Access to Ruthenium(0) Carbonyl Complexes via Dehydrogenation of a Tricyclopentylphosphine Ligand and Decarbonylation of Alcohols

Paul D. Bolton, Mary Grellier, Nicolas Vautravers, Laure Vendier, and
Sylviane Sabo-Etienne*

*Laboratoire de Chimie de Coordination du CNRS, 205 route de Narbonne,
31077 Toulouse Cedex 04, France*

Received June 3, 2008

The carbonylruthenium(0) complex $Ru(CO)\{PCyp_2(\eta^2\text{-}C_5H_7)\}_2$ (**4**) has been prepared by reaction of $RuH_2\{PCyp_2(\eta^2\text{-}C_5H_7)\}_2$ (**3**) with an excess of *tert*-butylethylene in the presence of ethanol. Decarbonylation of ethanol is also observed when reacting the bis(dihydrogen) complex $RuH_2(\eta^2\text{-}H_2)_2(PCyp_3)_2$ (**1**) with 2 equiv of ethanol. The reaction results formally in the substitution of one dihydrogen ligand by a carbonyl, and the corresponding complex $RuH_2(\eta^2\text{-}H_2)(CO)(PCyp_3)_2$ (**5**) was isolated. An excess of *tert*-butylethylene reacted with **5** to give $RuH_2(CO)\{PCyp_2(\eta^2\text{-}C_5H_7)\}(PCyp_3)$ (**6**), which corresponds to the formal loss of 2 equiv of dihydrogen: loss of the dihydrogen ligand and dehydrogenation of one cyclopentyl ring. The dihydride **6** can be dehydrogenated further by reaction with ethylene, affording the ruthenium(0) complex $Ru(\eta^2\text{-}C_2H_4)(CO)\{PCyp_2(\eta^2\text{-}C_5H_7)\}(PCyp_3)$ (**7**). Finally, the dicarbonyl complex $RuH_2(CO)_2(PCyp_3)_2$ (**8**) was isolated by exposing **1** to 3 bar of CO. **8** and the new complexes **4**−**7**, resulting from partial dehydrogenation of one or two cyclopentyl rings of the tricyclopentylphosphines and/or decarbonylation of alcohol, were characterized by multinuclear NMR, IR, elemental analysis, and X-ray diffraction.

Introduction

Steric and electronic substituent effects in phosphine compounds are key factors for tuning metal coordination, with applications in various fields, particularly in catalysis. These compounds can be grouped into different classes: for example, alkyl- versus arylphosphines. Within a class, some compounds display very similar properties. For example, the basicity and steric hindrance of tricyclohexylphosphine and tricyclopentylphosphine are believed to be quite similar. The coordination chemistry of tricyclopentylphosphine has been relatively neglected.[1−11] However, for a few catalytic systems it has already been demonstrated that small variations such as replacing tricyclohexylphosphine by tricyclopentylphosphine can induce large variations in catalyst activities.[12−20] We have recently reported the synthesis of the new bis(dihydrogen) complex $RuH_2(\eta^2\text{-}H_2)_2(PCyp_3)_2$ (**1**), incorporating two tricyclopentylphosphine ligands.[21] We have shown that this phosphine displays unique properties in dehydrogenation reactions and in catalysis.[22] Indeed, up to 10 hydrogen atoms can be removed from **1**, leading under ethylene to the formation of the ruthenium(0) complex $Ru(C_2H_4)\{PCyp_2(\eta^2\text{-}C_5H_7)\}_2$ (**2**). Interestingly, the reaction is reversible under a dihydrogen atmosphere. The dehydrogenation process involves not only the hydrides and the two dihydrogen ligands in the coordination sphere of the metal but also the partial dehydrogenation of the tricyclopentylphosphines. A dehydrogenation process involving such a phosphine has also been evidenced by Weller and coworkers in rhodium chemistry.[23−25] In our system, the dehydrogenation process occurs stepwise with the intermediate

---

* To whom correspondence should be addressed. Tel: 33 5 61 33 31 77. Fax: 33 5 61 55 30 03. E-mail: sylviane.sabo@lcc-toulouse.fr.

(1) Frost, P. W.; Howard, J. A. K.; Spencer, J. L. *J. Chem. Soc., Chem. Commun.* **1984**, 1362–1363.

(2) Brenndörfer, M.; Brune, H. A.; Debaerdemaeker, T.; Hemmer, R. *Z. Naturforsch., B* **1985**, *40B*, 357–362.

(3) Miller, T. M.; Whitesides, G. M. *Organometallics* **1986**, *5*, 1473–1480.

(4) Brainard, R. L.; Miller, T. M.; Whitesides, G. M. *Organometallics* **1986**, *5*, 1481–1490.

(5) Tomotake, Y.; Matsuzaki, T.; Murayama, K.; Watanabe, E.; Wada, K.; Onoda, T. *J. Organomet. Chem.* **1987**, *320*, 239–247.

(6) Howard, J. A. K.; Keller, P. A.; Vogt, T.; Taylor, A. L.; Dix, N. D.; Spencer, J. L. *Acta Crystallogr., Sect. B* **1992**, *B48*, 438–444.

(7) Schwab, P.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1996**, *118*, 100–110.

(8) Wolf, R.; Hey-Hawkins, E. *Angew. Chem., Int. Ed.* **2005**, *44*, 6241–6244.

(9) Douglas, T. M.; Molinos, E.; Brayshaw, S. K.; Weller, A. S. *Organometallics* **2007**, *26*, 463–465.

(10) Molinos, E.; Brayshaw, S. K.; Kociok-Köhn, G.; Weller, A. S. *Dalton Trans.* **2007**, 4829–4844.

(11) Huang, J.; Schanz, H. J.; Stevens, E. D.; Nolan, S. P. *Organometallics* **1999**, *18*, 5375–5380.

(12) Jan, D.; Delaude, L.; Simal, F.; Demonceau, A.; Noels, A. F. *J. Organomet. Chem.* **2000**, *606*, 55–64.

(13) Kisanga, P.; Widenhoefer, R. A. *J. Am. Chem. Soc.* **2000**, *122*, 10017–10026.

(14) Acemoglu, L.; Williams, J. M. J. *Adv. Synth. Catal.* **2001**, *343*, 75–77.

(15) Sanford, M. S.; Love, J. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **2001**, *123*, 6543–6554.

(16) Zhou, J.; Fu, G. C. *J. Am. Chem. Soc.* **2003**, *125*, 12527–12530.

(17) Moslin, R. M.; Jamison, T. F. *Org. Lett.* **2006**, *8*, 455–458.

(18) Nakao, Y.; Kanyiva, K. S.; Oda, S.; Hiyama, T. *J. Am. Chem. Soc.* **2006**, *128*, 8146–8147.

(19) Murakami, M.; Ashida, S.; Matsuda, T. *Tetrahedron* **2006**, *62*, 7540–7546.

(20) Ng, S.-S.; Jamison, T. F. *Tetrahedron* **2006**, *62*, 11350–11359.

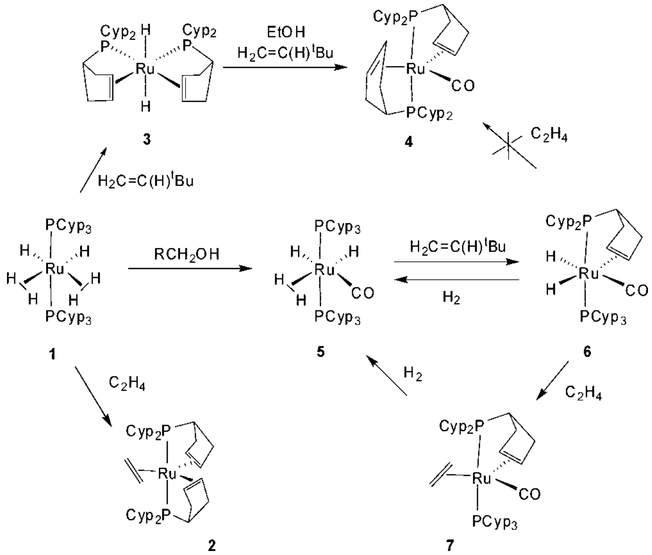
(21) Grellier, M.; Vendier, L.; Chaudret, B.; Albinati, A.; Rizzato, S.; Mason, S.; Sabo-Etienne, S. *J. Am. Chem. Soc.* **2005**, *127*, 17592–17593.

(22) Grellier, M.; Vendier, L.; Sabo-Etienne, S. *Angew. Chem., Int. Ed.* **2007**, *46*, 2613–2615.

(23) Douglas, T. M.; Nôtre, J. L.; Brayshaw, S. K.; Frost, C. G.; Weller, A. S. *Chem. Commun.* **2006**, 3408–3410.

10.1021/om8005118 CCC: $40.75

Scheme 1



formation of the *trans*-dihydride $RuH_2\{PCyp_2(\eta^2\text{-}C_5H_7)\}_2$ (**3**).[22] During the course of our studies to isolate the dihydride intermediate, we looked at the reactivity of **1** with various olefins. It turned out that reaction with triethoxyvinylsilane led to the isolation of some crystals characterized by X-ray diffraction as the carbonylruthenium species $Ru(CO)\{PCyp_2(\eta^2\text{-}C_5H_7)\}_2$ (**4**) (see below). We reasoned that the carbonyl ligand could come from decarbonylation of some alcohol adventitiously present in the olefin, as decarbonylation of alcohol by reaction with various ruthenium precursors is a well-established process.[26−30] Access to new ruthenium(0) carbonyl complexes is of particular interest for organic applications.[31] In addition, hydrido carbonyl complexes are key catalytic species in the Murai reaction,[32] and we had already obtained quite interesting results in this area by using **1** as a catalytic precursor.[21] This led us to examine the reactivity of our starting materials **1** and **3** with alcohols, and we report here the isolation of a series of carbonyl complexes resulting from decarbonylation of alcohols and dehydrogenation processes.

Results and Discussion

The results from our investigations are summarized in Scheme 1.

As briefly mentioned in the Introduction, a few crystals of the new carbonylruthenium(0) complex $Ru(CO)\{PCyp_2(\eta^2\text{-}C_5H_7)\}_2$ (**4**) were obtained after workup of a mixture of $RuH_2(\eta^2\text{-}H_2)_2(PCyp_3)_2$ (**1**) with an excess of triethoxyvinylsilane. **4** was better prepared by treatment of $RuH_2\{PCyp_2(\eta^2\text{-}C_5H_7)\}_2$ (**3**) with an excess of *tert*-butylethylene in the presence of 1.3 equiv of ethanol (Scheme 1). The complex was isolated in very good yield (79%) as a white powder and characterized by multinuclear NMR, IR, and microanalysis. The crystal structure of **4** shows a pseudo-trigonal-bipyramidal geometry with the two phosphorus atoms in the axial positions and a P−Ru−P angle of 171.49(2)° (Figure 1). A similar geometry was found in the analogous ethylene complex $Ru(C_2H_4)\{PCyp_2(\eta^2\text{-}C_5H_7)\}_2$ (**2**).[22] The C=C and Ru−C bond lengths involving the cyclopentenyl rings are of the same magnitude: ca. 1.43 and 2.21 Å, respectively. The single peak in the $^{31}P\{^1H\}$ NMR spectrum is in agreement with two equivalent phosphine ligands. The carbonyl is characterized by an IR stretching band at 1898 cm^{-1} and by a singlet at 219.2 ppm in the $^{13}C\{^1H,^{31}P\}$ NMR spectrum. The cyclopentenyl fragments display two multiplets at 3.83 and 3.05 ppm in the ^1H NMR spectrum and two singlets at 45.7 and 44.6 ppm in the $^{13}C\{^1H,^{31}P\}$ NMR spectrum. The shifts observed at higher field in comparison to the data obtained for **2** are the result of the replacement of ethylene by CO, the latter being a better π-acceptor ligand. **4** shows no reactivity toward H_2 at 3 bar of pressure in pentane (16 h) or in C_6D_6 (10 min). This is in contrast with the reversibility of the dehydrogenation process observed in the case of the analogous ethylene complex **2**. In that case, complete conversion into **1** upon exposure to H_2 at 1 bar was achieved within 150 min in cyclohexane-d_{12}.[22] Elimination of ethylene with concomitant hydrogenation to ethane is the driving force of the reaction.

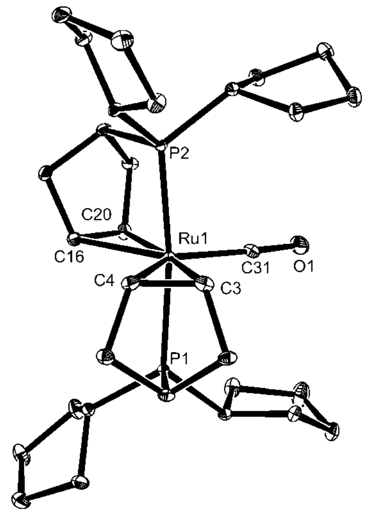


Figure 1. Structure of $Ru(CO)\{PCyp_2(\eta^2\text{-}C_5H_7)\}_2$ (**4**). Thermal ellipsoids are shown at the 30% probability level. Protons of cyclopentyl groups are omitted for clarity. Distances (Å) and angles (deg): Ru−P1 = 2.3392(10), Ru−P2 = 2.3268(10), Ru−C31 = 1.905(2), Ru−C3 = 2.196(2), Ru−C4 = 2.208(2), Ru−C16 = 2.224(2), Ru−C20 = 2.207(2), C31−O1 = 1.145(3), C3−C4 = 1.435(3), C16−C20 = 1.424(3); P1−Ru−P2 = 171.489(19).

An NMR tube scale reaction of the dihydride complex **3** with 2 equiv of ethanol in the absence of *tert*-butylethylene resulted in a 1:1 mixture of **4** and a new complex formulated as $RuH_2(\eta^2\text{-}H_2)(CO)(PCyp_3)_2$ (**5**) on the basis of NMR data. The carbonyl dihydrogen complex **5** was isolated in 74% yield by the reaction of **1** with 2 equiv of ethanol in pentane at 50 °C. **5** has been fully characterized by multinuclear NMR, IR, and elemental analysis. Orange crystals suitable for X-ray diffraction were grown by cooling a saturated pentane solution to −35 °C. The molecular structure of **5** is depicted in Figure 2. As in **1**, the two phosphines are in a trans configuration with a P−Ru−P angle of 159.64(2)°, even more bent toward the two hydrides

---

(24) Douglas, T. M.; Brayshaw, S. K.; Dallanegra, R.; Kociok-Köhn, G.; Macgregor, S. A.; Moxham, G. L.; Weller, A. S.; Wondimagegn, T.; Vadivelu, P. *Chem. Eur. J.* **2008**, *14*, 1004–1022.

(25) Douglas, T. M.; Weller, A. S. *New J. Chem.* **2008**, *32*, 966–969.

(26) Chaudret, B. N.; Cole-Hamilton, D. J.; Nohr, R. S.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1977**, 1546–1557.

(27) Van der Sluys, L. S.; Kubas, G. J.; Caulton, K. G. *Organometallics* **1991**, *10*, 1033–1038.

(28) Chen, Y.-Z.; Chan, W. C.; Lau, C. P.; Chu, H. S.; Lee, H. L.; Jia, G. *Organometallics* **1997**, *16*, 1241–1246.

(29) Coalter, J. N., III; Huffman, J. C.; Caulton, K. G. *Organometallics* **2000**, *19*, 3569–3578.

(30) Zhang, J.; Gandelman, M.; Shimon, L. J. W.; Rozenberg, H.; Milstein, D. *Organometallics* **2004**, *23*, 4026–4033.

(31) Park, Y. J.; Park, J.-W.; Jun, C.-H. *Acc. Chem. Res.* **2008**, *41*, 222–234.

(32) Kakiuchi, F.; Murai, S. *Acc. Chem. Res.* **2002**, *35*, 826–834.

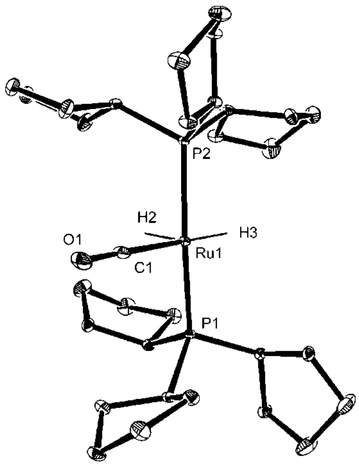


Figure 2. Structure of $RuH_2(\eta^2\text{-}H_2)(CO)(PCyp_3)_2$ (**5**). Thermal ellipsoids are shown at the 30% probability level. Protons of cyclopentyl groups are omitted for clarity. Distances (Å) and angles (deg): Ru−P1 = 2.3260(5), Ru−P2 = 2.3295(5), Ru−C1 = 1.896(2), C1−O1 = 1.146(3), Ru−H2 = 1.56(3), Ru−H3 = 1.63(3); P1−Ru−P2 = 159.640(19), C1−Ru−P1 = 97.23(6), C1−Ru−P2 = 98.15(6).

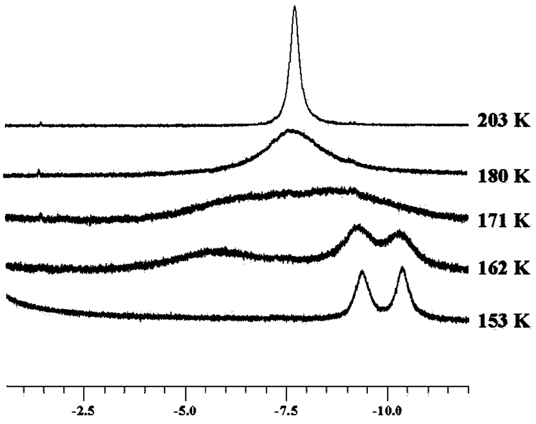


Figure 3. ^1H NMR spectra (500 MHz) of **5** in a mixture of toluene-d_8 with 5% of CH_2Cl_2 at various temperatures.

(168.64(2)° in **1**). The two hydrides could be located, but it was impossible to properly locate the dihydrogen ligand, probably as a result of a disorder due to its rotation. The ^1H NMR spectrum of **5** in toluene-d_8 at room temperature shows a broad triplet at −7.51 ppm with a small J_{PH} value of 9 Hz. The dihydride and dihydrogen ligands remain in fast exchange down to 193 K. The $T_{1,min}$ value of 42 ms at 233 K and 500 MHz is in agreement with the presence of a dihydrogen ligand.[33] When ^1H NMR spectra of **5** are recorded in a mixture of toluene-d_8 with 5% of CH_2Cl_2, decoalescence of the hydrides and dihydrogen ligands was observed at 174 K, leading at 159 K to a very broad signal at −6 ppm assigned to the dihydrogen ligand and two broad signals at −9.5 and −10.5 ppm corresponding to the inequivalent hydrides (Figure 3). The barrier for the exchange process is $\Delta G^\ddagger$ = ca. 30 kJ mol^{-1}. At 153 K, the lowest temperature we could reach, the signal at −6 ppm totally disappeared in the baseline. The analogous complex $RuH_2(\eta^2\text{-}H_2)(CO)(P^iPr_3)_2$, incorporating two triisopropylphosphines, was previously characterized by variable-temperature NMR and displayed a similar behavior.

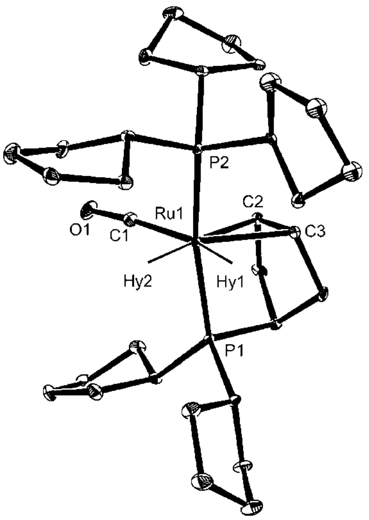


Figure 4. Structure of $RuH_2(CO)\{PCyp_2(\eta^2\text{-}C_5H_7)\}(PCyp_3)$ (**6**). Thermal ellipsoids are shown at the 30% probability level. Protons of cyclopentyl groups are omitted for clarity. Distances (Å) and angles (deg): Ru−P1 = 2.3023(16), Ru−P2 = 2.3447(16), Ru−C1 = 1.907(7), Ru−C2 = 2.301(6), Ru−C3 = 2.276(6), Ru−Hy1 = 1.63(6), Ru−Hy2 = 1.51(6), C1−O1 = 1.156(8), C2−C3 = 1.404(8); P1−Ru−P2 = 162.72(6).

Our attempt to generate **4** by dehydrogenation of **5** failed, as adding an excess of *tert*-butylethylene to **5** resulted in the formation of the new complex $RuH_2(CO)\{PCyp_2(\eta^2\text{-}C_5H_7)\}(PCyp_3)$ (**6**), isolated in 77% yield. **6** was characterized by multinuclear NMR, IR, elemental analysis, and X-ray diffraction. The formation of **6** corresponds to the formal loss of 2 equiv of dihydrogen: loss of the dihydrogen ligand and dehydrogenation of one cyclopentyl ring. The X-ray structure of **6** is depicted in Figure 4. As for **5** and **4,** the two phosphines are in a trans configuration with a P−Ru−P angle of 162.72(6)°. In **6**, the cyclopentenyl ring coordinated to Ru has a C(2)−C(3) bond length of 1.404(8) Å (1.424(3) and 1.435(3) Å in **4**) and Ru−C(2) and Ru−C(3) distances of 2.301(6) and 2.276(6) Å (ca. 2.21 Å in **4**). When the crystals of **6** are dissolved in toluene-d_8, the ^1H NMR spectrum shows two hydride resonances as one triplet at −8.55 ppm (J_{PH} = 20 Hz) and one broad resonance at −10.10 ppm in a 9:1 ratio. The ^{31}P NMR spectrum shows two AB patterns at 81.3 ppm ($^2J_{P-P}$ = 238 Hz, $PCyp_3$) and 63.9 ($^2J_{P-P}$ = 238 Hz, $PCyp_2(\eta^2\text{-}C_5H_7)$) for the major isomer and 82.5 ppm ($^2J_{P-P}$ = 239 Hz, $PCyp_3$) and 56.9 ($^2J_{P-P}$ = 239 Hz, $PCyp_2(\eta^2\text{-}C_5H_7)$) for the minor one. On the basis of multinuclear 2D experiments we can assign the X-ray structure depicted in Figure 4 to the major isomer and propose for the minor isomer a *trans*-dihydride formulation. In the case of the major isomer, decoalescence is observed at 233 K, leading to the formation of two triplets of equal intensity at −7.88 ppm (J_{PH} = 15 Hz) and −8.88 ppm (J_{PH} = 15 Hz) at 183 K. The barrier for the exchange process is $\Delta G^\ddagger$ = 43 kJ mol^{-1}. The minor signal at −10.10 ppm remains broad down to 183 K.

The dihydride complex **6** can be dehydrogenated further by the reaction with less bulky ethylene, and the new Ru(0) complex $Ru(\eta^2\text{-}C_2H_4)(CO)\{PCyp_2(\eta^2\text{-}C_5H_7)\}(PCyp_3)$ (**7**) can be isolated in 76% yield. The crystal structure of **7** reveals two independent molecules in the asymmetric unit (Figure 5). All

---

[33] Kubas, G. J. *Chem. Rev.* **2007**, *107*, 4152–4205.

[34] Gusev, D. G.; Vymenits, A. B.; Bakhmutov, V. I. *Inorg. Chem.* **1992**, *31*, 1–2.

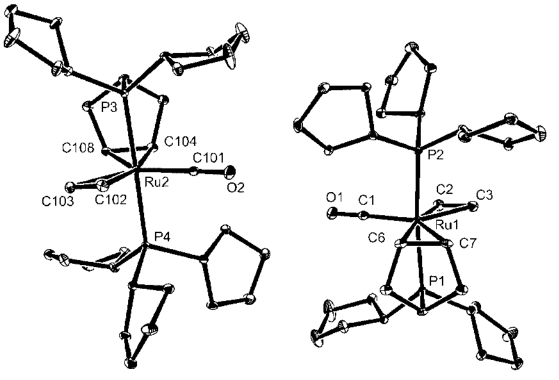


Figure 5. Structure of Ru(η^2-C_2H_4)(CO){PCyp$_2$(η^2-C_5H_7)}(PCyp$_3$) (**7**), showing the two independent molecules in the asymmetric unit. Thermal ellipsoids are shown at the 30% probability level. Protons of ethylene and cyclopentyl groups are omitted for clarity. Distances (Å) and angles (deg): Ru1−P1 = 2.3299(8), Ru1−P2 = 2.3932(8), Ru1−C1 = 1.898(4), Ru1−C2 = 2.229(3), Ru1−C3 = 2.223(3), Ru1−C6 = 2.164(3), Ru1−C7 = 2.216(3), C1−O1 = 1.142(4), C2−C3 = 1.399(6), C6−C7 = 1.427(5); P1−Ru1−P2 = 169.35(3); Ru2−P3 = 2.3292(8), Ru2−P4 = 2.4011(8), Ru2−C101 = 1.886(3), Ru2−C102 = 2.223(3), Ru2−C103 = 2.228(3), Ru2−C104 = 2.190(3), Ru2−C108 = 2.222(3), C101−O2 = 1.155(4), C103−C102 = 1.406(5), C104−C108 = 1.428(4); P3−Ru2−P4 = 173.67(3).

analogous bond lengths and angles are very similar in the two molecules. The two phosphines are in a trans configuration with a P−Ru−P angle of ca. 170°. The C−C bond length of 1.399(6) Å is much shorter than in Ru(η^2-C_2H_4)(CO)(PPh$_3$)$_3$, for which some ruthenacyclopropane character was proposed.[35] The cyclopentenyl ring coordinated to Ru displays bond lengths similar to those observed for the complexes described above. **7** was characterized by multinuclear NMR, IR, and elemental analysis. The ^{31}P NMR spectrum shows an AB pattern at 70.8 ppm ($^2J_{P-P}$ = 275 Hz, PCyp$_3$) and 19.7 ($^2J_{P-P}$ = 275 Hz, PCyp$_2$(η^2-C_5H_7)). The carbonyl is characterized by a IR stretching band at 1898 cm^{-1} and by a singlet at 219.1 ppm in the ^{13}C{^{1}H,^{31}P} NMR spectrum, values which are almost identical with those observed in **4**. The ethylene ligand resonates as two broad signals at 2.69 and 2.39 ppm in the ^{1}H NMR spectrum, whereas one singlet at 28.8 ppm is observed in the ^{13}C{^{1}H,^{31}P} NMR spectrum at room temperature. A similar value (29.8 ppm) was reported for the analogous complex Ru(η^2-C_2H_4)(CO)(PPh$_3$)$_3$.[35]

The dehydrogenation reactions leading to **6** and **7** are reversible, with quantitative formation of **5** under 3 bar of dihydrogen. In contrast, **4** showed no reactivity toward dihydrogen under the same conditions.

Finally, it is interesting to note that during the decarbonylation of alcohol promoted by **1**, the carbonyl dihydrogen complex **5** was formed, whereas no trace of the dicarbonyl complex RuH$_2$(CO)$_2$(PCyp$_3$)$_2$ (**8**) was detected. **8** could be isolated in 84% yield as a white solid by exposing **1** to 3 bar of CO. **8** has been fully characterized by multinuclear NMR, IR, and elemental analysis and by X-ray diffraction (Figure 6). The analogous complex incorporating two tricyclohexylphosphines was previously reported.[36]

Concluding Remarks

In this study we were able to isolate a series of carbonyl complexes with ruthenium adopting two oxidation states, 0 and II. This was achieved by combining two processes: dehydrogenation in the presence of an olefin and decarbonylation of alcohols. It is of particular interest that the dehydrogenation process, leading ultimately to the ruthenium(0) species Ru(η^2-C_2H_4)(CO){PCyp$_2$(η^2-C_5H_7)}(PCyp$_3$) (**7**), is fully reversible under a dihydrogen atmosphere. Significantly, the isolation of Ru(CO){PCyp$_2$(η^2-C_5H_7)}$_2$ (**4**) and **7** provides evidence that the dehydrogenation process may involve two or only one cyclopentyl rings. Moreover, the easy dehydrogenation/hydrogenation pathway of the tricyclopentylphosphine should have application in catalysis, as the generation of a vacant site is an important step. In our systems, such a step could occur without decoordination of the phosphine, one of the drawbacks using phosphine ligands in catalysis. Therefore, these results open up a new field of possibilities in catalysis (hydrogenation, C−C bond formation,...), as we will be able to benefit from easy access to Ru(0)/Ru(II) species.

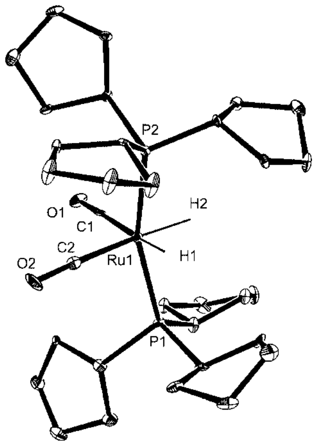


Figure 6. Structure of RuH$_2$(CO)$_2$(PCyp$_3$)$_2$ (**8**). Thermal ellipsoids are shown at the 30% probability level. Protons of cyclopentyl groups are omitted for clarity. Distances (Å) and angles (deg): Ru−P1 = 2.3250(18), Ru−P2 = 2.3258(18), Ru−C1 = 1.914(8), Ru−C2 = 1.867(7), C1−O1 = 1.149(7), C2−O2 = 1.170(7), Ru−H1 = 1.64(8), Ru−H2 = 1.64(6); P1−Ru−P2 = 160.47(6), C1−Ru−C2 = 96.3(3), C1−Ru−P1 = 97.27(19), C2−Ru−P2 = 97.8(2).

Experimental Section

General Methods and Instrumentation. All manipulations were carried out using standard Schlenk, Fisher−Porter bottle, or drybox techniques under an atmosphere of argon. Protio and deuterio solvents were refluxed over the appropriate drying agent, distilled, and stored under argon. ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectra were recorded on Bruker AV500, AV300, and DPX300 spectrometers. ^{1}H and ^{13}C assignments were confirmed when necessary with the use of DEPT-135 and two-dimensional ^{1}H−^{1}H and ^{13}C−^{1}H NMR experiments. ^{1}H and ^{13}C spectra were referenced internally to residual protio solvent (^{1}H) or solvent (^{13}C) resonances and are reported relative to tetramethylsilane (δ 0 ppm). ^{31}P{^{1}H} spectra were referenced to external H$_3$PO$_4$. Chemical shifts are quoted in δ (ppm) and coupling constants in hertz. Infrared spectra were prepared as Nujol mulls between KBr plates and were recorded on a Perkin-Elmer 1725 FTIR spectrometer. Infrared data are quoted in wavenumbers (cm^{-1}). Elemental analyses were carried out by the analytical laboratory of the LCC. The compounds RuH$_2$(η^2-H$_2$)$_2$(PCyp$_3$)$_2$ (**1**) and RuH$_2${PCyp$_2$(η^2-C_5H_7)}$_2$ (**3**) were prepared according to literature methods.[21,22] *tert*-Butylethylene was purchased, filtered through alumina, and degassed prior to use.

Ru(CO){PCyp$_2$(η^2-C_5H_7)}$_2$ (4). To a solution of RuH$_2${PCyp$_2$(η^2-C_5H_7)}$_2$ (312 mg, 0.54 mmol) in toluene (10 mL) were added *tert*-butylethylene (182 μL, 1.41 mmol) and ethanol (41 μL, 0.70 mmol).

---

(35) Jazzar, R. F. R.; Mahon, M. F.; Whittlesey, M. K. *Organometallics* **2001**, *20*, 3745–3751.

(36) Christ, M. L.; Sabo-Etienne, S.; Chaudret, B. *Organometallics* **1994**, *13*, 3800–3804.

The reaction mixture was heated to 50 °C in a sealed Fisher−Porter bottle for 48 h, resulting in a yellow solution. The solution was cooled to room temperature, the overpressure was vented, and then the solution was transferred to a Schlenk tube. The volatiles were removed under reduced pressure, affording a pale yellow solid. This was washed with pentane (4 × 1 mL), and the resulting white powder was dried in vacuo. Yield: 257 mg (79%). X-ray diffraction quality crystals of **4** were obtained from a solution of **1** in triethoxyvinylsilane contaminated by traces of ethanol. The solution was left at room temperature for 3 days, and a few white crystals were collected by filtration. ^{1}H NMR (500.3 MHz, C_6D_6, 296 K): 3.83 (br m, 2H, CH═CH), 3.05 (br m, 2H, CH═CH), 2.4−1.2 (overlapping m, 46H, Cyp). $^{31}P\{^1H\}$ NMR (202.6 MHz, C_6D_6, 296 K): 70.6 (s). $^{13}C\{^1H,^{31}P\}$ NMR (125.8 MHz, C_6D_6, 296 K): 219.2 (CO), 45.7 and 44.6 (C═C), 38.8, 37.1, 34.6, 34.1, 31.1, 30.3, 29.9, 28.6, 28.2, 26.6, 26.4, 25.6, 25.3 (CHP and CH_2 of $PCyp_2(\eta^2\text{-}C_5H_7)$). IR (Nujol mull, KBr plates, cm^{-1}): 1898 (s, ν_{CO}). Anal. Calcd for $C_{31}H_{50}OP_2Ru$: C, 61.88; H, 8.38. Found: C, 62.06; H, 8.02.

$RuH_2(\eta^2\text{-}H_2)(CO)(PCyp_3)_2$ (5). To a solution of $RuH_2(\eta^2\text{-}H_2)_2(PCyp_3)_2$ (425 mg, 0.73 mmol) in toluene (5 mL) was added ethanol (85 μL, 1.46 mmol). The reaction mixture was heated to 50 °C in a sealed Fisher−Porter bottle for 48 h, resulting in a deep yellow solution. The solution was cooled to room temperature, the overpressure was vented, and then the solution was transferred to a Schlenk tube. The volatiles were removed under reduced pressure, and the resulting orange solid was dissolved in pentane (5 mL). The solution was concentrated to approximately 2 mL and cooled to −40 °C with stirring. The resulting orange precipitate was filtered off, washed with pentane (3 × 0.5 mL), and dried in vacuo. Yield: 328 mg (74%). X-ray diffraction quality crystals of **5** were obtained by cooling a saturated pentane solution to −35 °C. ^{1}H NMR (300.1 MHz, C_6D_6, 298 K): 2.1−1.4 (overlapping m, 54H, Cyp), −7.51 (br t, 4H, $^2J_{P-H} = 9$ Hz, RuH). $^{31}P\{^1H\}$ NMR (121.5 MHz, C_6D_6, 298 K): 75.9 (s). $^{13}C\{^1H,^{31}P\}$ NMR (75.5 MHz, C_6D_6, 298 K): 204.9 (CO), 40.0 (CH of Cyp), 30.1, 26.5 (CH_2 of Cyp). $T_{1,min}$ (500.3 MHz, Tol-d_8, 233 K): 42 ms for the hydride/dihydrogen resonance. IR (Nujol mull, KBr plates, cm^{-1}): 1932 (s, ν_{CO}). Anal. Calcd for $C_{31}H_{58}OP_2Ru$: C, 61.06; H, 9.59. Found: C, 61.07; H, 9.57.

$RuH_2(CO)\{PCyp_2(\eta^2\text{-}C_5H_7)\}(PCyp_3)$ (6). To a solution of $RuH_2(\eta^2\text{-}H_2)(CO)(PCyp_3)_2$ (500 mg, 0.82 mmol) in pentane (5 mL) was added *tert*-butylethylene (232 μL, 1.80 mmol), resulting in a slight darkening of the yellow solution to orange-red. After it was stirred for 1 h, the solution was concentrated to approximately 2 mL and cooled to −40 °C with stirring. The resulting white precipitate was filtered off, washed with pentane (3 × 1 mL), and dried in vacuo. Yield: 383 mg (77%). X-ray diffraction quality crystals of **6** were obtained by cooling a saturated pentane solution to −35 °C. ^{1}H NMR (500.3 MHz, Tol-d_8, 298 K): 4.37 and 4.04 (br m, 2 × 1H, CH═CH), 2.1−1.2 (overlapping m, 50H, Cyp), −8.55 (t, 2H, $^2J_{P-H} = 20$ Hz, RuH). $^{31}P\{^1H\}$ NMR (202.5 MHz, Tol-d_8, 298 K): 81.3 (d, $^2J_{P-P} = 238$ Hz, $PCyp_3$), 63.9 (d, $^2J_{P-P} = 238$ Hz, $PCyp_2(\eta^2\text{-}C_5H_7)$). $^{13}C\{^1H,^{31}P\}$ NMR (125.8 MHz, Tol-d_8, 298 K): 213.4 (CO), 68.1 (C═C), 66.1 (C═C), 40.6 (CH of $PCyp_3$), 38.6, 38.0, 37.7, 35.9, 32.7, 30.9, 30.6 (CHP and CH_2 of $PCyp_2(\eta^2\text{-}C_5H_7)$), 30.5 and 30.3 ($CH_2$ of $PCyp_3$), 30.2, 29.9 (CH_2 of $PCyp_2(\eta^2\text{-}C_5H_7)$), 27.2 (2 × CH_2 of $PCyp_3$), 27.0, 26.8, 26.7, 26.4 (CH_2 of $PCyp_2(\eta^2\text{-}C_5H_7)$). A second minor species was also observed by NMR (approximate ratio 9:1 by integration of hydride resonances). This is tentatively assigned to an isomer of **6** having trans hydrides. ^{1}H NMR (500.3 MHz, Tol-d_8, 298 K): −10.16 (br s, RuH), other resonances obscured by Cyp of major isomer. $^{31}P\{^1H\}$ NMR (202.5 MHz, Tol-d_8, 298 K): 82.5 (d, $^2J_{P-P} = 239$ Hz, $PCyp_3$), 56.9 (d, $^2J_{P-P} = 239$ Hz, $PCyp_2(\eta^2\text{-}C_5H_7)$). $^{13}C\{^1H,^{31}P\}$ NMR (125.8 MHz, Tol-d_8, 298 K): 205.5 (CO), 39.2, 37.0, 31.5, 27.5 (CH and CH_2 of $PCyp_3$ or $PCyp_2(\eta^2\text{-}C_5H_7)$), other resonances too small too be observed or obscured by resonances of major isomer. IR (Nujol mull, KBr plates, cm^{-1}): 1943 (s, ν_{CO}), 1895 (w, ν_{RuH}). Anal. Calcd for $C_{31}H_{54}OP_2Ru$: C, 61.46; H, 8.98%. Found: C, 61.94; H, 9.00.

$Ru(\eta^2\text{-}C_2H_4)(CO)\{PCyp_2(\eta^2\text{-}C_5H_7)\}(PCyp_3)$ (7). A solution of $RuH_2(CO)\{PCyp_2(\eta^2\text{-}C_5H_7)\}(PCyp_3)$ (90 mg, 0.15 mmol) in pentane (2 mL) was placed under a dynamic 3 bar pressure of C_2H_4 for 1 h. During this time a white precipitate formed. The pressure was vented and the Fisher−Porter bottle back-filled with argon. The white solid was filtered off, washed with pentane (2 × 0.5 mL), and dried in vacuo. Yield: 71 mg (76%). X-ray diffraction quality crystals of **7** were obtained by cooling a saturated pentane solution to −35 °C. ^{1}H NMR (300.1 MHz, C_6D_6, 298 K): 3.62 and 3.56 (br m, 2 × 1H, CH═CH of $\eta^2\text{-}C_5H_7$), 2.69 and 2.39 (br m, 2 × 2H, C_2H_4), 2.2−1.1 (overlapping m, 50H, CHP and CH_2 of $\eta^2\text{-}C_5H_7$, Cyp). $^{31}P\{^1H\}$ NMR (121.5 MHz, C_6D_6, 298 K): 70.8 (d, $^2J_{P-P} = 275$ Hz, $PCyp_3$), 19.7 (d, $^2J_{P-P} = 275$ Hz, $PCyp_2(\eta^2\text{-}C_5H_7)$). $^{13}C\{^1H,^{31}P\}$ NMR (75.5 MHz, C_6D_6, 298 K): 219.1 (CO), 46.4 and 41.2 (CH═CH of $\eta^2\text{-}C_5H_7$), 38.7 (CH of $PCyp_3$), 38.3 and 37.1 (CH_2 of $PCyp_2(\eta^2\text{-}C_5H_7)$), 35.2 and 31.4 (CHP of $PCyp_2(\eta^2\text{-}C_5H_7)$), 30.6 and 30.1 ($CH_2$ of $PCyp_2(\eta^2\text{-}C_5H_7)$), 30.0 and 29.6 ($CH_2$ of $PCyp_3$), 29.1 (CH_2 of $PCyp_2(\eta^2\text{-}C_5H_7)$), 28.8 ($C_2H_4$), 28.4, 26.6, and 26.3 (CH_2 of $PCyp_2(\eta^2\text{-}C_5H_7)$), 25.7 (2 × CH_2 of $PCyp_3$), 25.6 and 25.0 (CH_2 of $PCyp_2(\eta^2\text{-}C_5H_7)$), one CHP resonance obscured. IR (Nujol mull, KBr plates, cm^{-1}): 1898 (s, ν_{CO}). Anal. Calcd for $C_{33}H_{56}OP_2Ru$: C, 62.73; H, 8.93%. Found: C, 62.55; H, 8.69.

$RuH_2(CO)_2(PCyp_3)_2$ (8). A suspension of $RuH_2(\eta^2\text{-}H_2)_2(PCyp_3)_2$ (310 mg, 0.53 mmol) in pentane (5 mL) at −30 °C was placed under 3 bar of CO. The mixture was immediately warmed to room temperature, resulting in a light orange solution which was stirred under a dynamic 3 bar pressure of CO for 1 h. During this time a white precipitate formed. The pressure was vented and the Fisher−Porter bottle back-filled with argon. The solution was cooled to −30 °C with stirring for 10 min to maximize precipitation, and then the white solid was filtered off, washed with pentane (3 × 1 mL), and dried in vacuo. Yield: 284 mg (84%). X-ray diffraction quality crystals of **8** were obtained by cooling a saturated pentane solution to −35 °C. ^{1}H NMR (300.1 MHz, C_6D_6, 298 K): 2.1−1.4 (overlapping m, 54H, Cyp), −8.57 (t, 2H, $^2J_{P-H} = 22.5$ Hz, RuH). $^{31}P\{^1H\}$ NMR (121.5 MHz, C_6D_6, 298 K): 70.3 (s). $^{13}C\{^1H\}$ NMR (75.5 MHz, C_6D_6, 298 K): 205.1 (t, $^2J_{C-P} = 8.0$ Hz, CO), 40.4 (t, $^1J_{C-P} = 13.6$ Hz, CH of Cyp), 30.0 (s, CH_2 of Cyp), 26.4 (t, $^2J_{C-P} = 4.2$ Hz, CH_2 of Cyp). IR (Nujol mull, KBr plates, cm^{-1}): 1987 (s, ν_{CO}), 1949 (s, ν_{CO}), 1871 (w, ν_{RuH}), 1827 (w, ν_{RuH}). Anal. Calcd for $C_{32}H_{56}O_2P_2Ru$: C, 60.45; H, 8.88. Found: C, 60.84; H, 8.81.

Crystal Structure Determinations of $Ru(CO)\{PCyp_2(\eta^2\text{-}C_5H_7)\}_2$ (4), $RuH_2(\eta^2\text{-}H_2)(CO)(PCyp_3)_2$ (5), $RuH_2(CO)\{PCyp_2(\eta^2\text{-}C_5H_7)\}(PCyp_3)$ (6), $Ru(\eta^2\text{-}C_2H_4)(CO)\{PCyp_2(\eta^2\text{-}C_5H_7)\}(PCyp_3)$ (7), and $RuH_2(CO)_2(PCyp_3)_2$ (8). Data were collected at low temperature (110 K) on an Xcalibur Oxford Diffraction diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å) and equipped with an Oxford Cryosystems Cryostream cooler device. The final unit cell parameters were obtained by means of a least-squares refinement. The structures were solved by direct methods using SIR92[37] and refined by means of least-squares procedures on F^2 with the aid of the program SHELXL97[38] included in the software package WinGX version 1.63.[39] The atomic scattering factors were taken from the International Tables for X-Ray Crystallography. All hydrogen atoms were geometrically placed and refined by using a riding model, except for the hydrogens coordinated to the Ru, which were located by calculating Fourier

---

(37) Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A. *J. Appl. Crystallogr.* **1993**, *26*, 343–350.

(38) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **2008**, *A64*, 112–122.

(39) Farrugia, L. *J. Appl. Crystallogr.* **1999**, *32*, 837–838.

(40) Farrugia, L. *J. Appl. Crystallogr.* **1997**, *30*, 565.

difference maps of the electronic density observed at small θ (<18°). They were refined isotropically. All non-hydrogen atoms were anisotropically refined, and in the last cycles of refinement a weighting scheme was used, where weights are calculated from the following formula: $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = (F_o^2 + 2F_c^2)/3$. Drawings of molecules were performed with the program ORTEP32 with 30% probability displacement ellipsoids for non-hydrogen atoms.[40] Concerning the structure of complex **7**, although the checkcif program detected a pseudo center of symmetry and suggested the possible pseudo/new space group $P2_1/c$, we carefully examined the extinctions, and it clearly appears that there is a single extinction on $(0k0)$ $k = 2n$, which corresponds well to the space group $P2_1$. After refinement, we found a Flack parameter of 0.09, not of 0.5, as it should be for a centrosymetric space group. Moreover, we could indeed solve in $P2_1/c$, but with a final R value of 13.5%, instead of 3.5% in $P2_1$.

Acknowledgment. Support from the CNRS as well as a postdoctoral CNRS fellowship to P.D.B. is gratefully acknowledged. This work was also supported by the ANR (Programme blanc ANR-06-BLAN-0060-01) and the European network IDECAT.

Supporting Information Available: CIF files giving crystallographic data for **4**−**8**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM8005118