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Versatile Reactivity of the Bis(dihydrogen) Complex $RuH_2(H_2)_2(PCy_3)_2$ toward Functionalized Olefins: Olefin Coordination versus Hydrogen Transfer via the Stepwise Dehydrogenation of the Phosphine Ligand

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Treatment of $RuH_2(H_2)_2(PCy_3)_2$ (**1**) with ethylene leads to the formation of $[RuH\{\eta^3\text{-}C_6H_8)PCy_2\}(C_2H_4)(PCy_3)]$ (**2**), which contains an η^3-cyclohexenyl ring. Upon addition of 3 equiv of an alkene bearing σ-donor substituents such as $CH_2{=}CH(SiEt_3)$ or $CH_2{=}CH^tBu$, **1** transforms in high yield into the trihydridoruthenium(IV) complex $[RuH_3\{(\eta^3\text{-}C_6H_8)PCy_2\}(PCy_3)]$ (**3**) and the corresponding alkane is obtained quantitatively. Further hydrogen abstraction from **1** can be achieved by using 5 equiv of alkene, leading to the hydridoruthenium(II) complex $[RuH\{(\eta^3\text{-}C_6H_8)PCy_2\}\{(\eta^2\text{-}C_6H_9)PCy_2\}]$ (**4**). This is the first complex where C−H activation within two cyclohexyl rings of two tricyclohexylphosphines has occurred. **4** can also be obtained by treatment of **3** with 2 equiv of alkene. The reactions can be reversed by bubbling dihydrogen into a solution of **2**−**4** yielding **1** at the final stage of hydrogenation. **3** and **4** undergo rapid H−D exchange with the deuterated solvent. Reaction of **1** with alkenes bearing electron-withdrawing substituents such as $CH_2{=}CHCO_2Me$ or *trans*-$MeO_2CCH{=}CHCO_2Me$ allows the formation of the hydrido dihydrogen complexes $[RuH(H_2)(\eta^2\text{-}O_2CCH_2CH_3)(PCy_3)_2]$ (**5**) and $[RuH(H_2)(\eta^2\text{-}O_2CCH_2CH_2CO_2Me)(PCy_3)_2]$ (**6**), respectively. An X-ray structure determination on **5** was carried out. Surprisingly, reaction of **1** with *cis*-$MeO_2CCH{=}CHCO_2Me$ yielded the alkene-coordinated complex $[RuH_2(\eta^2\text{-}CH_3O_2CCH{=}CHCO_2CH_3)(PCy_3)_2]$ (**7**). Variable-temperature NMR studies on **7** showed a barrier of rotation for the alkene of 10.5 kcal/mol. **7** was shown to catalyze *cis*−*trans* $MeO_2CCH{=}CHCO_2Me$ isomerization.

Introduction

Dihydrogen complexes[1] have been postulated as catalytic intermediates in numerous homogeneous processes such as hydrogenation of alkenes, alkynes, and ketones.[1d] The coordinated dihydrogen ligand is further easily substituted by several molecules and is considered in these catalytic processes as an intermediate on the way to oxidative addition. The first stable bis(dihydrogen) complex, $RuH_2(H_2)_2(PCy_3)_2$ (**1**), was synthesized in our group 10 years ago,[2] and its reactivity has been explored since then. The presence of two dihydrogen ligands has allowed the obtention of unusual structures. For example, stable 16-electron hydrido dihydrogen complexes $RuHX(H_2)(PCy_3)_2$ are obtained by reacting halocarbons or thiols with **1**.[3] Substitution of one dihydrogen ligand by silanes or germanes yields the new complexes $RuH_2(H_2)(\eta^2\text{-}HER_3)(PCy_3)_2$ in which the HER_3 (E = Si, Ge) ligand is weakly coordinated.[4] This last result prompted us to evaluate the catalytic activity of **1** toward hydrosilylation of olefins.

We found that treatment of **1** with triethylsilane and ethylene results in efficient production of vinylsilane. Dehydrogenative silylation of ethylene is favored over the hydrosilylation. Mechanistic studies have shown that **1** serves as a precursor to generate the catalyst resting state $[RuH\{(\eta^3\text{-}C_6H_8)PCy_2\}(C_2H_4)(PCy_3)]$ (**2**) by direct reaction of **1** with ethylene. **2** is the first complex presenting a dehydrogenated cyclohexyl ligand on a cyclohexylphosphine bound to the ruthenium in an η^3-mode and was reported in a preliminary communication.[5]

Stoichiometric studies are of importance for the understanding of catalytic processes. The reactivity of **1** toward functionalized alkenes was examined in an effort to develop other applications in catalytic reactions. In this paper, we describe the reactivity of the bis(dihydrogen) complex **1** toward substituted alkenes and demonstrate that **1** can cleanly and reversibly transfer up to 10 hydrogen atoms. We have chosen mono- and disubstituted alkenes that differ in coordination ability due to different steric and electronic properties of the functional groups.

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Results and Discussion

(1) Reaction of $RuH_2(H_2)_2(PCy_3)_2$ (1) with Alkenes L (L = C_2H_4, $CH_2{=}CHSiEt_3$, $CH_2{=}CH^tBu$). Synthesis of [RuH{(η^3-C_6H_8)PCy_2}(C_2H_4)(PCy_3)] (2). Treatment of a suspension of **1** in pentane with ethylene (3 bar) results in evolution of ethane (GC, NMR)) and formation of a white solid analyzed as [RuH{(η^3-C_6H_8))-PCy_2}(C_2H_4)(PCy_3)] (**2**) in 87% yield. Key spectroscopic features include an AB pattern in the $^{31}P\{^1H\}$ NMR spectrum with a large J_{P-P} value (283 Hz) indicative of a trans position for unequivalent phosphines and three doublets in the ^{13}C NMR spectrum for the allylic C_4, C_3, and C_5 carbons at δ 77.9 (J_{C-H} = 161 Hz), 67.0 (J_{C-H} = 150 Hz), and 45.8 (J_{C-H} = 156 Hz). The ethylenic carbons are presumably hidden by the multiplets of the cyclohexyl carbons between δ 27 and 33. The ^1H NMR spectrum is temperature dependent indicating the fluxionality of the molecule and fast rotation of the ethylene ligand at room temperature. At 297 K (400 MHz, C_7D_8) a very broad signal is observed for the hydride at δ −7.12 which becomes a doublet of doublets (J_{P-H} = 18.9 and 26.2 Hz) at 223 K. This signal resumes into a singlet upon phosphorus decoupling. At 297 K, broad peaks arising from the phosphine protons are observed between δ 1 and 3.3. The allylic protons appear as two broad signals at δ 5.13 and 3.52 in a 2:1 ratio. At low temperature the assignment is rendered difficult due to very broad resonances of the phosphine protons over a wide range of chemical shifts (between δ 1 and 3.3). At 223 K, the three broad signals at δ 5.32, 5.19, and 3.74 can be attributed to the allylic protons and three additional broad signals can be attributed to the ethylenic protons at δ 4.36, 3.49, and δ 2.73. All these signals are of equal intensity. The remaining ethylenic proton is presumably hidden by the phosphine protons.

The addition of 1 equiv of ^tBuNC to a solution of **2** in C_6D_6 in an NMR tube results in ethylene evolution as evidenced by an intense singlet at δ 5.36 and formation of a new complex tentatively formulated as [RuH{(η^3-C_6H_8)PCy_2}(PCy_3)(^tBuNC)]. All attempts to isolate the complex failed. An AB pattern is observed in the $^{31}P\{^1H\}$ NMR spectrum at δ 100.3 and 58.9 with J_{P-P} = 237 Hz. The ^1H NMR spectrum shows a hydride resonance at δ −8.42 as a doublet of doublets (J_{P-H} = 28.7 and 22 Hz), a singlet for the protons of ^tBuNC at δ 1.3, and allylic resonances at δ 5.3, 4.1, and 3.3. These data are very similar to the ones obtained for the hydridoruthenium(II) complex **4** (see below).

Synthesis of [RuH_3{(η^3-C_6H_8)PCy_2}(PCy_3)] (3). Reaction of **1** with a substituted alkene such as $CH_2{=}CH(SiEt_3)$ or $CH_2{=}CH^tBu$ did not result in the coordination of the alkene.

Addition of 3 equiv of $CH_2{=}CH(SiEt_3)$ to a suspension of **1** in pentane results in immediate dissolution of **1**, and within 20 s, precipitation of a white microcrystalline solid occurs; this analyzes as RuH_3[(η^3-C_6H_8)PCy_2]-(PCy_3) (**3**). This trihydride complex **3** was isolated in 81% yield. GC analysis of the mother liquor reveals the presence of $SiEt_4$ resulting from the hydrogenation of the alkene. The same results were obtained by using $CH_2{=}CH^tBu$ instead of $CH_2{=}CHSiEt_3$. The ^{31}P NMR shows, as for **2**, two inequivalent P nuclei with a typical trans coupling (J_{PP} = 254 Hz). The ^1H NMR spectrum at 297 K (C_7D_8) consists of a pseudotriplet at δ −7.57 (J_{P-H} = 17 Hz) for the hydrides, a quartet pattern at δ 5.08, and a broad singlet at δ 4.53 for the allylic protons at the 4 and 3,5 positions, respectively, of a cyclohexenyl ligand. The integration ratio for these three signals is respectively 3:1:2 which indicates the presence of 3 hydrides. Upon phosphorus decoupling, the high-field triplet is transformed into a singlet and the quartet pattern into a triplet (J_{H-H} = 6.2 Hz). The three hydrides exchange until the temperature limit of 203 K. The observed minimum T_1 value is 90 ms at 233 K (C_7D_8, 250 MHz) ruling out a hydrido dihydrogen formulation but not a short contact between the three hydrides. This complex is therefore formulated as a trihydridoruthenium(IV) complex, only a limited number of examples of which are known.[6] The presence of the (η^3-cyclohexenyl)(dicyclohexyl)phophine ligand was supported by the ^{13}C NMR spectrum. The allylic carbon at the 4 position resonates as a doublet at δ 81.3, while the two carbons in the 3 and 5 positions give a doublet at δ 58.9.

As the reaction is virtually instantaneous, it was not possible to obtain information on the reaction pathway. Monitoring the reaction by ^1H and ^{31}P NMR spectroscopy did not give any further information (see below: reactivity of **2**−**4** toward H_2). However, we can propose that substitution of one dihydrogen ligand by the competing alkene is followed by alkene insertion into the Ru−H bond to yield an alkyl hydrido intermediate which then eliminates the corresponding alkane. Effective C−H bond activations of one cyclohexyl ring could allow successive alkene insertion and elimination of the corresponding alkane.

Synthesis of [RuH{(η^3-C_6H_8)PCy_2}{(η^2-C_6H_9)-PCy_2}] (4). We have demonstrated that addition of 3 equiv of a substituted alkene to **1** resulted in hydrogenation of the alkene and formation of the trihydride **3**. When 5 equiv of alkene is added to **1**, total hydrogenation of the alkene is again achieved and a new hydridoruthenium(II) complex [RuH{(η^3-C_6H_8)PCy_2}{(η^2-C_6H_9)PCy_2}] (**4**) is obtained in good yield (74%). As opposed to the case of **3** where only one cyclohexyl group of one phosphine has been activated, both phosphine ligands in **4** exhibit a dehydrogenated cyclohexyl ring bound to the metal in an η^3 and η^2 mode, respectively. This represents the first example of such a double activation within the same complex. Support for structure **4** is provided by ^1H and ^{13}C NMR spectra.

The ^1H NMR spectrum of **4** consists of five separate signals of equal intensity between δ 5.2 and 3.4 attributed to the two olefinic and the three allylic protons, a doublet of doublets in the hydride region at δ −7.91 (J_{P-H} = 26.1 and 20.0 Hz), each of these six signals integrating for 1, and a complicated multiplet between δ 2.8 and 1.1 for the remaining cyclohexyl protons. Upon phosphorus decoupling the hydride signal transforms into a singlet and the multiplet at δ 5.16 simplifies into a triplet which can be assigned to the central allylic proton. All the other assignments derive from selective ^1H decoupling experiments (see Table 1 and Scheme 1 for assignments): olefinic hydrogens appear

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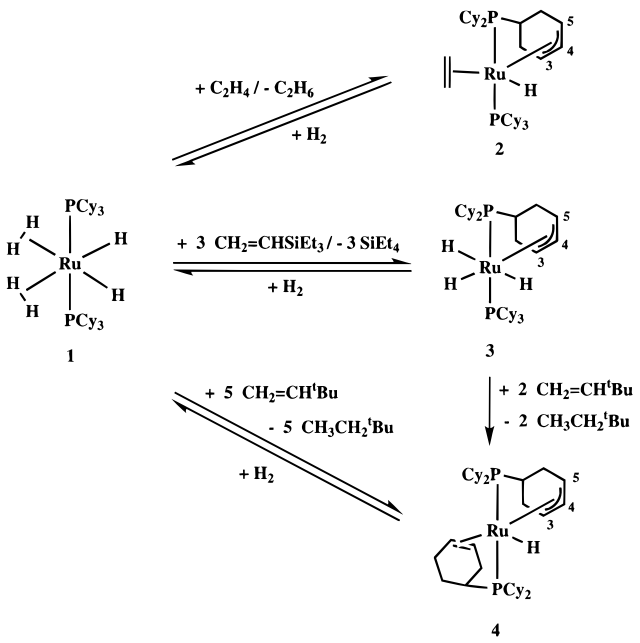
Table 1. Selected NMR Data (ppm) for Compounds 2−7

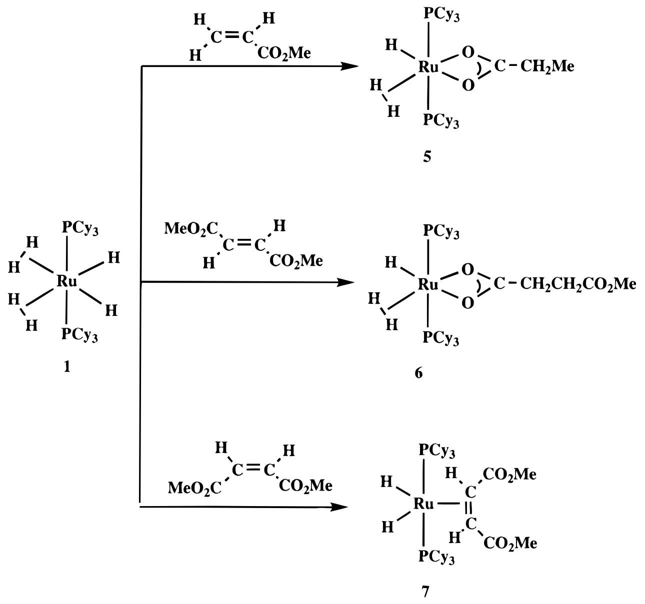
complexes	^{1}H NMR^a	^{31}P{^{1}H} NMR^a	^{13}C NMR^a
$[RuH\{(\eta^3\text{-}C_6H_8)PCy_2\}(C_2H_4)(PCy_3)]$ (**2**)	5.12 (br, 2H, η^3-$C_6H_8{}^{4,3}$),^{c} 3.52 (br, 1H, η^3-$C_6H_8{}^5$), −7.12 (br, Ru−H)	82.2 and 42.2 (J_{P-P} = 283 Hz)^e	77.9 (d, J_{C-H} = 161 Hz, C^4),^{h} 67.0 (d, J_{C-H} = 150 Hz, C^3), 45.8 (d, J_{C-H} = 156 Hz, C^5)
$[RuH_3\{(\eta^3\text{-}C_6H_8)PCy_2\}(PCy_3)]$ (**3**)	5.05 (m, 1H, η^3-$C_6H_8{}^4$),^{b} 4.51 (br, 2H, η^3-$C_6H_8{}^{3,5}$), −7.52 (pst, 3H, J_{P-H} = 17 Hz, Ru−H_3)	109.6 and 61.0 (J_{P-P} = 254 Hz)^e	81.3 (d, J_{C-H} = 163 Hz, C^4),^{g} 58.9 (d, J_{C-H} = 157 Hz, $C^{3,5}$)
$[RuH\{(\eta^3\text{-}C_6H_8)PCy_2\}\{(\eta^2\text{-}C_6H_9)PCy_2\}]$ (**4**)	5.16 (m, 1H, $J_{H^4-H^3}$ = 6.8 Hz, η^3-$C_6H_8{}^4$),^{c} 4.13 (br, 1H, η^3-$C_6H_8{}^3$), 3.47 (br, 1H, $J_{H^5-H^4}$ = 5.3 Hz, η^3-$C_6H_8{}^5$), 4.49 (br, 1H, η^2-C_6H_9), 3.93 (br, 1H, η^2-C_6H_9), −7.91 (dd, 1H, J_{P-H} = 26.1 and 20.0 Hz, Ru−H)	85.5 and 52.7 (J_{P-P} = 268 Hz)^f	75.3 (d, J_{C-H} = 162 Hz, η^2-C=C),^{h} 74.3 (d, J_{C-H} = 151 Hz, C^4), 52.7 (d, J_{C-H} = 166 Hz, $C^{3,5}$)
$[RuH(H_2)(O_2CCH_2CH_3)(PCy_3)_2]$ (**5**)	2.50 (q, 2H, J_{H-H} = 7.5 Hz, $O_2CCH_2CH_3$),^{b} 1.44 (t, 3H, J_{H-H} = 7.5 Hz, $O_2CCH_2CH_3$), −14.05 (t, 3H, J_{P-H} = 14.4 Hz, Ru−H(H_2))	51.9 (s)^e	182.8 (s, $O_2CCH_2CH_3$),^{h} 31.3 (t, J_{C-H} = 126 Hz, $O_2CCH_2CH_3$), 9.2 (q, J_{C-H} = 127 Hz, $O_2CCH_2CH_3$)
$[RuH(H_2)(O_2C(CH_2)_2CO_2CH_3)(PCy_3)_2]$ (**6**)	3.25 (s, 3H, $O_2C(CH_2)_2CO_2CH_3$),^{b} 2.85 (m, 4H, $O_2C(CH_2)_2CO_2CH_3$), −14.19 (t, 3H, J_{P-H} = 14.4 Hz, Ru−H(H_2))	52.0 (s)^e	180.5 (s, $O_2C(CH_2)_2CO_2CH_3$),^{i} 173.5 (s, $O_2C(CH_2)_2CO_2CH_3$), 51.5 (q, J_{C-H} = 146 Hz, $O_2C(CH_2)_2CO_2CH_3$) 33.1 (m, $O_2C(CH_2)_2CO_2CH_3$)
$[RuH_2(Z\text{-}CH_3O_2CCH{=}CHCO_2CH_3)(PCy_3)_2]$ (**7**)	3.92 (m, 2H, $CH_3O_2CCH{=}CHCO_2CH_3$),^{d} 3.44 (s, 6H, $CH_3O_2CCH{=}CHCO_2CH_3$), −19.8 (br, 2H, Ru−H_2)	59.1(s)^e	176.5 (s, $CH_3O_2CCH{=}CHCO_2CH_3$),^{g} 50.6 (q, J_{C-H} = 145 Hz, $CH_3O_2CCH{=}CHCO_2CH_3$), 49.0 (d, J_{C-H} = 165 Hz, $CH_3O_2CCH{=}CHCO_2CH_3$)

^{a} C_6D_6, 296 K. ^{b} 200.132 MHz. ^{c} 400.134 MHz. ^{d} 250.133 MHz. ^{e} 81.015 MHz. ^{f} 161.986 MHz. ^{g} 62.896 MHz. ^{h} 100.613 MHz. ^{i} 50.323 MHz.

Scheme 1



Scheme 2



at δ 3.93 and 4.49, while allylic hydrogens appear at δ 3.47, 4.13, and 5.16.

The ^{31}P NMR spectrum of **4** shows, as for **2** and **3**, an AB pattern with a typical trans coupling J_{P-P} = 268 Hz. Evidence for the η^3-C_6H_8 and η^2-C_6H_9 ligands is verified by ^{13}C NMR: the three allylic carbons resonate at δ 74.3 and 52.7 for the 4 and 3,5 positions, respectively, while the two olefinic carbons resonate at δ 75.3.

Note that one of us already reported two complexes $[Cp^*Ru\{(C_6H_9)PCy_2\}][BF_4]$ and $[Ru\{(C_6H_9)PCy_2\}(CF_3COO)]_2(\mu\text{-}CF_3COO)_2(\mu\text{-}OH_2)$ where dehydrogenation of a cyclohexyl ring resulted in the formation of an (η^2-C_6H_9)PCy_2 ligand but presenting in the former case a strong agostic interaction.[7,8]

It is interesting to note that **4** can also be obtained upon treatment of **3** with 2 equiv of 3,3-dimethyl-1-butene: **4** and 2-dimethylbutane are thus quantitatively produced as shown by ^{1}H and ^{31}P NMR.

Reactivity of 2−4 toward H_2. In all these reactions, the alkene serves as an hydrogen acceptor. The alkene:**1** ratios play a crucial role in obtaining **3** and **4**, since **1** is the only source of hydrogen. Thus, a 3-fold molar excess of the alkene is necessary to achieve total hydrogenation into the corresponding alkane and quantitative formation of **3**. In contrast, a 2-fold molar excess of the alkene affords **3** in the expected yield *ca.* 63% and the red dimer $Ru_2H_4(H_2)(PCy_3)_4$ characterized by ^{1}H and ^{31}P NMR.[2b]

Following the same strategy, **4** is prepared either from **1** using 5 equiv of alkene or from **3** using 2 equiv of

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alkene. A further dehydrogenation of the complex **4** is not observed when a 10-fold excess of the alkene over **1** is used.

In order to investigate whether hydrogen abstraction from the cyclohexyl rings is a reversible process, we have carried out a series of experiments aimed at a stepwise hydrogenation of complexes **2**−**4**. When the reactions of **1** with various amounts of alkene are carried out in NMR tubes and monitored by ^{1}H and ^{31}P NMR, no evidence of dihydrogen evolution is found. Gradual increase of the corresponding saturated alkane is observed together with the formation of the expected complexes **2**−**4**.

Bubbling dihydrogen (5 min) into a C_6D_6 solution of **2** results in the formation of **3** and **1** and evolution of ethane as monitored by ^{1}H and ^{31}P NMR. Further hydrogenation results in total conversion to **1**. Hydrogenation of complexes **3** or **4**, under the same conditions, results in the regeneration of the bis(dihydrogen) complex **1**. In the case of **4**, we assume that hydrogenation proceeds stepwise via formation of **3** as a short-lived intermediate.

H−D Exchange. Complexes **3** and **4** undergo H−D exchange with the deuterated solvent (C_6D_6 or C_7D_8). When **3** is kept in a deuterated solvent over a long period, two reactions occur: (i) further dehydrogenation leading to **4** and (ii) H−D exchange between the hydrides and the solvent. Deuterium was also incorporated within the cyclohexyl groups of the phosphine, but the allylic protons were not exchanged. The reactions were monitored by ^{1}H, ^{31}P, and ^{2}H NMR spectroscopy.

In the ^{1}H NMR spectrum the H−D exchange in the hydride region leads to the appearance of two new triplets for the isotopomers $[Ru]H_2D$ and $[Ru]HD_2$ with an isotopic shift of 44 and 84 ppb, respectively. After the NMR tube is kept at room temperature for 3 h, only the $[Ru]HD_2$ isotopomer is present. Integration of the hydride and the allylic signals indicates that the $[RuD_3$ isomer is the major one. The ^{2}H NMR spectrum (61.4 MHz) confirms the presence of $[Ru]D_3$ and indicates that some H−D exchange occurs within the cyclohexylphosphine protons but that the allylic ones are not affected.

Finally, the $^{31}P\{^1H\}$ NMR spectrum shows the formation of two new AB systems isotopically shifted by 160 and 940 ppb from the $[Ru]H_3$ isotopomer and respectively attributed to the $[Ru]HD_2$ and $[Ru]D_3$ isotopomers. The $[Ru]D_3$ isotopomer could also be obtained by starting from $RuD_6(PCy_3)_2$ in the presence of 2 equiv of alkene.

(2) Reaction of $RuH_2(H_2)_2(PCy_3)_2$ (1) with Alkenes L (L = $CH_2{=}CHCO_2Me$, *trans*- and *cis*-$MeO_2CCH{=}CHCO_2Me$). In the preceding section we have seen that the reactions of **1** with ethylene or substituted alkenes containing bulky σ-donor ligands cleanly lead to the formation of a new family of complexes where one or two cyclohexyl groups of the phosphines have been dehydrogenated. In this section we present the results obtained when **1** reacts with substituted alkenes bearing electron-withdrawing groups.

Synthesis of $[RuH(H_2)(\eta^2\text{-}O_2CCH_2CH_3)(PCy_3)_2]$ (5). Addition of 2 equiv of methyl acrylate $CH_2{=}CHCO_2Me$ to a suspension of **1** in pentane results in gas evolution and formation of a pale yellow solid analyzed as $[RuH(H_2)(\eta^2\text{-}O_2CCH_2CH_3)(PCy_3)_2]$ (**5**) in 44% yield. Single crystals of **5** were isolated from a benzene solution, and an X-ray diffraction study is discussed below.

All the data are consistent with the hydrogenation of the C=C double bond and demethylation of the ester group. The ^{1}H NMR spectrum of **5** in C_6D_6 shows a triplet at δ −14.05 (J_{P-H} = 14.4 Hz). No methyl ester group is observed in the expected region, but ethyl protons resonances are clearly identified at δ 2.50 as a quartet and δ 1.44 as a triplet. The relative intensities of the hydride signal to ethyl protons, using large relaxation delays (20 s), are in agreement with the presence of three hydrides. The lowest T_1 value found is 36 ms at 243 K (250 MHz, C_7D_8) for the hydride signal and is in favor of a hydrido dihydrogen formulation. The complex is fluxional since no decoalescence is observed for the hydride and dihydrogen ligands down to 203 K.

In contrast to **2**−**4**, the $^{31}P\{^1H\}$ NMR spectrum of **5** in C_6D_6 shows one singlet at δ 51.9 indicative of two equivalent phosphines. The IR spectrum of **5** (KBr disks) shows a very weak band at 2047 cm^{-1} attributed to a Ru−H stretch and two bands at 1543 and 1462 cm^{-1} typical for a bidentate chelating CO_2 group. The value found for $\Delta\nu = \nu_{\text{asymOCO}} - \nu_{\text{symOCO}}$ is in agreement with those previously reported.[9]

The ^{13}C NMR spectrum of **5** in C_6D_6 confirms the presence of the $\eta^2\text{-}O_2CCH_2CH_3$ ligand. A singlet at δ 182.8 is attributed to the quaternary carbon and the ethyl carbons resonate as a triplet at δ 31.3 (J_{C-H} = 126 Hz) and as a quartet at δ 9.2 (J_{C-H} = 127 Hz). The equivalent cyclohexyl groups of the phosphines are observed as three triplets at δ 27.1, 28.3, and 30.4 attributed to the methylene carbons and a broad doublet for the carbons α-bound to the phosphorus at δ 36.1 leading to a sharp triplet with J_{P-C} = 8.7 Hz upon ^{1}H decoupling.

All these spectroscopic data are in agreement with a hydrido dihydrogen complex containing a chelating carboxylate ligand and are similar to the data reported for a series of complexes obtained from the reaction of **1** with carboxylic acids. In particular, $RuH(H_2)(\eta^2\text{-}O_2CCH_3)(PCy_3)_2$ presents a triplet at δ −14.05 (J_{P-H} = 14.2 Hz) in the hydride region with a $T_{1\text{min}}$ value of 35 ms at 243 K (250 MHz) together with a singlet at δ 52.0 in the ^{31}P NMR spectrum.[10] The hydrogenation of the C=C bond and demethylation of the ester group are confirmed by the X-ray study. Due to the nucleophilic character of the hydrides of **1**,[3] demethylation may proceed by a mechanism derived from the general base-catalyzed hydrolysis of esters.[11]

X-ray Diffraction Study of 5. The molecular structure of **5** is depicted in Figure 1. Crystal data, data collection, and refinement parameters are reported in Table 2, and selected bond distances and angles are listed in Table 3. The structure is approximately octahedral with two *trans* phosphine ligands. The P−Ru−P angle and the Ru−P distances are similar to those in the hydridodihydrogenbis(tricyclohexylphosphine)ruthenium complex $RuH(H_2)I(PCy_3)_2$.[3a] The

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[9] Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 3rd ed.; John Wiley and Sons: New York, 1978; p 230.

[10] Chung, G.; Arliguie, T.; Chaudret, B. *New. J. Chem.* **1992**, *16*, 369.

[11] March, J. *Advanced Organic Chemistry, Reactions, Mechanism and Structure*, 4th ed.; Wiley-Interscience: New York, 1992; p 378.

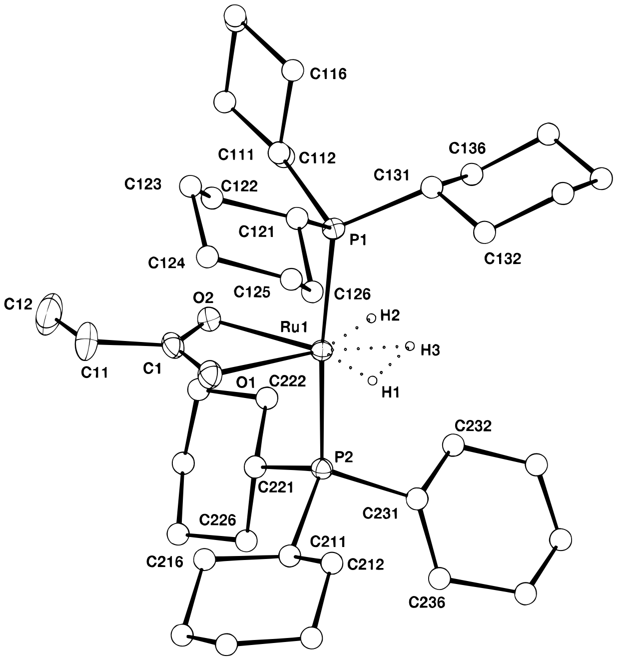

Figure 1. CAMERON view of $[RuH(H_2)(\eta^2\text{-}O_2CCH_2CH_3)(PCy_3)_2]$ (**5**).

parameters related to the bidentate carboxylate ligand are similar to those found for $RuH(CO_2Me)(PPh_3)_3$. In particular, the angle O(1)RuO(2) is 57.9° compared to 57.6° in $RuH(CO_2Me)(PPh_3)_3$.[12] Unfortunately, no X-ray diffraction study could be obtained at low temperature in order to confirm the hydrido dihydrogen structure established by ^1H NMR. Difference Fourier syntheses showed three peaks in the vicinity of the Ru atom. These peaks could be isotropically refined without any restraints either on x's or U(iso)'s as H atoms. The observed isotropic thermal parameters seem to have correct values for the H atoms. The large error shifts on H atoms coordinates prevent any discrimination between hydride and dihydrogen positions. The H−H distances are as follows: H(1)−H(2) 2.2(1) Å, H(1)−H(3) 1.2(1) Å, and H(2)−H(3) 1.4(1) Å. Therefore, if we have proposed in the CAMERON view that the hydrogen molecule is located in H(1)−H(3), it could also be in H(2)−H(3).

Synthesis of $[RuH(H_2)(\eta^2\text{-}O_2CCH_2CH_2CO_2CH_3)(PCy_3)_2]$ (6). Addition of 2 equiv of dimethyl fumarate, *trans*-$MeO_2CCH{=}CHCO_2Me$, to a suspension of **1** results in the same type of reaction as described above for the synthesis of **5**. A light green colored solid is obtained in 41% yield and analyzed as $[RuH(H_2)(\eta^2\text{-}O_2CCH_2CH_2CO_2CH_3)(PCy_3)_2]$ (**6**).

The hydride signal appears as a triplet at δ −14.19 (J_{P-H} = 14.4 Hz) and has the same T_{1min} value as **5** (36 ms at 243 K, 250 MHz, C_7D_8). The complex is also fluxional down to 203 K. As shown by ^1H and ^{13}C NMR measurements, the C=C double bond of the starting alkene has been hydrogenated and one ester group has lost its methyl group forming a chelate carboxylate bound to the ruthenium.

The two methylene groups give multiplets at δ 2.85 and 33.1 in the ^1H and ^{13}C NMR spectra, respectively. One ester group remains unaffected and is not involved in coordination with the metal center as shown by IR ($\nu_{C=O}$ at 1735 cm^{-1}) and ^{13}C NMR (δ(CO_2Me) 173.5 (s) and δ(CO_2CH_3) 50.6 (q)). The ^{13}C NMR spectra show three triplets at δ 27.5, 28.7, and 30.8 for the methylene carbons of the cyclohexyl rings at the 4, 3, and 2 positions, respectively. The carbons bound to phosphorus appear as a doublet at δ 36.5 leading to a sharp triplet with J_{P-C} = 8.5 Hz upon ^1H decoupling. Finally, the two *trans* phosphine ligands resonate as a singlet at δ 52.0 in the ^{31}P NMR spectrum. All the spectroscopic data are fully consistent with the proposed structure. The only difference between **5** and **6** is the presence of the ester group in **6**.

Table 2. Crystal Data, Data Collection, and Refinement Parameters

Crystal Data	
chem formula	$RuC_{39}H_{74}O_2P_2$
M_r	736.02
cryst system	triclinic
space group	$P\bar{1}$
a (Å)	11.750(6)
b (Å)	12.134(6)
c (Å)	14.342(4)
α (deg)	86.13(3)
β (deg)	84.44(4)
γ (deg)	82.63(6)
V (Å^3)	2015(2)
Z	2
ρ(calcd) (Mg·m^{-3})	1.213
radiation type	Mo Kα
wavelength (Å)	0.710 73
no. of reflcns for cell params	25
θ range for cell params (deg)	8−10
μ (mm^{-1})	48.750
F_{000}	789
temp (K)	293
Data Collection	
diffractometer	Enraf-Nonius CAD4
data collcn method	$\omega/2\theta$
no. of measd reflcns	3967
no. of indepdt reflcns	3762 (0.023)
no. of obsd reflcns	2469
observn criterion	$[I > 3\sigma(I)]$
θ_{max}	20
range of h,k,l	$-11 \rightarrow h \rightarrow 11$ $-11 \rightarrow k \rightarrow 11$ $0 \rightarrow l \rightarrow 13$
scan range θ (deg)	$0.8 + 0.35$ tg θ
monochromator	graphite
scan speed (deg·min^{-1})	2.9−20.1
Refinement	
refinement on	F
R^a	0.0483
$R_w{}^b$	0.0541
GOF (S)^c	1.17
abs corr	semi-empirical ψ-scan
min/max corr	0.92−1.07
weighting scheme^d	$\{w = w'[1 - (\Delta F/6\sigma(F_o))^2]^2\}$
Ar coeff	4.50, −2.08, 2.90
no. of reflcns used	2469
no. of params used	230

[a] $R = \sum(|F_o| - |F_c|)/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(|F_o|)^2]^{1/2}$. [c] Goodness of fit $= [\sum w(|F_o - F_c|)^2/(N_{obs} - N_{params})]^{1/2}$. [d] $w' = 1/\sum(r = 1,3)ArTr(X)$, where Ar are the coefficients for the Chebyshev polynomial Tr(X) with $X = F_c/F_c(max)(1)$.

Synthesis of $[RuH_2(\eta^2\text{-}CH_3O_2CCH{=}CHCO_2CH_3)(PCy_3)_2]$ (7). When a pentane suspension of **1** is treated with 2 equiv of dimethyl maleate, *cis*-$CH_3O_2CCH{=}CHCO_2CH_3$, the originally pale yellow solution turns deep orange. From that solution, an orange complex formulated as $[RuH_2(\eta^2\text{-}CH_3O_2CCH{=}CHCO_2CH_3)(PCy_3)_2]$ (**7**) is isolated in 77% yield. The formation of the dihydride **7** formally results from the loss of the

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[12] Skapski, A. C.; Stephens, F. A. *J. Chem. Soc., Dalton Trans.* **1974**, 390.

Table 3. Fractional Atomic Coordinates and Equivalent Thermal Parameters with Estimated Standard Deviations in Parentheses

atom	*x*/*a*	*y*/*b*	*z*/*c*	U_{eq},[a] Å^2
Ru(1)	0.19698(6)	0.07932(6)	0.21862(5)	0.0335
P(1)	0.2328(2)	−0.1055(2)	0.1789(1)	0.0341
P(2)	0.1784(2)	0.2696(2)	0.2444(1)	0.0334
O(1)	0.0859(5)	0.0359(5)	0.3508(4)	0.0510
O(2)	0.2700(5)	0.0362(4)	0.3548(4)	0.0461
C(1)	0.1725(8)	0.0220(7)	0.3965(6)	0.0447
C(11)	0.164(1)	−0.0099(9)	0.4992(7)	0.0700
C(12)	0.268(1)	−0.012(1)	0.5468(8)	0.0926
C(111)	0.3539(6)	−0.1856(6)	0.2380(5)	0.035(2)
C(112)	0.4596(7)	−0.1234(6)	0.2425(6)	0.040(2)
C(113)	0.5434(7)	−0.1878(7)	0.3086(6)	0.053(2)
C(114)	0.5800(8)	−0.3048(8)	0.2789(7)	0.062(3)
C(115)	0.4783(8)	−0.3659(8)	0.2700(7)	0.056(2)
C(116)	0.3935(7)	−0.3021(7)	0.2052(6)	0.044(2)
C(121)	0.1124(7)	−0.1940(6)	0.2102(5)	0.039(2)
C(122)	0.1096(7)	−0.2505(7)	0.3087(6)	0.052(2)
C(123)	0.0127(8)	−0.3252(8)	0.3238(7)	0.058(3)
C(124)	−0.1031(9)	−0.2618(9)	0.3097(8)	0.077(3)
C(125)	−0.102(1)	−0.2023(9)	0.2131(8)	0.081(3)
C(126)	−0.0053(8)	−0.1266(8)	0.1986(7)	0.059(3)
C(131)	0.2687(6)	−0.1335(6)	0.0526(5)	0.035(2)
C(132)	0.1707(8)	−0.0946(8)	−0.0094(7)	0.056(2)
C(133)	0.2038(9)	−0.1244(8)	−0.1105(7)	0.066(3)
C(134)	0.3147(9)	−0.0834(9)	−0.1505(8)	0.077(3)
C(135)	0.4096(8))	−0.1229(8)	−0.0888(7)	0.060(3)
C(136)	0.3778(7)	−0.0898(7)	0.0104(6)	0.049(2)
C(211)	0.0345(6)	0.3355(6)	0.2916(5)	0.034(2)
C(212)	−0.0595(8)	0.3100(8)	0.2337(7)	0.064(3)
C(213)	−0.1765(9)	0.3717(9)	0.2659(7)	0.071(3)
C(214)	−0.2098(9)	0.3452(9)	0.3682(7)	0.072(3)
C(215)	−0.1160(8)	0.3665(8)	0.4280(7)	0.062(3)
C(216)	0.0002(8)	0.3032(7)	0.3932(6)	0.055(2)
C(221)	0.2731(6)	0.2990(6)	0.3336(5)	0.036(2)
C(222)	0.3998(7)	0.2509(7)	0.3145(6)	0.046(2)
C(223)	0.4631(8)	0.2521(8)	0.4008(7)	0.058(3)
C(224)	0.4545(8)	0.3685(7)	0.4361(6)	0.055(2)
C(225)	0.3312(8)	0.4238(7)	0.4481(6)	0.057(2)
C(226)	0.2684(7)	0.4194(6)	0.3615(6)	0.040(2)
C(231)	0.2088(8)	0.3591(8)	0.1384(6)	0.053(2)
C(232)	0.3279(9)	0.3384(8)	0.0920(7)	0.067(3)
C(233)	0.348(1)	0.402(1)	−0.002(1)	0.119(5)
C(234)	0.293(1)	0.507(1)	−0.019(1)	0.116(5)
C(235)	0.173(1)	0.528(1)	0.0258(9)	0.092(4)
C(236)	0.154(1)	0.472(1)	0.125(1))	0.117(5)

[a] $U_{eq} = (U_{11}U_{22}U_{33})^{1/3}$.

two dihydrogen ligands and the coordination of the alkene.

The ^{1}H NMR spectrum of **7** in C_6D_6 shows, at 296 K, a very broad resonance in the hydride region at δ −19.8. A multiplet is observed for the two alkene protons shifted upfield from δ 5.71 for free *cis*-$MeO_2CCH{=}CHCO_2Me$ to δ 3.92 upon coordination to ruthenium. The six protons of the methyl ester groups resonate as a singlet at δ 3.44 while the cyclohexyl groups give multiplets between δ 2.7 and 1.2. The coordination of the CH=CH double bond to the ruthenium is confirmed by the ^{13}C NMR data. **7** shows at 296 K in C_6D_6 a doublet (J_{C-H} = 165 Hz) for the alkene carbons shifted upfield from δ 130.4 for the free alkene to δ 49.0 upon coordination to the ruthenium. The two methyl groups of the ester moiety resonate as a quartet at δ 50.6 (J_{C-H} = 145 Hz) and a singlet at δ 166.1 for the quaternary carbons. Thus the alkene proton and carbon atoms are largely shifted upfield upon coordination, indicating that there is strong π-back-bonding from the ruthenium center to the alkene.[13] The carbons of the cyclohexyl groups resonate as a doublet at δ 39.3 (J_{C-H} = 125 Hz) and three triplets at δ 30.5 (J_{C-H} = 127 Hz), 28.5 (J_{C-H} = 123 Hz), and 27.6 (J_{C-H} = 128 Hz) for the methylene carbons. The ^{31}P NMR spectrum (296 K, C_6D_6) shows a single peak at δ 59.1, which upon selective decoupling of the protons of the cyclohexyl groups transforms into a triplet with J_{P-H} ~ 30 Hz indicative of the presence of two hydrides.

Table 4. Selected Interatomic Bond Distances (Å) and Angles (deg) for 5 Where Esd's in Parentheses Refer to the Last Significant Digit

Ru(1)−P(1)	2.327(2)	P(1)−C(131)	1.862(8)
Ru(1)−P(2)	2.343(2)	P(2)−C(211)	1.860(7)
Ru(1)−O(1)	2.266(5)	P(2)−C(221)	1.855(8)
Ru(1)−O(2)	2.213(5)	P(2)−C(231)	1.841(9)
Ru(1)−H(1)	1.39(6)	O(1)−C(1)	1.25(1)
Ru(1)−H(2)	1.46(9)	O(2)−C(1)	1.266(9)
Ru(1)−H(3)	1.5(1)	C(1)−C(11)	1.50(1)
P(1)−C(111)	1.859(8)	C(11)−C(12)	1.45(2)
P(1)−C(121)	1.886(8)		

H(1)−Ru(1)−H(2)	104.2(46)	C(1)−C(11)−C(12)	116.8(9)
H(1)−Ru(1)−H(3)	49.5(45)	P(2)−Ru(1)−O(1)	94.4(2)
H(2)−Ru(1)−H(3)	54.9(48)	P(2)−Ru(1)−O(2)	91.4(1)
Ru(1)−P(1)−C(111)	113.1(3)	P(2)−Ru(1)−H(1)	90.3(26)
Ru(1)−P(1)−C(121)	116.8(3)	P(2)−Ru(1)−H(2)	89.1(37)
Ru(1)−P(1)−C(131)	117.8(2)	P(2)−Ru(1)−H(3)	93.8(40)
Ru(1)−P(2)−C(211)	117.2(2)	O(1)−Ru(1)−O(2)	57.9(2)
Ru(1)−P(2)−C(221)	111.5(2)	O(1)−Ru(1)−H(1)	99.0(27)
Ru(1)−P(2)−C(231)	114.3(3)	O(1)−Ru(1)−H(2)	156.6(40)
Ru(1)−O(1)−C(1)	90.4(5)	O(1)−Ru(1)−H(3)	147.4(44)
Ru(1)−O(2)−C(1)	92.5(5)	O(1)−C(1)−O(2)	119.1(7)
P(1)−Ru(1)−P(2)	173.11(8)	O(1)−C(1)−C(11)	121.8(8)
P(1)−Ru(1)−O(1)	92.4(1)	O(2)−Ru(1)−H(1)	156.9(27)
P(1)−Ru(1)−O(2)	91.1(1)	O(2)−Ru(1)−H(2)	98.9(40)
P(1)−Ru(1)−H(1)	90.0(26)	O(2)−Ru(1)−H(3)	153.1(44)
P(1)−Ru(1)−H(2)	84.2(37)	O(2)−C(1)−C(11)	119.0(9)
P(1)−Ru(1)−H(3)	81.1(40)		

The complex is fluxional on the NMR time scale. The process can be followed by ^{1}H and ^{31}P NMR spectroscopy. When the ^{31}P NMR spectra in C_7D_8 are monitored, the single peak observed at room temperature at δ 64.2 broadens and decoalesces at 243 K. At the slow-exchange limit, two broad signals are observed and resolved, at 193 K, as an ill-defined AB pattern at δ 67.9 and 60.7 (J_{P-P} = 124 Hz). Warming the sample to room temperature restores the starting singlet at δ 64.2 (observed at 59.1 in C_6D_6). The fluxional behavior can be also followed by ^{1}H NMR spectroscopy which shows a change of the hydride and methoxy signals. The very broad signal observed at δ −19.8 at 296K leads after decoalescence to two broad signals of equal intensity at δ −30.9 and −7.4. This last signal appears as an ill-resolved triplet at 203 K with J_{P-H} ~ 32 Hz. At low field the methoxy protons observed at δ 3.58 at 296 K decoalesces at 223 K and two broad signals are observed in the slow-exchange limit at δ 3.70 and 3.42.

This behavior could be explained by fast rotation of the alkene at room temperature. At low temperature, blocked rotation of the alkene could allow coordination to ruthenium of one oxygen of the carboxyl group bound to the ester, rendering the hydrides nonequivalent. The hydride *trans* to the oxygen is observed at high field at δ −30.9. The phosphine ligands are not equivalent as shown by the AB pattern in the ^{31}P NMR spectrum, and the rather small J_{P-P} value of 124 Hz indicates that the phosphines are pushed away from the alkene (see proposed structure **A**).

We have calculated the rotation barrier of the alkene using data from the hydride, the methoxy, and the

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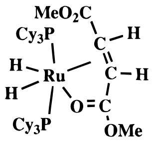
(13) (a) de Klerk-Engels, B.; Delis, J. G. P.; Vrieze, K.; Goubitz, K.; Fraanje, J. *Organometallics* **1994**, *13*, 3269. (b) Bianchini, C.; Frediani, P.; Masi, D.; Peruzzini, M.; Zanobini, F. *Organometallics* **1994**, *13*, 4616.



A

phosphorus signals (coalescence temperature and frequency difference between the coalescing signals in the limit of slow exchange). The values obtained for $\Delta G^{\ddagger}$ are equal within experimental error: 10.0, 10.7, and 10.6 kcal/mol, respectively.

When the reaction of **1** with 2 equiv of dimethyl maleate is performed in a closed NMR tube in C_6D_6 solution and followed by ^1H and ^{31}P NMR, we detect after 5 min the formation of **7** and of dimethyl succinate, $MeO_2CCH_2CH_2CO_2Me$, characterized by two singlets at δ 2.40 and 3.39 as well as traces of **6**. After 1.5 h, the main product of the reaction is **6** as shown by the very intense triplet in the hydride region at δ −14.2. A sharp singlet at δ 0.26 may correspond to methane evolution.

By reacting **1** with *cis*-$CH_3O_2CCH{=}CHCO_2CH_3$ in pentane suspensions, we observe the formation of two different complexes that could be isolated and characterized as **6** and **7**. Note that **6** is the main product obtained by treatment of **1** with *trans*-$CH_3O_2CCH{=}CHCO_2CH_3$. That fact suggests that an isomerization of the *cis*- to the *trans*-diester takes place in concentrated solutions. Isomerization of *cis*- to *trans*-diester is a well-established reaction, and complexes containing the two forms were isolated and recently characterized.[14] In order to test whether **7** was active in isomerization of *cis*-diester to the thermodynamically preferred *trans* isomer, we stirred a pentane suspension of **7** with *cis*-diester in a ratio of 1:40 for several days. A colorless crystalline product precipitated and was isolated and characterized by ^1H NMR, IR, and mass spectroscopy as *trans*-$MeO_2CCH{=}CHCCO_2Me$.

Finally, we have tested the catalytic activity of **1** toward hydrogenation of *cis*-$MeO_2CCH{=}CHCO_2Me$. The reaction was run in a Fisher−Porter bottle at room temperature in C_6D_6 under 2 bar of H_2 with a **1**/alkene ratio of 1:100. Examination of the solution by NMR spectroscopy, after 2 h stirring, showed total conversion to dimethyl succinate. **1** and **6** are the only organometallic complexes detected, the former being the major one.

Conclusions

We have described in this paper six new complexes **2**−**7** resulting from the reactivity of the bis(dihydrogen) complex **1** toward functionalized alkenes. **2** and **7** are the only examples in the series where π-coordination of the alkene is observed. In all the other cases, the C=C double bonds have been hydrogenated leading to two different types of complexes, depending on the nature of the alkene. For alkenes bearing substituents such as ester groups, coordination to the metal after the hydrogenation process allows for new reactivity. Namely, one ester group is dealkylated forming a chelating carboxylate ligand and complexes **5** and **6** are thus formed. To our knowledge, this demethylation process has no precedent. This confirms the nucleophilic behavior of **1**, as opposed to the electrophilic behavior we have recently described for the other bis(dihydrogen)ruthenium complex $Tp^*RuH(H_2)_2$.[15] The fact that **1** binds dimethyl maleate in an η^2 mode to form **7** but not dimethyl fumarate (synthesis of **6**) is most probably due to steric reasons. The alkenes have both the same electronic properties but dimethyl fumarate is more sterically demanding: when dimethyl fumarate apraoches the metal center after substitution of one dihydrogen ligand, one ester group comes very close to ruthenium. Activation of the ester group to form a carboxylate ligand can then occur. The same phenomenom can be observed with methyl acrylate.

In contrast to these results, no coordination is observed with alkenes bearing σ-donor substituents. Hydrogenation to the corresponding alkane is achieved, and depending upon the **1**/alkene ratios, complex **3** or **4** is obtained. These results indicate that the alkene serves as hydrogen acceptor. We reasoned that **1** is the only source of hydrogen and, thus, **3** and **4** formally result from the loss of respectively 6 and 10 hydrogen atoms from **1** leading to partial dehydrogenation of the cyclohexyl groups. **2**−**4** represent the first members of a new family of complexes stabilized by η^2- and/or η^3-cyclohexenylphosphines.

We have already reported that **2** is a powerful catalyst for the dehydrogenative silylation of ethylene, and we anticipate that these new structures will lead to the design of other active catalytic systems.

Experimental Section

All reactions were carried out under argon by using Schlenk glassware and vacuum line techniques. All solvents were freshly distilled from standard drying agents and thoroughly degassed under argon before use. Microanalysis were performed by the Laboratoire de Chimie de Coordination Microanalytical Service. Infrared spectra were obtained as Voltalef 35 oil mulls or KBr disks on a Perkin-Elmer 1725 FT-IR spectrometer. NMR spectra were recorded on a Bruker AC200 (at 200.13 MHz for ^1H and at 81.015 MHz for ^{31}P), while variable-temperature proton spectra and ^{13}C spectra were obtained by using an AM 250 (at 250.134 and 62.896 MHz, respectively), all these spectrometers operating on the Fourier transform mode. $RuCl_3{\cdot}3H_2O$ was purchased from Johnson Matthey Ltd, and all other reagents were purchased from Aldrich and degassed before use.

$[RuH_2(H_2)_2(P(C_6H_{11})_3)_2]$ (1). **1** was made by a modified method based on that described in 1985.[2] [Ru(COD)(COT)] (0.510 g; 1.62 mmol) was introduced into a Fischer−Porter bottle, and pentane (8 mL) was added. A solution of PCy_3 (0.908 g; 3.24 mmol) in pentane (10 mL) was then introduced, and the resulting yellow solution was degassed before admission of dihydrogen. The Fischer−Porter bottle was pressurized to 3 bar, and the stirred yellow solution became orange within 5 min followed by precipitation of a white solid. After 1 h the solution was filtered off and the cream-white solid was washed with cold pentane (3 × 3 mL) before drying in a stream of argon. Yield: 89%.

The same procedure was used to prepare $RuD_6(PCy_3)_2$ but using deuterium in place of dihydrogen.

$[RuH\{\eta^3\text{-}C_6H_8)P(C_6H_{11})_2\}(C_2H_4)P(C_6H_{11})_3]$ (2). A suspension of **1** (0.500 g; 0.75 mmol) in 30 mL of pentane was placed in a Fischer−Porter bottle, which was pressurized to 3 bar of ethylene. Immediate dissolution of **1** was observed with

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[14] (a) Helliwell, M.; Vessey, J. D.; Mawby, R. J. *J. Chem. Soc., Dalton Trans.* **1994**, 1193. (b) Bianchini, C.; Mealli, C.; Melli, A.; Penizzini, M.; Zanobini, F. *J. Am. Chem. Soc.* **1988**, *110*, 8725.

[15] Moreno, B.; Sabo-Etienne, S.; Chaudret, B.; Rodriguez, A.; Jalon, F.; Trofimenko, S. *J. Am. Chem. Soc.* **1995**, *117*, 7441.

formation of a red solution. After *ca*. 5 min, a white solid precipitated. The mixture was filtered, washed with pentane (2 × 5 mL), and dried under argon and then under vacuum. Yield: 87%. Anal. Calcd for $C_{38}H_{68}P_2Ru$: C, 66.3; H, 10.0. Found: C, 66.4; H, 10.4.

$[RuH_3\{(\eta^3\text{-}C_6H_8)P(C_6H_{11})_2\}P(C_6H_{11})_3]$ (3). To a suspension of $[RuH_2(H_2)_2(PCy_3)_2]$ (0.253 g; 0.38 mmol) in 5 mL of pentane was added $H_2C{=}CHSi(C_2H_5)_3$ (0.21 mL; 1.14 mmol). Immediate dissolution of **1** was observed with formation of a red solution from which after *ca*. 20 s a white microcrystalline solid was formed. The mixture was stirred for 1 h, after which the product was filtered out and washed with pentane (3 × 1.5 mL) before drying under vacuum. Yield: 81%. Recrystallization from THF/pentane gave thin white needles. Anal. Calcd for $C_{36}H_{66}P_2Ru$: C, 65.32; H, 10.05. Found: C, 65.47; H, 10.21.

$[RuH\{(\eta^3\text{-}C_6H_8)P(C_6H_{11})_2\}\{(\eta^2\text{-}C_6H_9)P(C_6H_{11})_2\}]$ (4). To a suspension of **1** (0.172 g; 0.26 mmol) in 5 mL of pentane was added 3,3-dimethyl-1-butene (0.166 mL; 1.3 mmol). The mixture was stirred for 2.5 h causing a color change from orange to red-brown. A pink solid was filtered off, washed with diethyl ether (4 × 2 mL), and dried under vacuum. Yield: 74%. Anal. Calcd for $C_{36}H_{62}P_2Ru$: C, 65.72; H, 9.50. Found: C, 65.82; H, 9.97.

4 is moderately stable and may be rapidly handled in air. It is sparingly soluble in most common solvents.

$[RuH(H_2)(O_2CCH_2CH_3)(P(C_6H_{11})_3)]$ (5). To a suspension of **1** (0.161 g; 0.24 mmol) in 3 mL of pentane was added methyl acrylate (44 μL; 0.46 mmol). An immediate dissolution of **1** was observed as well as gas evolution. The resulting red mixture was stirred overnight. A pale-yellow solid that formed was filtered off, washed with pentane (3 × 1.5 mL), and dried under vacuum. Yield: 44%. Anal. Calcd for $C_{39}H_{74}O_2P_2Ru$: C, 63.47; H, 10.11. Found: C, 63.18; H, 10.28.

X-ray Crystallographic Analyses. A selected crystal was mounted in Lindemann glass on an automatic CAD4-F Enraf-Nonius diffractometer. The data were collected at room temperature ($T = 293$ K). Graphite-monochromatized Mo Kα was used. Unit cell dimensions with esd's were obtained from least-squares refinement of the setting angles of 25 well-centered reflections. Three standard reflections were monitored periodically; they showed no change during data collection. Corrections were made for Lorentz and polarization effects; absorption corrections (Difabs) were applied.[16] Computations were performed by using CRYSTALS adapted on a PC.[17] Atomic form factors for neutral Ru, C, O, P, and H atoms were taken from ref 18. The structure was solved by direct methods using SHELXS86.[19] Owing to the low ratio (observations/variable parameters), only the Ru atom and the non-hydrogen atoms attached to it were anisotropically refined. Difference Fourier syntheses showed up three peaks in the vicinity of the Ru atom. These peaks could be isotropically refined without any restraints either on *x*'s or *U*(iso)'s as H atoms.

Refinements were carried out in three blocks approximation to the normal matrix by minimizing the function $\sum w(|F_o| - |F_c|)^2$, where F_o and F_c are the observed and calculated structure factors. Model reached convergence with R and R_w defined as

$$R = \sum ||F_o| - |F_c|| / \sum |F_o|$$

$$R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]$$

The criteria for a satisfactory complete analysis were the ratio of rms shift to standard deviation being less than 0.1 and no significant features in final difference maps. Further details of the crystal structure investigation are available on request from the Director of the Cambridge Crystallographic Data Centre, 12 Union Road, GB-Cambridge CB21EZ, U.K., on quoting the full journal citation.

$[RuH(H_2)(O_2CCH_2CH_2CO_2CH_3)(P(C_6H_{11})_3)_2]$ (6). To a suspension of **1** (0.145 g; 0.22 mmol) in 2 mL of pentane was added *E*-$CH_3O_2CCH{=}CHCO_2CH_3$ (63 μL; 0.44 mmol). An immediate change of color from pale yellow into orange was observed. After *ca*. 45 min a homogeneous orange-brown solution was obtained. Further stirring for 1 h afforded a pale green solid. The solvent was evaporated under a stream of argon, and the remaining solid was washed with diethyl ether (3 × 2 mL)) and then dried under vacuum. Yield: 41%. Anal. Calcd for $C_{41}H_{76}O_4P_2Ru$: C, 61.86; H, 9.62. Found: C, 61.59; H, 9.65.

$[RuH_2(\eta^2\text{-}Z\text{-}CH_3O_2CCH{=}CHCO_2CH_3)(P(C_6H_{11})_3)_2]$ (7). To a suspension of **1** (0.29 g; 0.43 mmol) in 7.5 mL of pentane, warmed to 30 °C, was added *Z*-$CH_3O_2CCH{=}CHCO_2CH_3$ (0.109 mL; 0.87 mmol). Slow gas evolution was observed, and the resulting orange mixture was stirred for 1.5 h. The solvent was evaporated to dryness, and the residue was washed with pentane (3 × 1 mL). The orange solid was dried under vacuum. Yield: 77%. Recrystallization was from diethyl ether. Anal. Calcd for $C_{42}H_{76}O_4P_2Ru$: C, 62.43; H, 9.48. Found: C, 62.01; H, 9.80.

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Supporting Information Available: Crystallographic data for **5** including tables of bond distances and angles, fractional atomic coordinates and equivalent isotropic thermal parameters for H atoms, and anisotropic thermal parameters (6 pages). Ordering information is given on any current masthead page.

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