Synthesis and Reactivity of Bis(ethene) Rhodium(I) and Iridium(I) Carboxylato Complexes☆

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$[Rh(\mu\text{-}O_2CCH_3)(C_2H_4)_2]_2$ (**3**) and analogous carboxylatobis(olefin)rhodium(I) complexes $[Rh(\mu\text{-}O_2CR)(olefin)_2]_2$ (**4**–**6**) were almost quantitatively prepared under heterogeneous conditions from $[RhCl(C_8H_{14})_2]_2$ (**1**) or $[RhCl(C_2H_4)_2]_2$ (**2**) and $CH_3CO_2Na \cdot 3\ H_2O$ or RCO_2H/NaOH, respectively. The X-ray crystal structure analysis of **3** confirmed the bridging position of the acetato ligands. The synthesis of $[Ir(\mu\text{-}O_2CCH_3)(C_2H_4)_2]_2$ (**10**) was carried out similarly by using $[IrCl(C_2H_4)_2]_2$ (**8**) and $CH_3CO_2Na \cdot 3\ H_2O$ as starting materials. The monoethene complex *trans*-$[Ir(\eta^1\text{-}O_2CCH_3)(C_2H_4)(P\mathit{i}Pr_3)_2]$ (**11**) was obtained from **10** and $P\mathit{i}Pr_3$; it reacted with H_2 and HC≡CPh by oxidative addition to give $[IrH_2(\eta^2\text{-}O_2CCH_3)(P\mathit{i}Pr_3)_2]$ (**12**) and $[IrH(C{\equiv}CPh)(\eta^2\text{-}O_2CCH_3)(P\mathit{i}Pr_3)_2]$ (**14**), respectively. Compound **12** was also prepared from $[IrH_2Cl(P\mathit{i}Pr_3)_2]$ (**13**) and $CH_3CO_2Na \cdot 3\ H_2O$. The new bis(ethene)complexes **3**, $[Rh(\mu\text{-}O_2CC_6H_5)(C_2H_4)_2]_2$ (**6**) and **10** are catalytically less active than **2** in the reaction of C_2H_4 and Ph_2CN_2 and gave as C–C coupling product not only 1,1-diphenylpropene (**16**) but also mixtures of **16** and 1,1-diphenylcyclopropane (**17**) in different ratios.

In the course of investigations into the synthesis of square-planar carbene-rhodium complexes of the general composition *trans*-$[RhCl(=CR_2)(P\mathit{i}Pr_3)_2]$ from highly reactive $[RhCl(P\mathit{i}Pr_3)_2]_2$ and diazoalkanes R_2CN_2 as precursors, we recently discovered that *trans*-$[RhCl(N_2CPh_2)(P\mathit{i}Pr_3)_2]$, which is formed from $[RhCl(P\mathit{i}Pr_3)_2]_2$ and diphenyldiazomethane, smoothly reacts with ethene to give *trans*-$[RhCl(C_2H_4)(P\mathit{i}Pr_3)_2]$ and, unexpectedly, 1,1-diphenylpropene[1]. This olefin, which *formally* is built up by linkage of the $:CPh_2$ fragment of the diazoalkane with the ethene isomer $:CHCH_3$, can be prepared catalytically from C_2H_4 and Ph_2CN_2 in the presence of various rhodium(I) and iridium(I) complexes[1,2]. While $[RhCl(C_2H_4)_2]_2$ is quite active and provides turnover numbers of about 500[3], the related rhodium acetylacetonate $[Rh(acac)(C_2H_4)_2]$ is rather inert. On reaction with C_2H_4/Ph_2CN_2 in benzene at 40°C, it does not support the formation of 1,1-diphenylpropene but of the isomeric 1,1-diphenylcyclopropane[4]. In contrast, the hexafluoro derivative $[Rh(acac\text{-}F_6)(C_2H_4)_2]$ behaves similarly to the chloro complex $[RhCl(C_2H_4)_2]_2$ and with C_2H_4/Ph_2CN_2 catalytically generates 1,1-diphenylpropene[5].

It was this puzzling result which prompted us to prepare the carboxylato compounds $[Rh(\eta^2\text{-}O_2CR)(C_2H_4)_2]_n$ and $[Ir(\eta^2\text{-}O_2CR)(C_2H_4)_2]_n$, and to study their catalytic activity with regard to the C_2H_4/Ph_2CN_2 system. We were surprised to learn that in contrast to the cycloocta-1,5-diene complexes $[M(\eta^2\text{-}O_2CR)(C_8H_{12})]_2$ (M = Rh[6], Ir[7]), the corresponding bis(ethene)rhodium(I) and -iridium(I) derivatives were unknown. In addition to the preparation, we were also interested in finding out whether the complexes $[M(\eta^2\text{-}O_2CR)(C_2H_4)_2]_n$ like the $M(C_8H_{12})$ counterparts are dimers or, in analogy to the recently described bis(phosphane)rhodium(I) compounds $[Rh(\eta^2\text{-}O_2CR)(P\mathit{i}Pr_3)_2]$[8], monomers in solution and in the solid state.

Preparation of Bis(olefin) Rhodium Carboxylato Complexes

The starting material for the synthesis of bis(ethene)rhodium(I) carboxylato complexes is $[RhCl(C_2H_4)_2]_2$ (**2**), which was prepared by Cramer from $RhCl_3 \cdot 3\ H_2O$ and methanol under ethene pressure of about 1 atm in 60–65% yield[9]. We used a modified procedure for the preparation of **2** which starts with $[RhCl(C_8H_{14})_2]_2$ (**1**) and gives compound **2** in 86% yield. While the attempts to prepare the acetato complex $[Rh(\mu\text{-}O_2CCH_3)(C_2H_4)_2]_2$ (**3**) from **2** and CH_3CO_2Na or CH_3CO_2K in methanol according to the route used by Chatt and Venanzi for the synthesis of $[Rh(\mu\text{-}O_2CCH_3)(C_8H_{12})]_2$[6a] failed, we found that **3** is formed almost quantitatively if **2** and sodium acetate react in ether at 0°C, i.e. under *heterogeneous* conditions. Compound **3** is an orange-red crystalline solid which is readily soluble in most common organic solvents and only moderately air-sensitive. The IR spectrum of **3** displays two bands at 1560 and 1420 cm^{-1}, assigned to the asymmetric and symmetric OCO stretching frequencies, the position of which indicates that the acetato ligand is in a bridging position[6d,10].

The bis(cyclooctene) complex $[Rh(\mu\text{-}O_2CCH_3)(C_8H_{14})_2]_2$ (**4**) is obtained in the same way as **3**, using **1** and sodium acetate as starting materials. Due to the low solubility of **1** in ether, the reaction takes longer (ca. 6 h) but affords compound **4** in excellent yields. Since we observed that both **3** and **4** can also be prepared from **1** or **2**, respectively, in ether by treatment with CH_3CO_2H and NaOH, we used

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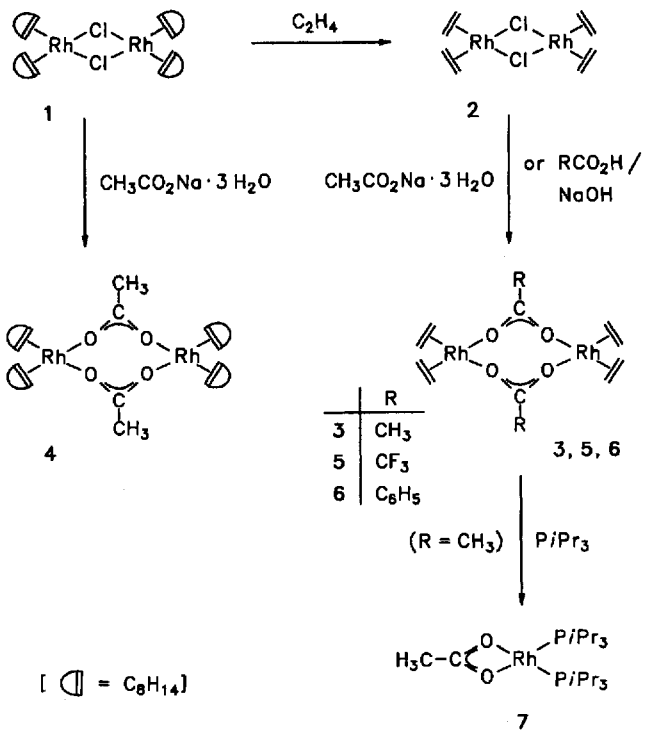
this procedure for the synthesis of the trifluoracetato and benzoato derivatives **5** and **6** (Scheme 1). In this case the yield was 70–75%. The IR data of **4**–**6** and the molecular weight measurements support the assumption that the complexes are dimeric and the RCO_2^- units behave as bridging ligands.

Scheme 1

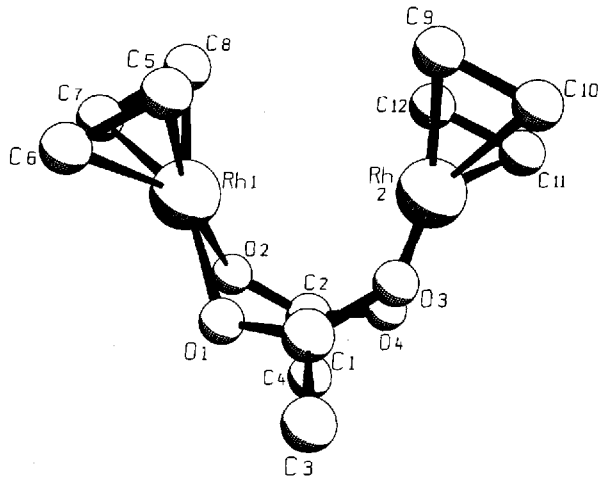


In contrast to $[Rh(\mu\text{-}O_2CCH_3)(C_7H_8)]_2$ which reacts with phosphanes to give $[Rh(\eta^1\text{-}O_2CCH_3)(PR_3)(C_7H_8)]$ without displacing the norbornadiene ligand[7], the bis(ethene) complex **3** on treatment with $PiPr_3$ yields $[Rh(\eta^2\text{-}O_2CCH_3)(PiPr_3)_2]$ (**7**). This compound, which is highly reactive toward CO, O_2, and H_2[11], was originally prepared from $[Rh(\eta^3\text{-}C_3H_5)(PiPr_3)_2]$ or $[Rh(\eta^3\text{-}CH_2C_6H_5)(PiPr_3)_2]$ by protolytic cleavage of the allyl- or benzyl-metal bond with acetic acid[8].

Molecular Structure of 3

The result of the X-ray structure analysis of **3** is shown in Figure 1. The coordination geometry around each rhodium center corresponds to a nearly square-planar configuration including one oxygen atom from each of the two bridging acetato ligands and the midpoints of the two olefinic bonds. This structure is consistent with other dimeric rhodium(I) complexes, in particular with $[Rh(\mu\text{-}O_2CCH_3)(C_7H_8)]_2$ (C_7H_8 = norbornadiene)[12]. The rhodium–rhodium distance of 3.225(1) Å [3.230(1) Å for the second independent molecule in the unit cell] is significantly larger than for $[Rh(\mu\text{-}O_2CCH_3)(C_7H_8)]_2$ [3.1050(7) Å][12], indicating the absence of a direct metal–metal interaction in compound **3**[13]. The average Rh–O distance is 2.095(7) Å which is almost identical with that in $[Rh(\mu\text{-}O_2CCH_3)(C_7H_8)]_2$ [2.106(7) Å][12] and in the monoacetato-bridged complex $[Rh_2(\mu\text{-}O_2CCH_3)(\mu\text{-}\eta^1\text{:}\eta^2\text{-}C_2Ph)(CO)_2(PCy_3)_2]$ [2.086(4) Å][14]. The ethene ligands of **3** are symmetrically and approximately perpendicularly bound to the rhodium atoms via the center of the olefin bonds. As has been expected, the average Rh–C distance of 2.11(2) Å is somewhat shorter than in the *cationic* complex $[\{(C_2H_4)_2Rh(\eta^6\text{-}C_6H_5)\}_2B(C_6H_5)_2]^+$ [2.162(2) Å] in which each rhodium is coordinated to one of the phenyl rings of a bridging tetraphenyloborate anion[15]. The C–C and C–O bond lengths within the two bridging acetate ligands of **3** agree with those found in $[Rh(\mu\text{-}O_2CCH_3)(C_7H_8)]_2$[12] and in the quadruple-bridged dirhodium(II) tetraacetate dihydrate[16].

Figure 1. Molecular structure (SCHAKAL drawing) of complex **3**; there are two independent molecules in the unit cell, the atoms of which are designated as Rh1, O1, ... and Rh1*, O1*, ... etc.



Selected bond lengths [Å] and angles [°]: Rh1–O1 2.091(4), Rh1*–O1* 2.103(4), Rh1–O2 2.097(4), Rh1*–O2* 2.088(4), Rh1–C5 2.128(6), Rh1*–C5* 2.096(7), Rh1–C6 2.112(6), Rh1*–C6* 2.097(7), Rh1–C7 2.117(7), Rh1*–C7* 2.117(7), Rh1–C8 2.107(6), Rh1*–C8* 2.105(6), Rh2–O3 2.094(4), Rh2*–O3* 2.095(4), Rh2–O4 2.100(4), Rh2*–O4* 2.093(4), Rh2–C9 2.118(7), Rh2*–C9* 2.122(7), Rh2–C10 2.105(6), Rh2*–C10* 2.130(6), Rh2–C11 2.116(6), Rh2*–C11* 2.114(6), Rh2–C12 2.119(6), Rh2*–C12* 2.115(7), C1–O1 1.248(7), C1*–O1* 1.254(8), C1–O3 1.261(7), C1*–O3* 1.249(7), C2–O2 1.252(8), C2*–O2* 1.247(7), C2–O4 1.244(7), C2*–O4* 1.259(7), C5–C6 1.38(1), C5*–C6* 1.37(1), C7–C8 1.35(1), C7*–C8* 1.40(1), C9–C10 1.36(1), C9*–C10* 1.39(1), C11–C12 1.38(1), C11*–C12* 1.39(1), Rh1–Rh2 3.225(1), Rh1*–Rh2* 3.230(1); C5–Rh1–C6 38.0(3), C5*–Rh1*–C6* 38.3(3), C7–Rh1–C8 37.4(3), C7*–Rh1*–C8* 38.8(3), O1–Rh1–O2 91.8(2), O1*–Rh1*–O2* 91.7(2), O3–Rh2–O4 91.2(2), O3*–Rh2*–O4* 91.6(2), C9–Rh2–C10 37.6(3), C9*–Rh2*–C10* 38.2(3), C11–Rh2–C12 38.2(3), C11*–Rh2*–C12* 38.5(3).

Preparation and Reactivity of Acetato Iridium Complexes

The doubly bridged acetato complex $[Ir(\mu\text{-}O_2CCH_3)(C_8H_{12})]_2$ was prepared from the related chloro derivative $[IrCl(C_8H_{12})]_2$ and silver acetate[7] while the corresponding tetrafluorobenzobarrelene iridium(I) compound $[Ir(\mu\text{-}O_2CCH_3)(TFB)]_2$ was obtained by treatment of $[Ir(\mu\text{-}OCH_3)(TFB)]_2$ with acetic acid[17]. In contrast to these synthetic routes, the bis(ethene) complex $[Ir(\mu\text{-}O_2CCH_3)(C_2H_4)_2]_2$ (**10**) was prepared similarly to the rhodium analogue **3** by using $[IrCl(C_2H_4)_2]_2$ (**8**) as starting

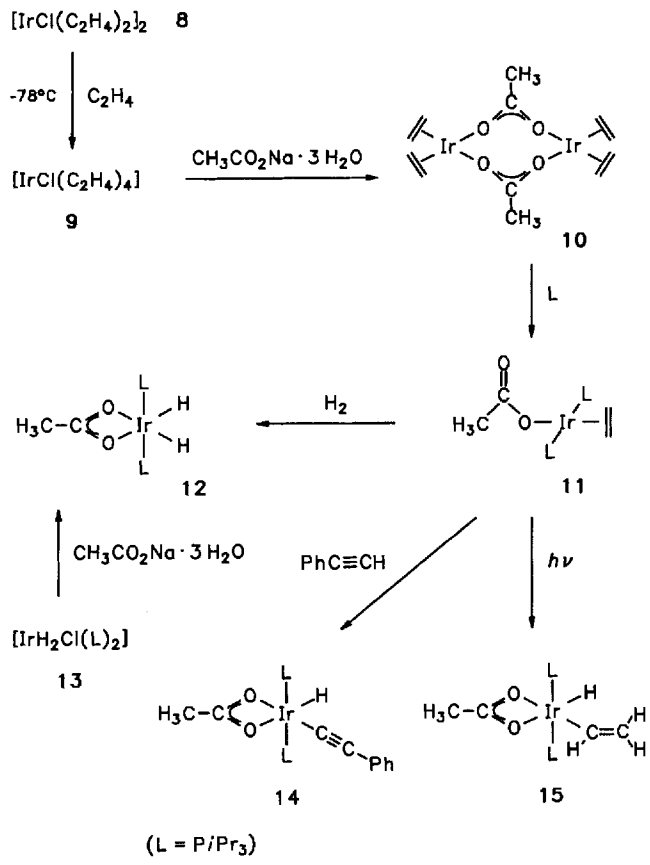
material. This dimer was first converted with an excess of ethene at −78 °C to the tetrakis(olefin) complex $[IrCl(C_2H_4)_4]$ (**9**)[18] which reacts with sodium acetate in ether to give the acetato derivative **10** in 85% yield. Compound **10** was isolated as a deep blue extremely air-sensitive solid which decomposes in solution (benzene, pentane, ether, chloroform) at room temperature in less than two hours. Since the positions of the asymmetric and symmetric OCO stretching frequencies in the IR spectrum of **10** are almost identical with those of **3**, we assume that the iridium complex is also dimeric both in solution and in the solid state.

The reaction of **10** with P*i*Pr$_3$ did not only lead to bridge cleavage but also to partial displacement of ethene and formation of the mononuclear compound *trans*-$[Ir(\eta^1\text{-}O_2CCH_3)(C_2H_4)(PiPr_3)_2]$ (**11**). In agreement with previous studies[10,11], in the IR spectrum of **11** the OCO stretching frequencies appear at higher wave numbers than in that of the bridged complex **10** while in the ^{1}H-NMR spectrum of **11** the signal of the O_2CCH_3 protons is shifted downfield if compared with **10**.

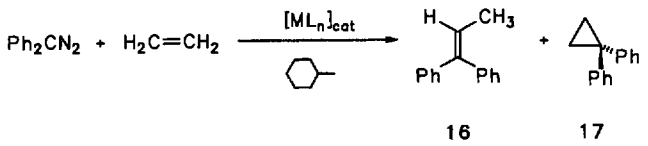
The ethene ligand of **11** is rather labile and easily displaced by H_2 and PhC≡CH (Scheme 2). The dihydrido complex $[IrH_2(\eta^2\text{-}O_2CCH_3)(PiPr_3)_2]$ (**12**) cannot only be prepared from **11** but also from the chloro derivative $[IrH_2Cl(PiPr_3)_2]$ (**13**) and $CH_3CO_2Na \cdot 3\,H_2O$ by ligand substitution. Related compounds of the general composition $[IrH_2(\eta^2\text{-}O_2CR)(PR_3)_2]$ are known and were obtained by treatment of $[Ir(\mu\text{-}O_2CR)(C_8H_{12})]_2$ with H_2 and phosphanes, from the cationic complexes $[IrH_2(OCMe_2)_2(PR_3)_2]^+$ and sodium carboxylates[9], or from $[IrH_5(PR_3)_2]$ and carboxylic acids[20]. The most characteristic feature of the NMR spectra of **12** and $[IrH(C{\equiv}CPh)(\eta^2\text{-}O_2CCH_3)(PiPr_3)_2]$ (**14**) is the appearance of a signal for the metal-bonded protons at high field (ca. $\delta = -31$) which is split into a triplet due to P−H coupling. We note that the rhodium analogues of **12** and **14**[11,21] are known and were purified from $[Rh(\eta^2\text{-}O_2CCH_3)(PiPr_3)_2]$ and H_2 or PhC≡CH.

In order to find out whether in analogy to $[Ir(\eta^2\text{-acac})(C_2H_4)(PiPr_3)]$, which reacts photochemically in the presence of P*i*Pr$_3$ to give the compound $[IrH(CH{=}CH_2)(\eta^2\text{-acac})(PiPr_3)_2]$[22], on irradiation of **11** an intramolecular C−H activation occurs we carried out a similar photochemical reaction of the acetato(ethene) complex. On irradiation of a solution of **11** in C_6D_6 with a 500 W Hg lamp at 10 °C for 1 h, a complete rearrangement to the isomer $[IrH(CH{=}CH_2)(\eta^2\text{-}O_2CCH_3)(PiPr_3)_2]$ (**15**) took place. The hydrido(vinyl) complex which is formed by intramolecular C−H activation was characterized by spectroscopic techniques. Since besides the signals for the acac and the acetato ligands there is a strong analogy in the ^{1}H-, ^{13}C-, and ^{31}P-NMR spectroscopic data of **15** and $[IrH(CH{=}CH_2)(\eta^2\text{-acac})(PiPr_3)_2]$ we assume that not only in the acetylacetonato complex[22] but also in **15** the two phosphane ligands are *trans*- and the hydrido and the vinyl ligands *cis*-disposed. No reversed isomerization of **15** to **11** could be observed, not even on heating a solution of **15** in toluene for 5 days at 100 °C.

Scheme 2



Scheme 3



Catalytic Studies

In contrast to the chloro complex **2**[1], the corresponding dimeric acetato compound **3** is catalytically less active in the reaction of ethene and diphenyldiazomethane. Moreover, it is also less *selective* and, depending on the reaction temperature, gives besides 1,1-diphenylpropene (**16**) also the isomeric 1,1-diphenylcyclopropane (**17**). At 20 °C in methylcyclohexane, the ratio of **16**/**17** is 1:5 while at 40 °C the ratio slightly decreases to 1:9 (Table 1). The same trend was observed with the acetatoiridium complex **10** as catalyst, which in analogy to the different catalytic activity of **2** and **8**[1,5], is significantly less reactive than **3** in the reaction shown in Scheme 3. We note, however, that whereas the turnover number for **3** as the catalyst becomes considerably *larger* if the temperature is increased from 20 °C to 40 °C, the reversed trend is found for the iridium analogue **10**. We assume that this difference is mainly due to the reduced

stability of **10** in solution which would agree with the observations made during the attempts to prepare the acetato derivatives **3** and **10** from the chlorometal precursors. The benzoatorhodium(I) complex **6** is nearly as active as the acetato counterpart **3** and at 20°C in methylcyclohexane generates the two isomers **16** and **17** in a molar ratio of 1:3. In all reactions, the C–C coupling products were separated from the metal-containing species by filtration through Al_2O_3 and identified by GC/MS analysis.

Table 1. Data on the catalytic activity of compounds **3**, **6**, and **10** in the reaction of ethene and diphenyldiazomethane (for details see Experimental)

Catalyst	T [°C]	TON[a]	ratio **16** : **17**
3	20	18	17 : 83
3	40	84	10 : 90
6	20	15	25 : 75
10	0	2	28 : 72
10	20	17	23 : 77
10	40	2	11 : 89

[a] TON = turnover number = mol product:mol catalyst.

Concluding Remarks

The work described here confirmed that the anionic ligand X^- of bis(ethene)rhodium(I) complexes $[RhX(C_2H_4)_2]_n$ (n = 1, 2) has a significant influence on (1) the turnover number and (2) the selectivity in the Rh-catalyzed reaction of ethene and diphenyldiazomethane to give 1,1-diphenylpropene and/or 1,1-diphenylcyclopropane. The dimeric carboxylato compound **3**, which is easily accessible from the corresponding chloro complex **2** and sodium acetate under heterogeneous conditions, is much more reactive than the related acetylacetonato derivative $[Rh(acac)(C_2H_4)_2]$, which could be due to the possibility of bridge cleavage and formation of a monomeric bis(ethene)rhodium(I) species from **3**. As far as both activity and selectivity are concerned, the first choice as catalyst still is the chloro compound **2**[1,3,5] which like the acetato complex **3**, is superior to the iridium counterparts **8** and **10**. A notable improvement may be obtained by the immobilization of the carboxylato compounds **3**–**6** or **10** on inorganic supports[23] and the results of this work will be reported in a forthcoming publication.

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Experimental

All operations were carried out under argon with the Schlenk tube technique. $[RhCl(C_8H_{14})_2]_2$ (**1**)[24], $[IrCl(C_2H_4)_2]_2$ (**8**)[18], and $[IrH_2Cl(PiPr_3)_2]$ (**13**)[25] were prepared by the published procedures. – IR: Perkin-Elmer 1420. – NMR: Bruker AC 200 and AMX 400; vt = virtual triplet. – MS: Finnigan MAT 90. – GC/MS: HP G1800A GCD System.

1. Modified Procedure for the Preparation of $[RhCl(C_2H_4)_2]_2$ (**2**)[9]: A suspension of 485 mg (0.86 mmol) of **1** in 60 ml of hexane was degassed at −30°C and then brought under 1 bar of ethene. Upon warming to room temp., the reaction mixture was stirred for 20 min to give an orange suspension. Part of the solvent was removed until a clear solution resulted which was filtered. The filtrate was concentrated to ca. 20 ml and after the concentrate had been saturated with ethene, an orange-yellow solid precipitated. It was filtered, repeatedly washed with small quantities of pentane (0°C) and dried. Orange crystals; yield 226 mg (86%).

2. Preparation of $[Rh(\mu\text{-}O_2CCH_3)(C_2H_4)_2]_2$ (**3**): A solution of 39 mg (0.10 mmol) of **2** in 10 ml of ether was treated at −30°C with 81 mg (0.60 mmol) of $CH_3CO_2Na \cdot 3\ H_2O$. With continuous stirring, the reaction mixture was slowly warmed to room temp. (1 h) and then filtered. The filtrate was concentrated to dryness in vacuo, and the residue was recrystallized from pentane to give orange-red crystals; yield 38 mg (92%); m.p. 115°C (dec.). – IR (KBr): $\tilde{\nu}$ = 1560, 1420 cm^{-1} [$\nu(O_2CMe)$ asym and sym]. – ^1H NMR (C_6D_6, 200 MHz): δ = 2.94 (s, br, 8H, C_2H_4), 1.67 (s, 3H, O_2CCH_3). – ^{13}C NMR (C_6D_6, 50.3 MHz): δ = 184.2 (s, O_2CCH_3), 61.1 [d, J(RhC) = 13.9 Hz, C_2H_4], 24.9 (s, O_2CCH_3). – $C_{12}H_{22}O_4Rh_2$ (436.1): calcd. C 33.05, H 5.09, Rh 47.19; found C 32.85, H 5.28, Rh 47.60.

3. Preparation of $[Rh(\mu\text{-}O_2CCH_3)(C_8H_{14})_2]_2$ (**4**): A suspension of 85 mg (0.12 mmol) of **1** in 10 ml of ether was treated at −30°C with 54 mg (0.40 mmol) of $CH_3CO_2Na \cdot 3\ H_2O$. After the reaction mixture had slowly been warmed to room temp., it was stirred for 6 h and then filtered. The filtrate was worked up as described for **3**. Orange microcrystalline solid; yield 75 mg (83%); m.p. 96°C (dec.). – IR (KBr): $\tilde{\nu}$ = 1555, 1420 cm^{-1} [$\nu(O_2CMe)$ asym and sym]. – ^1H NMR (C_6D_6, 200 MHz): δ = 2.35 (m, 4H, =CH of C_8H_{14}), 1.92, 1.54, 1.33 (all m, 24H, CH_2 of C_8H_{14}), 1.63 (s, 3H, O_2CCH_3). – ^{13}C NMR (C_6D_6, 50.3 MHz): δ = 191.9 (s, O_2CCH_3), 74.7 [d, J(RhC) = 14.5 Hz, =CH of C_8H_{14}], 30.5, 28.6, 27.5 (all s, CH_2 of C_8H_{14}), 24.2 (s, O_2CCH_3). – $C_{36}H_{62}O_4Rh_2$ (764.7): calcd. C 56.54, H 8.17; found C 56.72, H 8.24; mol. mass 725 (osmometr. in C_6H_6).

4. Preparation of $[Rh(\mu\text{-}O_2CCF_3)(C_2H_4)_2]_2$ (**5**): A solution of 40 mg (0.10 mmol) of **2** in 10 ml of ether was treated at −30°C with 16 μl (0.21 mmol) of CF_3CO_2H and 22 mg (0.60 mmol) of NaOH. After the reaction mixture had slowly been warmed to room temp. and stirred for 2 h, it was worked up as described for **3**. Yellow crystals; yield 37 mg (75%). – IR (KBr): $\tilde{\nu}$ = 1605, 1445 cm^{-1} [$\nu(O_2CCF_3)$ asym and sym]. – ^1H NMR (C_6D_6, 200 MHz): δ = 2.26 (s, br, C_2H_4). – ^{19}F NMR (C_6D_6, 188.3 MHz): δ = −137.9(s). – $C_{12}H_{16}F_6O_4Rh_2$ (544.1): calcd. C 26.49, H 2.96; found C 26.12, H 2.70; mol. mass 510 (osmometr. in C_6H_6).

5. Preparation of $[Rh(\mu\text{-}O_2CC_6H_5)(C_2H_4)_2]_2$ (**6**): Analogously as described for **5** by using 25 mg (0.07 mmol) of **2**, 16 mg (0.13 mmol) of benzoic acid and 15 mg (0.40 mmol) of NaOH as starting materials; orange crystals; yield 24 mg (67%). – IR (KBr): $\tilde{\nu}$ = 1590, 1415 cm^{-1} [$\nu(O_2CPh)$ asym and sym]. – ^1H NMR (C_6D_6, 200 MHz): δ = 7.82, 7.28, 7.18 (all m, 5H, C_6H_5), 3.17 (s, br, 8H, C_2H_4). – $C_{22}H_{26}O_4Rh_2$ (560.3): calcd. C 47.16, H 4.68, Rh 36.73; found C 47.52, H 4.87, Rh 36.12.

6. Preparation of $[Rh(\eta^2\text{-}O_2CCH_3)(PiPr_3)_2]$ (**7**) *from* **3**: A solution of 44 mg (0.10 mmol) of **3** in 10 ml of pentane was treated with 78 μl (0.40 mmol) of $PiPr_3$ and stirred for 1 h at room temp. The solution was filtered, the filtrate was concentrated to dryness in vacuo, and the residue was recrystallized from pentane to give dark red crystals of **7**[8]; yield 65 mg (68%).

7. Preparation of [Ir(μ-O_2CCH_3)(C_2H_4)$_2$]$_2$ (**10**): A solution of 79 mg (0.14 mmol) of **8** in 10 ml of ether was partly degassed at −78 °C and then stirred under 0.5 bar of ethene. A white solid of [IrCl(C_2H_4)$_4$] (**9**) precipitated. The reaction mixture was treated under ethene with 50 mg (0.37 mmol) of $CH_3CO_2Na \cdot H_2O$ and with continuous stirring slowly warmed to 0 °C (30 min). A characteristic change of color from pale yellow to red and finally to violet occurred. The solution was again cooled to −78 °C, briefly stored under 0.5 bar of ethene and slowly warmed to 0 °C. This procedure was repeated three times. The reaction mixture was finally warmed to room temp., the solvent was removed, and the residue was extracted with 30 ml of pentane. The extract was concentrated in vacuo to give a deep blue, extremely air-sensitive microcrystalline solid; yield 73 mg (85%); m.p.: 64 °C (dec.). − IR (hexane): $\tilde{\nu}$ = 1560, 1425 cm^{-1} [ν(O_2CMe) asym and sym]. − ^{1}H NMR (C_6D_6, 200 MHz): δ = 2.70 (s, br, 8H, C_2H_4), 1.67 (s, 3H, O_2CCH_3). − ^{13}C NMR ($C_6D_5CD_3$, −50 °C, 100.6 MHz): δ = 182.0 (s, O_2CCH_3), 41.7 (s, C_2H_4), 23.0 (s, O_2CCH_3). − $C_{12}H_{22}Ir_2O_4$ (614.7): calcd. C 23.45, H 3.61; found C 23.14, H 3.63.

8. Preparation of trans-[Ir(η^1-O_2CCH_3)(C_2H_4)(PiPr$_3$)$_2$] (**11**): A solution of 45 mg (0.07 mmol) of **10** in 10 ml of pentane was treated with 56 μl (0.30 mmol) of P*i*Pr$_3$ and stirred for 1 h at room temp. The solution was filtered, the solvent was removed and the residue was recrystallized from pentane to give dark brown crystals; yield 52 mg (58%). − IR (KBr): $\tilde{\nu}$ = 1625, 1445 cm^{-1} [ν(O_2CMe) asym and sym]. − ^{1}H NMR (C_6D_6, 200 MHz): δ = 2.10 (s, 3H, O_2CCH_3), 2.09 (m, 6H, PC*H*CH_3), 1.78 [t, *J*(PH) = 4.1 Hz, 4H, C_2H_4], 1.25 [dvt, *N* = 12.8, *J*(HH) = 7.0 Hz, 36H, PCHC*H*$_3$]. − ^{13}C NMR (C_6D_6, 50.3 MHz): δ = 173.8 (s, O_2CCH_3), 26.2 (s, O_2CCH_3), 22.9 (vt, *N* = 22.8 Hz, P*C*HCH$_3$), 20.9 (s, PCH*C*H$_3$), 16.0 (s, C_2H_4). − ^{31}P NMR (C_6D_6, 81.0 MHz): δ = 21.5 (s). − $C_{22}H_{49}IrO_2P_2$ (599.8): calcd. C 44.05, H 8.23; found C 44.50, H 8.80.

9. Preparation of [IrH$_2$(η^2-O_2CCH_3)(PiPr$_3$)$_2$] (**12**): (a) A stream of H_2 was passed through a solution of 49 mg (0.08 mmol) of **11** in 10 ml of pentane for 1 min at −50 °C. After warming to room temp., the solution was filtered and the solvent was removed from the filtrate to give an almost white solid; yield 30 mg (65%). − (b) A solution of 22 mg (0.04 mmol) of **13** in 5 ml of ether was treated with 20 mg (0.15 mmol) of $CH_3CO_2Na \cdot 3\ H_2O$ and stirred for 15 h at room temp. The solution was filtered and, after the solvent had been removed from the filtrate, a white solid was isolated; yield 20 mg (87%); m.p. 42−44 °C. − IR (C_6H_6): $\tilde{\nu}$ = 2242 cm^{-1} [ν(IrH)], 1545, 1445 [ν(O_2CMe) asym and sym]. − ^{1}H NMR (C_6D_6, 200 MHz): δ = 2.12 (m, 6H, PC*H*CH_3), 1.80 (s, 3H, O_2CCH_3), 1.19 [dvt, *N* = 13.0, *J*(HH) = 6.8 Hz, 36H, PCHC*H*$_3$], −31.77 [t, *J*(PH) = 15.3 Hz, 2H, IrH$_2$]. − ^{13}C NMR (C_6D_6, 50.3 MHz): δ = 181.6 (s, O_2CCH_3), 25.9 (vt, *N* = 26.8 Hz, P*C*HCH$_3$), 25.2 (s, O_2CCH_3), 20.3 (s, PCH*C*H$_3$). − ^{31}P NMR (C_6D_6, 81.0 MHz): δ = 45.8 (s). − $C_{20}H_{47}IrO_2P_2$ (573.8): calcd. C 41.87, H 8.26; found C 41.99, H 8.36; mol. mass (MS) 574 [M$^+$ for ^{193}Ir].

10. Preparation of [IrH(C≡CPh)(η^2-O_2CCH_3)(PiPr$_3$)$_2$] (**14**): A solution of 55 mg (0.09 mmol) of **11** in 10 ml of hexane was treated with 10.1 μl (0.09 mmol) of phenylacetylene and stirred for 20 h at 80 °C. After warming of the reaction mixture was brought to room temp., the solvent was removed and the residue was recrystallized from toluene to give a red oil; yield 50 mg (74%). − IR (C_6H_6): $\tilde{\nu}$ = 2272 cm^{-1} [ν(IrH)], 2088 [ν(C≡C)], 1535, 1440 [ν(O_2CMe) asym and sym]. − ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 6.95 (m, 5H, C_6H_5), 2.58 (m, 6H, PC*H*CH_3), 1.70 (s, 3H, O_2CCH_3), 1.25 [dvt, *N* = 16.4, *J*(HH) = 7.0 Hz, 36H, PCHC*H*$_3$], −30.68 [t, *J*(PH) = 12.8 Hz, 1H, IrH]. − ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ = 185.6 (s, O_2CCH_3), 131.4, 129.0, 128.3, 124.0 (all s, C_6H_5), 26.1 (s, O_2CCH_3), 24.2 (vt, *N* = 26.9 Hz, P*C*HCH$_3$), 20.4, 19.8 (both s, PCH*C*H$_3$); signals of the alkynyl carbon atoms not exactly located. − ^{31}P NMR ($CDCl_3$, 81.0 MHz): δ = 28.0 (s). − $C_{28}H_{51}IrO_2P_2$ (673.9): calcd. C 49.91, H 7.63; found C 49.64, H 7.40.

11. Photolysis of **11**: In an NMR tube, a solution of 44 mg (0.07 mmol) of **11** in 0.5 ml of C_6D_6 was irradiated at 10 °C (water cooling) for 1 h with a 500 W-Hg lamp (Osram). Although no change of color could be observed, the NMR spectra confirmed a complete rearrangement of **11** to the isomer [IrH(CH=CH_2)(η^2-O_2CCH_3)(P*i*Pr$_3$)$_2$] (**15**). Spectroscopic data of **15**: ^{1}H NMR (C_6D_6, 200 MHz): δ = 8.30 [dd, $J(HH)_{trans}$ = 16.9, $J(HH)_{cis}$ = 9.5 Hz, 1H, C*H*=CH_2], 5.94, 4.90 (both m, 1H each, =CH_2), 2.57 (m, 6H, PC*H*CH_3), 1.78 (s, 3H, O_2CCH_3), 1.26 [dvt, *N* = 13.2, *J*(HH) = 6.9 Hz, 36H, PCHC*H*$_3$], −28.42 [t, *J*(PH) = 14.8 Hz, 1H, IrH]. − ^{13}C NMR (C_6D_6, 50.3 MHz): δ = 183.5 (s, O_2CCH_3), 121.7 [t, *J*(PC) = 8.5 Hz, IrCH], 118.1 (s, =CH_2), 26.3 (s, O_2CCH_3), 23.9 (vt, *N* = 25.9 Hz, P*C*HCH$_3$), 20.1, 19.6 (both s, PCH*C*H$_3$). − ^{31}P NMR (C_6D_6, 81.0 MHz): δ = 24.7 (s).

12. Catalytic Reaction of Ph_2CN_2 and C_2H_4 with **3**, **6** *or* **10** *as Catalyst:* A solution of 10 mg (0.02 mmol) of **3** or 20 mg (0.035 mmol) of **6** or 30 mg (0.05 mmol) of **10** in 6 ml of methylcyclohexane was treated dropwise at 20 °C with a 0.1 M solution of Ph_2CN_2 in methylcyclohexane while bubbling ethene through the solution. The catalytic reaction was finished when the violet color of the diazoalkane solution did not disappear on addition to the reaction mixture. The solvent was removed in vacuo, and the oily residue was dissolved in 2−3 ml of hexane. In order to destroy excess Ph_2CN_2 and separate the catalyst, the mixture was filtered through Al_2O_3 (neutral, activity grade III, height of column 3 cm). After evaporation, a white solid of **16** or an oil containing a mixture of **16** and **17** was isolated from the eluate. The ratio of the two products was determined by integration of characteristic signals in the ^{1}H-NMR spectra and by GC/MS analysis. − With **3** as catalyst, the catalytic reaction of Ph_2CN_2 and C_2H_4 was also performed at 40 °C, and with **10** as catalyst at 0 °C and 40 °C. The results are summarized in Table 1.

13. Determination of the X-ray Crystal Structure of **3**[26]: Single crystals were grown from pentane. Crystal data (from 23 reflections, 10° < Θ < 14°): triclinic, space group *P*-1 (No. 2); *a* = 8.069(6) Å, *b* = 12.36(1) Å, *c* = 16.18(1) Å, α = 102.12(5)°, β = 104.48(4)°, γ = 90.12(5)°, *V* = 1524(2) Å^3, *Z* = 4, d_{calcd} = 1.90 gcm^{-3}, μ(Mo-K_α) = 21.4 cm^{-1}; crystal size 0.08 × 0.13 × 0.15 mm; Enraf-Nonius CAD4 diffractometer, Mo-K_α radiation (0.70930 Å), graphite monochromator, zirconium filter (factor 15.41); *T* = 293 K; ω/Θ-scan, max 2Θ = 48°; 5161 reflections measured, 4393 independent reflections, 3103 reflections with $F_o > 3\sigma(F_o)$. Intensity data were corrected for Lorentz and polarization effects, a linear decay correction (loss of intensity −12.7%) and an empirical absorption correction (ψ-scan method) were applied (minimum transmission 90.62%). The structure was solved by the Patterson method (SHELXS-86). Atomic coordinates and the anisotropic thermal parameters of the non-hydrogen atoms were refined by full-matrix least squares (325 parameters, unit weights, Enraf-Nonius SDP). The positions of all hydrogen atoms were calculated according to ideal geometry (distance C−H = 0.95 Å). There are two independent molecules in the unit cell which differ only slightly in respect of bond lengths and bond angles (Figure 1). *R* = 0.033, R_w = 0.036; reflex/parameter ratio 9.55; residual electron density +0.49/−0.58 eÅ^{-3}.

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