New *N*,*N*-Diisopropylcarbamato Complexes of Ruthenium(II) as Catalytic Precursors for Olefin Hydrogenation

Daniela Belli Dell'Amico,*[a] Fausto Calderazzo,[a] Ulli Englert,[b] Luca Labella,[a] Fabio Marchetti,[a] and Monica Specos[a]

Keywords: *N*,*N*-Dialkylcarbamato complexes / Ruthenium / Hydrogenation

During the synthesis of [Ru($O_2CNi$$Pr_2$)$_2$($PPh_3$)$_2$] (**1**), the [$RuCl_2(PPh_3)_3$]/NH*i*$Pr_2$/$CO_2$ system produces the intermediates [NH_2*i*Pr_2][$Ru_2Cl_2(\mu\text{-}Cl)_3(PPh_3)_4$] (**2**) and [RuCl($O_2C$-N*i*$Pr_2$)($PPh_3$)$_3$] (**3**) which have been isolated and fully characterised. Compound **2** contains the dinuclear anionic triply chloride-bridged ruthenium(II) species. Compound **3** is mononuclear, the octahedral ruthenium centre being coordinated to the bidentate carbamato ligand. The reactions of compounds **1** and **3** with dihydrogen have been studied at room temperature and atmospheric pressure with respect to their catalytic hydrogenation of 1-octene.

Introduction

Olefin hydrogenation using ruthenium(II) complexes has been studied extensively.[1] Some precursors containing carboxylato ligands have been shown to be catalytically active under homogeneous conditions.[2] *N*,*N*-Dialkylcarbamato complexes of ruthenium(II) with tertiary phosphanes as ancillary ligands have been prepared in our laboratories[3] and elsewhere.[4] The *N*,*N*-dialkylcarbamato group, R_2NCO_2, is geometrically similar to the carboxylato ligand and is a good leaving group, prompt CO_2 evolution being observed in the presence of proton-active substances.[5] Moreover, this ligand may undergo a change of hapticity from bidentate to monodentate, thus allowing coordination of a further ligand. This observation has been established for the reaction of **1** with CO, the two bidentate carbamato groups being sequentially converted into monodentate groups by addition of carbon monoxide yielding [Ru(O_2C-N*i*Pr_2)$_2$(CO)(PPh_3)$_2$] and [Ru(O_2CN*i*Pr_2)$_2$(CO)$_2$(PPh_3)$_2$].[3a] This is reminiscent of earlier data on the hexacoordinate ruthenium(II) cation [$Ru(O_2CNMe_2)(PMe_2Ph)_4$]$^+$ which is converted into [$Ru(CO)(O_2CNMe_2)(PMe_2Ph)_4$]$^+$. Both were isolated as their hexafluorophosphate derivatives.[4a,4b] Such coordination flexibility is an important prerequisite for catalysis.

In relation to the use of carboxylato and carbamato derivatives of ruthenium(II) in catalysis, [$Ru(O_2CMe)_2(PPh_3)_2$] was reported to assist olefin hydrogenation in the presence of strong protic acids such as CF_3SO_3H,[2a] with [$Ru(PPh_3)_n$]$^{2+}$ being postulated as the catalytically active species. Moreover, it is worth noting that in the ruthenium-catalysed conversion of $CO_2/HNMe_2/H_2$ to $HCONMe_2$ at 125 °C, the intermediacy of a (carbamato)ruthenium complex was excluded on the basis of deuteration studies.[6a] The possible role played by the *N*,*N*-dialkylcarbamato group in this process urged us to study the behaviour of this ligand in ruthenium-promoted catalytic hydrogenation. This paper reports some new data regarding the reaction of [$RuCl_2(PPh_3)_3$], a pentacoordinate mononuclear ruthenium complex,[6b] with the NH*i*Pr_2/CO_2 system leading to new derivatives of ruthenium(II). Moreover, results are presented on the reaction of the (carbamato)ruthenium(II) complexes with dihydrogen, some of them acting as catalyst precursors for olefin hydrogenation.

Results and Discussion

Synthesis and Characterisation of the Ruthenium Complexes

The reaction of [$RuCl_2(PPh_3)_3$] with NH*i*Pr_2 and CO_2 to afford **1** is rather slow, the conversion of 4 g of the precursor requiring several days at room temperature in the presence of a large excess of the amine [Equation (1)].[3a]

$$[\mathrm{RuCl_2(PPh_3)_3}] + 4\ \mathrm{NH}i\mathrm{Pr_2} + 2\ \mathrm{CO_2} \longrightarrow \underset{\mathbf{1}}{[\mathrm{Ru(O_2CN}i\mathrm{Pr_2)_2(PPh_3)_2}]} + 2\ [\mathrm{NH_2}i\mathrm{Pr_2}]\mathrm{Cl} + \mathrm{PPh_3} \quad (1)$$

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[a] Dipartimento di Chimica e Chimica Industriale, Università di Pisa,
Via Risorgimento 35, 56126 Pisa, Italy
Fax: (internat.) + 39-050-2219-246
E-mail: belli@dcci.unipi.it
[b] Institut für Anorganische Chemie der RWTH,
Professor-Pirlet-Strasse 1, 52074 Aachen, Germany

DOI: 10.1002/ejic.200400014

A more appropriate synthesis of **1** has now been found (vide infra) and this required further work on the reactivity of $[RuCl_2(PPh_3)_3]$. In spite of its low solubility in toluene, $[RuCl_2(PPh_3)_3]$ rapidly dissolves in the presence of $NHi Pr_2$ and CO_2. We have now found that two intermediates, **2** and **3**, can be intercepted, presumably formed according to Equation (2).

$$3\,[RuCl_2(PPh_3)_3] + 2\,NH\textit{i}Pr_2 + CO_2 \longrightarrow \underset{\mathbf{2}}{[NH_2\textit{i}Pr_2][Ru_2Cl_5(PPh_3)_4]} + \underset{\mathbf{3}}{[RuCl(O_2CN\textit{i}Pr_2)(PPh_3)_3]} + 2\,PPh_3 \tag{2}$$

It is reasonable to assume that the relatively slow substitution of one chloro ligand by the carbamate anion $[O_2CNi Pr_2]^-$, formed in situ from carbon dioxide and the amine, yields **3** and $[NH_2i Pr_2]Cl$, the latter being promptly sequestered by the unchanged starting material to afford **2**. The formation of **2** in a 69% yield has been established independently by treating $[RuCl_2(PPh_3)_3]$ with $[NH_2i Pr_2]Cl$ in toluene in a molar ratio of 2 [Equation (3)].

$$2\,[RuCl_2(PPh_3)_3] + [NH_2\textit{i}Pr_2]Cl \longrightarrow \underset{\mathbf{2}}{[NH_2\textit{i}Pr_2][Ru_2Cl_5(PPh_3)_4]} + 2\,PPh_3 \tag{3}$$

The successful replacement of the phosphane ligand by chloride in this reaction can be easily understood since the starting compound $[RuCl_2(PPh_3)_3]$, which is mononuclear with a pentacoordinate ruthenium atom, is converted into the anionic dinuclear product containing a hexacoordinate ruthenium atom (vide infra).

The salt-like product **2** has been found to be a convenient starting material for the synthesis of **1**. Since it contains two phosphane ligands per ruthenium atom, the poorly soluble phosphane is not released and **1** is obtained pure, in a satisfactory yield of about 55%, without contamination by **3** [Equation (4)].

$$\underset{\mathbf{2}}{[H_2N\textit{i}Pr_2][Ru_2Cl_5(PPh_3)_4]} + 8\,NH\textit{i}Pr_2 + 4\,CO_2 \longrightarrow 2\,\underset{\mathbf{1}}{[Ru(O_2CN\textit{i}Pr_2)_2(PPh_3)_2]} + 5\,[NH_2\textit{i}Pr_2]Cl \tag{4}$$

The ^{31}P NMR spectrum of **2** in C_6D_6 shows a singlet at $\delta = 46.8$ ppm. This suggests a symmetrical arrangement of the ligands which was subsequently confirmed by X-ray diffraction methods.

The anion contains two hexacoordinate ruthenium centres bridged by three chloro ligands, the coordination of each ruthenium atom being completed by two phosphane ligands and one terminal chloro ligand (Figure 1). In addition, hydrogen interactions are present between the cation and the terminal chloro ligands of the anion, the N(1)···Cl(4) and N(1)···Cl(5) distances being 3.29 and 3.23 Å, respectively. Similar interactions have already been reported in $[Et_2NH_2][Ru_2Cl_2(\mu\text{-}Cl)_3(DPB)_2]$ [DPB = 1,2-bis(diphenylphosphanyl)benzene],[7a] $[t Bu_2MePH][Ru_2Cl_2(\mu\text{-}Cl)_3(CO)_2(Pt Bu_2Me)_2]$[7b] and in $[Et_2NH_2][Ru_2Cl_2(\mu\text{-}Cl)_3\{(R)\text{-}p\text{-}MeO\text{-}BINAP\}_2]$ [*p*-MeO-BINAP = 2,2′-bis(diphenylphosphanyl)-1,1′-binaphthyl].[8a] The formation of ion pairs is presumably responsible for the high solubility of these species in aromatic solvents. Crystal packing is created by the ion pairs where the two partners are tightly linked, the shortest distance separating the centroids of neighbouring pairs being 11.8 Å.

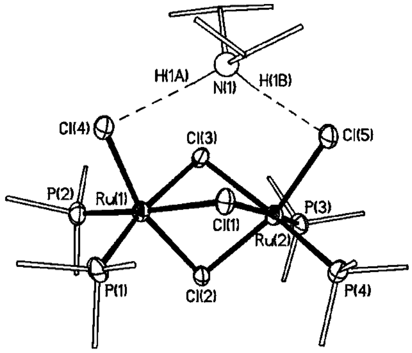

Figure 1. View of the molecular structure of the ion pair $[i Pr_2NH_2][Ru_2Cl_2(\mu\text{-}Cl)_3(PPh_3)_4]$ (**2**) with thermal ellipsoids at the 30% probability level; the phenyl groups of triphenylphosphane and the isopropyl hydrogen atoms have been omitted for clarity

Table 1. Bond lengths [Å] and angles [°] around the Ru atoms in **2**

Ru(1)−Cl(1)	2.466(7)	Ru(2)−Cl(1)	2.437(6)
Ru(1)−Cl(2)	2.439(6)	Ru(2)−Cl(2)	2.411(6)
Ru(1)−Cl(3)	2.478(6)	Ru(2)−Cl(3)	2.487(6)
Ru(1)−Cl(4)	2.404(6)	Ru(2)−Cl(5)	2.414(7)
Ru(1)−P(1)	2.288(7)	Ru(2)−P(3)	2.311(7)
Ru(1)−P(2)	2.308(8)	Ru(2)−P(4)	2.302(7)
N(1)···Cl(4)	3.29(2)	N(1)···Cl(5)	3.23(2)
P(1)−Ru(1)−P(2)	98.9(3)	P(3)−Ru(2)−Cl(5)	95.5(2)
P(1)−Ru(1)−Cl(4)	93.2(3)	P(4)−Ru(2)−Cl(2)	100.1(2)
P(2)−Ru(1)−Cl(4)	92.8(2)	P(3)−Ru(2)−Cl(2)	93.4(2)
P(1)−Ru(1)−Cl(2)	98.3(3)	Cl(5)−Ru(2)−Cl(2)	163.8(2)
P(2)−Ru(1)−Cl(2)	98.4(2)	P(4)−Ru(2)−Cl(1)	89.6(2)
Cl(4)−Ru(1)−Cl(2)	162.5(2)	P(3)−Ru(2)−Cl(1)	169.0(3)
P(1)−Ru(1)−Cl(1)	90.3(2)	Cl(5)−Ru(2)−Cl(1)	89.4(2)
P(2)−Ru(1)−Cl(1)	170.7(3)	Cl(2)−Ru(2)−Cl(1)	79.7(2)
Cl(4)−Ru(1)−Cl(1)	88.2(2)	P(4)−Ru(2)−Cl(3)	167.5(2)
Cl(2)−Ru(1)−Cl(1)	78.6(2)	P(3)−Ru(2)−Cl(3)	92.2(2)
P(1)−Ru(1)−Cl(3)	167.5(2)	Cl(5)−Ru(2)−Cl(3)	88.9(2)
P(2)−Ru(1)−Cl(3)	93.2(2)	Cl(2)−Ru(2)−Cl(3)	77.2(2)
Cl(4)−Ru(1)−Cl(3)	89.1(2)	Cl(1)−Ru(2)−Cl(3)	78.0(2)
Cl(2)−Ru(1)−Cl(3)	76.9(2)	Ru(2)−Cl(1)−Ru(1)	86.8(2)
Cl(1)−Ru(1)−Cl(3)	77.6(2)	Ru(2)−Cl(2)−Ru(1)	88.0(2)
P(4)−Ru(2)−P(3)	100.1(3)	Ru(1)−Cl(3)−Ru(2)	85.5(2)
P(4)−Ru(2)−Cl(5)	91.6(3)		

As can be seen in Table 1, the coordination environment around the ruthenium centre is pseudo-octahedral. The Ru(1)···Ru(2) distance is 3.370 Å, a value beyond the maximum generally accepted for a bonding interaction. A significant difference is found between the ruthenium−chlorine distances *trans* to the phosphane ligands (mean value 2.467 Å) and those *trans* to the terminal chloro ligands (mean value 2.425 Å).

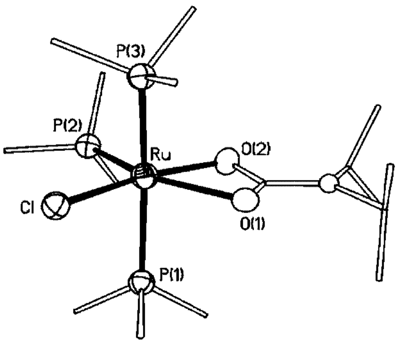

Figure 2. View of the molecular structure of [$RuCl(O_2CNi Pr_2)(PPh_3)_3$] (**3**) with thermal ellipsoids at the 30% probability level; the phenyl groups of the triphenylphosphane and isopropyl hydrogen atoms have been omitted for clarity

The presence of two face-bridged octahedra with three bridging chloro ligands is common in ruthenium chemistry. On the other hand, a few examples exist in the literature of *anionic* species containing tertiary phosphanes as ligands, namely those mentioned above as well as [Et_2NH_2][$Ru_2Cl_2(\mu\text{-}Cl)_3(dppb)_2$] [dppb = 1,4-bis(diphenylphosphanyl)butane].[8b] A rational synthesis of this class of anionic species was reported for [H_2NR_2][($Ru_2Cl_2(\mu\text{-}Cl)_3(dppb)_2$][8b] involving the addition of [R_2NH_2]Cl to the pentacoordinate [$RuCl_2(dppb)(PPh_3)$]. Closely connected are the results by Caulton and co-workers[7b] on the reaction of $RuX_2(CO)L_2$ with M^IX (M^I = alkali metal; X = halide) which affords M^I[$Ru_2X_5(CO)_2L_2$]. Reactions which involve elimination of a ligand L from the metal coordination sphere, followed by dimerization of the metal-containing fragments through bridging halo ligands, can be explained by the need torelieve steric congestion and to obtain the 18-electron configuration in the triply bridged anion.

To obtain pure **3**, it is necessary to use an excess of the amine (amine/Ru molar ratio ca. 4) in a relatively dilute toluene solution [Equation (5)]. In fact, with a $i Pr_2NH$/[$RuCl_2(PPh_3)_3$] molar ratio of 2, the reaction according to Equation (2) still operates and a mixture of **2** and **3** was found even after long reaction times together with unchanged starting material. It is important to note that contamination of **3** with **1** does not occur since complete removal of the chloro ligands from the ruthenium atom requires a large excess of the amine [Equation (1)]. The reaction of **3** towards the amine/(carbon dioxide) system is slow [Equation (6)].

$$[RuCl_2(PPh_3)_3] + 2\ NH\mathit{i}Pr_2 + CO_2 \rightleftharpoons \underset{\mathbf{3}}{[RuCl(O_2CN\mathit{i}Pr_2)(PPh_3)_3]} + [NH\mathit{i}Pr_2]Cl \tag{5}$$

$$\underset{\mathbf{3}}{[RuCl(O_2CN\mathit{i}Pr_2)(PPh_3)_3]} + 2\ NH\mathit{i}Pr_2 + CO_2 \longrightarrow \underset{\mathbf{1}}{[Ru(O_2CN\mathit{i}Pr_2)_2(PPh_3)_2]} + [NH\mathit{i}Pr_2]Cl + PPh_3 \tag{6}$$

Moreover, the formation of **1** would be accompanied by PPh_3 elimination which is clearly counteracted by the presence of free triphenylphosphane. Thus, when good yields of pure **3** are required, addition of some free triphenylphosphane to the reaction mixture totally prevents the formation of **1**. A similar situation has already been encountered with [$RuCl(O_2CNR_2)(\eta^6\text{-cymene})$] (R = Et, *i*Pr) which does not yield [$Ru(O_2CNR_2)_2(\eta^6\text{-cymene})$] even under severe conditions of temperature and pressure and with elevated amine/Ru molar ratios.[3c]

The ruthenium complex **3**, recrystallized from a toluene/heptane mixture, has been studied by single-crystal X-ray diffraction (Figure 2, Table 2). The compound has a mononuclear structure with the metal centre in a distorted octahedral geometry. The coordination sites are occupied by a chloro ligand, an asymmetric bidentate carbamato ligand and three phosphane ligands in *mer* positions.

Table 2. Bond lengths [Å] and angles [°] around the Ru atom in **3**

Ru−Cl	2.415(6)	Ru−P(3)	2.419(7)
Ru−P(1)	2.375(7)	Ru−O(1)	2.27(2)
Ru−P(2)	2.271(6)	Ru−O(2)	2.12(2)
O(2)−Ru−P(2)	91.2(5)	O(1)−Ru−Cl	106.5(4)
O(1)−Ru−O(2)	60.0(6)	P(1)−Ru−Cl	81.8(2)
P(2)−Ru−O(1)	151.1(4)	O(2)−Ru−P(3)	98.9(5)
O(2)−Ru−P(1)	94.9(5)	P(2)−Ru−P(3)	98.2(2)
P(2)−Ru−P(1)	98.8(2)	O(1)−Ru−P(3)	89.5(5)
O(1)−Ru−P(1)	82.4(5)	P(1)−Ru−P(3)	157.9(2)
O(2)−Ru−Cl	166.5(5)	Cl−Ru−P(3)	80.9(2)
P(2)−Ru−Cl	102.2(2)		

Major distortions from ideal octahedral geometry are due to the small O(1)−Ru−O(2) angle of 60.0° and the P(1)−Ru−P(3) bond angle, involving the two *trans*-phosphane ligands, of 157.9°. The Ru−O(1) bond of 2.27 Å is longer than Ru−O(2) (2.12 Å), possibly due to O(1) being *trans* to P(2). The Ru−P(2) bond is significantly shorter than the other two distances, as found elsewhere for other *mer* complexes.[9a,9b] The easy displacement of one of the weakly bonded phosphane ligands leading to [*cis*-$Ru(O_2CN\mathit{i}Pr_2)_2(PPh_3)_2$] can therefore be easily understood.

Compound **3** was subjected to conventional spectroscopic investigations. The presence of bidentate carbamato ligands was confirmed by the absence of IR bands above 1600 cm^{-1}.[5b] The ^{31}P NMR solution spectrum of **3** at −40 °C shows the presence of free PPh_3 with a signal at $\delta = -4.2$ ppm and two doublets at $\delta = 27.7$ and 51.0 ppm ($J = 68$ Hz) as well as a triplet at $\delta = 46.5$ ppm coupled with the doublet at $\delta = 50.1$ ppm ($J = 66$ Hz). For comparison, [$RuCl(O_2CMe)(PPh_3)_3$][9c] shows signals at $\delta = 31.0$ (t) and 50.5 (d) ppm. At room temperature the signals of **3** are broad. These results may be explained by assuming that equilibrium [Equation (7)] occurs in solution, the dinuclear species being responsible for the additional signals.

$$2\ \underset{\mathbf{3}}{[RuCl(O_2CN\mathit{i}Pr_2)(PPh_3)_3]} \rightleftharpoons [Ru_2(\mu\text{-}Cl)_2(O_2CN\mathit{i}Pr_2)_2(PPh_3)_4] + 2\ PPh_3 \tag{7}$$

Similar to other examples in the literature,[10] the equilibrium is suppressed by addition of an excess of phosphane. In the dinuclear compound, each ruthenium atom is assumed to be hexacoordinate with two bridging chloro ligands, two phosphane ligands and a terminal bidentate carbamato ligand, the ruthenium(II) centre again reaching the 18-electron configuration.[10a] The rather simple NMR spectra of [RuCl(O_2CMe)(PPh_3)$_3$][9c] suggest the absence of ligand dissociation.

Reactivity of the Ruthenium Complexes with Dihydrogen

Olefin complexation is believed to be the primary process in a catalytic hydrogenation cycle and a few olefin complexes of ruthenium(II) have been isolated and crystallographically characterised.[11−15] RuHCl(PPh_3)$_3$[16] was reported to be unreactive towards 1-hexene, 1-heptene and 2-octene, whereas an alkyl derivative was detected (NMR) with ethylene at 35 atm. We have observed that the carbamato complexes **1** and **3** do not react with 1-octene, although it was conceivable that they could add the olefin by converting the carbamato ligand from a bidentate to a monodentate ligating mode.

Compound **3** is converted by dihydrogen at room temperature and atmospheric pressure in toluene solution into both the soluble [Ru(H)$_2$(H_2)(PPh_3)$_3$] and the poorly soluble violet [RuHCl(PPh_3)$_3$]. These compounds have been identified on the basis of their spectroscopic data and by comparison with data in the literature.[16,17] The intermediate [RuH(O_2CNiPr_2)(PPh_3)$_3$] (**4**) was also detected by ^{31}P NMR spectroscopy in solution (vide infra). These results are consistent with the reactions shown in Equations (8) and (9). On the other hand, direct hydrogenation of **3** may lead to [RuH(Cl)(PPh_3)$_3$] [Equation (10)]. We have also established that when **3** is hydrogenated in the presence of an excess of NH*i*Pr$_2$, only the soluble [Ru(H)$_2$(H_2)(PPh_3)$_3$] is formed, together with [NH$_2$*i*Pr$_2$]Cl. HCl elimination from [RuH(Cl)(PPh_3)$_3$] is favoured under these conditions. It is interesting to note that [Ru(H)$_2$(H_2)(PPh_3)$_3$][17,18] is prepared by the action of relatively strong reducing agents such as $NaBH_4$ or AlR_3 on [RuCl$_2$(PPh_3)$_3$].[19a,19b] Our synthesis operates under mild conditions in aromatic hydrocarbons.

$$\underset{\mathbf{3}}{[\mathrm{RuCl(O_2CN}i\mathrm{Pr_2)(PPh_3)_3}]} + \mathrm{H_2} \longrightarrow \underset{\mathbf{4}}{[\mathrm{RuH(O_2CN}i\mathrm{Pr_2)(PPh_3)_3}]} + \mathrm{HCl} \qquad (8)$$

$$\underset{\mathbf{4}}{[\mathrm{RuH(O_2CN}i\mathrm{Pr_2)(PPh_3)_3}]} + 2\,\mathrm{H_2} \rightleftharpoons [\mathrm{Ru(H)_2(H_2)(PPh_3)_3}] + \mathrm{CO_2} + \mathrm{NH}i\mathrm{Pr_2} \qquad (9)$$

$$\underset{\mathbf{3}}{[\mathrm{RuCl(O_2CN}i\mathrm{Pr_2)(PPh_3)_3}]} + \mathrm{H_2} \longrightarrow [\mathrm{RuH(Cl)(PPh_3)_3}] + \mathrm{CO_2} + \mathrm{NH}i\mathrm{Pr_2} \qquad (10)$$

The carbamato derivative **1** does not react with dihydrogen at room temperature and atmospheric pressure. By gradually increasing the temperature, a reaction was found to occur at about 80 °C, accompanied by some decomposition, presumably due to the low thermal stability of the intermediate [Ru(H)$_2$(H_2)$_2$(PPh_3)$_2$].[17a,17b] The experiment at 80 °C was therefore repeated in the presence of 1 equiv. of triphenylphosphane. Under these conditions, [Ru(H)$_2$(H_2)(PPh_3)$_3$] was detected as the sole final ruthenium-containing compound [Equation (11)].

$$[\mathrm{Ru(O_2CN}i\mathrm{Pr_2)_2(PPh_3)_2}] + 3\,\mathrm{H_2} + \mathrm{PPh_3} \longrightarrow [\mathrm{Ru(H)_2(H_2)(PPh_3)_3}] + 2\,\mathrm{CO_2} + 2\,\mathrm{NH}i\mathrm{Pr_2} \qquad (11)$$

Upon monitoring the reaction by ^{31}P NMR spectroscopy, signals attributable to the intermediate formation of [RuH(O_2CNiPr_2)(PPh_3)$_3$] [Equation (12)] were detected, namely a triplet at $\delta = 76.8$ ppm coupled with a doublet at $\delta = 41.7$ ppm ($J = 68$ Hz). These signals can be attributed to three phosphane ligands in a *mer* configuration if a comparison is made with [*mer*-RuH(O_2CMe)(PPh_3)$_3$], the latter showing resonances at $\delta = 77.6$ (t) and 43.8 (d) ppm.[10b]

$$\underset{\mathbf{1}}{[\mathrm{Ru(O_2CN}i\mathrm{Pr_2)_2(PPh_3)_2}]} + \mathrm{H_2} + \mathrm{PPh_3} \longrightarrow [\mathrm{RuH(O_2CN}i\mathrm{Pr_2)(PPh_3)_3}] + \mathrm{CO_2} + \mathrm{NH}i\mathrm{Pr_2} \qquad (12)$$

The ^1H NMR spectrum of [RuH(O_2CNiPr_2)(PPh_3)$_3$] shows a quadruplet at $\delta = -17.6$ ppm, equivalent to an overlapping doublet of triplets which would be expected for the coupling with the three phosphorus atoms. This is analogous with the quadruplet at $\delta = -19.8$ ppm exhibited by [RuH(O_2CMe)(PPh_3)$_3$].[1d] A possible structure for [RuH(O_2CNiPr_2)(PPh_3)$_3$], similar to that of **3** with three *mer*-phosphane ligands, is consistent with the observed spectrum (Figure 2).

The reaction according to Equation (9) is reversible: in toluene, [Ru(H)$_2$(H_2)(PPh_3)$_3$] rapidly reverts to [RuH(O_2CNiPr_2)(PPh_3)$_3$] in the presence of *i*Pr$_2$NH/CO_2 (amine/ruthenium molar ratio ca. 8) which is the only species present in solution after 1 h. By adding a large excess of amine, [Ru(O_2CNiPr_2)$_2$(PPh_3)$_2$] was obtained after one week.

Catalysis

All ruthenium derivatives reported in this paper have been tested as potential catalysts for the hydrogenation of 1-octene in toluene at room temperature, with activity being shown by **1** and **3**.

Once it was established that **1** does not react at room temperature and atmospheric pressure either with 1-octene or with H_2, hydrogenation of 1-octene was observed using $10^{-2}/10^{-3}$ M solutions of **1**, as evidenced by both gas chromatography, ^1H NMR spectroscopy and gas-volumetric measurements. Immediately after the catalyst precursor comes into contact with the reaction mixture, olefin hydrogenation occurs with no induction time being observed. The initial rate was found to correspond to approximately 300 mmol·L^{-1} h^{-1}, the olefin/ruthenium molar ratio being 28 and the initial olefin concentration being 2.6×10^{-1} M. After normalization with respect to the concentration of both the catalyst precursor and the olefin and to the H_2

partial pressure, the initial reaction rate (r_i), was calculated to be 163 mol·L^{-1} h^{-1}. No other ruthenium complexes other than the starting material were detected in solution by NMR spectroscopy after hydrogenation. More than 90% of **1** remained unchanged.[19c] It is reasonable to assume that in the course of the process, vacant sites for olefin or hydrogen coordination are made available on **1** by a hapticity change of the carbamato ligand from bidentate to monodentate.

Hydrogenation of 1-octene was also studied in the presence of **3** as a catalytic precursor. After about 6 h in toluene at room temperature, complete hydrogenation was established as indicated by gas chromatography and ruthenium was recovered as [RuHCl(PPh$_3$)$_3$]. No [RuH$_2$(H$_2$)(PPh$_3$)$_3$] was present in the solution and gas-volumetric measurements showed that 89% of the olefin was hydrogenated in about 3 h.

In contrast to the earlier report on the use of the anionic complex [Ru$_2$Cl$_2$(μ-Cl)$_3${(*R*)-*p*-MeO-BINAP}$_2$]$^-$ [8a] in the asymmetric hydrogenation of olefins, [*i*Pr$_2$NH$_2$][Ru$_2$Cl$_5$(PPh$_3$)$_4$] was found to be inactive for the hydrogenation of 1-octene, the latter being slowly converted into (*E*)-4-octene. Similarly, in an attempted hydrogenation of 1-octene, the carbonyl complex [Ru(CO)(O$_2$CN*i*Pr$_2$)$_2$(PPh$_3$)$_2$] gave only a slow olefin isomerization.

Conclusions

In the reaction of [RuCl$_2$(PPh$_3$)$_3$] with *i*Pr$_2$NH and CO$_2$, optimum conditions have been identified for the preparation of the new species **3**. Moreover, a new convenient synthesis of **1** was carried out using **2** as a precursor.

The hydrogenation of some (carbamato)ruthenium(II) complexes was found to depend on the nature of the ligands. Compound **3** promptly reacts at room temperature, producing a mixture of [RuHCl(PPh$_3$)$_3$] and [RuH$_2$(H$_2$)(PPh$_3$)$_3$]. When the reaction was carried out in the presence of an HCl scavenger, for instance *i*Pr$_2$NH, only [RuH$_2$(H$_2$)(PPh$_3$)$_3$] was detected as the final ruthenium-containing product through the intermediate [RuH(O$_2$CN*i*Pr$_2$)(PPh$_3$)$_3$].

No reaction with dihydrogen was observed for **1** at room temperature with [RuH$_2$(H$_2$)(PPh$_3$)$_3$] being formed at 80 °C in the presence of PPh$_3$. Both **1** and **3** promote the hydrogenation of 1-octene at room temperature and atmospheric pressure, the highest activity being exhibited by the former which was largely recovered unchanged after catalysis in toluene. No other complexes were detected in solution by ^{31}P NMR spectroscopy. This suggests that catalysis does not require complete cleavage of the Ru−O$_2$CN*i*Pr$_2$ bond. The flexibility of the carbamato ligand changing its coordination mode from η^2 to η^1 and allowing easy access to the metal atom may explain the results. Consistent with this interpretation both [Ru(O$_2$CN*i*Pr$_2$)$_2$CO(PPh$_3$)$_2$] and [Ru(O$_2$CN*i*Pr$_2$)$_2$(CO)$_2$(PPh$_3$)$_2$], which contain monodentate carbamato groups and strongly bonded ancillary ligands, are inactive towards olefin hydrogenation under comparable conditions. The importance of the carbamato ligand in the dihydrogen activation is apparent from the observation that the chloride-bridged anion of ruthenium(II) in the [*i*Pr$_2$NH$_2$][Ru$_2$Cl$_5$(PPh$_3$)$_4$] derivative was found to be inactive. As a result of recent mechanistic studies on ruthenium-catalysed hydrogenations,[20a−20c] the hydrogenation experiments reported in this paper will be extended to other unsaturated substrates.

Experimental Section

General: All procedures were carried out in standard Schlenk tubes. Solvents were freshly distilled from conventional drying agents under nitrogen and all manipulations were carried out under nitrogen, unless otherwise specified. The compounds [RuCl$_2$(PPh$_3$)$_3$],[21] [Ru(CO)(O$_2$CN*i*Pr$_2$)$_2$(PPh$_3$)$_2$],[3a] and [Ru(CO)$_2$(O$_2$CN*i*Pr$_2$)$_2$(PPh$_3$)$_2$][3a] were prepared according to the literature. Commercial (Aldrich) triphenylphosphane, 1-octene and diisopropylamine were purified by conventional methods. Elemental analyses (C, H, N) were performed by the Laboratorio di Microanalisi della Facoltà di Farmacia, Università di Pisa, with a Carlo Erba model 1106 elemental analyser. IR spectra were recorded with a Perkin-Elmer FT-IR model 1725X spectrophotometer. Nuclear magnetic resonance spectra were recorded using a Varian Gemini 200BB instrument, the data being expressed in ppm relative to TMS for ^{1}H and ^{13}C and to 85% H$_3$PO$_4$ in D$_2$O for ^{31}P.

Synthesis of [RuCl(O$_2$CN*i*Pr$_2$)(PPh$_3$)$_3$] (3): To a solution of diisopropylamine (2.6 mL, 18.4 mmol) in toluene (300 mL), saturated with carbon dioxide, [RuCl$_2$(PPh$_3$)$_3$] (4.35 g, 4.54 mmol) was quickly added together with PPh$_3$ (3.63 g, 13.8 mmol). After stirring under carbon dioxide for 4 d, [*i*Pr$_2$NH$_2$]Cl was removed by filtration. The ^{31}P NMR spectroscopic measurements on the filtrate gave the following results: δ = −4.2 ppm, 27.7 ppm (br. s), 46.5 (t, *J* = 66.0 Hz), 50.1 (d, *J* = 66.0 Hz), 51.0 (br., s) ppm. After removing the volatiles in vacuo, the resultant residue was dissolved in toluene (25 mL). By addition of heptane (75 mL), the title compound was recovered by filtration and then dried in vacuo at room temperature for 3 h (3.48 g, 71.8% yield). C$_{68}$H$_{75}$ClNO$_2$P$_3$Ru (1167.8): calcd. C 69.9, H 6.5, N 1.2; found C 70.5, H 5.5, N 0.8. ^{31}P NMR (C$_6$D$_6$): δ = 27.7 (br. s), 46.5 (br. t, *J* = 68 Hz), 50.1 (br. d, *J* = 68 Hz), 51.0 (br. s) ppm. ^{1}H NMR (C$_6$D$_6$): δ = 0.9 (d, *J* = 68 Hz, C*H*$_3$ *i*Pr), 1.2 (d, C*H*$_3$ *i*Pr), 1.3 (d, C*H*$_3$ *i*Pr), 3.7 (m, C*H* *i*Pr), 4.4 (m, C*H* *i*Pr), 6.7 (m, 27 H, *m,p*-C*H*), 7.7 (m, 18 H, *o*-C*H*) ppm. ^{13}C NMR (C$_6$D$_6$): δ = 21.7 (s, *C*H$_3$ *i*Pr), 21.8 (s, *C*H$_3$ *i*Pr), 44.4 (s, *C*H *i*Pr), 44.5 (s, *C*H *i*Pr), 44.6 (s, *C*H *i*Pr), 163.5 (s) and 164.0 (s) (*C*O$_2$) ppm. Addition of triphenylphosphane caused the signals at δ = 27.7 and 51.0 ppm to decrease leading to a better resolution of the signals at δ = 50.1 (d) and 46.5 (t) ppm.

Synthesis of [NH$_2$*i*Pr$_2$][Ru$_2$Cl$_5$(PPh$_3$)$_4$] (2): A suspension of [RuCl$_2$(PPh$_3$)$_3$] (0.44 g, 0.46 mmol) in toluene (25 mL) was treated with [*i*Pr$_2$NH$_2$]Cl (0.03 g, 0.22 mmol) under argon. The resultant dark-red solution showed a single ^{31}P NMR peak at δ = 46.9 ppm. After filtration and evaporation of the solvent to a small volume, the title crystalline compound was precipitated by addition of heptane (20 mL), filtered and dried in vacuo (0.23 g, 69% yield). C$_{78}$H$_{76}$Cl$_5$NP$_4$Ru$_2$ (1530.8): calcd. C 61.2, H 5.0, N 0.9; found C 59.6, H 5.2, N 0.6. ^{31}P NMR (C$_6$D$_6$): δ = 46.8 (s) ppm. ^{1}H NMR (C$_6$D$_6$): δ = 1.2 (dd, *J* = 6.0 Hz, 12 H, C*H*$_3$ *i*Pr), 3.5 (m, 2 H, C*H* *i*Pr), 6.8 (m, 36 H, *m,p*-C*H*), 7.6 (m, 24 H, *o*-C*H*), 8.2 (br. s, 2 H, N*H*) ppm. IR (nujol, KBr): ṽ = 3049 (m), 1586 (w),1482 (m), 1434 (s), 1311 (w) cm^{-1}.

Synthesis of $[Ru(O_2CNiPr_2)_2(PPh_3)_2]$ (1) from $[NH_2iPr_2][Ru_2Cl_5(PPh_3)_4]$ (2): Under carbon dioxide, iPr_2NH (25 mL) was added to a toluene solution of **2** prepared from $[RuCl_2(PPh_3)_3]$ (3.61 g, 3.76 mmol) and iPr_2NH_2Cl (0.25 g, 1.82 mmol). After stirring at ambient temperature for 4 d, the ammonium salt was removed by filtration and the filtrate was concentrated to dryness in vacuo. The resultant residue was suspended in heptane and the product was recovered by filtration and subsequent drying in vacuo (1.96 g, 57% yield).^{31}P NMR (C_6D_6): $\delta = 66.2$ (s) ppm.^{1}H NMR (C_6D_6): $\delta = 1.1$ (d, CH_3, *i*Pr), 3.6 (sept, CH, *i*Pr), range 6.6−7.5 (aromatic, m, CH) ppm.[3a]

Reaction of $[RuCl(O_2CNiPr_2)(PPh_3)_3]$ (3) with H_2: A solution of **3** (1.21 g, 1.13 mmol) in toluene (100 mL) was placed under hydrogen. After 4 h, a violet precipitate was observed and a ^{31}P NMR spectrum of the liquid phase showed signals at $\delta = 58.5$ $[RuH_2(H_2)(PPh_3)_3]$[17a] and 76.9 (t) and 41.7 (d) $\{[RuH(O_2CNiPr_2)(PPh_3)_3]\}$ ppm. The latter signals disappeared with time such that after 1 d only the signal at $\delta = 58.5$ was present. The violet solid was filtered and dried in vacuo (0.52 g, 49.6% yield). ^{31}P NMR ($C_2D_2Cl_4$): $\delta = 59.0$ (br. s) ppm. ^{1}H NMR ($C_2D_2Cl_4$): $\delta = -18.4$ (q, $J = 26.0$ Hz), 1.4 (br. s, CH_3), 3.4 (m, CH *i*Pr), 6.9 (m, *m,p*-CH), 7.7 (m, *o*-CH), 9.0 (br. s, NH) ppm. IR (Nujol, KBr, range 2200−1900 cm^{-1}): $\tilde{\nu} = 2030$ cm^{-1}. To a solution of $[RuCl(O_2CNiPr_2)(PPh_3)_3]$ (0.73 g, 0.68 mmol) in toluene (50 mL), iPr_2NH (0.4 mL, 2.86 mmol) was added and the mixture was stirred under dihydrogen for 4 h. The ^{31}P NMR spectrum of the liquid phase showed peaks due to $[RuH(O_2CNiPr_2)(PPh_3)_3]$. After 24 h of stirring, the ^{31}P NMR of the liquid phase showed only a signal at $\delta = 58.5$ $\{[RuH_2(H_2)(PPh_3)_3]\}$ ppm.[17a]

Treatment of $[Ru(O_2CNiPr_2)_2(PPh_3)_2]$ with H_2. Reversible Formation of $[RuH_2(H_2)(PPh_3)_3]$: A solution of $[Ru(O_2CNiPr_2)_2(PPh_3)_2]$ (0.38 g, 0.42 mmol) in toluene (50 mL) was stirred under hydrogen at room temperature for 3 h. No change was indicated by ^{31}P NMR spectroscopy even after treatment at 30 and 60 °C. Treatment at 80 °C for 4 h led to a mixture with a complex ^{31}P NMR spectrum containing a resonance at $\delta = 58.5$ $\{[RuH_2(H_2)(PPh_3)_3]\}$ ppm. Longer treatment led to extensive decomposition. In an experiment where 1 equiv. of PPh_3 had been added, a solution of $[Ru(O_2CNiPr_2)_2(PPh_3)_2]$ (0.32 g, 0.35 mmol) and PPh_3 (0.10 g, 0.38 mmol) in C_6D_6 (4 mL) was treated with hydrogen at atmospheric pressure. As in the previous experiment, no NMR spectroscopic changes were noted at room temperature, 40 or 60 °C, whereas a reaction did occur at 80 °C. After 12 h at 80 °C under hydrogen, the solution showed the following ^{31}P NMR resonances: $\delta = 76.8$ (t, $J = 68$ Hz) and 41.7 (d, $J = 68$ Hz) $\{[RuH(O_2CNiPr_2)(PPh_3)_3]\}$, 58.5 {s, $[RuH_2(H_2)(PPh_3)_3]$} ppm. ^{1}H NMR: $\delta = -17.6$ (q, $J = 26.0$ Hz), −7.1 (br. s), 0.75 (d, CH_3), 0.9 (d, CH_3 of free amine), 1.05 (d, CH_3 of the carbamato group), 2.7 (m, C*H* of free amine), 3.1 and 4.1 (m, C*H*), range 6.6−7.8 (aromatic C*H*), 9.0 (s, amine N*H*) ppm. ^{13}C NMR: $\delta = 164.6$ (br. s), 45.4 (amine C*H*), 44.0 (C*H* of the carbamato group), 23.7 (amine CH_3), 21.8 (CH_3 of the carbamato group) ppm. After an additional 12 h at 80 °C, the solution turned yellow and only the resonance at $\delta = 58.5$ $\{[RuH_2(H_2)(PPh_3)_3]\}$ ppm was observed. To this solution was added iPr_2NH (0.2 mL, 1.42 mmol) under carbon dioxide. After 1 h, the solution turned red and had the following spectroscopic features. ^{31}P NMR: $\delta = 76.8$ (t, $J = 68$ Hz), 41.7 (d, $J = 68$ Hz) and 58.5 ppm. ^{1}H NMR: $\delta = -17.6$ (q, $J = 26$ Hz), −7.1 (br. s), 0.75 (d, CH_3 of the carbamato groups), 0.9 (d, amine CH_3), 1.05 (d, CH_3 of the carbamato groups), 2.7 (m, amine C*H*), 3.1 and 4.1 (m, C*H* of the carbamato groups), range 6.6−7.8 (aromatic C*H*), 9.0 (s, amine N*H*) ppm. After 12 h, the ^{31}P NMR showed signals at $\delta = 76.8$ (t) and 41.6 (d) $\{[RuH(O_2CNiPr_2)(PPh_3)_3]\}$ ppm. By addition of an excess (5 mL) of iPr_2NH, a signal at $\delta = 66.4$ {s, $[Ru(O_2CNiPr_2)_2(PPh_3)_2]$} ppm[3a] was present in the ^{31}P NMR spectrum after 1 week.

Reaction of $[Ru(CO)_2(O_2CNiPr_2)_2(PPh_3)_2]$ with H_2: A solution of $[Ru(CO)_2(O_2CNiPr_2)_2(PPh_3)_2]$ (0.19 g, 0.19 mmol) in toluene (10 mL) was placed under hydrogen and heated at 50 °C for 1 d. ^{31}P NMR spectra of the solution showed the progressive decrease of the signal of the starting material ($\delta = 29.9$ ppm), the presence of an intermediate signal at $\delta = 43.5$ ppm and the increase of the final signal at $\delta = 57.8$ ppm attributable to $[RuH_2(CO)_2(PPh_3)_2]$.[2g,22] Once the reaction was complete, the pale-yellow $[RuH_2(CO)_2(PPh_3)_2]$ precipitated upon cooling to room temperature (30 mg, 22.4% yield). ^{31}P NMR (C_6D_6): $\delta = 57.7$(s) ppm. ^{1}H NMR (C_6D_6): $\delta = -6.35$ (t, $J = 25$ Hz), range 6.9−7.8 (aromatic C*H*) ppm. IR (Nujol): $\tilde{\nu} = 2010$, 1974 (CO stretching), 1880 and 1815 (Ru−H stretching) cm^{-1}.

Treatment of $[iPr_2NH_2][Ru_2Cl_5(PPh_3)_4]$ (2) with 1-Octene and with 1-Octene/H_2: To a C_6D_6 (3 mL) solution of **2** (0.37 g, 0.24 mmol) was added 1-octene (0.1 mL, 0.64 mmol). The solution was monitored by ^{31}P NMR spectroscopy with no change being noted. After introducing hydrogen, ^{1}H NMR signals due to (*E*)-4-octene [$\delta = 5.4$ (m), 1.9 (m), 1.5 (m), 0.85 (t) ppm] were noted in addition to those of 1-octene.

Hydrogenation of 1-Octene in the Presence of $[Ru(O_2CNiPr_2)_2(PPh_3)_2]$ (1) or $[RuCl(O_2CNiPr_2)(PPh_3)_3]$ (3): The olefin (1-octene, 1.46 mmol) in C_6D_6 (4 mL) was stirred under H_2 at room temperature in the presence of **1** (0.15 mmol). After 12 h, the ^{1}H NMR spectrum of the reaction mixture showed the absence of the signals of 1-octene, the latter being completely converted into octane (gas chromatography, ATWAX capillary column). A hydrogenation experiment was carried out directly in an NMR tube: 1-octene (1.02 mmol) and **1** (86 mg, 9.44×10^{-2} mmol) were dissolved in C_6D_6 (0.7 mL) under N_2 with aqueous 85% H_3PO_4 contained in a flame-sealed capillary being used as a reference. The ^{31}P NMR spectrum showed signals at $\delta = 0$ ppm due to phosphoric acid and at $\delta = 66.2$ ppm due to **1** with an intensity ratio of 7.3. The content of the tube was then exposed to H_2 ($p = 760$ Torr) for 3 d. A new ^{31}P NMR spectrum showed signals at $\delta = 0$ and 66.2 ppm with a ratio of 7.7, corresponding to more than 90% of the original complex **1** being unconverted. No other resonances were observed, while the ^{1}H NMR spectrum showed that complete hydrogenation to octane had occurred. A solution of **3** (0.14 g, 0.13 mmol) and 1-octene (0.2 mL, 1.27 mmol) in toluene (50 mL) was stirred for a few hours with no change in the ^{31}P NMR spectrum being noted. The solution was then placed under H_2 and stirred for 6 h. A violet solid was formed. A gas chromatogram of the liquid phase with an ATWAX capillary column showed a single peak due to octane. The violet solid spectroscopically identified as $[RuHCl(PPh_3)_3]$ was filtered and dried (50 mg, 41.2% yield). ^{31}P NMR ($C_2D_2Cl_4$): $\delta = 59.0$ (br. s) ppm. ^{1}H NMR ($C_2D_2Cl_4$): $\delta = -18.4$ (q, $J_{H,P} = 26$ Hz), range 6.9−7.8 (m) ppm. The hydrogenation of 1-octene was monitored by gas volumetry, using both **1** and **3** as catalytic precursors. In a typical experiment, the solution of the olefin in toluene (20 mL) was prepared and a fragile flame-sealed ampoule containing the ruthenium complex was introduced. After thermostatting the system under H_2 ($p_{H2} = 740$ Torr), the ampoule was broken by magnetic stirring and the hydrogen absorption with time was noted, no induction being observed. The hydrogenation of 1-octene (0.8 mL, 5.1 mmol) in the presence of **1** (0.16 g, 0.18 mmol) at 20.6 °C in toluene (20 mL) gave a dihydrogen absorption corresponding to a conversion of about 70% in 165 min, the initial rate being 300 mmol·L^{-1} h^{-1} ([Ru] = 9.0×10^{-3} M).

The hydrogenation of 1-octene (0.3 mL, 1.91 mmol) in the presence of **3** (0.21 g, 0.20 mmol) at 21.2 °C in toluene (20 mL) was similarly monitored, the absorption of dihydrogen corresponding to 88.8% of the theoretical amount in 165 min. The initial rate was 153 $\text{mmol·L}^{-1}\ \text{h}^{-1}$, the ruthenium concentration being 1.0×10^{-2} м.

X-ray Crystallographic Studies: The crystallographic measurements on both samples were carried out on four-circle diffractometers. Cu-K_α radiation ($\lambda = 1.54184$ Å) was used for **3** due to the length of the *b* parameter, whereas Mo-K_α radiation ($\lambda = 0.71073$ Å) was used for **2**. All data were collected in the ω-2θ scan mode and three standard reflections were monitored every 97 measurements in order to check for crystal decay and equipment stability. For both samples, particularly for **3**, weak diffractions which rapidly dropped below the observation threshold were measured at increasing 2θ angles. Data reduction was performed using the DARX2000 and SDP program packages.[23,24] Crystals of **2**, prepared as described before, are red-brown blocks. An approximately tetrahedral splinter cut from one of them, with the edge about 0.30 mm long, was sealed in a glass capillary under N_2 and the unit cell parameters listed in Table 3 were derived from the setting angles of 35 strong reflections. A set of 6633 reflections were collected between $\theta = 1.8$ and 22.5° which were corrected for Lorentz and polarization effects and for absorption using the Ψ-scan method. After merging the equivalent reflections $\{R_{\text{int}} = [\Sigma|F_o^2 - F_o^2(\text{mean})|/\Sigma(F_o^2)] = 0.0483\}$, 4553 unique reflections satisfying the condition $I > 2\sigma(I)$ were obtained. The systematic absences indicated the $P2_1/c$ space group. After location of all the heavy atoms of the $[Ru_2Cl_5(PPh_3)_4]^-$ anion and of the $[i\text{Pr}_2NH_2]^+$ cation and the introduction of the hydrogen atoms in calculated positions, several large peaks were found in the difference Fourier map in the cavities between the ion pairs. These peaks were attributed to a disordered lattice solvent (heptane), but a reliable model for this substance was not found. This contributed to the relatively high reliability factors of the refinement which was carried out with anisotropic thermal factors for the Ru, Cl and P atoms only. The final reliability factors are listed in Table 3. Calculations were carried out using the SHELX-97 program.[25] Crystals of **3** are red prisms. A crystal of dimensions 0.20 × 0.25 × 0.38 mm, sealed in a glass capillary under N_2, exhibited the cell parameters listed in Table 3. Due to the poor diffraction properties of the crystal, only 3157 independent intensities having $I > 2\sigma(I)$ were collected in the range $3.69° \le \theta \le 70.0°$. They were corrected for Lorentz and polarization effects and for absorption using the Ψ-scan method. The structure was solved in the $P2_1/n$ space group by direct methods and refined by least-squares methods based on *F* (SHELXTL).[26] As in the structure of **2**, several peaks present in the difference Fourier map were attributed to a disordered lattice solvent (heptane) molecule. The last refinement cycle was carried out using anisotropic thermal factors for Ru, Cl and P atoms only. The final reliability factors are listed in Table 3. Final atomic parameters, thermal factors and the details of the structural determinations have been deposited in the form of a CIF file with the Cambridge Crystallographic Data Centre. CCDC-228267 (for **2**) and -228268 (for **3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

Table 3. Crystal data and structural refinements for **2** and **3**

	2·heptane	**3**·heptane
Empirical formula	$C_{85}H_{92}Cl_5NP_4Ru_2$	$C_{68}H_{75}ClNO_2P_3Ru$
Formula mass	1630.87	1167.72
Wavelength [Å]	0.71069	1.54184
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$ (No. 14)	$P2_1/n$ (No. 14)
a [Å]	19.922(5)	10.583(2)
b [Å]	15.385(2)	46.516(9)
c [Å]	27.423(4)	12.990(3)
β [°]	91.15(2)	104.29(3)
V [Å^3]	8403(3)	6197(2)
Z	4	4
$D_{\text{calcd.}}$ [Mg·m^{-3}]	1.289	1.252
μ [mm^{-1}]	0.636	3.507
No. observed [$I > 2\sigma(I)$]	4553	3157
No. parameters	296	367
R, *wR*	0.1226, 0.3116	0.1061, 0.2769
Goodness of fit on F^2	1.607	0.994

Acknowledgments

The authors wish to thank the Ministero dell' Istruzione Universitaria e della Ricerca (MIUR), Programmi di Rilevante Interesse Nazionale 2002-3 and the Consiglio Nazionale delle Ricerche, Progetto CNR/MIUR "Sviluppo di microcelle a combustibile" for financial support.

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Received January 9, 2004
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