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Preparation of Cyanoguanidine and Ethylcyanamide Complexes of Ruthenium(II) and Osmium(II)

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Cyanoguanidine complexes $[MCl\{\eta^1\text{-}N{\equiv}CN(H)C(NH_2){=}NH\}(\eta^6\text{-}p\text{-cymene})(PR_3)]BPh_4$ [M = Ru, Os; PR_3 = $P(OEt)_3$, $PPh(OEt)_2$, PPh_2OEt, $PiPr_3$] were prepared by treating compounds $[MCl_2(\eta^6\text{-}p\text{-cymene})(PR_3)]$ with cyanamide $N{\equiv}CNH_2$. Alternatively, complexes $[MCl\{\eta^1\text{-}N{\equiv}CN(H)C(NH_2){=}NH\}(\eta^6\text{-}p\text{-cymene})(PR_3)]BPh_4$ were prepared by treating $[MCl_2(\eta^6\text{-}p\text{-cymene})(PR_3)]$ with cyanoguanidine. Diethylcyanamide complexes $[MCl(N{\equiv}CNEt_2)(\eta^6\text{-}p\text{-cymene})(PR_3)]BPh_4$ were also obtained by treating $[MCl_2(\eta^6\text{-}p\text{-cymene})(PR_3)]$ with an excess amount of $N{\equiv}CNEt_2$. Complexes were characterised spectroscopically (IR, ^1H, ^{31}P, ^{13}C NMR) and in the case of $[RuCl\{N{\equiv}CN(H)C(NH_2){=}NH\}(\eta^6\text{-}p\text{-cymene})\{PPh(OEt)_2\}]BPh_4$ by X-ray crystal structure determination.

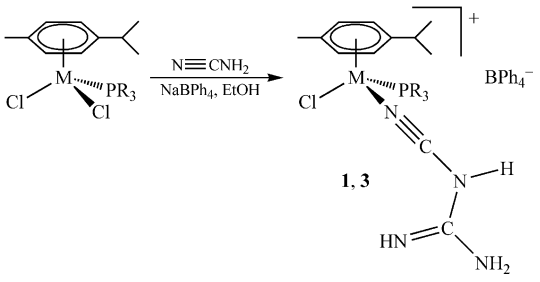
Introduction

Cyanamides $N{\equiv}CNR_2$ (R = H, alkyl or aryl) are aminofunctionalised nitriles whose coordination chemistry is still relatively unexplored[1–7] in comparison to the rich and various coordination chemistry of organonitriles $RC{\equiv}N$ (R = alkyl or aryl).[8]This is somewhat surprising in light of the biological and synthetic interest of these compounds, particularly cyanamide itself, $N{\equiv}CNH_2$, and its dimeric form, cyanoguanidine, $N{\equiv}CN(H)C(NH_2){=}NH$.[9,10] Only a small number of papers on the synthesis and reactivity of cyanamide complexes of transition metals have recently been reported, mainly molybdenum,[6] platinum,[5] and copper[4] as central metal. Instead, only one report is known for ruthenium[11] and none for osmium.

We are interested in the chemistry of "diazo" and "triazo" complexes of transition metals with d^6 configuration and have reported the synthesis not only of diazene and hydrazine derivatives[12] but also of amidrazone complexes obtained by nucleophilic attack of hydrazine on coordinated nitrile.[13] We have now extended these studies to cyanamide, and this paper reports the preparation of cyanoguanidine and diethylcyanamide complexes of ruthenium and osmium stabilised by half-sandwich *p*-cymene fragments.

Results and Discussion

p-Cymene complexes of ruthenium and osmium $[MCl_2(\eta^6\text{-}p\text{-cymene})(PR_3)]$[24a] react with an excess amount of cyanamide, $N{\equiv}CNH_2$, in the presence of $NaBPh_4$, to give cyanoguanidine complexes $[MCl\{N{\equiv}CN(H)C(NH_2){=}NH\}(\eta^6\text{-}p\text{-cymene})(PR_3)]BPh_4$ (**1** and **3**), as shown in Scheme 1.



Scheme 1. M = Ru (**1**), Os (**3**); PR_3 = $P(OEt)_3$ (**a**), $PPh(OEt)_2$ (**b**), PPh_2OEt (**c**), $PiPr_3$ (**d**).

Cyanoguanidine complexes **1** and **3** were also prepared by treating the dichloride precursor $[MCl_2(\eta^6\text{-}p\text{-cymene})(PR_3)]$ with an excess amount of free cyanoguanidine, $N{\equiv}CN(H)C(NH_2){=}NH$, in ethanol. In both cases, the reaction proceeds with substitution of one chloride by the N-donor ligand, yielding cationic complexes **1** and **3**.

The formation of cyanoguanidine complexes **1** and **3** from the reaction of cyanamide is not unexpected and may be explained on the basis of the initial coordination of one molecule of $N{\equiv}CNH_2$ to give cyanamide complex [**A**] (Scheme 2). Nucleophilic attack of a second $N{\equiv}CNH_2$ species on the cyanide carbon atom of the coordinated cyanamide, followed by a H-shift, gives N-imine-bonded cyano-

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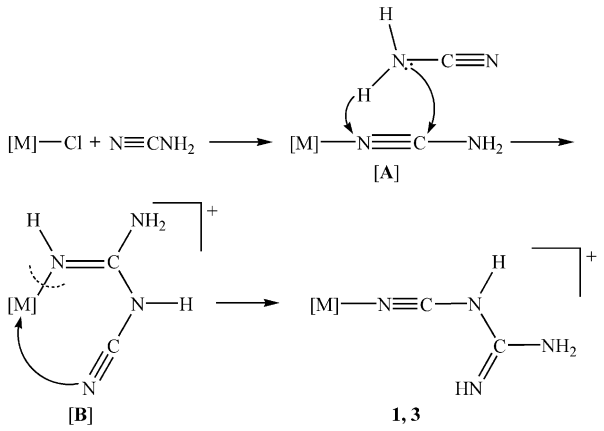
guanidine complex [**B**]. The linkage isomerisation of this ligand gives the final N-nitrile bonded [M]–N≡CN(H)C-(NH_2)=NH derivatives **1** and **3**.

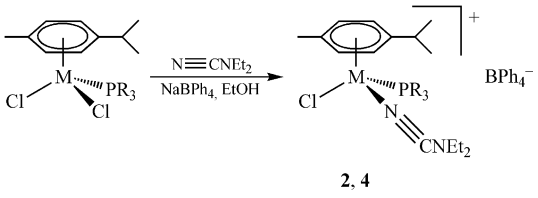


Scheme 2. [M] = [MCl(η⁶-*p*-cymene)(PR_3)].

Nucleophilic attack on coordinated nitrile is well documented[8] for several transition metals, and these precedents support the proposed path for the metal-mediated dimerisation of the N≡CNH_2 to give cyanoguanidine.

We also attempted to prepare cyanamide complexes like [**A**] by slow addition of a solution of N≡CNH_2 to the starting complexes [MCl_2(η⁶-*p*-cymene)(PR_3)] in a low ratio (0.8:1), but only cyanoguanidine complexes **1** and **3** were isolated under all conditions. Nucleophilic attack of free N≡CNH_2 to give cyanoguanidine is probably faster than the coordination of cyanamide, affording exclusively complexes **1** and **3** as final products.

Ethylcyanamide N≡$CNEt_2$ also reacts with *p*-cymene complexes [MCl_2(η⁶-*p*-cymene)(PR_3)] to give the cyanamide derivatives [MCl(N≡$CNEt_2$)(η⁶-*p*-cymene)(PR_3)]-BPh_4 (**2** and **4**), which were isolated in good yields and characterised (Scheme 3). Also in this case, the reaction proceeds by substitution of one chloride by ethylcyanamide and the formation of cationic complexes **2** and **4**.



Scheme 3. M = Ru (**2**), Os (**4**); PR_3 = $PPh(OEt)_2$ (**b**).

Examples of cyanamide and cyanoguanidine complexes have been reported[1–7] mainly for Mo, Pt and Cu as central metals, whereas only one example is known for ruthenium[11] and none for osmium. The use of *p*-cymene fragments [MCl(η⁶-*p*-cymene)(PR_3)] with phosphane or phosphite allowed the synthesis of both new ruthenium complexes and of the first osmium ones containing cyanoguanidine and ethylcyanamide as ligands.

Complexes **1**–**4** were isolated as yellow or yellowish-green solids, stable in air and in solution of polar organic solvents, where they behave as 1:1 electrolytes.[14] Their formulation is supported by analytical and spectroscopic data (IR and ^1H, ^{31}P, ^{13}C NMR) and by X-ray crystal structure determination of the complex [RuCl{N≡CN(H)C(NH_2)=NH}(η⁶-*p*-cymene){$PPh(OEt)_2$}]BPh_4 (**1b**), whose ORTEP diagram is shown in Figure 1. The structure of the complex consists of a ruthenium atom η⁶-coordinated to a *p*-cymene molecule, one chlorine atom, one diethoxyphenylphosphane bonded through the phosphorus atom and one *N*-cyanoguanidine bonded through the nitrile nitrogen atom in an η¹-fashion.[15] The overall coordination around the metal consists of a classic "three-legged piano stool" structure. The geometry of the complex is octahedral and is marked by near-90° values for angles P1–Ru–Cl1 87.0(1), N1–Ru–P1 86.2(1), N1–Ru–Cl1 83.5(1)°. The chloride ligand and *N*-cyanoguanidine are bonded through a hydrogen bond (see Table 1 for their metrical parameters), as found also for the polymeric complex [$ZnCl_2(C_2H_4N_4)]_n$.[16]

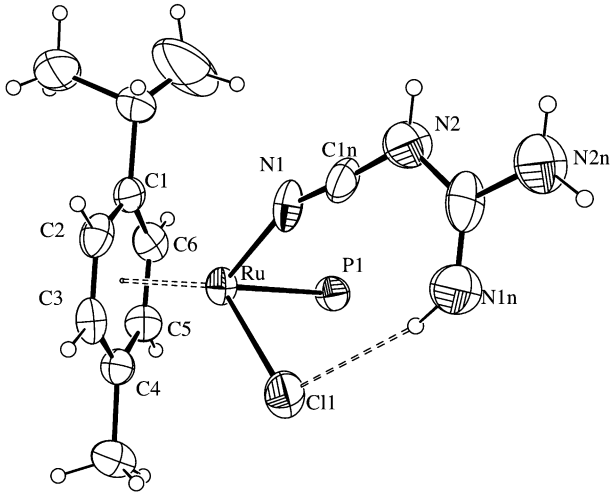


Figure 1. ORTEP view of the cation of **1b**. The ethoxy and phenyl groups of the phosphonite group are not drawn. The atoms are drawn at the 30% probability level.

The Ru–P bond and Ru–Cl bonds are 2.287(2) and 2.408(2) Å, respectively, which are in good agreement with other *p*-cymene ruthenium complexes.[17] The Ru–N(1) bond [2.026(6) Å] is slightly shorter than that found in related nitrile compounds of ruthenium.[18] It is worth noting that the CCDC database (CSD version 5.30, Feb. 2009 updated)[19] only lists 51 structures of coordination compounds with *N*-cyanoguanidine and none with ruthenium. The coordination of *N*-cyanoguanidine preferentially occurs through nitrile nitrogen N1, as occurs in **1b**, and the N1–C1N bond length [1.138(8) Å] matches well with a triple bond.[15,16,20] The angle N1–C1n–N2 is almost linear [176.7(8)°], and the C1n–N1–Ru angle of only 158.9(6)° may be explained by formation of a hydrogen bond between the cyanoguanidine ligand and the coordinated chlorine atom.[20,21] The planarity (rms = 0.0246) and distances around the C2n carbon atom (Table 1) correspond to large π-electron delocalisation in the ligand.[20]

Table 1. Selected bond lengths [Å] and angles [°] for **1b**.[a]

Bonds			
Ru–C1	2.207(6)	Ru–C2	2.252(6)
Ru–C3	2.257(6)	Ru–C4	2.232(7)
Ru–C5	2.192(6)	Ru–C6	2.195(6)
Ru–N1	2.026(6)	Ru–P1	2.2876(17)
Ru–Cl1	2.4086(18)	Ru–Ct	1.7225(5)
N1–C1N	1.138(8)	N2–C1N	1.330(9)
N2–C2N	1.337(10)	C2N–N1N	1.298(10)
C2N–N2N	1.322(9)		
Angles			
Ct–Ru–N1	129.00(15)	Ct–Ru–P1	129.40(5)
Ct–Ru–Cl1	126.55(5)	P1–Ru–Cl1	86.99(7)
N1–Ru–P1	86.19(15)	N1–Ru–Cl1	83.46(17)
N1–C1N–N2	176.7(8)	C1N–N1–Ru	158.9(6)
Dihedral angles			
C1–Ct–Ru–N1	33.1(4)	C2–Ct–Ru–N1	–26.7(4)
C3–Ct–Ru–Cl1	28.6(3)	C4–Ct–Ru–Cl1	–32.0(3)
C5–Ct–Ru–P1	30.5(3)	C6–Ct–Ru–P1	–29.8(3)

Hydrogen bond

D–H···A	*d*(D–H)	*d*(H···A)	∠DHA	*d*(D···A)
N1n–H1n1···Cl1	1.1(1)	2.42(10)	156(7)	3.493(9)

[a] Ct represents the centroid of the benzene ring for the *p*-cymene ligand.

The distance from the ruthenium atom to the centroid of the benzene ring of the cymene ligand is 1.722(2) Å. The rms value for this plane is 0.019, with maximum deviation for C1 (isopropyl substituted) and C4 (methyl substituted) of 0.026(4) and 0.027(4) Å, respectively. The benzene plane could be considered slightly bent in a boat-shaped conformation, with the substituted carbon atoms facing the metal atom (Figure 2).

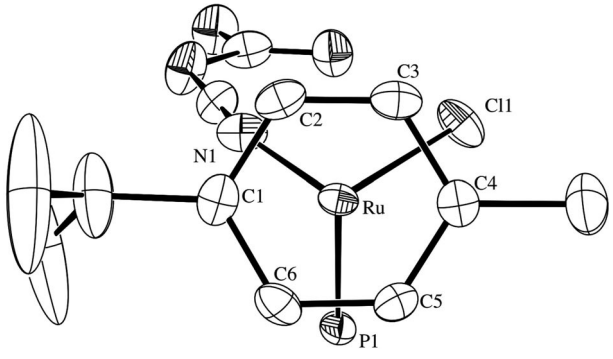


Figure 2. ORTEP drawn of the cation view along the Ct–Ru vector.

Infrared and NMR spectroscopic data fit the proposed formulation for cyanamide complexes **1**–**4**. The IR spectra of cyanoguanidine derivatives **1** and **3** show strong absorption at 2259–2241 cm^{-1}, attributed to ν_{CN} of the nitrile group, and two or three bands of medium or strong intensity at 3446–3339 cm^{-1}, due to ν_{NH} of the amine NH_2 and imine =NH groups of the cyanoguanidine ligand. In the 1630–1627 cm^{-1} region, the δ_{NH_2} band also occurs. At room temperature, the ^1H NMR spectra of cyanoguanidine complexes **1** and **3** show not only the multiplet of the BPh_4 anion, but also the characteristic signals of the *p*-cymene and phosphite or phosphane ligands. One broad signal also appears between δ = 5 and 4 ppm, which was attributed to the NH_2 or NH protons of the cyanamide ligand. Lowering the sample temperature caused a change in the spectra, with the appearance, at –40 °C, of a new broad signal near 3.6 ppm for **1a**. However, further lowering of the temperature did not change the profiles of the spectra in the case of ruthenium complexes **1** and, even at –90 °C, the expected third signal, attributable to NH_2 or one of the two NH groups, did not appear. Instead, at –80 °C, the ^1H NMR spectrum of osmium complex **3b** showed a slightly broad doublet at δ = 4.34 ppm attributed to the NH_2 protons, and two broad singlets at δ = 5.58 and 4.52 ppm due to the two NH signals. These attributions are supported by both the 2:1:1 intensity ratio of the signals and the correlations observed in the COSY spectra. The ^{13}C NMR spectra of complexes **1** and **3** fit the proposed formulation, showing the characteristic signals of the *p*-cymene and phosphane ligands and a singlet at δ = 162.9–162.7 ppm for the CNH_2 carbon atom of cyanoguanidine. Instead, the resonance of the nitrile carbon atom N≡C–N(H) was identified as a broad singlet at δ = 156.5 ppm only for complex **3b**.

The IR spectra of the diethylcyanamide complexes $[MCl(N{\equiv}CNEt_2)(\eta^6\text{-}p\text{-cymene})(PR_3)]BPh_4$ (**2** and **4**) show a strong band at 2273–2266 cm^{-1}, attributed to ν_{CN} of the nitrile group. The ^1H NMR spectra confirm the presence of the cyanamide ligand, showing a quartet at δ = 3.09–2.69 ppm and a triplet at δ = 1.25–0.91 ppm of the ethyl group of the ligand. At temperature ranges between +20 and –80 °C, the ^{31}P NMR spectra appears as a sharp singlet, whereas the $^{13}C\{^1H\}$ NMR spectra support the proposed formulation, showing the characteristic signals of *p*-cymene and the phosphite carbon resonance. A singlet at δ = 166.6 ppm, attributed to the nitrile carbon resonance, and two signals at δ = 46.7 and 13.4 ppm of the ethyl group of $N{\equiv}CNEt_2$ also appear in the ^{13}C NMR spectra of **4c**, fitting the presence of the cyanamide ligand.

Conclusions

In this paper we report the synthesis of cyanoguanidine complexes of ruthenium and osmium stabilised by the *p*-cymene fragment $[MCl(\eta^6\text{-}p\text{-cymene})(PR_3)]$ containing phosphite or phosphane as a supporting ligand. The structural parameters for ruthenium complex $[RuCl\{N{\equiv}CN(H)\text{-}C(NH_2){=}NH\}(\eta^6\text{-}p\text{-cymene})\{PPh(OEt)_2\}]BPh_4$ (**1b**) were determined. Ethylcyanamide derivatives $[MCl(N{\equiv}CNEt_2)\text{-}(\eta^6\text{-}p\text{-cymene})(PR_3)]BPh_4$ were also prepared and spectroscopically characterised.

Experimental Section

General: All synthetic work was carried out under an appropriate atmosphere (Ar, N_2) by using standard Schlenk techniques or a vacuum/atmosphere dry box. All solvents were dried with appropriate drying agents, degassed on a vacuum line, and distilled into

vacuum-tight storage flasks. $RuCl_3 \cdot 3H_2O$ and $(NH_4)_2OsCl_6$ were purchased from Pressure Chemical Co. (USA) and used as received. Phosphites $PPh(OEt)_2$ and PPh_2OEt were prepared by the method of Rabinowitz and Pellon;[22] $P(OEt)_3$ (Aldrich) and $PiPr_3$ (Strem) were used as received. 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 FTIR spectrophotometer. NMR spectra (^1H, ^{31}P, ^{13}C) were obtained with AC200 or Avance 300 Bruker spectrometers at temperatures between –80 and +30 °C, unless otherwise noted. ^1H and ^{13}C spectra are referred to internal tetramethylsilane; $^{31}P\{^1H\}$ chemical shifts are reported with respect to 85% H_3PO_4, with downfield shifts considered positive. The COSY, HMQC, and HMBC NMR experiments were performed by using Bruker standard programs. The SwaN-MR and iNMR software packages[23] were used to treat NMR spectroscopic data. The conductivity of 10^{-3} mol L^{-1} solutions of the complexes in CH_3NO_2 at 25 °C were measured with a Radiometer CDM 83. Elemental analyses were determined in the Microanalytical Laboratory of the Dipartimento di Scienze Farmaceutiche of the University of Padua, Italy.

Synthesis of the Complexes: Complexes $[MCl_2(\eta^6\text{-}p\text{-cymene})(PR_3)]$ [M = Ru, Os; PR_3 = $P(OEt)_3$, $PPh(OEt)_2$, PPh_2OEt, $PiPr_3$] were prepared by our method,[24a] as follows: an excess amount of the appropriate phosphite or phosphane (3.5 mmol) was added to a solution of the dimeric complex $[MCl_2(\eta^6\text{-}p\text{-cymene})]_2$[24b,24c] (0.7 mmol) in CH_2Cl_2 (10 mL), and the reaction mixture was stirred at room temperature for 3 h. The solvent was removed under reduced pressure to give an oil, which was triturated with *n*-hexane (10 mL). A yellow solid slowly separated out, which was filtered and crystallised from dichloromethane and hexane; yield ≥90%.

$[RuCl\{NCN(H)C(NH_2)=NH\}(\eta^6\text{-}p\text{-cymene})(PR_3)]BPh_4$ (1) [PR_3 = $P(OEt)_3$ (a), $PPh(OEt)_2$ (b), PPh_2OEt (c), $PiPr_3$ (d)]

Method 1: In a 25-mL, three-necked, round-bottomed flask was placed the appropriate complex $[MCl_2(\eta^6\text{-}p\text{-cymene})(PR_3)]$ (0.42 mmol), an excess amount of cyanamide $N{\equiv}CNH_2$ (1.26 mmol, 53 mg), a slight excess amount of $NaBPh_4$ (0.50 mmol, 171 mg), and ethanol (10 mL). The reaction mixture was stirred for 24 h and the yellow-green solid formed was filtered and crystallised from CH_2Cl_2 and ethanol.

Method 2: In a 25-mL, three-necked, round-bottomed flask was placed the appropriate complex $[MCl_2(\eta^6\text{-}p\text{-cymene})(PR_3)]$ (0.42 mmol), an excess amount of cyanoguanidine $N{\equiv}CN(H)\text{-}C(NH_2){=}NH$ (0.84 mmol, 71 mg), a slight excess amount of $NaBPh_4$ (0.50 mmol, 171 mg), and ethanol (10 mL). The reaction mixture was stirred for 24 h and the yellow-green solid formed was filtered and crystallised from CH_2Cl_2 and ethanol.

1a: Yield: 254 mg (72%). IR (KBr pellet): $\tilde{\nu}$ = 3435 (ν_{NH}, s), 3351 (ν_{NH}, s), 2245 (ν_{CN}, s) 1627 (δ_{NH_2}, s) cm^{-1}. ^1H NMR (CD_2Cl_2, 25 °C): δ = 7.40–6.89 (m, 20 H, BPh_4), 5.70, 5.63, 5.55, 5.33 (d, 4 H, Ph *p*-cym), 4.30 (br. s, 4 H, NH, NH_2), 4.07 (quint, 6 H, CH_2), 2.67 (m, 1 H, CH), 2.08 (s, 3 H, CH_3 *p*-cym), 1.31 (t, 9 H, CH_3 phos), 1.23, 1.21 (d, 6 H, CH_3 *i*Pr) ppm. ^1H NMR (CD_2Cl_2, –40 °C): δ = 7.40–6.88 (m, 20 H, BPh_4), 5.67, 5.63, 5.47, 5.26 (d, 4 H, Ph *p*-cym), 4.73 (br., 2 H, NH), 3.63 (br., 2 H, NH_2), 3.98 (quint, 6 H, CH_2), 2.59 (m, 1 H, CH), 2.03 (s, 3 H, CH_3 *p*-cym), 1.26 (t, 9 H, CH_3 phos), 1.17, 1.13 (d, 6 H, CH_3 *i*Pr) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C): δ = 114.2 ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 25 °C): δ = 165–122 (m, BPh_4), 162.7 (s, $=CNH_2$), 110.3 (s, C1 *p*-cym), 103.2 (s, C4), 94.1, 94.0, 87.1 (s, C3), 92.3, 92.2, 88.81, 88.77 (s, C2), 63.9 (d, CH_2), 31.4 (s, CH), 22.3, 22.0 (s, CH_3 *i*Pr), 18.6 (s, CH_3 *p*-cym), 16.3 (d, CH_3 phos) ppm. Λ_M = 54.6 Ω^{-1} mol^{-1} cm^2. $C_{42}H_{53}BClN_4O_3PRu$ (840.20): calcd. C 60.04, H 6.36, Cl 4.22, N 6.67; found C 60.27, H 6.28, Cl 4.05, N 6.59.

1b: Yield: 256 mg (70%). IR (KBr pellet): $\tilde{\nu}$ = 3446 (ν_{NH}, s), 3353 (ν_{NH}, s), 2245 (ν_{CN}, s), 1628 (δ_{NH_2}, s) cm^{-1}. ^1H NMR (CD_2Cl_2, 25 °C): δ = 7.58–6.88 (m, 25 H, Ph), 5.64, 5.58, 5.43, 5.24 (d, 4 H, Ph *p*-cym), 4.12 (br. s, 4 H, NH, NH_2), 4.03, 3.95 (m, 4 H, CH_2), 2.55 (m, 1 H, CH), 1.97 (s, 3 H, CH_3 *p*-cym), 1.35, 1.34 (t, 6 H, CH_3 phos), 1.18, 1.16 (d, 6 H, CH_3 *i*Pr) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C): δ = 142.0 ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 25 °C): δ = 165–122 (m, Ph), 162.8 (s, $=CNH_2$), 111.1 (s, C1 *p*-cym), 102.6 (s, C4), 94.5, 94.4, 86.7 (s, C3), 91.7, 91.6, 88.1 (s, C2), 64.5 (d, CH_2), 31.4 (s, CH), 22.3, 22.2 (s, CH_3 *i*Pr), 18.4 (s, CH_3 *p*-cym), 16.4 (d, CH_3 phos) ppm. Λ_M = 52.8 Ω^{-1} mol^{-1} cm^2. $C_{46}H_{53}BClN_4O_2PRu$ (872.25): calcd. C 63.34, H 6.12, Cl 4.06, N 6.42; found C 63.12, H 6.24, Cl 3.89, N 6.27.

1c: Yield: 273 mg (72%). IR (KBr pellet): $\tilde{\nu}$ = 3434 (ν_{NH}, s), 3339 (ν_{NH}, s), 2247 (ν_{CN}, s), 1628 (δ_{NH_2}, s) cm^{-1}. ^1H NMR (CD_2Cl_2, 25 °C): δ = 7.70–6.83 (m, 30 H, Ph), 5.59, 5.48, 5.24, 5.20 (d, 4 H, Ph *p*-cym), 4.10 (br. s, 4 H, NH, NH_2), 3.72, 3.63 (m, 2 H, CH_2), 2.47 (m, 1 H, CH), 1.93 (m, 3 H, CH_3 *p*-cym), 1.21 (t, 3 H, CH_3 phos), 1.11, 1.06 (d, 6 H, CH_3 *i*Pr) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C): δ = 121.6 ppm. Λ_M = 50.9 Ω^{-1} mol^{-1} cm^2. $C_{50}H_{53}BClN_4O$-PRu (904.29): calcd. C 66.41, H 5.91, Cl 3.92, N 6.20; found C 66.15, H 6.03, Cl 3.74, N 6.06.

1d: Yield: 266 mg (76%). IR (KBr pellet): $\tilde{\nu}$ = 3435 (ν_{NH}, s), 3357 (ν_{NH}, m), 2241 (ν_{CN}, s), 1630 (δ_{NH_2}, s) cm^{-1}. ^1H NMR (CD_2Cl_2, 25 °C): δ = 7.43–6.90 (m, 20 H, BPh_4), 5.59, 5.40 (d, 4 H, Ph *p*-cym), 4.06 (br. s, 4 H, NH, NH_2), 2.35, 2.33 (m, 4 H, CH), 1.81 (m, 3 H, CH_3 *p*-cym), 1.21 (m, 24 H, CH_3 *i*Pr) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C): δ = 51.6 ppm. Λ_M = 55.4 Ω^{-1} mol^{-1} cm^2. $C_{45}H_{59}BClN_4PRu$ (834.28): calcd. C 64.78, H 7.13, Cl 4.25, N 6.72; found C 64.60, H 7.25, Cl 4.19, N 6.55.

$[RuCl(N{\equiv}CNEt_2)(\eta^6\text{-}p\text{-cymene})(PR_3)]BPh_4$ (2) [PR_3 = $P(OEt)_3$ (a), $PPh(OEt)_2$ (b), PPh_2OEt (c), $PiPr_3$ (d)]: In a 25-mL, three-necked, round-bottomed flask was placed the appropriate complex $[MCl_2(\eta^6\text{-}p\text{-cymene})(PR_3)]$ (0.42 mmol), an excess amount of diethylcyanamide $N{\equiv}CNEt_2$ (1.26 mmol, 146 µL), a slight excess amount of $NaBPh_4$ (0.50 mmol, 171 mg), and ethanol (10 mL). The reaction mixture was stirred for 24 h and the yellow solid formed was filtered and crystallised from CH_2Cl_2 and ethanol.

2a: Yield: 301 mg (84%). IR (KBr pellet): $\tilde{\nu}$ = 2273 (ν_{NH}, s) cm^{-1}. ^1H NMR (CD_2Cl_2, 25 °C): δ = 7.35–6.88 (m, 20 H, BPh_4), 5.68, 5.65, 5.60, 5.23 (d, 4 H, Ph *p*-cym), 4.12 (quint, 6 H, CH_2 phos), 3.09 (q, 4 H, CH_2 cyanam), 2.67 (m, 1 H, CH), 2.06 (s, 3 H, CH_3 *p*-cym), 1.34 (t, 9 H, CH_3 phos), 1.25, 1.23 (d, 6 H, CH_3 *i*Pr), 1.24 (t, 6 H, CH_3 cyanam) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C): δ = 113.8 ppm. Λ_M = 54.3 Ω^{-1} mol^{-1} cm^2. $C_{45}H_{59}BClN_2O_3PRu$ (854.27): calcd. C 63.27, H 6.96, Cl 4.15, N 3.28; found C 63.06, H 6.88, Cl 4.01, N 3.21.

2b: Yield: 305 mg (82%). IR (KBr pellet): $\tilde{\nu}$ = 2260 (ν_{CN}, s) cm^{-1}. ^1H NMR (CD_2Cl_2, 25 °C): δ = 7.65–6.89 (m, 25 H, Ph), 5.69, 5.63, 5.56, 5.23 (d, 4 H, Ph *p*-cym), 4.14, 4.03 (m, 4 H, CH_2 phos), 2.75 (m, 4 H, CH_2 cyanam), 2.63 (m, 1 H, CH), 2.03 (s, 3 H, CH_3 *p*-cym), 1.49, 1.40 (t, 6 H, CH_3 phos), 1.24, 1.22 (d, 6 H, CH_3 *i*Pr), 1.03 (t, 6 H, CH_3 cyanam) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C): δ = 144.6 ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 25 °C): δ = 165–122 (m, Ph), 111.2 (s, C1 *p*-cym), 104.7 (s, C4), 95.6, 95.5, 85.9 (s, C3), 92.32, 92.25, 89.0 (s, C2), 64.8, 64.6 (d, CH_2 phos), 46.3 (s, CH_2 cyanam), 31.4 (s, CH), 22.6, 22.1 (s, CH_3 *i*Pr), 18.4 (s, CH_3 *p*-cym), 16.4 (d, CH_3 phos), 13.1 (s, CH_3 cyanam) ppm. Λ_M = 49.5 Ω^{-1} mol^{-1} cm^2. $C_{49}H_{59}BClN_2O_2PRu$ (886.31): calcd. C 66.40, H 6.71, Cl 4.00, N 3.16; found C 66.22, H 6.83, Cl 3.82, N 3.04.

2c: Yield: 308 mg (80%). IR (KBr pellet): $\tilde{\nu}$ = 2269 (ν_{NH}, s) cm^{-1}. ^1H NMR (CD_2Cl_2, 25 °C): δ = 7.95–6.80 (m, 30 H, Ph), 5.65, 5.57, 5.39, 5.30 (d, 4 H, Ph *p*-cym), 3.81, 3.68 (m, 2 H, CH_2 phos), 2.84 (q, 4 H, CH_2 cyanam), 2.58 (m, 1 H, CH), 1.87 (s, 3 H, CH_3 *p*-cym), 1.31 (t, 3 H, CH_3 phos), 1.22, 1.19 (d, 6 H, CH_3 *i*Pr), 1.06 (t, 6 H, CH_3 cyanam) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C): δ = 122.5 ppm. Λ_M = 50.2 Ω^{-1} mol^{-1} cm^2. $C_{53}H_{59}BClN_2OPRu$ (918.36): calcd. C 69.32, H 6.48, Cl 3.86, N 3.05; found C 69.07, H 6.59, Cl 3.70, N 2.95.

2d: Yield: 303 mg (85%). IR (KBr pellet): $\tilde{\nu}$ = 2258 (ν_{NH}, s) cm^{-1}. ^1H NMR (CD_2Cl_2, 25 °C): δ = 7.35–6.87 (m, 20 H, BPh_4), 5.75, 5.71, 5.69, 5.38 (d, 4 H, Ph *p*-cym), 3.11 (q, 4 H, CH_2), 2.59 (m, 4 H, CH), 2.01 (s, 3 H, CH_3 *p*-cym), 1.36–1.26 (m, 24 H, CH_3 *i*Pr), 1.25 (t, 6 H, CH_3 cyanam) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C): δ = 45.9 ppm. Λ_M = 52.5 Ω^{-1} mol^{-1} cm^2. $C_{48}H_{65}BClN_2PRu$ (848.35): calcd. C 67.96, H 7.72, Cl 4.18, N 3.30; found C 68.09, H 7.81, Cl 4.04, N 3.35.

[OsCl{NCN(H)C(NH$_2$)=NH}(η^6-*p*-cymene)(PR$_3$)]BPh$_4$ (3) [PR$_3$ = PPh(OEt)$_2$ (b), PPh$_2$OEt (c)]: These complexes were prepared exactly like the related ruthenium derivatives **1b** and **1c**, following both Method 1 and 2, crystallising the solid obtained from CH_2Cl_2 and ethanol.

3b: Yield: 319 mg (79%). IR (KBr pellet): $\tilde{\nu}$ = 3446 (ν_{NH}, s), 3350 (ν_{NH}, s), 2246 (ν_{CN}, s), 1630 (δ_{NH_2}, s) cm^{-1}. ^1H NMR (CD_2Cl_2, 0 °C): δ = 7.50–6.90 (m, 25 H, Ph), 5.69, 5.61, 5.55, 5.43 (d, 4 H, Ph *p*-cym), 5.50 (br. s, 2 H, NH), 4.52 (br. s, 2 H, NH_2), 4.02, 3.87 (m, 4 H, CH_2), 2.54 (m, 1 H, CH), 2.12 (s, 3 H, CH_3 *p*-cym), 1.31 (m, 6 H, CH_3 *i*Pr), 1.18 (t, 6 H, CH_3 phos) ppm. ^1H NMR (CD_2Cl_2, –80 °C): δ = 5.58, 4.52 (br. s, 2 H, NH), 4.34 (br. d, 2 H, NH_2) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 0 °C): δ = 98.0 ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 25 °C): δ = 166–121 (m, Ph), 162.9 (s, =CNH_2), 156.5 (br. s, N≡C), 102.5 (s, C1 *p*-cym), 96.2 (s, C4), 85.8, 85. 7, 78.6 (s, C3), 84.1, 84.0, 79.90, 79.87 (s, C2), 64.0 (d, CH_2), 31.1 (s, CH), 22.6, 22.5 (s, CH_3 *i*Pr), 18.1 (s, CH_3 *p*-cym), 16.3 (d, CH_3 phos) ppm. Λ_M = 51.7 Ω^{-1} mol^{-1} cm^2. $C_{46}H_{53}BClN_4O_2OsP$ (961.41): calcd. C 57.47, H 5.56, Cl 3.69, N 5.83; found C 57.23, H 5.69, Cl 3.84, N 5.79.

3c: Yield: 321 mg (77%). IR (KBr pellet): $\tilde{\nu}$ = 3451 (ν_{NH}, s), 3356 (ν_{NH}, s), 2259 (ν_{CN}, s), 1629 (δ_{NH_2}, s) cm^{-1}. ^1H NMR (CD_2Cl_2, 25 °C): δ = 7.60–6.86 (m, 30 H, Ph), 5.74, 5.63, 5.53, 5.50 (d, 4 H, Ph *p*-cym), 4.17 (br., 4 H, NH, NH_2), 3.78, 3.65 (m, 2 H, CH_2), 2.53 (m, 1 H, CH), 2.20 (s, 3 H, CH_3 *p*-cym), 1.20, 1.15 (d, 6 H, CH_3 *i*Pr), 1.19 (t, 3 H, CH_3 phos) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C): δ = 81.1 ppm. Λ_M = 53.8 Ω^{-1} mol^{-1} cm^2. $C_{50}H_{53}BClN_4OOsP$ (993.45): calcd. C 60.45, H 5.38, Cl 3.57, N 5.64; found C 60.61, H 5.24, Cl 3.26, N 5.51.

[OsCl(N≡CNEt$_2$)(η^6-*p*-cymene)(PPh$_2$OEt)]BPh$_4$ (4c): This complex was prepared exactly like the related ruthenium derivative **2c**, crystallising the solid obtained from CH_2Cl_2 and ethanol. Yield: 355 mg (84%). IR (KBr pellet): $\tilde{\nu}$ = 2266 (ν_{CN}, s) cm^{-1}. ^1H NMR (CD_2Cl_2, 25 °C): δ = 7.80–6.86 (m, 30 H, Ph), 5.62, 5.51, 5.48, 5.42 (d, 4 H, Ph *p*-cym), 2.93, 2.83 (quint, 2 H, CH_2 phos), 2.70, 2.69 (d, 4 H, CH_2 cyanam), 2.26 (m, 1 H, CH), 1.96 (s, 3 H, CH_3 *p*-cym), 1.26, 1.24 (d, 6 H, CH_3 *i*Pr), 0.96 (t, 3 H, CH_3 phos), 0.91 (t, 6 H, CH_3 cyanam) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C): δ = 88.2 ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 25 °C): δ = 166.6 (s, N≡C), 165–122 (m, Ph), 101.4 (s, C1 *p*-cym), 96.6 (s, C4), 87.0, 86.6, 85.0, 84.8 (s, C3), 84.5, 84.0, 80.1, 78.7 (s, C2), 46.7 (s, CH_2 cyanam), 43.7 (d, CH_2 phos), 32.3 (s, CH), 22.6, 22.4 (s, CH_3 *i*Pr), 18.4 (s, CH_3 *p*-cym), 16.2 (d, CH_3 phos), 13.4 (s, CH_3 cyanam) ppm. Λ_M = 51.1 Ω^{-1} mol^{-1} cm^2. $C_{53}H_{59}BClN_2OOsP$ (1007.52): calcd. C 63.18, H 5.90, Cl 3.52, N 2.78; found C 62.96, H 5.80, Cl 3.35, N 2.90.

X-ray Crystallography: Crystallographic data were collected with a Bruker Smart 1000 CCD diffractometer at CACTI (Universidade de Vigo) by using graphite monochromated Mo-K_α radiation (λ = 0.71073 Å) and were corrected for Lorentz and polarisation effects. The software SMART[25] was used for collecting frames of data, indexing reflections, and the determination of lattice parameters, SAINT[26] for integration of intensity of reflections and scaling, and SADABS[27] for empirical absorption correction. The structure was solved and refined with the Oscail program[28] by Patterson methods and refined by a full-matrix least-squares based on F^2.[29] Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in idealised positions and refined with isotropic displacement parameters except that corresponding with the C=N–H group, which was found in the final density map and refined with isotropic displacement parameters. The phenyl and ethoxy substituents of the phosphane ligand are disordered over two positions, with factor occupancy of 56/44%. Details of crystal data and structural refinement are given in Table 2. CCDC-739178 (for **1b**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 2. Crystal data and structure refinement for **1b**.

	1b
Empirical formula	$C_{46}H_{53}BClN_4O_2PRu$
Formula weight	872.22
Temperature [K]	293(2)
Wavelength [Å]	0.71073
Crystal system	triclinic
Space group	$P\bar{1}$
a [Å]	9.9275(16)
b [Å]	13.978(2)
c [Å]	16.662(3)
α [°]	98.675(3)
β [°]	103.182(4)
γ [°]	93.388(3)
Volume [Å^3]	2214.9(6)
Z	2
$D_{calcd.}$ [Mg m^{-3}]	1.308
μ [mm^{-1}]	0.491
F(000)	908
Crystal size [mm]	0.47 × 0.42 × 0.14
θ range for data collection [°]	1.48 to 28.07
Index ranges	$-12 \le h \le 13$
	$-18 \le k \le 18$
	$-21 \le l \le 16$
Reflections collected	14414
Independent reflections	10085 [*R*(int) = 0.0461]
Reflections observed (>2σ)	4279
Data completeness	0.939
Absorption correction	semiempirical from equivalents
Max. and min. transmission	1.000 and 0.772
Refinement method	full-matrix least-squares on F^2
Data/restraints/parameters	10085/0/571
Goodness-of-fit on F^2	0.970
Final *R* indices [$I > 2\sigma(I)$]	R_1 = 0.0654 wR_2 = 0.1483
R indices (all data)	R_1 = 0.1691 wR_2 = 0.2009
Largest diff. peak/hole [e Å^{-3}]	0.833/–1.307

Supporting Information (see footnote on the first page of this article): Additional perspective views of **1b** and the complete list of bond lengths and angles for **1b**.

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