Preparation and Reactivity of Mixed-Ligands Hydride Complexes [RuHCl(CO)(PPh₃)₂{P(OR)₃}]

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Abstract. Mixed-ligands hydride complexes [RuHCl(CO)(PPh₃)₂{P(OR)₃}] (2) (R = Me, Et) were prepared by allowing [RuHCl(CO)(PPh₃)₃] (1) to react with an excess of phosphites P(OR)₃ in refluxing benzene. Treatment of hydrides **2** first with triflic acid and next with an excess of hydrazine afforded hydrazine complexes [RuCl(CO)(κ^1 -NH₂NHR1)(PPh₃)₂{P(OR)₃}]BPh₄

 $)(PPh_3)_2\{P(OR)_3\}]BPh_4$

Introduction

Previous reports from our laboratories dealt with studies on the synthesis and reactivity of hydride-carbonyl complexes of osmium [OsHCl(CO)(PPh₃)L] [L = P(OMe)₃ and P(OEt)₃], which allowed the preparation of new organic azide and hydrazine derivatives [OsCl(κ^1 -N₃R)(CO)(PPh₃)₂L]BPh₄ and [OsCl(CO)(κ^1 -NH₂NHR)(PPh₃)₂L]BPh₄.^[1] The interesting properties shown by these mixed-ligands carbonyl complexes prompted us to extend study to ruthenium^[2] with the aim of testing whether related hydride-carbonyl complexes may be prepared and how they properties change. The results of these studies, which involve the preparation of mixed-ligands hydrazine and diethylcyanamide complexes of ruthenium and the crystallographic structure determination of [RuHCl(CO)– (PPh₃)₂{P(OEt)₃}], are reported herein.

Results and Discussion

The hydride-carbonyl complex $[RuHCl(CO)(PPh_3)_3]$ (1) had been prepared by reacting $RuCl_3 \cdot 3H_2O$ with PPh_3 in refluxing 2-methoxyethanol and aqueous formaldehyde.^[3] We found that 1 can be prepared in good yield by refluxing the dichloro compound $[RuCl_2(PPh_3)_3]$ in ethanol in the presence of Zn dust. The addition of the metal is crucial for successful synthesis, otherwise only traces of hydride complex are obtained. No other characterizable species was obtained from this reaction, which represents an easy and efficient method for the preparation of this precursor.

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(3, 4) $(R1 = H, CH_3)$. Diethylcyanamide derivatives [RuCl(CO)(N=CNEt₂)(PPh₃)₂{P(OR)₃}]BPh₄ (5) were also prepared by reacting **2** first with HOTf and then with N=CNEt₂. The complexes were characterized spectroscopically and by X-ray crystal structure determination of [RuHCl(CO)(PPh₃)₂{P(OEt)₃}] (**2b**).

The hydride $[RuHCl(CO)(PPh_3)_3]$ (1) reacts with an excess of phosphite $P(OR)_3$ in benzene to give mixed-ligands derivatives $[RuHCl(CO)(PPh_3)_2\{P(OR)_3\}]$ (2), which were isolated and characterized (Scheme 1).





The reaction proceeds with the substitution of only one PPh₃ ligand affording the new hydride-carbonyl derivatives containing two PPh₃ and one phosphite as supporting ligands. Good analytical data were obtained for complexes **1** and **2**, which were isolated as yellow solids stable in air and in solution of common organic solvents, where they behave as either nonelectrolytes.^[4] Their IR and NMR spectroscopic data support the proposed formulation, which was further confirmed by X-ray crystal structure determination of the complex [RuHCl(CO)(PPh₃)₂{P(OEt)₃}] (**2b**). Figure 1 shows the ORTEP^[5] plot and selected bond lengths and angles are given in Table 1.



Figure 1. ORTEP^[5] view of the complex $[RuHCl(CO)(PPh_3)_2{P(OEt)_3}]$ (2b).

The compound contains three phosphane ligands, organized in a meridional configuration, and one carbonyl and one chlorine ligands, *trans* to each other. One hydride ligand completes



Table 1. S	selected bor	d lengths	/Å and	angles /	∕° for	2b
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Ru(1)-H(1)	1.60(4)	Ru(1)–C(1)	1.825(7)
Ru(1) - P(1)	2.3604(17)	Ru(1)-P(2)	2.3775(15)
Ru(1)–P(3)	2.3602(15)	Ru(1)-Cl(1)	2.4630(15)
C(1)–O(1)	1.137(7)		
C(1)-Ru(1)-P(1)	88.7(2)	C(1)-Ru(1)-P(2)	92.42(18)
C(1)-Ru(1)-P(3)	90.00(18)	C(1)-Ru(1)-Cl(1)	176.2(2)
P(1)-Ru(1)-P(2)	101.06(6)	P(2)-Ru(1)-P(3)	159.75(5)
P(1)-Ru(1)-P(3)	99.10(6)	P(1)-Ru(1)-Cl(1)	95.17(6)
P(2)-Ru(1)-Cl(1)	87.09(5)	P(3)-Ru(1)-Cl(1)	89.15(5)
H(1)-Ru(1)-C(1)	85.1(15)	H(1)-Ru(1)-P(1)	173.4(15)
H(1)-Ru(1)-P(2)	81.2(14)	H(1)-Ru(1)-P(3)	79.0(14)
H(1)-Ru(1)-Cl(1)	91.1(15)	Ru(1)-C(1)-O(1)	178.8(6)

the octahedral environment for the Ru^{II} metal atom. Among phosphanes, there is one phosphite ligand, situated *trans* to the hydride ligand, and two triphenylphosphines *trans* to each other.^[6]

The Ru–P bond lengths range between 2.3602(15) and 2.3775(15) Å, and there is no difference between the phosphine and phosphite coordination distances.

This could sound surprising, since differences due to σ - and π -bonding of phosphane and phosphine ligands are wellknown and, for example, Ru–P distances are clearly different when they are *trans* to similar ligand, as Cp or related ones.^[2d,7] But in the case of the title compound **2b**, probably the higher π -acidity of the phosphite is balanced out by the hydride in *trans* position.^[8] In any case, the Ru–P distances formed by the phosphines (2.37 Å in average) are comparable to those found for complexes with similar arrangements, as the *trans* Ru–P distances of 2.358 and 2.396 Å found for RuH(CO)Cl(PPh₃)₃.^[9]

The carbonyl Ru–C bond length, 1.825(7) Å, is only slightly shorter than that found in the tris(triphenylphosphine) compound RuH(CO)Cl(PPh₃)₃ [1.837(6) Å],^[9] whereas the C–O distance, 1.137(7) Å, does not show difference with reported values for that compound, 1.141(6) Å. The Ru–Cl bond length 2.4630(15) Å (*trans* to the carbonyl ligand) is also slightly shorter than that in the aforementioned compound [2.499(1) Å].

The two trans PPh₃ ligands are bent towards the position occupied by the hydride ligand, with a trans P-Ru-P angle of 159.75(5)° and obtuse cis P-Ru-P angles of 99.10(6) and 101.06(6)°. This bending is usual in hydride compounds, probably due to the scarce steric hindrance of the hydrogen atom,^[9,10] together with the high steric requirements of the PPh₃ ligands. The *trans* Cl–Ru–carbonyl angle, 176.2(2)°, is however close to theoretical 180°. Cis angles in the Cl-Ru-carbonyl meridional plane are acute for OC-Ru-P(1), 88.7(2)°, and obtuse for Cl-Ru-P(1) angle, 95.17(6)°, undoubtedly due to the relative disposition of $P(OEt)_3$ as can be seen in Figure 2(left), where is apparent the steric limitation on the chlorine position due to the ethoxy group of the phosphite ligand (whose phosphorus atom is hidden by the metal atom). Obviously the inaccuracy of the position of the hydride in X-ray diffraction technique prevents any comment about its geometrical parameters. The Ru(1)-C(1)-O(1)angle, 178.8(6)°, is not surprising.



The IR spectra of the mixed-ligands hydride complexes $[RuHCl(CO)(PPh_3)_2 \{P(OR)_3\}]$ (2) show one strong band at 1957 (2a) and 1956 cm⁻¹ (2b) attributed to the v(CO) of the carbonyl ligand. These bands fall at a value slightly higher than that of the related complex 1, in agreement with the better π -acceptor properties of phosphite P(OR)₃ with respect to PPh₃. In the spectra a weak band at 1886 (**2a**) and 1903 cm^{-1} (2b) is also present and was attributed to the v(RuH) of the hydride. The presence of such a ligand is confirmed by the ¹H NMR spectra, which show a doublet of triplets at -5.62 (2a) and -5.74 ppm (2b) due to the hydride ligand coupled with the ³¹P nuclei of phosphine. The value of one $J_{\rm HP}$ is in the range 177-174 Hz, whereas the other falls at 21.0-20.5 Hz suggesting that the hydride is *trans* to one phosphine and *cis* to the other two. In addition, in the temperature range between +20 and -80 °C, the ³¹P{¹H} NMR spectra appear as AX_2 multiplets suggesting that the two PPh₃ are magnetically equivalent and different from the phosphite. On this basis, mer arrangement II (Scheme 1) may be proposed in solution for mixed-ligands hydrides 2, like that found in the solid state (Figure 1).

Hydrazine and Cyanamide Complexes

Hydride complexes **1** and **2** reacted with triflic acid at low temperature (-80 °C) with evolution of H₂ – detected by ¹H NMR – and probable formation of a triflate species like [RuCl(κ^1 -OTf)(CO)(PPh₃)₂{P(OR)₃}] [**A**]. Unfortunately, these species are unstable also in solution and cannot be isolated. However, they can be used as precursors to prepare new complexes. In fact, treatment of the triflate complexes formed by protonation of **2** with an excess of hydrazine afforded the cationic complexes [RuCl(CO)(κ^1 -NH₂NHR1)(PPh₃)₂{P(OR)₃}]⁺ (**3**, **4**) [*R*1 = H (**3**), CH₃ (**4**); *R* = Me (**a**), Et (**b**)] which were isolated as tetraphenylborate salts and characterized (Scheme 2).

Diethylcyanamide $N \equiv CNEt_2$ also reacted with the triflate species [A] to give the cyanamide derivatives [RuCl(CO)(N \equiv CNEt_2)(PPh_3)_2{P(OR)_3}]BPh_4 (5) in good yields (Scheme 3).

Instead, treatment of the triflate complex [A] with organic azide $R2N_3$ did not afford any stable compound but only decomposition products (Scheme 4).

This result is rather unexpected because the related osmium triflate compounds $[OsCl(\kappa^1-OTf)(CO)(PPh_3)_2\{P(OR)_3\}]$

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Scheme 2. R1 = H(3), $CH_3(4)$; R = Me(a), Et(b).



Scheme 3. R = Me(a), Et(b).



Scheme 4. $R2 = ArCH_2$ or Ph.

quickly reacted with organic azides to give azide derivatives $[OsCl(CO)(\kappa^1-N_3R2)(PPh_3)_2\{P(OR)_3\}]BPh_4$, which are stable and isolable.^[1] The ruthenium fragment, instead, is not able to stabilize azide as a ligand. However, both hydrazine and diethylcyanamide can be stabilized by the carbonyl fragments $[RuCl(CO)(PPh_3)_2\{P(OR)_3\}]^+$ allowing the preparation of new derivatives.^[11] Hydrazine complexes of ruthenium have been previously reported with several ligands including arene, phosphine, isocyanide, cyclopentadienyl, and tris(pyrazolyl)borate and have been studied as models of the dinitrogen fixation process.^[2d,e,h,12,13] The use of the hydride $[RuHCl(CO)(PPh_3)_2\{P(OR)_3\}]$ as a precursor allowed the synthesis of mixed-ligands hydrazine derivatives.

The new complexes **3–5** were all isolated as yellow or orange solids stable in air and in solution of polar organic solvents, where they behave as 1:1 electrolytes.^[4] Analytical and spectroscopic data (IR and NMR) supported the proposed formulation.

The IR spectra of the hydrazine complexes [RuCl(CO)(κ^1 -NH₂NH*R*1)(PPh₃)₂{P(O*R*)₃}]BPh₄ (**3**, **4**) show two or three bands of medium or weak intensity in the 3353–3267 cm⁻¹ region attributed to the v(NH) of the hydrazine ligand, the presence of which is confirmed by the ¹H NMR spectra, which, for complex **3b**, show two broad resonances at δ = 3.40 and 2.95 ppm attributed to the coordinated and free NH₂

groups of the NH₂NH₂ ligand, respectively. The presence of two resonances for the NH₂ protons also suggests end-on coordination of the hydrazine. The proton NMR spectra of methylhydrazine complexes **4a** and **4b** also show a broad signal at 2.55–2.50 ppm attributed to the metal-bonded NH₂ group and a multiplet at 3.11–3.06 ppm of the NH protons of methylhydrazine. A doublet at 1.62 ppm (**4a**) and 1.59 ppm (**4b**) also appears in the spectra of methylhydrazine derivatives due to the methyl substituent of the CH₃NHNH₂ ligand. In the temperature range between +20 and -80 °C the ³¹P{¹H} NMR spectra of **3** and **4** appear as AX_2 multiplets suggesting the magnetic equivalence of the two phosphines PPh₃ different from the phosphite P(OR)₃.

These spectroscopic data support the proposed formulation for the hydrazine complexes **3** and **4** but do not allow to unambiguously assign them one among arrangements **I**, **II**, or **III** in solution (Scheme 5).



Scheme 5. Possible geometries.

However, the IR spectra of complexes **3** and **4** show the v(CO) as a strong band at 1971–1982 cm⁻¹, a value, which is only slightly higher than those of the precursors [RuHCl(CO)(PPh₃)₂{P(OR)₃}] (**2**) (due to complex charge), suggesting that a good σ -donor ligand such as Cl⁻ should be in *trans* position with respect to the CO, as observed in **2**. On these bases, arrangement **II** may be tentatively proposed in solution for the hydrazine derivatives.

The IR spectra of the cyanamide complexes $[RuCl(CO)(N \equiv CNEt_2)(PPh_3)_2 \{P(OR)_3\}]BPh_4$ (5) show a medium-intensity band at 2273 cm⁻¹ (**5a**) and 2278 cm⁻¹ (**5b**) attributed to the v(NC) of the diethylcyanamide. In the spectra a strong band at 1975–1977 cm⁻¹ also appears due to the v(CO) of the carbonyl ligand. The ¹H NMR spectra confirm the presence of the cyanamide ligand showing the characteristic signals of the substituents at 2.52 ppm q (5a) and 2.55 ppm q (5b) of the methylene and at 0.70 ppm t (5a) and 0.73 ppm t (5b) of the methyl protons of the CH_3CH_2 group of the N=CNEt₂ ligand. In the spectra the signals of the PPh₃ and $P(OR)_3$ and of the BPh₄ anion also appear. The ³¹P NMR spectra are AX_2 multiplets suggesting that the two PPh₃ are magnetically equivalent and different from the phosphite. On the basis of these data and taking into account that the v(CO) values are comparable with those of hydrazine derivatives 3 and 4, we tentatively propose a geometry in solution of type IV for diethylcyanamide derivatives 5 (Scheme 6).



Scheme 6.

Conclusions

In this paper we report the preparation of mixed-ligands hydride complexes [RuHCl(CO)(PPh₃)₂{P(OR)₃}], which behave as a precursor for the synthesis of both hydrazine [RuCl(CO)(κ^1 -NH₂NHR1)(PPh₃)₂{P(OR)₃}]BPh₄ and diethyl-cyanamide [RuCl(CO)(N=CNEt₂)(PPh₃)₂{P(OR)₃}]BPh₄ derivatives.

Experimental Section

General Comments: The synthetic work was carried out in an appropriate atmosphere (Ar, N2) using standard Schlenk techniques or in an inert-atmosphere glove box. Once isolated, the compounds were found to be relatively stable in air. All solvents were dried with appropriate drying agents, degassed on a vacuum line, and distilled into vacuumtight storage flasks. RuCl₃·3H₂O was a Pressure Chemical Co. (USA) product, used as received. Phosphites P(OMe)₃ and P(OEt)₃ were Aldrich products and were purified by distillation in a nitrogen atmosphere. Other reagents were purchased from commercial sources in the highest available purity and used as received. Infrared spectra were recorded with a Perkin-Elmer Spectrum-One FT-IR spectrophotometer. ¹H and ³¹P{¹H} NMR spectra were obtained with AVANCE 300 and AVANCE III 400 Bruker spectrometers at temperatures between -90 and +30 °C, unless otherwise noted. ¹H spectra are referred to internal tetramethylsilane; ${}^{31}P{}^{1}H$ chemical shifts were reported with respect to 85% H₂PO₄, with downfield shifts considered positive. COSY, HMQC, and HMBC NMR experiments were performed with standard programs. The iNMR software package^[14] was used to process NMR spectroscopic data. The conductivity of 10⁻³ mol·dm⁻³ solutions of the complexes in CH₃NO₂ at 25 °C was measured with a Radiometer CDM 83. Elemental analyses were determined in the Microanalytical Laboratory of the Dipartimento di Scienze Farmaceutiche, University of Padova (Italy).

Synthesis of Complexes: The precursor compound [RuCl₂(PPh₃)₃] was prepared following the reported method.^[15]

[RuHCl(CO)(PPh₃)₃] (1): In a 25-mL three-necked round-bottomed flask were placed [RuCl₂(PPh₃)₃] (0.25 g, 0.26 mmol), zinc dust (60 mg, 0.9 mmol), and 15 mL ethanol. The reaction mixture was refluxed for 3 h, filtered, and the volume was reduced to about 3 mL by evaporation of the solvent under reduced pressure. A yellow solid slowly separated out, which was filtered and crystallized from CH₂Cl₂ and ethanol; yield ≥ 55%. **IR** (KBr): $\tilde{v} = (vRuH)$ 2011 (w); (vCO) 1925 (s) cm⁻¹. ¹H NMR (CD₂Cl₂, -60 °C): $\delta = 7.70-7.00$ (m, 45 H, Ph), -6.96 (dt, *J*_{HP} = 10.3, *J*_{HP} = 23,3, 1 H, hydride) ppm. ³¹P{¹H} NMR (CD₂Cl₂, 20 °C): $\delta = A_2B$ spin syst, δ_A 41.6, δ_B 13.4, *J*_{AB} = 16.4 Hz. C₅₅H₄₆ClOP₃Ru (852.40): calcd. C 69.36, H 4.87, Cl 3.72%; found C 69.61, H 4.78, Cl 3.58%.

 $[RuHCl(CO)(PPh_3)_2 \{P(OR)_3\}]$ (2) [R = Me (a), Et (b)]: Method 1: In a 25-mL three-necked round-bottomed flask were placed

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[RuCl₂(PPh₃)₃] (0.25 g, 0.26 mmol), zinc dust (60 mg, 0.9 mmol), and 15 mL of ethanol. The reaction mixture was refluxed for 3 h, cooled to room temperature, and an excess of the appropriate phosphite $P(OR)_3$ (0.52 mmol) was added. The reaction mixture was refluxed for 45 min, filtered, and the volume was reduced to about 3 mL by evaporation of the solvent under reduced pressure. By slow cooling to -25 °C of the resulting solution vellow microcrystals separated out, which were filtered and crystallized from ethanol (vield $\geq 35\%$). Method 2: An excess of the appropriate phosphite P(OR)₃ (0.45 mmol) was added to a solution of [RuHCl(CO)(PPh₃)₃] (0.16 mmol, 250 mg) in 10 mL of benzene and the reaction mixture was refluxed for 45 min. The solvent was removed under reduced pressure to give an oil, which was triturated with ethanol (2 mL). By slow cooling to -25 °C of the resulting solution a yellow solid slowly separated out, which was filtered and crystallized from ethanol (yield $\geq 80\%$). 2a: IR (KBr): $\tilde{v} = (vCO)$ 1957 (s); (vRuH) 1886 (w) cm⁻¹. ¹H NMR (CD₂Cl₂, 20 °C): δ = 7.79– 7-30 (m, 30 H, Ph), 3.27 (dd, 9 H, CH₃), -5.62 (dt, $J_{\rm HP}$ = 177.0, $J_{\rm HP}$ = 21.0, 1 H, hydride) ppm. ³¹P{¹H} NMR (CD₂Cl₂, 20 °C): $\delta = AX_2$ spin syst, $\delta_A 132.0$, $\delta_X 41.3$, $J_{AX} = 26.7$ Hz. $C_{40}H_{40}ClO_4P_3Ru$ (814.19): calcd. C 59.01, H, 4.95, Cl 4.35 %; found C 59.15, H 4.84, Cl 4.49 %. **2b**: **IR** (KBr): $\tilde{v} = (vCO)$ 1956 (s); (vRuH) 1903 (w) cm⁻¹. ¹H NMR $(CD_2Cl_2, 20 \circ C): \delta = 7.78-7.35 \text{ (m, 30 H, Ph)}, 3.64 \text{ (m, 6 H, CH}_2),$ 1.00 (t, 9 H, CH₃), -5.74 (dt, $J_{\rm HP}$ = 174.0, $J_{\rm HP}$ = 20.5, 1 H, hydride) ppm. ³¹P{¹H} NMR (CD₂Cl₂, 20 °C): $\delta = AX_2$ spin syst, δ_A 130.1, δ_X 41.2, $J_{AX} = 26.7$ Hz. $C_{43}H_{46}ClO_4P_3Ru$ (856.27): calcd. C 60.32, H, 5.41, Cl 4.14%; found C 60.11, H 5.54, Cl 4.01%.

 $[RuCl(CO)(\kappa^{1}-NH_{2}NHR1)(PPh_{3})_{2}\{P(OR)_{3}\}]BPh_{4}(3,4)[R1 = H(3),$ Me (4); R = Me (a), Et (b)]: Triflic acid HOTf (0.11 mmol, 9.7 µL) was added to a solution of the appropriate complex $[RuHCl(CO)(PPh_3)_2{P(OR)_3}]$ (2) (0.1 mmol) in 5 mL of toluene cooled to -196 °C. The reaction mixture was brought to 0 °C, stirred for 40 min, and cooled again to -196 °C. An excess of the appropriate hydrazine (0.22 mmol) in 5 mL of dichloromethane was added to the reaction mixture, which was brought to 0 °C and stirred for 2 h. The solvent was removed under reduced pressure to give an oil which was treated with ethanol (2 mL) containing an excess of NaBPh4 (0.2 mmol, 68 mg). A pale-yellow solid slowly separated out, which was filtered and crystallized from CH_2Cl_2 and EtOH (yield $\geq 70\%$). **3b**: **IR** (KBr): $\tilde{v} = (vNH)$ 3353 (w), 3293 (m), 3267 (w); (vCO) 1982 (s) cm⁻¹. ¹**H** NMR (CD₂Cl₂, 20 °C): δ = 7.80–6.88 (m, 50 H, Ph), 3.59 (qnt, 6 H, CH₂), 3.40 (br., 2 H, RuNH₂), 2.95 (br., 2 H, NNH₂), 1.03 (t, 9 H, CH₃) ppm. ³¹P{¹H} NMR (CD₂Cl₂, 20 °C): $\delta = AX_2$ spin syst, δ_A 121.13, δ_X 35.73, J_{AX} = 34.6 Hz. Λ_M = 54.9 $\Omega^{-1} \cdot \text{mol}^{-1} \cdot \text{cm}^2$. C₆₇H₆₉BClN₂O₄P₃Ru (1206.53): calcd. C 66.70, H, 5.76, N 2.32, Cl 2.94%; found C 66.48, H 5.65, N, 2.43, Cl 3.06%. 4a: IR (KBr): v = (vNH) 3326, 3275 (w); (vCO) 1971 (s) cm⁻¹. ¹H NMR (CD₂Cl₂, 20 °C): δ = 7.79–6.86 (m, 50 H, Ph), 3.34 (d, 9 H, CH₃ phos), 3.11 (m, 1 H, NH), 2.55 (br., 2 H, NH₂), 1.62 (d, 3 H, CH₃N) ppm. ${}^{31}P{^{1}H}$ **NMR** (CD₂Cl₂, 20 °C): $\delta = AX_2$ spin syst, δ_A 126.0, δ_X 32.23, $J_{AX} =$ 33.1 Hz. $\Lambda_{\rm M}$ = 55.1 Ω^{-1} ·mol⁻¹·cm². C₆₅H₆₅BClN₂O₄P₃Ru (1178.48): calcd. C 66.25, H, 5.56, N 2.38, Cl 3.01 %; found C 66.07, H 5.42, N 2.30, Cl 3.16%. **4b**: **IR** (KBr): $\tilde{v} = (vNH)$ 3339, 3268 (w); (vCO) 1977 (s) cm⁻¹. ¹**H** NMR (CD₂Cl₂, 20 °C): δ = 7.77–6.87 (m, 50 H, Ph), 3.54 (m, 6 H, CH₂), 3.01 (br., 1 H, NH), 2.50 (br., 2 H, NH₂), 1.59 (d, 3 H, CH₃N), 1.05 (t, 9 H, CH₃) ppm. ³¹P{¹H} NMR (CD₂Cl₂, 20 °C): $\delta = AX_2$ spin syst, δ_A 119.8, δ_X 36.0, $J_{AX} = 34.0$ Hz. $\Lambda_M =$ 53.7 Ω⁻¹·mol⁻¹·cm². C₆₈H₇₁BClN₂O₄P₃Ru (1220.56): calcd. C 66.91, H, 5.86, N 2.30, Cl 2.90%; found C 66.75, H 5.98, N 2.18, Cl 3.04%.

[RuCl(CO)(N=CNEt₂)(PPh₃)₂{P(OR)₃}]BPh₄ (5) [R = Me (a), Et (b)]: This complex was prepared exactly like the related hydrazine derivatives 3 and 4 by treating [RuHCl(CO)(PPh₃)₂{P(OR)₃}] (2) first



with triflic acid and then with an excess of diethylcyanamide N=CNEt₂. The yellow solid obtained was filtered and crystallized from CH₂Cl₂ and EtOH; yield \geq 75 %. **5a**: **IR** (KBr): $\tilde{v} = (vCN)$ 2273 (m); (vCO) 1977 (s) cm⁻¹. ¹H NMR (CD₂Cl₂, 20 °C): δ = 7.81–6.87 (m, 50 H, Ph), 3.31 (d, 9 H, CH₃ phos), 2.52 (q, 6 H, CH₂), 0.70 (t, 6 H, CH₃ NEt) ppm. ³¹P{¹H} NMR (CD₂Cl₂, 20 °C): $\delta = AX_2$ spin syst, δ_A 124.64, δ_X 33.22, J_{AX} = 32.81 Hz. Λ_M = 54.6 $\Omega^{-1} \cdot \text{mol}^{-1} \cdot \text{cm}^2$. C₆₀H₆₀BClN₂O₄P₃Ru (1230.55): calcd. C 67.35, H. 5.65, N. 2.28, Cl 2.88%; found C 67.21, H 5.50, N, 2.37, Cl 2.99%. 5b: IR (KBr): v = (vCN) 2278 (m); (vCO) 1975 (s) cm⁻¹. ¹H NMR (CD₂Cl₂, 20 °C): δ = 7.83–6.86 (m, 50 H, Ph), 3.56 (m, 6 H, CH₂ phos), 2.55 (q, 4 H, CH₂ NEt), 1.11 (t, 9 H, CH₃ phos), 0.73 (t, 6 H, CH₃ NEt) ppm. ³¹P{¹H} NMR (CD₂Cl₂, 20 °C): $\delta = AX_2$ spin syst, δ_A 121.3, δ_X 35.8, $J_{AX} = 34.7 \text{ Hz}. \Lambda_{M} = 55.0 \ \Omega^{-1} \cdot \text{mol}^{-1} \cdot \text{cm}^{2}. C_{72}H_{75}BCIN_{2}O_{4}P_{3}Ru$ (1272.63): calcd. C 67.95, H, 5.94, N 2.20, Cl 2.79%; found C 67.73, H 6.06, N, 2.08, Cl 2.66%.

X-ray Data Collection and Refinement: Crystallographic data for compound hydridechloridecarbonyl(triethoxyphosphine)[bis(triphenyl phosphine)]ruthenium(II) (2b) were collected at room temperature with a Bruker Smart 1000 CCD diffractometer at CACTI (Universidade de Vigo) using graphite monochromated Mo- K_{α} radiation (λ = 0.71073 Å), and were corrected for Lorentz and polarization effects. The software SMART^[16] was used for collecting frames of data, indexing reflections, and the determination of lattice parameters, SAINT^[16] for integration of intensity of reflections and scaling, and SADABS^[16] for scaling and empirical absorption correction. The crystallographic treatment was performed with the Oscail program.^[17] The structure of the compound was solved by using the SHELXT program^[18] and refined by a full – matrix least – squares based on F^2 , SHELXL program.^[19] Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in idealized positions and refined with isotropic displacement parameters. Five atoms on the ethoxy substituents in the phosphite ligands may be split into two different positions, but this disorder was not modeled. Details of crystal data and structural refinement are given in Table 2.

Crystallographic data (excluding structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository number CCDC-1899488 for **2b** (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

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Table 2.	Crystal	data	and	structure	refinement	for	2b .
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	2b
Empirical formula	C ₄₃ H ₄₆ ClO ₄ P ₃ Ru
Formula weight	856.23
Temperature /K	293(2)
Wavelength /Å	0.71073
Crystal system	monoclinic
Space group	$P2_{1}/c$
Unit cell dimensions:	
a /Å	17.771(3)
b /Å	10.0406(14)
c /Å	24.379(3)
β /°	110.371(3)
Volume /Å ³	4078.1(10)
Z	4
Density (calculated) /Mg·m ⁻³	1.395
Absorption coefficient /mm ⁻¹	0.608
F(000)	1768
Crystal size /mm	$0.270 \times 0.200 \times 0.070$
Theta range for data collection	1.222 to 28.013°
Index ranges	$-14 \le h \le 23$
-	$-13 \le k \le 13$
	$-31 \le l \le 29$
Reflections collected	26626
Independent reflections	9766 $[R_{int} = 0.0780]$
Reflections observed (> 2σ)	4687
Data completeness	0.991
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.7029
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	9766 / 0 / 476
Goodness-of-fit on F^2	1.007
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0542$
	$wR_2 = 0.1134$
R indices (all data)	$R_1 = 0.1542$
	$wR_2 = 0.1583$
Largest diff. peak and hole /e·Å ⁻³	1.193 and -0.879

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Journal of Inorganic and General Chemistry ZAAAC Zeitschrift für anorganische und allgemeine Chemie

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