{-}H)_2$,[16] $Ir_2H_2(\mu\text{-}H)_3$,[17] $Ir_2H_2(\mu\text{-}H)$,[18] $Ir_2H(\mu\text{-}H)_2$,[19] $Ir_2H(\mu\text{-}H)$,[20] $Ir_2(\mu\text{-}H)_3$,[21] $Ir_2(\mu\text{-}H)_2$,[22] and $Ir_2(\mu\text{-}H)$.[23] Our complex represents the first example of a hydrido-bridged dinuclear iridium compound with the $Ir_2H_2(\mu\text{-}H)_2$ unit characterized by X-ray diffraction.

Results and Discussion

Synthesis, Characterization and Reactivity of $IrH_2(\eta^2\text{-}O_2CR)(PPh_3)_2$. Treatment of suspensions of $IrH_5(PPh_3)_2$ with RCO_2H (R = (*S*)-CH(NaphOMe)Me, (*R*)-CH(OMe)Ph, (*R*)-$C(CF_3)(OMe)Ph$, (*S*)-$\overline{CHOC({=}O)CH_2CH_2}$) in toluene under reflux results in the formation of colourless solutions, from which complexes **2–5** (eq 1) were isolated, by addition of methanol, as white solids in 60–80% yield.



1

2-5

(1)

R = (S)-CH(NaphOMe)Me (**2**), (R)-CH(OMe)Ph (**3**), (R)-$C(CF_3)(OMe)Ph$ (**4**), (S)-$\overline{CHOC(=O)CH_2CH_2}$ (**5**)

These compounds are formulated as octahedral derivatives containing chelating carboxylate ligands on the basis of assignments for $\nu_{asym}(OCO)$ and $\nu_{sym}(OCO)$ at ca. 1565–1520 and 1430–1400 cm^{-1}, respectively. In this line, the values found for $\Delta\nu$ ($\nu_{asym}(OCO) - \nu_{sym}(OCO)$) coincide with those previously observed for related ruthenium and osmium derivatives.[24] Furthermore, the complexes contain two hydrides. Their presence is strongly supported by the $^{31}P\{^1H\}$ NMR spectra, which show singlets that under *off-resonance* conditions split into triplets due to P–H coupling. The existence of two hydrides is also inferred from IR and ^1H NMR spectra. The IR spectra have one or two strong absorptions at about 2200 cm^{-1}, attributable to ν(Ir–H), in agreement with a cis arrangement. The ^1H NMR spectra show a triplet between −28.7 and −29.8 ppm, with P–H coupling constants of about 17 Hz.

Two useful synthetic routes for the preparation of complexes of the type $IrH_2(\eta^2\text{-}O_2CR)(PPh_3)_2$ have been previously reported.[11a] The first, which is more useful for arylphosphine complexes, involves treatment of $[IrH_2(\eta^1\text{-}OCMe_2)_2(PR_3)_2]^+$ with the sodium salt of the carboxylic acid. The second is shown in eq 2.

$$[Ir(\mu\text{-}Cl)(COD)]_2 \xrightarrow[-AgCl]{AgOCOR} [Ir(\mu\text{-}OCOR)(COD)]_2 \xrightarrow[(ii)\ H_2]{(i)\ 4PR_3} IrH_2(\eta^2\text{-}O_2CR)(PR_3)_2 + C_8H_{16} \quad (2)$$

The formation of **2–5** can be rationalized in terms of the loss of four hydrogen atoms as molecular hydrogen, accompanied by binding of the carboxylate anion to the central metal in an η^2-fashion. We suggest that the first step of the reaction shown in eq 1 may be the protonation of **1** to give the cationic intermediate $[IrH_2(\eta^2\text{-}H_2)_2(PPh_3)_2]^+$, which rapidly reacts with RCO_2^- by liberation of molecular hydrogen to give **2–5**. In this context, it

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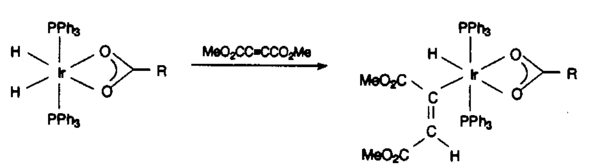
is noteworthy that a variety of polyhydrides of tungsten, rhenium, osmium and iridium react with HBF_4 in acetonitrile to form molecular hydrogen and solvento complexes.[10k] Crabtree and Lavin have also investigated the protonation of $IrH_5(PCy_3)_2$ with HBF_4, which leads to the cationic dihydrogen complex $[IrH_2(\eta^2\text{-}H_2)_2(PCy_3)_2]^+$; in acetonitrile the nitrogen donor ligand displaces the two dihydrogen ligands to give $[IrH_2(NCMe)_2(PCy_3)_2]^+$.[10m]

The complexes **2–5** react with acetylenedicarboxylic dimethyl ester. Treatment of **2–5** with the alkyne in toluene leads, after 1 h at room temperature, to yellow solutions from which, by addition of methanol, white solids precipitate. According to the elemental analyses, the composition of the solids correspond to 1:1 adducts of the fragments $IrH_2(\eta^2\text{-}O_2CR)(PPh_3)_2$ and acetylenedicarboxylic dimethyl ester. The IR and ^1H and $^{31}P\{^1H\}$ NMR spectra of these compounds suggest that the insertion of the unsaturated substrate into one of the two Ir–H bonds of **2–5** has taken place. With regard to the spectroscopic data, there is no doubt that the products obtained from these reactions are complexes **6–9** (eq 3).



2-5 **6-9** (2)

R = (S)-CH(NaphOMe)Me (**2**, **6**), (R)-CH(OMe)Ph (**3**, **7**), (R)-C(CF3)(OMe)Ph (**4**, **8**), (S)-CHOC(=O)CH2CH2 (**5**, **9**)

The carboxylate groups in **6–9** are formulated as bidentate-chelate ligands on the basis of the values observed for $\Delta\nu$, which coincide with those determined for **2–5**. The ^1H NMR spectra contain the signals due to the carboxylate and phosphine ligands together with characteristic resonances of the hydride and vinyl ligands. The hydride resonances appear as triplets between −27.29 and −29.00 ppm, with P–H coupling constants of about 16.7 Hz. The characteristic signals of the vinyl ligands are three singlets, of intensity ratio 1:3:3, at about 4.2, 3.6, and 3.3 ppm, which are assigned to the vinyl proton and the two chemically inequivalent methyl groups, respectively. The proposal that the ester units are not coordinated is substantiated by the IR spectra, which have ν(CO) bands at about 1710 cm^{-1}. The Ir–H absorptions appear between 2240 and 2210 cm^{-1}. The trans orientation of the phosphine ligands was inferred from the $^{31}P\{^1H\}$ NMR spectra, which show singlets at about 16 ppm.

The formation of **6–9** most probably involves dihydride intermediates, where the carboxylate groups act as monodentate ligands. In this way, the metal center of **2–5** could coordinate the alkyne, which should subsequently undergo an insertion reaction.

The insertion of a second molecule of alkyne into the Ir–H bonds of **6–9** was not observed, even working with an excess of alkyne. In this context, it is interesting to note that the compounds **2–5** show the same behaviour toward the alkynes as the complex $[IrH_2(\eta^1\text{-}OCMe_2)(Hpz)(PPh_3)_2]BF_4$. This cation reacts with methyl propiolate and acetylenedicarboxylic dimethyl ester to afford the corresponding hydridovinyl derivatives, by insertion of the alkynes into one of the two Ir–H bonds of the starting complex. Again, these hydridovinyl derivatives do not react with more alkyne.[25]

The complexes **2** and **3** also react with HBF_4 in diethyl ether to yield the compounds $[Ir_2H_2(PPh_3)_4(\mu\text{-}H)_2(\mu\text{-}O_2CR)]BF_4$ (R = (S)-CH(NaphOMe)Me (**10**), (R)-CH(OMe)Ph (**11**)), which contain two terminal and two bridging hydride ligands (eq 4).

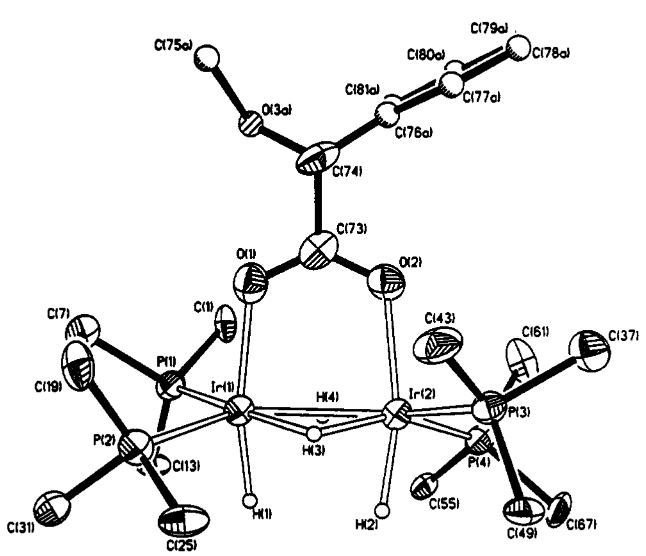
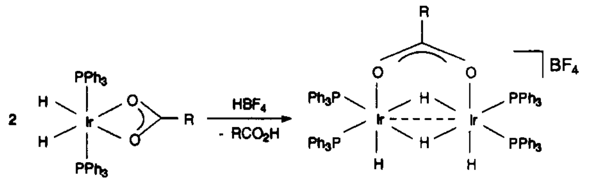


Figure 1. Molecular representation of the $[Ir_2H_2(PPh_3)_4(\mu\text{-}H)_2(\mu\text{-}\eta^2\text{-}O_2C\{(R)\text{-}CH(OMe)Ph\})]^+$ cation with the labeling scheme used. Only one of the disordered phenyl and methoxy groups of the carboxylate ligand have been represented (atoms labeled with a). Only the ipso carbon atoms of the phenyl groups of the phosphine ligands have been drawn for clarity.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for the Complex $[Ir_2H_2(PPh_3)_4(\mu\text{-}H)_2(\mu\text{-}\eta^2\text{-}O_2C\{(R)\text{-}CH(OMe)Ph\})]BF_4\cdot 1.7Et_2O$ (**11**)

Ir(1)–Ir(2)	2.6592(6)	Ir(2)–P(4)	2.280(3)
Ir(1)–P(1)	2.277(3)	Ir(2)–O(2)	2.208(8)
Ir(1)–P(2)	2.276(3)	O(1)–C(73)	1.263(15)
Ir(1)–O(1)	2.157(8)	O(2)–C(73)	1.260(15)
Ir(2)–P(3)	2.271(3)	C(73)–C(74)	1.545(19)
Ir(2)–Ir(1)–P(1)	130.15(7)	Ir(1)–Ir(2)–O(2)	84.3(2)
Ir(2)–Ir(1)–P(2)	128.11(8)	P(3)–Ir(2)–P(4)	100.3(1)
Ir(2)–Ir(1)–O(1)	85.1(2)	P(3)–Ir(2)–O(2)	87.9(2)
P(1)–Ir(1)–P(2)	101.5(1)	P(4)–Ir(2)–O(2)	106.7(2)
P(1)–Ir(1)–O(1)	89.5(2)	Ir(1)–O(1)–C(73)	121.9(8)
P(2)–Ir(1)–O(1)	101.9(2)	Ir(2)–O(2)–C(73)	119.8(8)
Ir(1)–Ir(2)–P(3)	131.83(6)	O(1)–C(73)–O(2)	128(1)
Ir(1)–Ir(2)–P(4)	127.47(8)		



2, 3 **10, 11** (3)

R = (S)-CH(NaphOMe)Me (**2**, **10**), (R)-CH(OMe)Ph (**3**, **11**)

These complexes were characterized by elemental analysis and IR and ^1H and $^{31}P\{^1H\}$ NMR spectroscopies. **11** was furthermore identified by an X-ray crystallographic study. An ORTEP drawing of the molecular structure of the cation of **11** is presented in Figure 1. Selected bond distances and angles are listed in Table 1.

This cation can be described as a dinuclear species of 32 valence electrons. Electron counting, to satisfy the 18-electron rule, suggests an iridium-iridium double bond, which is consistent with the separation observed between the metals (2.6592(6) Å).[19a] The existence of a strong metal–metal bonding interaction, either a direct interaction or one through the bridging atoms, is also supported by the mass spectra of **10** and **11** which show ions with the natural diiridium isotope distribution centered at m/e 1665 and 1604, respectively.

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[25] Esteruelas, M. A.; García, M. P.; Martín, M.; Nürnberg, O.; Oro, L. A.; Werner, H. *J. Organomet. Chem.* **1994**, *466*, 249.

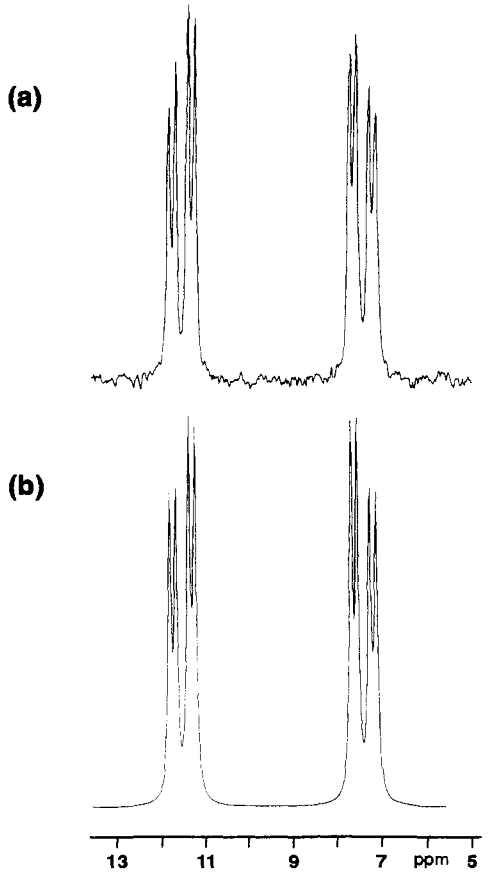

Figure 2. Experimental (a) and computed (b) NMR $^{31}P\{^1H\}$ spectrum of the compound $[Ir_2H_2(PPh_3)_4(\mu\text{-}H)_2(\mu\text{-}\eta^2\text{-}O_2C\{(R)\text{-}CH(OMe)Ph\})]BF_4$ (**11**) (121.4 MHz, 25 °C, $CDCl_3$, 85% H_3PO_4 reference).

Without taking into account the iridium–iridium interaction, the coordination environment of both iridium atoms can be formally described as distorted octahedral with an oxygen atom of the carboxylate ligand and a terminal hydrido ligand occupying two mutually trans positions. The remaining perpendicular coordination plane on each metal is formed by the two bridging hydrido ligands, mutually cis disposed, and two phosphorus atoms of the triphenylphosphine ligands (P(1)–Ir(1)–P(2) = 101.5(1)°, P(3)–Ir(2)–P(4) = 100.3(1)°).

The intrinsic asymmetry of the carboxylate group leads to a loss of symmetry in the molecule displayed in the structural parameters by the two different Ir–O bond distances (2.157(8) or 2.208(8) Å). This fact can also be observed in the $^{31}P\{^1H\}$ and ^1H NMR spectra. The $^{31}P\{^1H\}$ NMR spectrum of **11**, shown in Figure 2a, can be simulated by using an AA′BB′ model (Figure 2b). The ^1H NMR spectrum of **11** shows in the hydride region two resonances at −8.69 and −21.88 ppm. The first one, assigned to the bridging hydrido ligands, can be described as a virtual triplet of virtual triplets with P–H coupling constants of 66.1 and 9 Hz. No H–H coupling constant is observed. The $^{31}P\{^1H\}$ NMR spectrum of **10** is not very informative, as it exhibits unresolved resonances at 5.0 and 13.2 ppm, from room temperature to −55 °C. In the ^1H NMR spectrum the resonance due to the bridging hydrido ligands appears as a very complicated signal centered at −8.65 ppm, while the terminal hydridos appear as a broad triplet at −21.7 ppm. Although geometrically reasonable electronic residuals were observed in the last cycles of refinement of the X-ray experiment, the hydride ligands could not stand proper refinement. Their positions (Figure 1), concordant with those inferred from the ^1H NMR spectrum, were evaluated from electrostatic potential energy calculations.[26]

In addition, it should be mentioned that the spectroscopic characterization of the complex $[(triphos)IrH(\mu\text{-}H)_2HIr(triphos)](BPh_4)_2$ has been recently reported.[27a] This compound, which also has an $Ir_2H_2(\mu\text{-}H)_2$ unit in the core of its structure, has been prepared by reaction of $[(triphos)IrH_2(C_2H_4)]BPh_4$ with molecular hydrogen. In contrast to **10** and **11**, it is stereochemically nonrigid in solution; the bridging–terminal interconversion of the four hydride ligands is rapid on the NMR time scale to −90 °C.

Previously, it has been also reported that the reaction of $RuH(\eta^2\text{-}O_2CCH_3)(CO)(PPh_3)_2$ with $H_2C(SO_2CF_3)_2$ yields the cationic binuclear compound $[(PPh_3)_4Ru_2(CO)_2(\mu\text{-}H)(\mu\text{-}\eta^2\text{-}O_2CCH_3)][HC(SO_2CF_3)]$.[27b]

The most noticeable features of the IR spectra of **10** and **11** are the absorptions due to the $[BF_4]^-$ anion with T_d symmetry together with bands characteristic of the coordinated carboxylate ligands and $\nu(Ir\text{–}H_{terminal})$ at about 2240 cm^{-1}. The values calculated for $\Delta\nu$, 140 (**10**) and 135 (**11**) cm^{-1}, are from 55 to 25 cm^{-1} higher than those calculated for the related mononuclear complexes **2**, **3**, **6**, and **7**, which is in agreement with the general trend observed for these types of compounds.[28]

The complexes **10** and **11** as well as **2–5** are effective catalysts for the hydrogen transfer reaction from 2-propanol to acetophenone. In 2-propanol–toluene (3:1) as solvent, at 80 °C and under atmospheric pressure of argon, the initial reaction rates for the reduction of 0.25 M solutions of acetophenone with 2.5×10^{-3} M solutions of catalyst, if it is mononuclear, or 1.25×10^{-3} M, if it is dinuclear, are between 3.0×10^{-6} and 21.8×10^{-6} M s^{-1}. Although these compounds have a chiral center on the carboxylate ligands, they are not enantioselective catalysts for the reduction of the ketone.

EHT-MO Calculations on the Model Cation $[Ir_2H_2(PH_3)_4(\mu\text{-}H)_2(\mu\text{-}\eta^2\text{-}O_2CH)]^+$. Previously it has been mentioned that for complexes **10** and **11**, a simple electron count shows that the EAN rule predicts the existence of a double bond between the iridium atoms. The iridium–iridium separation obtained from the X-ray analysis of **11** (2.6592(6) Å)[19a] is in agreement with this proposal. However, the short iridium–iridium separation could be also related with the nature of the bridging ligands. With the aim of casting light on the bonding mode of the unit $Ir_2(\mu\text{-}H)_2$ of **10** and **11**, an EHT-MO calculation on the model cation $[Ir_2H_2(PH_3)_4(\mu\text{-}H)_2(\mu\text{-}\eta^2\text{-}O_2CH)]^+$ (**12**) of C_{2v} symmetry has been carried out. The electronic structure of **12** has been analyzed using the extended Hückel methodology (Appendix).

In order to perform a fragment analysis, **12** was partitioned as a $[(\mu\text{-}H)_2]^{2-}$ group which interacts with a $[Ir_2H_2(PH_3)_4(\mu\text{-}\eta^2\text{-}O_2CH)]^{3+}$ moiety.

The pattern of the frontier orbitals of the latter fragment corresponds to that of the two interacting ML_4 (C_{2v}) building blocks. The frontier orbitals of the ML_4 building block are well-known. They can be easily derived from those of an octahedral complex (i.e.: e_g above t_{2g}) by removing two cis ligands.[29] Interactions of two ML_4 blocks give rise to the splitting of the d orbitals by forming the corresponding bonding and antibonding linear combinations.[30] Filling all orbitals derived from the t_{2g} group with 12 electrons, as in this case, means the total absence of a metal–metal bond, unless other effects are in play.

The interaction diagram between the $[(\mu\text{-}H)_2]^{2-}$ group and the $[Ir_2H_2(PH_3)_4(\mu\text{-}\eta^2\text{-}O_2CH)]^{3+}$ fragment is shown in Figure 3. A Mulliken population analysis shows a net positive reduced overlap population, 0.121, between the iridium atoms. After the removal

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[26] Orpen, A. G. *J. Chem. Soc., Dalton, Trans.* **1980**, 2509.

[27] (a) Barbaro, P.; Bianchini, C.; Meli, A.; Peruzzini, M.; Vacca, A.; Vizza, F. *Organometallics* **1991**, *10*, 2227. (b) Siedle, A. R.; Newmark, R. A.; Korba, G. A.; Pignolet, L. H.; Boyle, P. D. *Inorg. Chem.* **1988**, *27*, 1593.

[28] Deacon, G. B.; Phillips, R. J. *Coord. Chem. Rev.* **1980**, *33*, 227.

[29] Albright, T. A.; Hwanbo, W. *Orbital interactions in Chemistry;* J. Wiley: New York, 1985.

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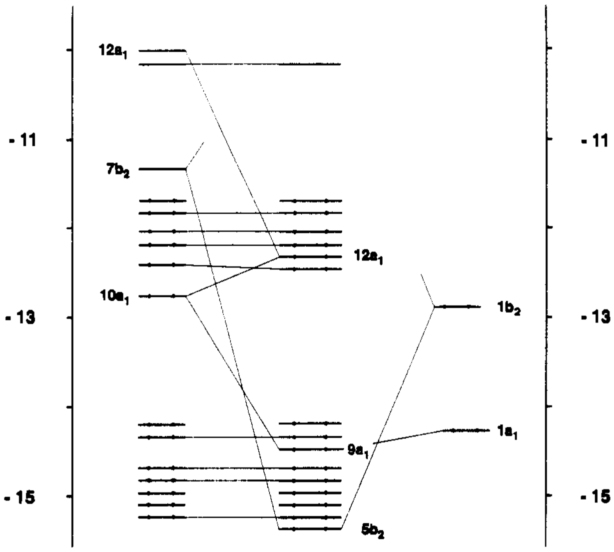

Figure 3. Molecular orbital interaction diagram between the $[(\mu\text{-H})_2]^{2-}$ group and the $[Ir_2H_2(PH_3)_4(\mu\text{-}\eta^2\text{-}O_2CH)]^{3+}$ fragment to give the cation $[Ir_2H_2(PH_3)_4(\mu\text{-H})_2(\mu\text{-}\eta^2\text{-}O_2CH)]^+$ (**12**).

Table 2. Atomic Composition of Selected Molecular Orbitals

orbital	%Ir	% H
$9a_1$	26	30
$5b_2$	54	28

of 12 electrons from the first occupied orbitals in **12**, which cancels the effects due to direct interaction between d orbitals, the reduced overlap population remains substantially unchanged, 0.119. This fact clearly suggests that this metal–metal interaction has its origin at the core level.

The hydride ligands give rise to two linear combinations (σ_g and σ^*_u) which are of a_1 and b_2 symmetry in the C_{2v} global symmetry environment. These interact with the corresponding orbitals of the same symmetry of the $[Ir_2H_2(PH_3)_4(\mu\text{-}\eta^2\text{-}O_2CH)]^{3+}$ fragment, as is shown in the interaction diagram of Figure 3. The greatest overlaps are those of the a_1 orbital of group $[(\mu\text{-H})_2]^{2-}$ with the $12a_1$ orbital of the fragment $[Ir_2H_2(PH_3)_4(\mu\text{-}\eta^2\text{-}O_2CH)]^{3+}$ and the b_2 orbital of group $[(\mu\text{-H})_2]^{2-}$ with the $7b_2$ orbital of the fragment $[Ir_2H_2(PH_3)_4(\mu\text{-}\eta^2\text{-}O_2CH)]^{3+}$. They give rise to two occupied bonding linear combinations ($9a_1$ and $5b_2$, Figure 4), which are essentially delocalized over the bridge, although they have an extensive metal centered orbital character (Table 2). From the point of view of the metal–metal interaction, these combinations have σ- and π-bonding character respectively, but they are mainly responsible for the metal–hydride bond. Because of this metal-metal-bonding character it can be said that there is a "partial" double bond between the metal atoms. This agrees well with the proposal of Green, who views the bridging hydrido ligand as a 3-electron donor, with one electron to one metal and an agostic M–H interaction with the adjacent metal.[31]

A noticeable feature of the frontier MO levels of **12** is that the LUMO appears 1.5 eV apart from the HOMO but there is a larger gap from the LUMO to the following empty orbital (2.25 eV). This suggests that the LUMO can be easily occupied, leading to a reduction product, and prompted us to test the accessibility of this orbital to incoming electrons by using cyclic voltammetry. The cyclic voltammogram of a CH_2Cl_2 solution of compound **11** is shown in Figure 5, which shows a single reduction process at around −1.2 V. The value of ΔE_p (0.07 V) suggests that the process corresponds to a single electron transfer. The value observed for the i_a/i_c ratio remains virtually constant at the scan rates investigated (0.05, 0.10, and 0.20 V s^{-1}), showing that the process is diffusion controlled. On the other hand, it is a chemically and electrochemically reversible process, as it is shown by the constant value of the $(i_a)_0 v^{1/2}$ function, at the different scan rates studied. This reduction process should lead to occupation of the LUMO (Figure 6), which has an antibonding character with respect to the metal–metal interaction. As a consequence, the partial or total occupation of this level, by reduction of the complex, would weaken the metal–metal interaction.

Concluding Remarks. This study has shown that the reactions of the pentahydride $IrH_5(PPh_3)_2$ with carboxylic acids lead to complexes of the type $IrH_2(\eta^2\text{-}O_2CR)(PPh_3)_2$, which are effective catalysts for the hydrogen transfer reaction from 2-propanol to acetophenone.

Studies aimed to elucidate the reactivity of these compounds show that the reactions with acetylenedicarboxylic dimethyl ester afford the hydride–vinyl derivatives $IrH\{C(CO_2Me){=}CH(CO_2Me)\}(\eta^2\text{-}O_2CR)(PPh_3)_2$ by insertion of the alkyne into one of the two Ir–H bonds of the starting complexes, while the reactions with HBF_4 give hydrido-bridged dinuclear cations of formula $[Ir_2H_2(PPh_3)_4(\mu\text{-H})_2(\mu\text{-}\eta^2\text{-}O_2CR)]^+$.

For these cationic species, a simple electron count using the EAN rule predicts a double bond between the iridium atoms. The iridium–iridium separation obtained from the X-ray analysis of a single crystal of the complex $[Ir_2H_2(PPh_3)_4(\mu\text{-H})_2(\mu\text{-}\eta^2\text{-}O_2C\text{-}\{(R)\text{-}CH(OMe)Ph\})]BF_4$, 2.6592(6) Å, seems to support this idea. EHT-MO calculations on the model $[Ir_2H_2(PH_3)_4(\mu\text{-H})_2(\mu\text{-}\eta^2\text{-}O_2CH)]^+$ suggest that there is a "partial" double bond between the metal atoms. However, the interaction between them does not have its origin in the direct overlap of the iridium orbitals but instead at the three-center bonds formed by the bridging system.

Experimental Section

General Considerations. All reactions were carried out under an atmosphere of argon by using Schlenk tube techniques. Solvents were dried by known procedures and distilled under argon prior to use. Carboxylic acids were used as purchased from Fluka. The starting complex $IrH(COD)(PPh_3)_2$ was prepared by a published method.[12a] $IrH_5(PPh_3)_2$ was prepared as described below.

Physical Measurements. IR spectra were recorded on Perkin-Elmer 783 infrared spectrophotometer and NMR spectra on Varian XL 200 and UNITY 300 spectrophotometers. Chemical shifts are expressed in parts per million upfield from Me_4Si (^1H) and 85% H_3PO_4 (^{31}P) as external references. C, H, and N analyses were carried out with a Perkin-Elmer 240C microanalyzer. MS were recorded in a VG Autospec double-focusing mass spectrometer operating in the positive mode; ions were produced with the standard Cs^+ gun at ca. 30 kV; 3-nitrobenzylalcohol (NBA) was used as the matrix. Cyclic voltammetric experiments were performed by employing an EG&G PARC Model 273 potentiostiat. A three-electrode system was used, consisting of a platinum-disk working electrode, a platinum-wire auxiliary electrode, and a saturated calomel reference electrode. The measurements were carried out in CH_2Cl_2 solutions with 0.1 M Bu_4NPF_6 as supporting electrolyte. Under the present experimental conditions, the ferrocenium/ferrocene couple was located at 0.47 V. The analysis of the products of the catalytic reactions was carried out on a Hewlett Packard 5890 gas chromatograph with a flame ionization detector and using a WCOT fused silica at stationary phase CP-cyclodextrin-B-2,3,6-M-19 (50 m × 0.25 mm) column, at 110 °C. The reduction product was identified by comparison of its retention time with that observed for a pure sample. Initial rate data were fitted by conventional linear regression programs by plotting n_{SH2} (moles of hydrogenated substrate) *versus* time.

Preparation of $IrH_5(PPh_3)_2$ (1). A suspension of $IrH(COD)(PPh_3)_2$ (998.6 mg, 1.2 mmol) in 10 mL of ethanol was treated with $NaBH_4$ (5 g, 131.6 mmol). The mixture was stirred at room temperature for 18 h. The solid formed was filtered off, repeatedly washed with ethanol, and dried in vacuo. Yield: 724 mg (84%). Anal. Calcd for $C_{36}H_{35}IrP_2$: C, 59.90; H, 4.88. Found: C, 59.85; H, 4.67. IR (Nujol): ν(IrH) 1950 vs cm^{-1}.

Preparation of $IrH_2(\eta^2\text{-}O_2C\{(S)\text{-}CH(NaphOMe)Me\})(PPh_3)_2$ (2). To a suspension of $IrH_5(PPh_3)_2$ (1) (72.1 mg, 0.10 mmol) in 6 mL of toluene was added an excess of *S*-2-(6-methoxy-2-naphthyl)propionic acid ({(*S*)-CH(NaphOMe)Me}CO_2H; 104.3 mg, 0.11 mmol) and stirred for 30

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[31] (a) Berry, M.; Cooper, N. J.; Green, M. L. H.; Simpson, S. J. *J. Chem. Soc., Dalton Trans.* **1980**, 29. (b) Brookhart, M.; Green, M. L. H.; Wong, L. L. *Prog. Inorg. Chem.* **1988**, *36*, 1.

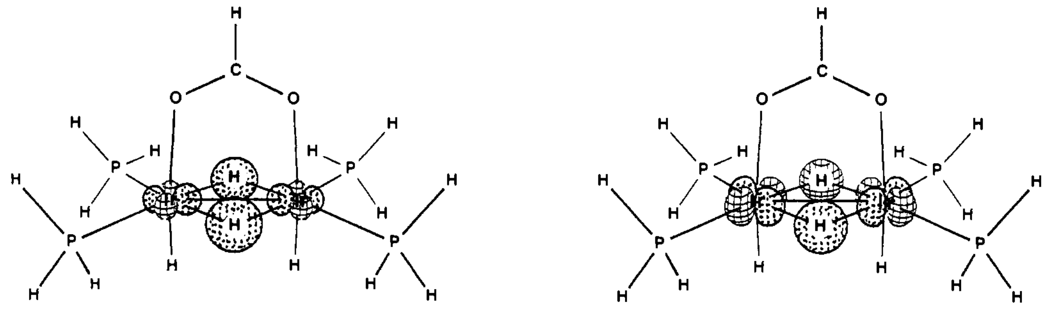

Figure 4. Molecular orbitals $9a_1$ (left) and $5b_2$ (right) corresponding to the cation $[Ir_2H_2(PH_3)_4(\mu\text{-}H)_2(\mu\text{-}\eta^2\text{-}O_2CH)]^+$ (**12**).

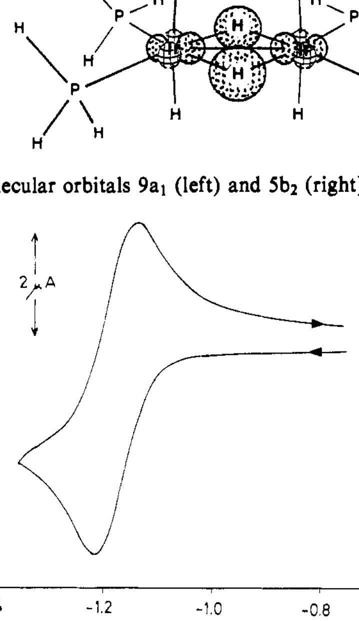

Figure 5. Cyclic voltammogram scan of a solution 5×10^{-4} M of **11** in CH_2Cl_2 containing 0.1 M $[NBu_4][PF_6]$ at room temperature (ν = 0.10 V s^{-1}; Pt electrode).

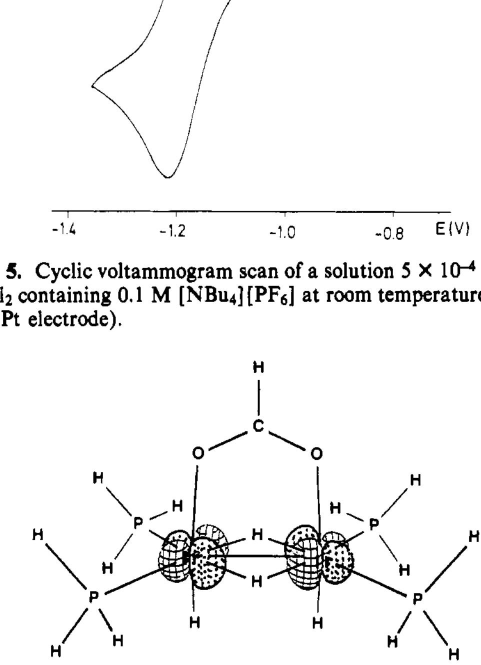

Figure 6. Molecular orbital $7a_2$ corresponding to the cation $[Ir_2H_2(PH_3)_4(\mu\text{-}H)_2(\mu\text{-}\eta^2\text{-}O_2CH)]^+$ (**12**).

min under reflux. After being cooled to room temperature, the yellow solution was filtered through kieselguhr and concentrated to ca. 1 mL. Addition of methanol led to the formation of a white precipitate, which was repeatedly washed with methanol and dried in vacuo. Yield: 75.8 mg (80%). Anal. Calcd for $C_{50}H_{45}IrO_3P_2$: C, 63.34; H, 4.78. Found: C, 63.11; H, 4.85. IR (Nujol): ν(IrH) 2210 s, ν(C=C) 1605 s, ν_{asym}(OCO) 1520 s, ν_{sym}(OCO) 1420 s cm^{-1}. ^1H NMR (300 MHz, C_6D_6): δ 7.7–7.0 (m; PPh_3 and O_2C–CH(*Naph*OMe)Me), 3.35 (s, 3H; (O_2CCH(NaphO*Me*)Me), 3.09 (q, 1H; *J*(HH) = 7 Hz; O_2CC*H* (NaphOMe)Me), 1.05 (d, 3H; *J*(HH) = 7 Hz; O_2C–CH(NaphOMe)*Me*), –28.67 (t, *J*(PH) = 16.9 Hz; IrH). $^{31}P\{^1H\}$ NMR (80.9 MHz, C_6D_6): δ 23.5 (s).

Preparation of $IrH_2(\eta^2\text{-}O_2C\{(R)\text{-}CH(OMe)Ph\})(PPh_3)_2$ (3). This compound was prepared analogously as described for **2**, starting from $IrH_5(PPh_3)_2$ (**1**) (72.1 mg, 0.10 mmol) and α-methoxyphenylacetic acid ({(*R*)-CH(OMe)Ph}CO_2H; 18.3 mg, 0.11 mmol). A white solid was obtained. Yield: 68.9 mg (78%). Anal. Calcd for $C_{45}H_{41}IrO_3P_2$: C, 61.14; H, 4.67. Found: C, 61.35; H, 4.66. IR (Nujol): ν(IrH) 2240 s, 2220 s, ν_{asym}(OCO) 1540 vs, ν_{sym}(OCO) 1420 s cm^{-1}. ^1H NMR (300 MHz, C_6D_6): δ 7.7–6.9 (m; PPh_3 and O_2C-CH(OMe)*Ph*), 4.19 (s, 1H; O_2C-C*H*(OMe)Ph), 2.89 (s, 3H; O_2C-CH (O*Me*)Ph), –29.12 (t, J(PH) = 17.2 Hz; IrH). ^{31}P $\{^1H\}$NMR (80.9 MHz, C_6D_6): δ 23.5 (s).

Preparation of $IrH_2(\eta^2\text{-}O_2C\{(R)\text{-}C(CF_3)(OMe)Ph\})(PPh_3)_2$ (4). This compound was prepared analogously as described for **2**, starting from $IrH_5(PPh_3)_2$ (**1**) (72.1 mg, 0.10 mmol) and *R*-α-methoxy-α-(trifluoromethyl)phenylacetic acid ({(*R*)-C(CF_3)(OMe)Ph}CO_2H; 25.7 mg, 0.11 mmol). A white solid was obtained. Yield: 66.6 mg (70%). Anal. Calcd for $C_{46}F_3H_{40}IrO_3P_2$: C, 58.04; H, 4.23. Found: C, 58.03; H, 4.33. IR (Nujol): ν(IrH) 2260 s, ν_{asym}(OCO) 1565 vs, ν_{sym}(OCO) 1400 s cm^{-1}. ^1H NMR (300 MHz, C_6D_6): δ 7.7–6.9 (m; PPh_3 and O_2CC(CF_3)(OMe)-*Ph*), 3.06 (s, 3H; O_2C–C(CF_3)(O*Me*)Ph), –29.77 (t, *J*(PH) = 17.7 Hz; IrH). $^{31}P\{^1H\}$ NMR (80.9 MHz, C_6D_6): δ 23.3 (s).

Preparation of $IrH_2(\eta^2\text{-}O_2C\{(S)\text{-}\overline{CHOC(=O)CH_2CH_2}\})(PPh_3)_2$ (5). This compound was prepared analogously as described for **2**, starting from $IrH_5(PPh_3)_2$ (**1**) (72.1 mg, 0.10 mmol) and *S*-5-oxotetrahydrofuran-2-carboxylic acid ({(*S*)-$\overline{CHOC(=O)CH_2CH_2}$}$CO_2H$; 14.2 mg, 0.11 mmol). A white solid was obtained. Yield: 48.33 mg (57%). Anal. Calcd for $C_{41}H_{37}IrO_4P_2$: C, 58.07; H, 4.40. Found: C, 58.08; H, 4.68. IR (Nujol): ν(IrH) 2310 m, 2210 m, ν(CO) 1790 vs, ν_{asym}(OCO) 1560 s, ν_{sym}(OCO) 1430 s cm^{-1}. ^1H NMR (300 MHz, C_6D_6): δ 7.8–7.0 (PPh_3), 3.68 (m, 1H; $O_2C\overline{C\textit{H}OC(=O)CH_2CH_2}$), 1.43 and 1.10 and 0.77 (all br, 2H the first, 1H each of the others; $O_2C\overline{CHOC(=O)C\textit{H}_2C\textit{H}_2}$), –29.27 (t, J(PH) = 16.6 Hz; IrH). $^{31}P\{^1H\}$ NMR (80.9 MHz, C_6D_6): δ 24.4 (s).

Preparation of $[IrH\{C(CO_2Me)=CH(CO_2Me)\}(\eta^2\text{-}O_2C\{(S)\text{-}CH(NaphOMe)Me\})(PPh_3)_2]$ (6). A solution of $IrH_2(\eta^2\text{-}O_2C\{(S)\text{-}CH(NaphOMe)Me\})(PPh_3)_2$ (**2**) (94.8 mg, 0.10 mmol) in 5 mL of toluene was treated with acetylenedicarboxylic dimethyl ester ($MeO_2CC{\equiv}CCO_2Me$; 14 μL, 0.11 mmol) and stirred for 1 h. The solution was concentrated to ca. 1 mL in vacuo and methanol was added. After the solution was cooled to –78 °C a white solid was formed, which was washed with methanol and dried in vacuo. Yield: 35.9 mg (33%). Anal. Calcd for $C_{56}H_{51}IrO_7P_2$: C, 61.69; H, 4.71. Found: C, 61.88; H, 4.68. IR (Nujol): ν(IrH) 2210 m, ν(C=O) 1710 vs, ν(C=C) 1605 s, ν_{asym}(OCO) 1570 s and 1520 s, ν_{sym}(OCO) 1435 s cm^{-1}. ^1H NMR (300 MHz, C_6D_6): δ 7.8–7.0 (m; PPh_3 and O_2CCH(*Naph*OMe)Me), 4.45 (s, 1H; =C*H*R), 3.62, 3.41, and 3.26 (all s, each 3H; OCH_3), 2.84 (q, 1H; *J*(HH) = 7.4 Hz; O_2CC*H*(NaphOMe)Me), 0.89 (d, 3H; *J*(HH) = 7.4 Hz; O_2CCH(NaphOMe)*Me*), –27.29 (t, *J*(PH) = 16.8 Hz; IrH). $^{31}P\{^1H\}$ NMR (80.9 MHz, C_6D_6): δ 15.9 (s).

Preparation of $IrH\{C(CO_2Me)=CH(CO_2Me)\}(\eta^2\text{-}O_2C\{(R)\text{-}CH(OMe)Ph\})(PPh_3)_2$ (7). This compound was prepared analogously as described for **6**, starting from $IrH_2(\eta^2\text{-}O_2C\{(R)\text{-}CH(OMe)Ph\})(PPh_3)_2$ (**3**) (88.4 mg, 0.10 mmol) and acetylenedicarboxylic dimethyl ester ($MeO_2CC{\equiv}CCO_2Me$; 14 μL, 0.11 mmol). A white solid was obtained. Yield: 28.7 mg (28%). Anal. Calcd for $C_{51}H_{47}IrO_7P_2$: C, 59.70; H, 4.62. Found: C, 59.78; H, 4.71. IR (Nujol): ν(IrH) 2230 m, ν(CO) 1720 vs, ν_{asym}(OCO) 1570 and 1540 both s, ν_{sym}(OCO) 1430 s cm^{-1}. ^1H NMR (300 MHz, C_6D_6): δ 7.7–7.0 (m; PPh_3 and O_2CCH(OMe)*Ph*), 4.33 (s, 1H; =C*H*R), 3.81 (s, 1H; O_2CC*H*(OMe)Ph), 3.57, 3.29, and 2.70 (all s, each 3H; OCH_3), –27.83 (t, *J*(PH) = 17.1 Hz; IrH). $^{31}P\{^1H\}$ NMR (80.9 MHz, C_6D_6): δ 16.1 (s).

Preparation of $[IrH\{C(CO_2Me)=CH(CO_2Me)\}(\eta^2\text{-}O_2C\{(R)\text{-}C(CF_3)(OMe)Ph\})(PPh_3)_2]$ (8). This compound was prepared analogously as described for **6**, starting from $IrH_2(\eta^2\text{-}O_2C\{(R)\text{-}C(CF_3)(OMe)Ph\})(PPh_3)_2$ (**4**) (95.2 mg, 0.10 mmol) and acetylenedicarboxylic dimethyl ester ($MeO_2CC{\equiv}CCO_2Me$; 14 μL, 0.11 mmol). A white solid was obtained. Yield: 30 mg (27%). Anal. Calcd for $C_{52}F_3H_{46}IrO_7P_2$: C, 57.09; H, 4.24. Found: C, 57.08; H, 4.18. IR (Nujol): ν(IrH) 2240 m, ν(CO) 1710 vs, ν_{asym}(OCO) 1570 vs, ν_{sym}(OCO) 1415 s cm^{-1}. ^1H NMR (300 MHz, C_6D_6): δ 7.7–6.6 (m; PPh_3 and O_2CC(CF_3)(OMe)*Ph*), 3.78 (s, 1H; =C*H*R), 3.58, 3.17, and 2.87 (all s, each 3H; OCH_3), –29.00 (t, *J*(PH) = 16.6 Hz; IrH). $^{31}P\{^1H\}$ NMR (80.9 MHz, C_6D_6): δ 15.9 (s).

Table 3. Atomic Coordinates (×10^4; ×10^5 for Ir Atoms) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$; $Å^2 \times 10^4$ for Ir Atoms) for the Compound $[Ir_2H_2(PPh_3)_4(\mu\text{-}H)_2(\mu\text{-}\eta^2\text{-}O_2C\{(R)\text{-}CH(OMe)Ph\})]BF_4\cdot 1.7Et_2O$ (11)

atom	X/a	Y/b	Z/c	$U_{eq}{}^a/U_{iso}$
Ir(1)	17762(3)	103712(2)	99102(2)	263(1)
Ir(2)	2424(3)	97028(2)	98753(2)	265(1)
P(1)	3332(2)	10134(1)	10026(1)	29(1)
P(2)	1878(2)	11336(1)	9751(1)	32(1)
P(3)	−1326(2)	9904(1)	9974(1)	28(1)
P(4)	162(2)	8758(1)	9626(1)	30(1)
O(1)	1577(6)	10350(4)	10756(3)	41(3)
O(2)	362(6)	9711(3)	10746(3)	38(3)
C(1)	3393(8)	9472(4)	10435(5)	30(4)
C(2)	3060(7)	8966(5)	10212(5)	33(4)
C(3)	3046(9)	8452(6)	10488(6)	45(5)
C(4)	3373(12)	8455(6)	10986(7)	64(7)
C(5)	3679(15)	8947(7)	11208(7)	86(8)
C(6)	3739(14)	9448(6)	10936(5)	70(7)
C(7)	4070(8)	10621(5)	10416(5)	35(5)
C(8)	5054(9)	10694(5)	10301(6)	51(6)
C(9)	5601(11)	11047(7)	10611(8)	74(7)
C(10)	5197(11)	11326(6)	11052(7)	59(6)
C(11)	4259(12)	11262(6)	11169(7)	59(6)
C(12)	3687(11)	10905(5)	10846(6)	47(5)
C(13)	4009(9)	9949(5)	9426(5)	30(4)
C(14)	3841(9)	10244(5)	8975(5)	38(5)
C(15)	4314(10)	10114(5)	8506(6)	49(5)
C(16)	4986(10)	9651(7)	8531(6)	58(6)
C(17)	5151(10)	9362(5)	8986(6)	42(5)
C(18)	4661(9)	9515(5)	9432(6)	40(5)
C(19)	1867(8)	11848(4)	10291(6)	39(5)
C(20)	2212(8)	12423(5)	10224(6)	43(5)
C(21)	2181(9)	12804(6)	10626(6)	41(5)
C(22)	1811(10)	12649(6)	11100(6)	42(5)
C(23)	1477(10)	12117(6)	11166(6)	52(6)
C(24)	1479(10)	11708(6)	10778(6)	47(5)
C(25)	799(9)	11538(5)	9366(5)	36(5)
C(26)	482(10)	11174(6)	8956(6)	45(5)
C(27)	−287(10)	11322(6)	8646(6)	52(6)
C(28)	−718(11)	11876(8)	8750(8)	70(8)
C(29)	−438(12)	12203(7)	9142(7)	59(7)
C(30)	355(9)	12042(5)	9430(6)	48(6)
C(31)	2843(9)	11593(5)	9352(5)	31(5)
C(32)	3748(9)	11686(4)	9560(6)	37(5)
C(33)	4500(10)	11870(5)	9243(7)	52(6)
C(34)	4342(11)	11960(6)	8717(7)	56(6)
C(35)	3478(10)	11884(6)	8488(6)	50(5)
C(36)	2749(10)	11706(5)	8803(5)	41(5)
C(37)	−2095(9)	9373(5)	10305(6)	41(5)
C(38)	−3010(9)	9267(5)	10181(6)	51(5)
C(39)	−3545(11)	8871(6)	10485(7)	68(7)
C(40)	−3129(10)	8566(6)	10861(7)	55(6)
C(41)	−2187(10)	8665(5)	11002(6)	46(5)
C(42)	−1681(10)	9063(5)	10722(5)	38(5)
C(43)	−1424(10)	10544(5)	10393(6)	47(5)
C(44)	−1119(8)	11066(5)	10212(7)	50(5)
C(45)	−1163(10)	11552(5)	10524(7)	54(6)
C(46)	−1459(12)	11516(6)	11038(7)	63(7)
C(47)	−1772(12)	10979(6)	11245(6)	61(6)
C(48)	−1758(9)	10502(5)	10916(6)	43(5)
C(49)	−2015(9)	10127(5)	9393(5)	34(5)
C(50)	−1778(11)	9950(6)	8911(6)	53(6)
C(51)	−2312(12)	10124(7)	8486(7)	70(7)
C(52)	−3072(11)	10481(7)	8538(8)	70(7)
C(53)	−3328(11)	10670(6)	9025(8)	60(7)
C(54)	−2801(8)	10497(5)	9454(6)	40(5)
C(55)	1256(8)	8595(5)	9240(5)	28(4)
C(56)	1617(9)	8998(5)	8912(5)	36(5)
C(57)	2438(11)	8890(6)	8644(6)	53(6)
C(58)	2937(10)	8359(6)	8703(6)	46(5)
C(59)	2550(9)	7956(6)	9038(6)	43(5)
C(60)	1714(9)	8072(5)	9315(5)	39(5)
C(61)	144(7)	8192(4)	10136(7)	39(4)
C(62)	−193(8)	7640(5)	10019(6)	46(5)
C(63)	−193(11)	7222(6)	10388(7)	54(6)
C(64)	176(11)	7326(6)	10858(8)	59(7)
C(65)	533(10)	7885(6)	11008(6)	53(6)
C(66)	516(10)	8313(5)	10634(5)	39(5)
C(67)	−782(9)	8563(5)	9161(6)	32(5)
C(68)	−1641(12)	8401(5)	9363(7)	62(6)
C(69)	−2392(12)	8307(8)	9034(9)	79(8)
C(70)	−2328(15)	8331(9)	8529(12)	107(12)
C(71)	−1453(18)	8471(8)	8310(9)	115(11)
C(72)	−695(12)	8598(7)	8636(7)	62(7)
C(73)	920(9)	10060(5)	10968(5)	35(5)
C(74)	771(10)	10161(6)	11566(5)	45(5)
O(3a)[b]	1654(18)	10275(14)	11810(11)	50(8)
C(75a)	1410(40)	10866(24)	12188(22)	84(19)
O(3b)	1596(16)	10479(12)	11737(10)	52(7)
C(75b)	1605(24)	10691(15)	12227(14)	50(10)
C(76a)[c]	332(22)	9693(11)	11847(12)	53(11)
C(77a)	−620	9697	12001	55(10)
C(78a)	−1011	9213	12246	91(15)
C(79a)	−452	8726	12338	64(12)
C(80a)	499	8723	12183	114(17)
C(81a)	891	9207	11938	86(14)
C(76b)	567(16)	9601(8)	11834(10)	47(9)
C(77b)	1261	9186	11934	64(10)
C(78b)	1013	8667	12179	74(11)
C(79b)	72	8565	12323	50(9)
C(80b)	−622	8980	12222	48(10)
C(81b)	−374	9499	11978	58(9)
B	9474(7)	1847(4)	2535(4)	96(8)
F(lac)[d]	8905(10)	2301(6)	2690(6)	108(6)
F(2a)	9021(17)	1333(6)	2646(15)	161(20)
F(3a)	9645(25)	1883(12)	2000(6)	112(13)
F(4a)	10323(15)	1870(11)	2806(13)	235(33)
F(1b)	9641(25)	1393(10)	2195(9)	151(17)
F(2b)	8601(12)	2088(12)	2424(10)	91(11)
F(3b)	9481(19)	1648(10)	3049(5)	72(10)
F(4b)	10173(15)	2258(11)	2473(13)	161(21)
F(2c)	9945(15)	1628(7)	2969(6)	54(6)
F(3c)	8919(14)	1420(7)	2314(10)	148(14)
F(4c)	10126(15)	2037(9)	2168(9)	140(13)
C(201)[e]	3651(21)	7546(19)	2774(18)	112(16)
C(202)	4497(20)	7724(13)	2431(15)	78(12)
O(203)	5266(17)	7332(9)	2515(11)	85(9)
C(204)	6089(20)	7536(24)	2241(16)	145(26)
C(205)	6984(17)	7320(21)	2520(19)	99(15)
C(401)	3873(20)	7887(18)	2529(17)	79(13)
C(402)	4821(23)	7950(19)	2239(15)	88(15)
O(403)	5540(20)	7637(15)	2516(12)	109(13)
C(404)	6398(25)	7635(30)	2214(23)	137(30)
C(405)	6825(68)	7027(37)	2215(58)	368(95)
C(301)	6746(21)	4526(22)	2250(21)	129(24)
C(302)	5863(18)	4910(13)	2238(12)	64(11)
O(303)	5205(10)	4724(6)	2632(6)	106(5)
C(304)	4497(35)	5157(14)	2712(28)	158(33)
C(305)	3667(24)	4901(20)	3024(24)	141(24)
C(501)	6689(25)	4734(20)	2151(22)	83(17)
C(502)	5959(22)	5090(10)	2458(22)	102(20)
C(504)	4469(25)	5065(11)	2863(23)	82(18)
C(505)	3832(29)	4682(21)	3205(22)	119(21)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor. [b] A complementary occupancy factor has been refined for the disordered methoxy and phenyl groups, O(3a) to C(81b) atoms (0.46(5) for a-labeled atoms, and 0.54(5) for the b-labeled ones). From this atom downwards isotropic displacement parameters are displayed. [c] A geometrically constrained refinement has been applied to both disordered phenyl groups (C(76a) to C(8ab)). [d] Three different BF_4^- groups were included in the refinement to take account for the disorder observed. They share the B atom, and two of them share the F(1ac) atom. [e] The atoms from C(201) to C(505) are involved in solvent disorder.

Preparation de $IrH\{C(CO_2Me)=CH(CO_2Me)\}(\eta^2\text{-}O_2C\{(S)\text{-}CHOC(=O)CH_2CH_2\})(PPh_3)_2$ (9). This compound was prepared analogously as described for **6**, starting from $IrH_2(\eta^2\text{-}O_2C\{(S)\text{-}CHOC(=O)CH_2CH_2\})(PPh_3)_2$ (**5**) (84.8 mg, 0.10 mmol) and acetylenedicarboxylic dimethyl ester ($MeO_2CC\equiv CCO_2Me$; 14 μL, 0.11 mmol). A white solid was obtained. Yield: 37.6 mg (38%). Anal. Calcd for $C_{47}H_{43}IrO_8P_2$: C, 57.02; H, 4.38. Found: C, 57.51; H, 4.47. IR (Nujol): ν(IrH) 2220 w, ν(CO) 1790 vs and 1710 vs, ν_{asym}(OCO) 1570 s, ν_{sym}(OCO) 1440 s cm^{-1}. ^1H NMR (300 MHz, C_6D_6): δ 7.7–7.0 (m; PPh_3), 4.47 (s, 1H; $=CHR$), 3.53 and 3.17 (both s, each 3H; OCH_3), 3.38 (m, 1H; $O_2CCHOC(=O)CH_2CH_2$), 1.34 and 0.91 and 0.53 (all br, 2H the first, 1H each of the others; $O_2CCHOC(=O)CH_2CH_2$), −27.96 (t, J(PH) = 16.2 Hz; IrH). $^{31}P\{^1H\}$ NMR (80.9 MHz, C_6D_6): δ 17.5 (s).

Preparation of $[H(PPh_3)_2Ir(\mu\text{-}H)_2(\mu\text{-}\eta^2\text{-}O_2C\{(S)\text{-}CH(NaphOMe)\ Me\})$-

Table 4. Crystallographic Data for $[Ir_2H_2(PPh_3)_4(\mu\text{-}H)_2(\mu\text{-}\eta^2\text{-}O_2C\{(R)\text{-}CH(OMe)Ph\})]BF_4{\cdot}1.7Et_2O$ (**11**)

formula: $C_{81}H_{73}B_1F_4Ir_2O_3P_4{\cdot}1.7C_4H_{10}O$	fw = 1798.48
a = 14.082(1) Å	T = 233 K
b = 23.169(2) Å	λ = 0.710 73 Å
c = 25.291(3) Å	ρ_{calcd} = 1.447 g cm^{-3}
V = 8252(1) Å	μ = 3.34 mm^{-1}
Z = 4	abs cor = 1.230, 0.844
cryst syst: orthorhombic	R^a = 0.0414
space group: $P2_12_12_1$	R_w = 0.0389

[a] $R = (\Sigma[|F_o| - |F_c|])/\Sigma F_o$; $R_w = (\Sigma([|F_o| - |F_c|])w^{1/2})/\Sigma(|F_o|w^{1/2})$, $w^{-1} = \sigma^2(F_o) + 0.0008(F_o)^2$.

Table 5. Extended Hückel Parameters

atom	orbital	H_{ii}, eV	ξ_1	ξ_2	c_1	c_2
Ir	6s	−11.36	2.5040			
	6p	−4.50	2.4840			
	5d	−12.70	5.7960	2.5570	0.635	0.556
C	2s	−21.40	1.5500			
	2p	−11.40	1.3250			
O	2s	−32.30	2.2000			
	2p	−14.80	1.9750			
P	3s	−18.60	1.7500			
	3p	−14.00	1.3000			
H	1s	−13.60	1.3000			

$IrH(PPh_3)_2]BF_4$ (10). To a suspension of $IrH_2(\eta^2\text{-}O_2C\{(S)\text{-}CH(NaphOMe)Me\})(PPh_3)_2$ (**2**) (94.8 mg, 0.10 mmol) in 7 mL of diethyl ether was added HBF_4 (15 μL, 0.11 mmol). After the mixture was stirred for 3 h at room temperature, a orange solid precipitated which was repeatedly washed with diethyl ether and dried in vacuo. The solid was recrystallized from dichloromethane/diethyl ether. Yield: 70.1 mg (80%). Anal. Calcd for $BC_{86}F_4H_{77}Ir_2O_3P_4$: C, 58.90; H, 4.42. Found: C, 58.41; H, 4.55. IR (Nujol): ν(IrH) 2240 s, ν(C═C) 1610 s, ν_{asym}(OCO) 1540 s, ν_{sym}(OCO) 1400 s cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.6–6.8 (m; PPh_3 and O_2CCH(*Naph*OMe)Me), 3.99 (s, 3H; (O_2CCH(NaphO*Me*)-Me), 3.45 (q, 1H; J(HH) = 6.9 Hz; $O_2CC(CH_3)$*H*(NaphOMe)Me), 1.22 (d, 3H; *J*(HH) = 6.9 Hz; O_2CCH(NaphOMe)*Me*), −8.65 (m, 2H; Ir(μ-H)Ir), −21.70 (br, 2H; IrH). $^{31}P\{^1H\}$ NMR (121.4 MHz, $CDCl_3$, −55 °C): δ 5.0 and 13.2 (both br). MS (FAB): *m/e* 1665.

Preparation of $[Ir_2H_2(PPh_3)_4(\mu\text{-}H)_2(\mu\text{-}\eta^2\text{-}O_2C\{(R)\text{-}CH(OMe)Ph\})]BF_4$ (11). This compound was prepared analogously as described for **10** starting from $IrH_2(\eta^2\text{-}O_2C\{(R)\text{-}CH(OMe)Ph\})(PPh_3)_2$ (**3**) and HBF_4 (15 μL, 0.11 mmol). The red solid was recrystallized from dichloromethane/diethyl ether. Yield: 59.1 mg (70%). Anal. Calcd for $BC_{81}F_4H_{73}Ir_2O_3P_4$ (powder habit): C, 57.58; H, 4.35. Found: C, 57.49; H, 4.21. IR (Nujol): ν(IrH) 2240 w, ν_{asym}(OCO) 1565 s, ν_{sym}(OCO) 1435 s cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.6–6.7 (m; PPh_3 and O_2C-CH(OMe)*Ph*), 4.05 (s, 1H; O_2CC*H*(OMe)Ph), 3.11 (s, 3H; O_2-CCH(O*Me*)Ph), −8.69 (vtt, 2H; *N* = 132.2 Hz, *N′* = 18 Hz; Ir(μ-H)Ir), −21.88 (vt, 2H; *N* = 36.4 Hz; IrH). $^{31}P\{^1H\}$ NMR (121.4 MHz, $CDCl_3$): δ spin system AA′BB′; δ_A = 11.5 and δ_B = 7.4; *J*(AA′) = *J*(BB′) = 0 Hz; *J*(AB) = *J*(A′B′) = 51.78 Hz; *J*(AB′) = *J*(A′B) = 16.96 Hz. MS (FAB): *m/e* 1604.

X-ray Structure Analysis of $[Ir_2H_2(PPh_3)_4(\mu\text{-}H)_2(\mu\text{-}\eta^2\text{-}O_2C\{(R)\text{-}CH(OMe)Ph\})]BF_4{\cdot}1.7Et_2O$ (11). Crystals suitable for the X-ray diffraction study were obtained by slow diffusion of diethyl ether into a saturated dichloromethane solution of the compound. Atomic coordinates and U_{eq} values are listed in Table 3. A summary of crystal data is reported in Table 4. A red prismatic block of approximate dimensions 0.333 × 0.342 × 0.487 mm was mounted in a glass fiber. A set of randomly searched reflections was indexed to orthorhombic symmetry. A fast data collection in the range $20 \le 2\theta \le 38°$ showed strong reflections from which a group of 56 were carefully centered and used to obtain by least-squares methods the unit cell dimensions. A Siemens AED four-circle diffractometer was used for data acquisition ($\omega/2\theta$ scan mode), with graphite-monochromated Mo Kα radiation and 2θ range 3.0–45° ($-15 \le h \le 0$; $-25 \le k \le 0$; $0 \le l \le 27$ and $0 \le h \le 15$; $0 \le k \le 25$; $-27 \le l \le 5$). A total of 13486 reflections were measured; from 10 742 unique reflections (R_{merg} = 0.023), 8343 having $F_o \ge 4.0\ \sigma(F_o)$ were considered observed and used in the refinement. Three orientation and intensity standards were monitored every 55 min of measuring time; no variation was observed. Reflections were also corrected for absorption by an empirical method.[32]

The structure was solved by Patterson (iridium atoms) and conventional Fourier techniques. The phenyl and methoxy groups of the carboxylate ligand were found to be disordered. This disorder could result from a small rotation (18° aproximately) around the C(73)–C(74) bond. The disordered groups were modeled by including two different moieties (atoms C(75) to C(81) and O(3)) with a complementary occupancy factor initially assigned on the basis of thermal parameters and refined to a final value of 0.46(5) for the *a*-labeled atoms, and with the phenyl ring geometry constrained to a regular hexagon. Hydrogens, except those bonded to disordered groups, were included in the refinement in calculated positions (C–H = 0.96 Å) riding on carbon atoms with a common isotropic thermal parameter. The BF_4^- anion and the solvent molecules (Et_2O) were also observed severely disordered. The diethyl ether molecules exhibit static disorders in two different spatial regions. Both molecules were modelled on the base of two sites for each atom (atoms C(201) to C(505)), and refined including geometrical restrictions for the values of bond distances and angles (DFIX facility). On the other hand, a common B atom and three sites for each fluorine (atoms F(1ac) to F(4c)) were included in the model established for the BF_4^- anion. The occupancy factors for the latter disordered groups (solvent and BF_4^-) were estimated based on the thermal parameters and maintained fixed during refinement. Atomic scattering factors, corrected for anomalous dispersion of iridium and phosphorus atoms, were taken from ref 33. The function minimized was $\Sigma w(|F_o|-|F_c|)^2$ with the weighting-factor defined as $w^{-1} = \sigma^2(F_o) + 0.0008(F_o)^2$. Final R and R_w values are 0.0414 and 0.0389, respectively. The chirality of the molecule has been checked using the Rogers method (η = 1.02(2)). All calculations were performed by use of the SHELXTL-PLUS system of computer programs.[34]

Hydrogen Transfer Reactions. The reactions were carried out under an atmosphere of argon in a mixture of 2-propanol–toluene (3:1) with magnetic stirring. The equipment consisted of a 50-mL two-necked flash fitted with a Suba-seal to allow samples to be removed without opening the system. In a typical procedure, a solution of the catalyst (0.02 mmol, if it is mononuclear, or 0.01 mmol, if it is dinuclear) in 1 mL of toluene and 3 mL of 2-propanol was refluxed, and a solution of the substrate (acetophenone) in mixture of 1 mL of toluene and 3 mL of 2-propanol was then injected. Initial rates (r) for each of the catalysts (compounds **2–5** and **10**, **11**) were as follows: $r = 10.4 \times 10^{-6}$ M s^{-1} (**2**), $r = 21.6 \times 10^{-6}$ M s^{-1} (**3**), $r = 21.8 \times 10^{-6}$ M s^{-1} (**4**), $r = 7.1 \times 10^{-6}$ M s^{-1} (**5**), $r = 13.6 \times 10^{-6}$ M s^{-1} (**10**) and $r = 3.0 \times 10^{-6}$ M s^{-1} (**11**).

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Appendix

All calculations performed in this paper have been performed by the Extended Hückel method[35] using the programs ICON8 and CACAO[36]. The atomic parameters used are listed in Table 5. The geometrical parameters were taken from the crystal structure data and idealized to a C_{2v} symmetry. The P–H bond distance was set to 1.45 Å and the environment around the phosphorus atom was assumed to be tetrahedral.

Supplementary Material Available: Tables of positional and displacement parameters, crystallographic data, and bond lengths and angles (18 pages). Ordering information is given on any current masthead page.

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