

Activation of the N–H bond of ethyl carbamate and urea by ruthenium hydride complexes. Unexpected loss of alcohol or ammonia to yield isocyanato complexes†

Fabio Ragaini,^a Tatiana Longo,^a Sergio Cenini^{*a} and Francesco Demartin^b

^a Dipartimento di Chimica Inorganica, Metallorganica e Analitica and CNR Center, V. G. Venezian 21, I-20133 Milano, Italy

^b Dipartimento di Chimica Strutturale e Stereochimica Inorganica and CNR Center, V. G. Venezian 21, I-20133 Milano, Italy

The complex $[\text{RuH}_2(\text{CO})(\text{PPh}_3)_3]$ **1** reacted with ethyl carbamate (urethane), $\text{H}_2\text{NCO}_2\text{Et}$, or urea to yield the complex $[\text{RuH}(\text{NCO})(\text{CO})(\text{PPh}_3)_3]$ **2**, which was spectroscopically characterised. The analogous reaction of $[\text{RuH}_2(\text{PPh}_3)_4]$ **3** gave a mixture of products in which $[\text{RuH}(\text{NCO})(\text{C}_6\text{H}_5\text{Me})(\text{PPh}_3)_3]$ **4** predominates. Treatment of this mixture with CO allowed the isolation of $[\text{RuH}(\text{NCO})(\text{CO})_2(\text{PPh}_3)_2]$ **5** the crystal structure of which was solved by X-ray diffraction. The reactions appear to proceed through the intermediate formation of a N-bonded carbamato or ureido complex, formed by elimination of H_2 , followed by irreversible elimination of alcohol or ammonia. This synthesis of isocyanate complexes appears to be quite general. The reactivity of the complexes obtained with olefins has been investigated. Only isomerisation was observed, with no evidence for organic isocyanate formation.

Transition-metal-promoted activation and functionalisation of N–H bonds is a topic of high industrial and academic interest.^{1,2} However, reactions employing amines as substrates are not yet sufficiently effective to meet the requirements for application in organic synthesis.³ In another perspective, the development of phosgene (COCl_2) free routes to organic isocyanates and carbamates has also attracted academic and especially industrial interest. Urethane, $\text{H}_2\text{NCO}_2\text{Et}$, and urea, $\text{H}_2\text{NC(O)NH}_2$, are cheap, large-scale industrial products⁴ that are not produced *via* phosgene. We therefore decided to investigate the reactivity of these molecules with respect to several transition-metal complexes, with the aim of developing catalytic systems able to effect the addition of the N–H bond of these substrates to olefins. Up to now very few studies on the reactions of urethane and urea with transition-metal complexes have been reported.^{5–11}

It has been reported¹² that $[\text{RuH}_2(\text{CO})(\text{PPh}_3)_3]$ **1** reacts with amides and perfluoroamides to yield products containing a Ru–N bond, derived from the activation of a N–H bond of the amide, and, apparently, dihydrogen. Since the acidity of the N–H group of urethane should be quite similar to that of the N–H bond of a perfluoroamide, we decided to start our investigation with the reaction of urethane with complex **1**.

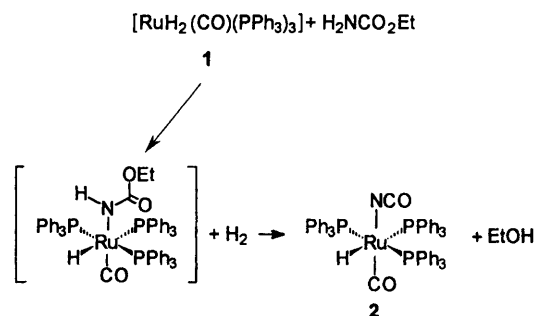
Results and Discussion

Reactions of $[\text{RuH}_2(\text{CO})(\text{PPh}_3)_3]$ **1** with urethane and urea

The reaction of $[\text{RuH}_2(\text{CO})(\text{PPh}_3)_3]$ **1** with an equimolar amount of $\text{H}_2\text{NCO}_2\text{Et}$ in refluxing toluene afforded a complex **2** showing in the IR spectrum (in toluene) two bands at 2227 and 1933 cm^{-1} . The first is strongly indicative of an isocyanato group, whereas the latter can be attributed to the initially present CO group. No band was observed that may be attributed to an NH or OH group. The mass spectrum (FAB) of the isolated product showed a parent peak at $m/z = 959$ (M^+ , highest peak of the multiplet), consistent with **2** having the formula $[\text{RuH}(\text{NCO})(\text{CO})(\text{PPh}_3)_3]$. Elemental analysis was

also consistent with this formulation. The presence of an isocyanato group is also supported by the presence of an intense peak at $M - 42$ ($M - \text{NCO}$) in the mass spectrum. This spectrum also showed the presence of a very small peak at $m/z = 1393$ (M^+ , highest peak of the multiplet), attributable to the presence of the dimeric product $[\text{Ru}_2\text{H}_2(\text{NCO})_2(\text{CO})_2(\text{PPh}_3)_4]$, formed by loss of PPh_3 from **2** followed by dimerisation. It is impossible to say whether this product has formed during the analysis or if it was present in the beginning. In the latter case it should be a very minor impurity, since elemental analysis was perfectly consistent for **2**. The signal for the hydridic hydrogen ($\delta - 7.12$, in CDCl_3) is present as doublet [$J(\text{PH}) = 103.8$] of triplets [$J(\text{PH}) = 24.4$ Hz] indicating the presence of one phosphine *trans* and two equivalent phosphines *cis* to the hydride ligand, thus establishing for **2** the stereochemistry shown in Scheme 1. The ^{31}P NMR spectrum (see Experimental section) also supports this attribution. The isocyanate ligand has been depicted as N-bonded. This appears to be the most common co-ordination mode of this ligand in transition-metal complexes. Although the assignment based on the IR stretching frequency is problematic,¹³ the correctness of this attribution is supported by the crystal structure determination of the related complex **5** (see below).

Given the identity of complex **2** we can now write the reaction leading to its synthesis as in Scheme 1. The intermediate formation of a carbamato complex can be postulated, but this is



Scheme 1

† Non-SI unit employed: bar = 10^5 Pa.

not observable even when conducting the reaction at 45 °C instead of reflux. Under these last conditions, in fact, the reaction does not proceed at all.

To the best of our knowledge, the easy loss of an alcohol from a carbamate complex has only one precedent,⁵ but the eliminated alcohol in this case was phenol and phenyl carbamates are much less stable than those derived from alkyl alcohols, analogously to the situation found for organic esters. Water elimination has also been reported to be an easy reaction, occurring from an O-bonded isomer of a carbamate complex, $[\text{Ru}(\eta\text{-C}_5\text{H}_5)\{(\text{C}_6\text{H}_{11})_2\text{P}(\text{CH}_2)_2\text{P}(\text{C}_6\text{H}_{11})_2\}\{\text{OC}(\text{O})\text{NH}_2\}]$.¹⁴ In this last case it is not known whether water elimination is preceded by an isomerisation reaction leading to a complex similar to the one proposed by us, which appears likely, or it follows a different route.

The second hydride ligand of the complex appears to be less reactive. Indeed, when the same reaction was performed by using a two-fold molar amount of urethane with respect to complex and for longer times, only **2** was obtained, with no evidence for the formation of a diisocyanate complex.

In the hope that the second step of the reaction were reversible, we conducted it in the presence of a large excess of ethanol. However, in this case the reaction proceeded to afford $[\text{Ru}(\text{CO})_3(\text{PPh}_3)_2]$ ¹⁵ as the largely dominant product, where the ruthenium atom has been reduced from the oxidation state two to zero. Such a reducing power of alcohols has many precedents. Indeed, by conducting the same reaction in the absence of urethane, the same product was obtained. However, we note that the reaction is now much slower. Thus the presence of urethane allows for a different, faster, reaction pathway. It is also to be noted that, during the reaction performed in the presence of urethane, the intermediate formation of **2** is observable by IR spectroscopy. Thus, loss of ethanol does not appear to be a reversible process in this case. On the contrary, the complexes $[\text{M}(\text{NCO})_2(\text{PPh}_3)_2]$ ($\text{M} = \text{Pt}$ or Pd) have been reported to react with CO and methanol or ethanol to yield urethanes $\text{H}_2\text{NCO}_2\text{R}$ ($\text{R} = \text{Me}$ or Et) and $[\text{M}(\text{NCO})(\text{CO}_2\text{R})(\text{PPh}_3)_2]$.¹⁶ Intermediate complexes having NHCO_2Et and even $\text{H}_2\text{NCO}_2\text{Et}$ ligands could be isolated if the reactions of the aforementioned complexes were conducted in the presence of HBF_4 and in the absence of CO.¹⁷

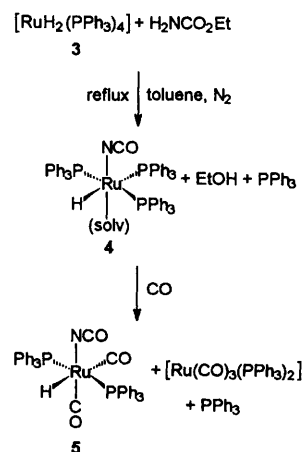
By conducting the reaction in the presence of urea instead of urethane, complex **2** was again obtained as the only metal-containing product. The other product, in place of ethanol, is likely ammonia, although its formation has not been directly observed (Scheme 2).

Reaction of $[\text{RuH}_2(\text{PPh}_3)_4]$ **3** with urethane

When the reaction was conducted by using $[\text{RuH}_2(\text{PPh}_3)_4]$ **3** as substrate in place of **1** and using an excess of urethane a mixture of products was obtained. The IR spectrum of the solution showed an intense absorption at 2227 cm^{-1} , accompanied by a weak band at 2178 cm^{-1} , which indicate the presence of at least two complexes containing the NCO ligand, one of which largely predominates over the other.* A weak band at 1931 cm^{-1} was also present which may be tentatively attributed to a Ru–H stretching. In the ^1H NMR spectrum of the isolated solid a

hydride signal was observed at $\delta -7.08$ (CDCl_3), split into a doublet [$J(\text{PH}) = 103.6$] of triplets [$J(\text{PH}) = 24.3\text{ Hz}$], together with a weak hydride signal (about 12% of the first) at $\delta -18.61$ (q, $J = 25.6\text{ Hz}$). A singlet was also present at $\delta 2.31$, with an intensity ratio 3:1 with respect to the more intense hydridic signal, which can be attributed to the methyl hydrogen atoms of a toluene molecule. The position and coupling constants of the more intense hydride peak are almost identical to those found in the spectrum of complex **2** and strongly suggest that the main product of the reaction between **3** and urethane is $[\text{RuH}(\text{NCO})(\text{C}_6\text{H}_5\text{Me})(\text{PPh}_3)_3]$ **4**, with the geometry depicted in Scheme 3.

This formulation is further supported by the ^{31}P NMR spectrum (hydrogen decoupled) of the isolated solid in which the two most intense signals [$\delta 40.8$, d, $J(\text{PP}) = 15.2$, 2 P; 17.49 , t, $J(\text{PP}) = 15.2\text{ Hz}$, 1 P] closely parallel those observed for complex **2**. However, other weaker signals were present indicating that the complex is not pure. The presence of the toluene molecule in the structure is supported by the



Scheme 3

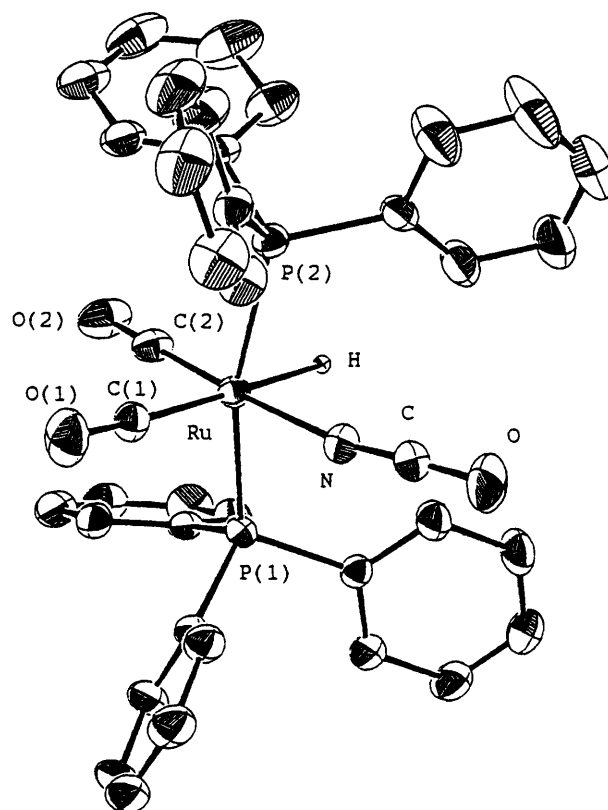


Fig. 1 An ORTEP¹⁹ drawing of $[\text{RuH}(\text{NCO})(\text{CO})_2(\text{PPh}_3)_2]$ **5**. Thermal ellipsoids are drawn at the 30% probability level



Scheme 2

* Since $[\text{RuH}_2(\text{PPh}_3)_4]$ is known easily to dissociate a phosphine ligand in solution and to co-ordinate even weak ligands such as dinitrogen,¹⁸ to afford a complex showing an IR absorption at 2143 cm^{-1} , we considered the possibility that the band at 2178 cm^{-1} was due to a N–N vibration of a dinitrogen complex. However, treating the solution with CO (see later) did not lead to the disappearance of this band. So the formation of a dinitrogen complex is excluded.

Table 1 Selected interatomic distances (Å) and angles (°) for complex **5**

Ru–P(1)	2.378(1)	N–C	1.119(4)
Ru–P(2)	2.373(1)	O–C	1.214(4)
Ru–N	2.115(3)	P(1)–C(111)	1.825(3)
Ru–C(1)	1.968(4)	P(1)–C(121)	1.835(3)
Ru–C(2)	1.857(4)	P(1)–C(131)	1.835(3)
Ru–H	1.79(3)	P(2)–C(211)	1.836(3)
O(1)–C(1)	1.122(4)	P(2)–C(221)	1.823(3)
O(2)–C(2)	1.138(4)	P(2)–C(231)	1.832(3)
P(1)–Ru–P(2)	163.62(3)	N–Ru–C(2)	176.0(1)
P(1)–Ru–N	87.74(8)	N–Ru–H	90.1(10)
P(1)–Ru–C(1)	98.1(1)	C(1)–Ru–C(2)	92.9(2)
P(1)–Ru–C(2)	92.1(1)	C(1)–Ru–H	178.8(11)
P(1)–Ru–H	82.2(10)	C(2)–Ru–H	85.9(10)
P(2)–Ru–N	86.75(8)	Ru–N–C	167.0(3)
P(2)–Ru–C(1)	97.4(1)	Ru–C(1)–O(1)	176.5(3)
P(2)–Ru–C(2)	92.3(1)	Ru–C(2)–O(2)	179.7(7)
P(2)–Ru–H	82.4(10)	N–C–O	177.5(4)
N–Ru–C(1)	91.1(1)		

forementioned detection of a signal for the methyl hydrogens in the ^1H NMR spectrum, in the correct intensity ratio with respect to the hydridic signal. However, we cannot exclude that the toluene molecule is only clathrated in the solid and not actually co-ordinated. Complex **4** would then be unsaturated, which is not unusual for complexes containing the $\text{Ru}(\text{PPh}_3)_3$ moiety. A referee has suggested that the hydride signal at $\delta -18.61$ may be due to the non-toluene-containing five-co-ordinated complex $[\text{RuH}(\text{NCO})(\text{PPh}_3)_3]$. The fluxional nature of such complexes may indeed explain the observed splitting, a quartet, as arising from three equivalent phosphines.

Reaction of $[\text{RuH}(\text{NCO})(\text{C}_6\text{H}_5\text{Me})(\text{PPh}_3)_3]$ **4** with CO

Since attempts to isolate complex **4** in a pure state or to obtain good mass spectra failed, we attempted to substitute the solvent molecule of the complex by CO, in order to observe the formation of **2**. On bubbling CO through the solution it was possible to observe the growth of several new bands at 2043, 1981, 1953 and 1899 cm^{-1} , the relative intensities of which changed with the reaction time. The last band is attributable to $[\text{Ru}(\text{CO})_3(\text{PPh}_3)_2]$. Only a very weak band at 1932 cm^{-1} , attributable to **2**, was observed a few minutes after the beginning of the bubbling, indicating that the previously isolated isomer of **2** is surely not the kinetic product of substitution of toluene by CO in **4**. The position of the NCO band shifted to 2235 cm^{-1} , in accord with the lower back donation of the metal to the NCO ligand due to the contemporary presence of at least one CO ligand in the product. The weak band at 2178 cm^{-1} did not shift appreciably.

After 1 h of bubbling the two most intense carbonyl bands were those at 2043 and 1981 cm^{-1} . Dissolution of the isolated solid product in tetrahydrofuran (thf) and layering with hexane afforded some yellow crystals of the complex $[\text{RuH}(\text{NCO})(\text{CO})_2(\text{PPh}_3)_2]$ **5**, the structure of which has been solved by X-ray crystallography.

Crystal structure of $[\text{RuH}(\text{NCO})(\text{CO})_2(\text{PPh}_3)_2]$ **5**

Crystals of compound **5** contain $[\text{RuH}(\text{NCO})(\text{CO})_2(\text{PPh}_3)_2]$ and tetrahydrofuran molecules separated by normal van der Waals interactions with a molar ratio of ca. 1 : 1 (Fig. 1, Table 1). The clathrated thf molecules display high displacement parameters and are partially disordered; no assignment of the C and O atoms could be made on the basis of the bond distances and angles which are affected by high estimated standard deviations (e.s.d.s) and therefore all the atoms were refined as C atoms. The complex molecule possesses an almost C_s symmetry, with the idealised mirror plane passing through the metal atom,

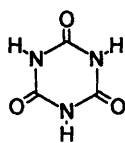
the two carbonyls, the isocyanate and the hydride ligands. The ruthenium atom displays a slightly distorted octahedral co-ordination geometry, with the P–Ru–P moiety bent towards the less hindering hydride ligand [163.62(3)°]. From an inspection of the bond distances of the carbonyl ligands the high *trans* influence of the hydride ligand can be clearly seen: the Ru–C(1) distance is about 0.1 Å longer than Ru–C(2). Conversely the C(1)–O(1) distance is slightly but within the limit of significance shorter than C(2)–O(2).

The isocyanato moiety is almost linearly co-ordinated to the ruthenium atom, through the N atom. In spite of their purported existence on the basis of spectroscopic data,¹³ no structure determination of compounds containing terminal monodentate O-co-ordinated isocyanates has been reported. Only a few examples are known where the cyanate ligand bridges two metal atoms in a end-to-end (*exo*-bidentate) fashion, thus involving the O atom in the co-ordination (see for instance ref. 20). Other than being in agreement with spectroscopic results, N-co-ordination can be confirmed in the present complex by a crystallographic test. If we assume O-co-ordination here, the following improbable values for the atomic displacement parameters (B_{equiv}) are obtained for the OCN ligand: O, 5.8; C, 4.5 and N, 6.0 Å². These values do not follow the correct sequence $\text{N} > \text{C} > \text{O}$ that would be expected for a terminally bound appendage. The geometrical parameters are also in line with those reported for other terminal N-co-ordinated isocyanate moieties [compare, for instance, the N–C and C–O bond lengths of 1.119(4) and 1.214(4) Å respectively, with the corresponding interactions of 1.157(5) and 1.206(5) Å reported in ref. 21].

Reactions of complexes **1–3** with olefins and urethane

On treating complexes **1** and **2** with an excess of hex-1-ene no reaction could be observed by IR (toluene) and ^1H NMR (CDCl_3) spectroscopy at temperatures up to 57 °C. Even on mixing **2** and norbornene [bicyclo[2.2.1]hept-2-ene], an olefin known to give stable insertion products because of the accompanying release of steric strain,² at 90 °C no reaction was observed. By comparison, it should be noted that $[\text{RuH}(\text{Cl})(\text{PPh}_3)_3]$ is known to insert olefins,²² but the activity of $[\text{RuH}(\text{X})(\text{CO})(\text{PPh}_3)_3]$ has been reported to depend on the identity of X,²³ and $[\text{RuH}(\text{Cl})(\text{CO})(\text{PPh}_3)_3]$ inserts allylamines only after the amine group has co-ordinated, displacing a phosphine ligand,²⁴ otherwise pressure is required to observe insertion of ethylene.²⁵ However, some reaction must occur, at least at high temperatures. Indeed when we attempted catalytic reactions using either **1** or **2** as catalyst, in the presence of urethane or urea and hex-1-ene (molar ratio urethane or urea to Ru = 100 : 1 and olefin : Ru = 100 : 1) at temperatures up to 180 °C,* no organic isocyanate was obtained, but the starting hexene was completely isomerised to a thermodynamic mixture of hex-1-, -2- and -3-ene. This isomerisation indicates that **2**, or a complex derived from it by loss of a ligand at high temperature, is able reversibly to insert an olefin, to afford an alkyl complex which may then react by β -H elimination to afford the eventually isomerised olefin. It is important to realise that the alkyl and the isocyanato group are necessarily in *cis* position in the intermediate complex. However, there seems not to be any thermodynamic driving force towards the reductive elimination of the alkyl isocyanate. However, at the end of the reactions conducted at 180 °C, some white insoluble residue was also present which, from its mass spectrum, mainly contains the trimer of isocyanic acid. The mass spectrum also shows the presence of minor amounts of two other products which correspond to the formulations $(\text{HN})_2(\text{CO})_3$ and

* Reactions at high temperatures were conducted inside an autoclave under 10 bar dinitrogen, to avoid evaporation of the solvent and of the olefin.



(HN)₃(CO)₄. It is not clear whether the formation of these products derives from a reductive elimination of HCNO from **2** or not. Direct thermolysis of **2** under the reaction conditions failed to yield detectable amounts of isocyanic acid trimer, but this may be due to the very low amount of such a product that would be formed in a stoichiometric reaction. Anyway, the metal surely plays a role, since, in the absence of it, urethane was stable under the same conditions. Only a trace amount of HCNO and no trimer were detected at the end of the reaction.

Use of complex **3** in place of **1** or **2** in catalytic reactions also failed to yield any alkyl isocyanate, even when activated olefins or alkynes were used as substrates and even in the presence of Lewis-acid cocatalysts or photostimulation.

Conclusion

We have examined the reactivity of urethane and urea with respect to two different ruthenium hydride complexes and found that easy loss of alcohol or ammonia from an intermediate N-bonded carbamate or ureido complex affords isocyanato complexes in good yields. The reactivity of these complexes towards unsaturated ligands such as olefins and CO has been investigated. Whereas with olefins only isomerisation reactions were observed, CO substituted other ligands to yield carbonyl complexes, the structure of one of which has been solved by X-ray crystallography. Although only the reactions of two complexes have been discussed in detail, preliminary results in our laboratories²⁶ show that the reactivity pattern disclosed is much more general. The presence of an hydride ligand on the starting complex is not necessary, since we found that reaction of [Ru₃(CO)₁₂] with urethane in refluxing toluene also afforded a mixture of isocyanate complexes. It should be noted that the same reaction, at lower temperatures, had previously been reported to yield a carbamate complex analogous to the ones here suggested as intermediates, albeit in low yield.⁶ We observed the formation of isocyanate complexes even in palladium-based systems, where palladium acetate and several proligands were used as starting materials.²⁶ Thus this reaction appears to be a new and quite general entry to isocyanato complexes, which does not require the use of hazardous materials. Attempts to effect the catalytic synthesis of organic carbamates or isocyanates by reaction of these complexes with olefins failed, due to the high stability of the co-ordinated isocyanato group. We have now succeeded in performing the catalytic synthesis of alkyl carbamates by reaction of urethane with olefins using a different catalytic system and the results will be reported elsewhere.²⁷ What emerges even from these other studies is that in order for the reaction to be successful the carbamate must directly attack a co-ordinated olefin without previously interacting with the metal. Whenever interaction of the carbamate with the metal occurs, formation of stable isocyanate complexes takes place and the catalytic reaction does not proceed.

Experimental

General procedures

Unless otherwise stated, all reactions and manipulations were conducted under a dinitrogen atmosphere, using standard Schlenk apparatus and cannula techniques. Solvents were dried by standard procedures and stored under dinitrogen before use. The complexes [RuH₂(CO)(PPh₃)₃],²⁸ [RuH₂(PPh₃)₄],²⁹ and [Ru(CO)₃(PPh₃)₂]¹⁵ were prepared by literature methods.

All other reagents were commercial products used as received. The IR spectra were recorded on a Bio-Rad FTS-7 FT-IR spectrophotometer, NMR spectra on a Bruker AC 200 FT (200 MHz). The GC mass spectrometric analyses were performed on a Hewlett-Packard 5890 gas chromatograph, coupled with a 5971A mass-selective detector, quantitative GC analyses on a Perkin-Elmer 8420 capillary gas chromatograph, equipped with a PSS 255 column.

Synthesis of [RuH(NCO)(CO)(PPh₃)₃] **2**

To a Schlenk flask (50 cm³) was added [RuH₂(CO)(PPh₃)₃] **1** (300 mg, 0.33 mmol) and dissolved in toluene (10 cm³). Urethane (29 mg, 0.33 mmol) was then added and heating started. Essentially no reaction was observed at temperatures lower than the reflux one (110 °C). After 3 h at reflux the reaction was stopped by cooling at 0 °C and the product precipitated by addition of hexane (20 cm³) at this temperature. The yellow-green solid was filtered off, washed with hexane (10 cm³) and dried *in vacuo* (253 mg, 0.26 mmol, 80% isolated yield) [Found: C, 69.8; H, 5.05; N, 1.3%; *m/z* (FAB) 959 (*M*⁺, highest peak of the multiplet). C₅₆H₄₆NO₂-P₃Ru requires C, 70.1; H, 4.8; N, 1.5%; *m/z* 959 (highest peak of the simulated multiplet)]. $\tilde{\nu}_{\max}/\text{cm}^{-1}$ (Nujol) 2231vs (NCO), 1987vw (M-H) and 1925vs (CO); (toluene) 2227vs (NCO) and 1933vs cm⁻¹ (CO). δ_{H} (200 MHz, solvent CDCl₃, internal deuterium lock) -7.12 [d, *J*(PH) = 103.8, of t, *J*(PH) = 24.4]. δ_{P} (200 MHz, solvent CDCl₃, decoupling hydrogen) 40.66 [2 P, d, *J*(PP) 15] and 17.31 [1 P, t, *J*(PP) 15 Hz]. The reaction between **1** and urea was conducted similarly and afforded the same product.

Reaction of [RuH₂(CO)(PPh₃)₃] **1** with urethane in the presence of EtOH

The same procedure was used as for the previous reaction, but EtOH (2 cm³) was also added. The solution was refluxed and additional EtOH (2 cm³) was added every 2 h. After 6 h the largely dominant absorption in the IR spectrum was at 1899 cm⁻¹, although a small absorption at 1941 cm⁻¹ due to the starting material was still observable, together with weaker bands due to complex **2**. The attribution of the most intense band to [Ru(CO)₃(PPh₃)₂]¹³ (based on a comparison with an authentic sample) was also confirmed by the mass spectrum of the solid obtained by precipitation of the reaction mixture with hexane [*m/z* (FAB) 710 (*M*⁺, highest peak in the multiplet); subsequent loss of three CO groups was also observed). C₃₉H₃₀O₃P₂Ru requires *m/z* 710 (*M*⁺, highest peak of the multiplet)]. The same procedure was used for a reaction in the absence of urethane, but refluxing for about 30 h was necessary to reach the same extent of conversion.

Reaction of [RuH₂(PPh₃)₄] **3** with urethane

To a Schlenk flask (50 cm³) was added [RuH₂(PPh₃)₄] (176 mg, 0.153 mmol) and dissolved in toluene (10 cm³). Urethane (138 mg, 1.55 mmol) was then added and the solution refluxed for 1 h. The IR spectrum of a small portion of the solution at this stage, dried *in vacuo*, showed absorptions at $\tilde{\nu}_{\max}/\text{cm}^{-1}$ (Nujol) 2227vs (NCO), 2178w (NCO), 1931vw (M-H) and 1738vs (H₂NCO₂Et). The reaction was stopped by cooling at 0 °C and the product precipitated by addition of hexane (20 cm³) at this temperature. δ_{H} (200 MHz, solvent CDCl₃, internal deuterium lock) 2.31 (s), -7.08 [d, *J*(PH) = 103.6, of t, *J*(PH) = 24.3] and -18.61 (q, *J* = 25.6 Hz). δ_{P} (200 MHz, solvent CDCl₃, decoupling hydrogen) 40.8 [2 P, d, *J*(PP) 15.2] and 17.49 [1 P, t, *J*(PP) 15.2]; weaker signals at 78.5 (t, *J* = 25), 53.9 (t, *J* = 25), 44.79 (d, *J* = 27.7), 44.2 (s) and 31.6 (d, *J* = 27.3 Hz); strong signals were also observed at δ_{P} 29.60 (s, PPh₃O) and -4.92 (s, PPh₃). See the Results and Discussion section.

Reaction of $[\text{RuH}(\text{NCO})(\text{C}_6\text{H}_5\text{Me})(\text{PPh}_3)_3]$ **4** with CO

The reaction described in the previous paragraph was repeated, but instead of adding hexane at the end CO was bubbled through the solution at ambient temperature. After 1 h the solution showed IR absorptions at $\tilde{\nu}_{\text{max}}/\text{cm}^{-1}$ (toluene) 2235vs (NCO), 2178w (NCO), 2043ms (CO), 2014w (CO), 1981vs (CO), 1950w (CO), 1899m (CO) and 1738vs ($\text{H}_2\text{NCO}_2\text{Et}$). Half of the solution was separated, evaporated *in vacuo* and dissolved in thf. Yellow-green crystals of compound **5** suitable for X-ray diffraction were obtained by slow diffusion of hexane in this solution. The IR spectrum of one of these crystals dissolved in toluene (recorded with a micro IR cell) showed absorptions at $\tilde{\nu}_{\text{max}}/\text{cm}^{-1}$ (toluene) 2235s (NCO), 2043s (CO) and 1981vs (CO). The remaining part of the reaction solution was subjected to additional bubbling of CO. The band at 1899 cm^{-1} , attributable to $[\text{Ru}(\text{CO})_3(\text{PPh}_3)_2]$ by comparison with an authentic sample, gradually increased over 12 h, with the relative intensity of the other bands remaining almost unchanged. After this time no further variation was observed over 24 h.

General procedures for the reactions with olefins and urethane or urea

In a typical reaction the catalyst (complex **1**, **2** or **3**; 0.0655 mmol), hex-1-ene (550 mg, 6.55 mmol), urethane or urea (6.55 mmol) and toluene (10 cm^3) were added to a glass liner. The liner was placed inside an autoclave, frozen at -78°C , evacuated and filled with N_2 (10 bar, measured at room temperature). The autoclave was then heated in an oil-bath for 3 h, cooled with ice and vented. Modification of the above-mentioned procedure included prolonging the reaction time, changing the solvent or the olefin (see the Results and Discussion section). Reactions at lower temperatures were also performed. At the end of many reactions a white residue was present on the bottom of the glass liner, the mass spectrum of which showed a parent peak at m/z 129 (electron impact, EI) ($\text{H}_3\text{C}_3\text{N}_3\text{O}_3$) and lower-intensity peaks at m/z 114 and 157. After a reaction employing diphenylacetylene instead of an olefin the mass spectrum of the residue included peaks at m/z 178 (diphenylacetylene) and 533 (hexaphenylbenzene). Similar concentrations were also employed for reactions run under milder conditions in a Schlenk flask.

Crystallography

Crystal data. Crystals of complex **5** are triclinic, space group $P\bar{1}$ (no. 2), $a = 10.218(4)$, $b = 11.388(3)$, $c = 17.404(3)$ Å, $\alpha = 96.43(2)$, $\beta = 91.68(2)$, $\gamma = 97.26(2)^\circ$, $U = 1994(1)$ Å³, $Z = 2$, $D_c = 1.33$ g cm^{-3} , $\mu(\text{Mo-K}\alpha) = 5.0$ cm^{-1} , $F(000) = 820$.

Preliminary examination of a crystal ($0.08 \times 0.10 \times 0.25$ mm), mounted on a glass fibre in a random orientation, and data collection were performed with graphite-monochromatised Mo-K α radiation ($\lambda = 0.71073$ Å) on an Enraf-Nonius CAD4 diffractometer. Cell constants and an orientation matrix for data collection were obtained from least-squares refinement, using the setting angles of 25 reflections, measured by the computer-controlled diagonal-slit method of centring. 6662 Reflections were collected at room temperature using an ω -scan mode with variable scan rate. As a check on crystal and electronic stability, three representative reflections were measured every 2 h and showed a decay of the scattering power during the data collection, probably due to the loss of solvent molecules, which was about 15% on I at the end of data collection.

Lorentz-polarisation and an empirical absorption correction were applied to the data. The structure was solved by Patterson and Fourier methods and refined by full-matrix least squares minimising the function $\Sigma w(|F_o| - |F_c|)^2$. Scattering factors were taken from ref. 30. Anomalous dispersion effects were

included in F_c ; the values for $\delta f'$ and $\delta f''$ were taken from ref. 31. The location of the hydride bound to the metal atom was possible by inspection of a Fourier-difference map: its coordinates and displacement parameter were included in the refinement. All the remaining hydrogen atoms were placed at calculated positions (C–H 0.95 Å) and not refined. The final conventional R and R' indices, $\Sigma(F_o - k|F_c|)/\Sigma F_o$; and $[\Sigma w(F_o - k|F_c|)^2/\Sigma wF_o^2]^{1/2}$, are 0.037 and 0.049, respectively, for 4875 observed reflections having $I > 3\sigma(I)$; $w = 1/[\sigma(F_o)] = [\sigma^2(I) + (0.04I)^2]^{1/2}/2F_oL_p$. Calculations were performed on a 80486/33 computer using Personal SDP software.³²

Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/117.

Acknowledgements

One of us (T. L.) thanks the Italian CNR (Consiglio Nazionale delle Ricerche) for a fellowship. Thanks are also due to Progetto Strategico Tecnologie Chimiche Innovative of CNR for financial support.

References

- 1 D. M. Roundhill, *Chem. Rev.*, 1992, **92**, 1 and refs. therein.
- 2 A. L. Casalnuovo, J. C. Calabrese and D. J. Milstein, *J. Am. Chem. Soc.*, 1988, **110**, 6738.
- 3 S. Cenini, M. Pizzotti and C. Crotti, in *Aspects of Homogeneous Catalysis*, ed. R. Ugo, D. Reidel, Dordrecht, 1988, vol. 6, pp. 97–198.
- 4 *Ullmann's Encyclopedia of Industrial Chemistry*, VCH, Weinheim, 1989, vol. A5, p. 51; *Kirk-Othmer Encyclopedia of Chemical Technology*, 3rd edn., Wiley, New York, 1983, vol. 23, p. 548.
- 5 C. Woodcock and R. Eisenberg, *Organometallics*, 1982, **1**, 886.
- 6 T. Jenke, H. Stoeckli-Evans, U. Bodensieck and G. Suss-Fink, *J. Organomet. Chem.*, 1991, **401**, 347.
- 7 U. Bodensieck, J. Santiago, H. Stoeckli-Evans and G. Suss-Fink, *J. Organomet. Chem.*, 1992, **433**, 141.
- 8 U. Bodensieck, H. Stoeckli-Evans and G. Suss-Fink, *Chem. Ber.*, 1990, **123**, 1603.
- 9 U. Bodensieck, H. Stoeckli-Evans, G. Rheinwald and G. Suss-Fink, *J. Organomet. Chem.*, 1992, **433**, 167.
- 10 E. Boroni, G. Predieri, A. Tiripicchio and M. Tiripicchio Camellini, *Organometallics*, 1992, **11**, 3456.
- 11 S. Okeya, S. Koshino, M. Namie, I. Nagasawa and Y. Kushi, *J. Chem. Soc., Chem. Commun.*, 1995, 2123.
- 12 M. B. Hursthouse, M. A. Mazid, S. D. Robinson and A. Sahajpal, *J. Chem. Soc., Chem. Commun.*, 1991, 1146; *J. Chem. Soc., Dalton Trans.*, 1993, 2835; S. D. Robinson, A. Sahajpal and D. A. Tocher, *J. Chem. Soc., Dalton Trans.*, 1995, 3497.
- 13 A. H. Norbury, *Adv. Inorg. Chem. Radiochem.*, 1975, **17**, 231 and refs. therein.
- 14 F. L. Joslin, M. Pontier Johnson, J. T. Mague and D. M. Roundhill, *Organometallics*, 1991, **10**, 2781.
- 15 N. Ahmad, J. J. Levison, S. D. Robinson and M. F. Uttley, *Inorg. Synth.*, 1974, **15**, 50.
- 16 W. Beck and C. v. Werner, *Chem. Ber.*, 1971, **104**, 2901.
- 17 C. v. Werner and W. Beck, *Chem. Ber.*, 1972, **105**, 3947.
- 18 T. Ito, S. Kitazume, A. Yamamoto and S. Ikeda, *J. Am. Chem. Soc.*, 1970, **92**, 3011.
- 19 C. K. Johnson, ORTEP, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.
- 20 A. Escuer, R. Vicente, J. Ribas, M. S. El Fallah, X. Solans and M. Font-Bardia, *Inorg. Chim. Acta*, 1994, **216**, 5 and refs. therein; L. Walz and W. Haase, *J. Chem. Soc., Dalton Trans.*, 1985, 1243 and refs. therein.
- 21 C.-M. Che, W.-T. Tang, W.-O. Lee, W.-T. Wong and T.-F. Lai, *J. Chem. Soc., Dalton Trans.*, 1989, 2011.
- 22 G. Alibrandi and B. E. Mann, *J. Chem. Soc., Dalton Trans.*, 1994, 951.
- 23 J. T. Poulton, M. P. Sigalas, O. Eisenstein and K. G. Caulton, *Inorg. Chem.*, 1993, **32**, 5490.
- 24 K. Hiraki and T. Matsunaga, *Organometallics*, 1994, **13**, 1878.

- 25 P. S. Hallman, B. R. McGarvey and G. Wilkinson, *J. Chem. Soc. A*, 1968, 3143.
- 26 F. Ragaini, T. Longo and S. Cenini, unpublished work.
- 27 F. Ragaini, T. Longo and S. Cenini, *J. Mol. Catal. A*, submitted for publication.
- 28 N. Ahmad, J. J. Levison, S. D. Robinson and M. F. Uttley, *Inorg. Synth.*, 1974, **15**, 45.
- 29 J. J. Levison and S. D. Robinson, *J. Chem. Soc. A*, 1970, 2947.
- 30 D. T. Cromer and J. T. Waber, *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4, Table 2.2B.
- 31 D. T. Cromer, *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4, Table 2.3.1.
- 32 B. Frenz, *Comput. Phys.*, **2**, 1988, No. 3 (May/June), pp. 42–48; B. Frenz, *Crystallographic Computing 5*, Oxford University Press, 1991, ch. 11, pp. 126–135.

Received 19th February 1996; Paper 6/01182I