

Monomeric ruthenium(II) complexes containing diazene and isocyanide ligands: preparation and properties. Crystal structure of $[\text{Ru}(\text{4-CH}_3\text{C}_6\text{H}_4\text{N=NH})\text{-(4-CH}_3\text{C}_6\text{H}_4\text{NC)}\{\text{P(OEt)}_3\}_4](\text{PF}_6)_2$

Gabriele Albertin, Stefano Antoniutti, Emilio Bordignon *

Dipartimento di Chimica dell'Università di Venezia, 30123 Venice (Italy) and

Giancarlo Pelizzi and Francesca Vitali

Istituto di Chimica Generale, Centro Strutturistica CNR, Università di Parma, 43100 Parma (Italy)

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Abstract

The complexes $[\text{Ru}(\text{ArN=NH})(\text{RNC})\{\text{P(OEt)}_3\}_4](\text{BPh}_4)_2$ (**1**: $\text{Ar} = \text{4-CH}_3\text{C}_6\text{H}_4$, $\text{4-CH}_3\text{OC}_6\text{H}_4$, $\text{4-FC}_6\text{H}_4$; $\text{R} = \text{4-CH}_3\text{C}_6\text{H}_4$, $\text{4-CH}_3\text{OC}_6\text{H}_4$, C_6H_5), $[\text{Ru}(\text{RNC})_2\text{-}\{\text{P(OEt)}_3\}_4](\text{BPh}_4)_2$ (**2**) and $[\text{Ru}(\text{RNC})_3\{\text{P(OEt)}_3\}_3](\text{BPh}_4)_2$ (**3**) ($\text{R} = \text{4-CH}_3\text{-C}_6\text{H}_4$) derivatives were prepared by treating the bis(diazene) $[\text{Ru}(\text{ArN=NH})_2\text{-}\{\text{P(OEt)}_3\}_4]^{2+}$ cations with isocyanides: they were characterized by IR and ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy. The crystal structure of $[\text{Ru}(\text{4-CH}_3\text{C}_6\text{H}_4\text{N=NH})(\text{4-CH}_3\text{C}_6\text{H}_4\text{NC})\{\text{P(OEt)}_3\}_4](\text{PF}_6)_2$ was determined by X-ray diffraction. Crystals are monoclinic, of space group $P2_1/n$ with unit-cell dimensions a 23.527(4), b 22.597(3), c 11.565(1) Å, β 92.78(1)°, and $Z = 4$. The structure was solved by the heavy-atom method and refined by least-squares procedures to an R value of 0.0906 for 4812 independent observed reflections. The ruthenium atom lies within an essentially octahedral array of ligands with the diazene and isocyanide groups *cis* to one another. Reactions of the mono(diazene) derivatives **1** with NaBH_4 and LiCl gave the new complexes $[\text{RuH}(\text{ArN=NH})(\text{RNC})\{\text{P(OEt)}_3\}_3]\text{BPh}_4$ and $[\text{RuCl}(\text{RNC})\{\text{P(OEt)}_3\}_4]\text{BPh}_4$.

Introduction

In previous reports [1,2] we describe the synthesis, characterization, and X-ray crystal structure of salts of the cation bis(aryldiazene) $[\text{M}(\text{ArN=NH})_2\text{L}_4]^{2+}$ where M was iron(II) or ruthenium(II), and showed that the compound underwent a range of interesting reactions [2]. For example, π -acceptor ligands such as CO and

phosphite can substitute only one diazene ligand in $[\text{Ru}(\text{ArN}=\text{NH})_2\text{L}_4]^{2+}$ complexes, affording new ruthenium(II) derivatives. As no diazene complex containing RNC as coligand had been up to now described, and as isocyanide ligands [3,4] are known to cause less steric crowding around a metal than phosphites, while their bonding properties are generally intermediate between CO and phosphite, we decided to undertake a detailed investigation of the reactivity of bis(diazene)- $[\text{Ru}(\text{ArN}=\text{NH})_2\text{L}_4]^{2+}$ derivatives toward isocyanides, which allowed us to synthesize the first complexes containing both diazene and isocyanide ligands bonded to the same central metal, and the results are reported below. The results of studies of the reactivity of these isocyanide-diazene derivatives are also presented.

Experimental

General. All the solvents used were dried over appropriate drying agents, degassed on a vacuum line, and distilled into vacuum-tight storage flasks. Ethanol was dried over calcium hydride and dichloromethane by refluxing over phosphorus pentoxide. Triethyl phosphite (Ega Chemie) was purified by distillation under nitrogen. Substituted phenyl isocyanides were prepared as described by Ziehn et al. [5]. Diazonium salts were made in the usual way [6]. The labeled diazonium salt $[4\text{-CH}_3\text{C}_6\text{H}_4\text{N}=\text{N}^{15}\text{N}]\text{BF}_4$ was prepared from $\text{Na}^{15}\text{NO}_2$ (99% enriched, Stohler Isotope Chemicals) and *p*-toluidine. Other reagents were purchased from commercial sources in the highest available purity and used as received.

Infrared spectra (Table 1) were recorded on a Perkin–Elmer spectrometer model 683. Potassium bromide discs were used for solid state spectra and KBr cells (path length 0.5 mm) for solutions. Proton magnetic resonance spectra were recorded on Varian EM390 or Varian FT-80A instruments, with SiMe_4 as internal standard. Fourier-mode, proton-noise-decoupled ^{31}P NMR spectra were recorded on a Varian FT-80A spectrometer operating at 32.203 MHz; chemical shifts are reported with respect to 85% H_3PO_4 , with downfield shifts positive. Conductivities of 10^{-3} M solutions of the complexes in acetone at 25°C were measured with a “Halosis” bridge. Solution susceptibilities were determined by the Evans method [7].

Synthesis of the complexes. All syntheses work was performed under an inert atmosphere by standard Schlenk techniques. Once isolated, the complexes were found to be stable in air for 1 day. The bis(aryldiazene) complexes $[\text{Ru}(\text{ArN}=\text{NH})_2\{\text{P}(\text{OEt})_3\}_4]\text{Y}_2$ ($\text{Ar} = 4\text{-CH}_3\text{C}_6\text{H}_4$, $4\text{-CH}_3\text{OC}_6\text{H}_4$, $4\text{-FC}_6\text{H}_4$; $\text{Y} = \text{BPh}_4^-$ and PF_6^-) were prepared as previously described [3].

cis- $[\text{Ru}(\text{ArN}=\text{NH})(\text{RNC})\{\text{P}(\text{OEt})_3\}_4](\text{BPh}_4)_2$ (**1a**: $\text{Ar} = \text{R} = 4\text{-CH}_3\text{C}_6\text{H}_4$; **1b**: $\text{Ar} = 4\text{-CH}_3\text{C}_6\text{H}_4$ and $\text{R} = 4\text{-CH}_3\text{OC}_6\text{H}_4$; **1c**: $\text{Ar} = 4\text{-CH}_3\text{C}_6\text{H}_4$ and $\text{R} = \text{C}_6\text{H}_5$; **1d**: $\text{Ar} = 4\text{-CH}_3\text{OC}_6\text{H}_4$ and $\text{R} = 4\text{-CH}_3\text{C}_6\text{H}_4$; **1e**: $\text{Ar} = 4\text{-FC}_6\text{H}_4$ and $\text{R} = 4\text{-CH}_3\text{C}_6\text{H}_4$). An excess of the appropriate isocyanide (1.2 mmol) was added to a solution of $[\text{Ru}(\text{ArN}=\text{NH})_2\{\text{P}(\text{OEt})_3\}_4](\text{BPh}_4)_2$ (0.4 mmol) in 30 ml of CH_2Cl_2 and the mixture was refluxed for 9 h. The solvent was removed under reduced pressure to leave an oil, which was triturated with ethanol. The resulting white solid was filtered off and crystallized from CH_2Cl_2 (5 ml)/ethanol (20 ml); yield $\geq 85\%$. The physical constants and elemental analyses follow. Anal. Found: C, 63.61; H, 7.13; N, 2.49. **1a** $\text{C}_{87}\text{H}_{115}\text{B}_2\text{N}_3\text{O}_{12}\text{P}_4\text{Ru}$ calcd.: C, 63.66; H, 7.06; N, 2.56%. m.p. 169°C dec. Λ_M 178.9 $\text{cm}^2 \Omega^{-1} \text{M}^{-1}$. ^1H NMR: 13.63 [m, 1 H, NH]; 7.57, 7.32, 6.87 [m, 48 H, H phen.]; 4.32 [m, 24 H, CH_2]; 2.39 [s, 3 H, CH_3 diaz.]; 2.42 [s, 3 H, CH_3

Table 1
Selected infrared and $^3\text{P}\{^1\text{H}\}$ NMR data for ruthenium(II) complexes

Compounds ^a	$\nu(\text{CN})$ ^b (cm^{-1})	Spin system	$^3\text{P}\{^1\text{H}\}$ NMR ^{c,d} chemical shifts (δ ppm) and coupling constants (Hz)
<i>cis</i> -[Ru(4-CH ₃ C ₆ H ₄ N=NH)(4-CH ₃ C ₆ H ₄ NC)L ₄](BPh ₄) ₂ (1a)	2170s (2165s)	AB ₂ C	δ_A 128.1 δ_B 116.5 δ_C 116.3 J_{AB} 55.0 J_{AC} 58.5 J_{BC} 54.0
<i>cis</i> -[Ru(4-CH ₃ C ₆ H ₄ N=NH)(4-CH ₃ OC ₆ H ₄ NC)L ₄](BPh ₄) ₂ (1b)	2174s (2170s)	AB ₂ C	δ_A 128.3 δ_B 116.6 δ_C 116.4 J_{AB} 56.0 J_{AC} 58.5 J_{BC} 54.0
<i>cis</i> -[Ru(4-CH ₃ C ₆ H ₄ N=NH)(C ₆ H ₃ NC)L ₄](BPh ₄) ₂ (1c)	2170s (2162s)	AB ₂ C	δ_A 127.9 δ_B 116.3 δ_C 116.1 J_{AB} 56.0 J_{AC} 57.9 J_{BC} 54.0
<i>cis</i> -[Ru(4-CH ₃ OC ₆ H ₄ N=NH)(4-CH ₃ C ₆ H ₄ NC)L ₄](BPh ₄) ₂ (1d)	2172s (2165s)	AB ₂ C	δ_A 128.4 δ_B 116.7 δ_C 116.5 J_{AB} 55.0 J_{AC} 57.0 J_{BC} 54.0
<i>cis</i> -[Ru(4-FC ₆ H ₄ N=NH)(4-CH ₃ C ₆ H ₄ NC)L ₄](BPh ₄) ₂ (1e)	2172s (2163s)	AB ₂ C	δ_A 127.7 δ_B 116.2 δ_C 116.0 J_{AB} 56.0 J_{AC} 58.5 J_{BC} 54.0
<i>cis</i> -[Ru(4-CH ₃ C ₆ H ₄ N=NH)(4-CH ₃ C ₆ H ₄ NC)L ₄](PF ₆) ₂ (1f)	2168s (2160s)	AB ₂ C	δ_A 128.1 δ_B 116.5 δ_C 116.3 J_{AB} 55.0 J_{AC} 58.5 J_{BC} 54.0
<i>cis</i> -[Ru(4-CH ₃ C ₆ H ₄ NC) ₂ L ₄](BPh ₄) ₂ (2)	2202s (2198s)	A ₂ B ₂	δ_A 118.7 δ_B 117.0 J_{AB} 58.0
[Ru(4-CH ₃ C ₆ H ₄ NC) ₃ L ₃](BPh ₄) ₂ (3)	2204m (2200m)		117.3s
[RuH(4-CH ₃ C ₆ H ₄ N=NH)(4-CH ₃ C ₆ H ₄ NC)L ₃](BPh ₄) (4)	2138s (2133s)	ABX ^e	δ_A 140.7 δ_B 137.6 δ_X 149.8 J_{AB} 45.0 J_{AX} 62.8 J_{BX} 39.4
<i>trans</i> -[RuCl(4-CH ₃ C ₆ H ₄ NC)L ₄](BPh ₄) (5)	2131s (2129s)		120.1s

^a L = P(OEt)₃. ^b In CH₂Cl₂ and (KBr). ^c At room temperature in (CD₃)₂CO. ^d Positive shift downfield from 85% H₃PO₄. ^e At room temperature in CD₂Cl₂.

isocy.]; 1.44, 1.41, 1.22 [t, 36 H, CH₃]. Anal. Found: C, 63.00; H, 7.05; N, 2.57. **1b**, C₈₇H₁₁₅B₂O₁₃P₄Ru calcd.: C, 63.04; H, 6.99; N, 2.54%. m.p. 154°C dec. Λ_M 170.2 cm² Ω⁻¹ M⁻¹. ¹H NMR: 13.63 [m, 1 H, NH]; 7.57, 7.33, 6.89 [m, 48 H, H phen.]; 4.30 [m, 24 H, CH₂]; 3.79 [s, 3 H, CH₃ isocy.]; 2.41 [s, 3 H, CH₃ diaz.]; 1.43, 1.40, 1.12 [t, 36 H, CH₃]. Anal. Found: C, 63.38; H, 6.91; N, 2.45. **1c**, C₈₆H₁₁₄B₂N₂O₁₂P₄Ru calcd.: C, 63.47; H, 7.00; N, 2.58%. m.p. 144°C dec. Λ_M 176.5 cm² Ω⁻¹ M⁻¹. ¹H NMR: 13.62 [m, 1 H, NH]; 7.58, 7.35, 6.87 [m, 49 H, H phen.]; 4.32 [m, 24 H, CH₂]; 2.42 [s, 3 H, CH₃ diaz.]; 1.44, 1.41, 1.21 [t, 36 H, CH₃]. Anal. Found: C, 62.88; H, 7.07; N, 2.54. **1d**, C₈₇H₁₁₅B₂N₃O₁₃P₄Ru calcd.: C, 63.04; H, 6.99; N, 2.54%. m.p. 163°C dec. Λ_M 172.9 cm² Ω⁻¹ M⁻¹. ¹H NMR: 13.27 [m, 1 H, NH]; 7.33, 6.88 [m, 48 H, H phen.]; 4.29 [m, 24 H, CH₂]; 3.83 [s, 3 H, CH₃ diaz.]; 2.38 [s, 3 H, CH₃ isocy.]; 1.44, 1.39, 1.21 [t, 36 H, CH₃]. Anal. Found: C, 62.73; H, 6.94; N, 2.39. **1e**, C₈₆H₁₁₁B₂FN₃O₁₂P₄Ru calcd.: C, 62.77; H, 6.86; N, 2.55%. m.p. 154°C. Λ_M 171.7 cm² Ω⁻¹ M⁻¹. ¹H NMR: 13.68 [m, 1 H, NH]; 7.35, 6.87 [m, 48 H, H phen.]; 4.25 [m, 24 H, CH₂]; 2.35 [s, 3 H, CH₃ isocy.]; 1.41, 1.38, 1.19 [t, 36 H, CH₃].

cis-[Ru(4-CH₃C₆H₄N=NH)(4-CH₃C₆H₄NC){P(OEt)₃}₄](PF₆)₂ (**1f**). This compound was prepared by the procedure used for **1** but starting from [Ru(4-CH₃C₆H₄N=NH)₂L₄](PF₆)₂. Anal. Found: C, 36.15; H, 5.85; N, 3.17. **1f**, C₃₉H₇₅F₁₂N₂O₁₂P₆Ru calcd.: C, 36.23; H, 5.85; N, 3.25%. Λ_M 240.3 cm² Ω⁻¹ M⁻¹. ¹H NMR: 13.68 [m, 1 H, NH]; 7.59 [m, 8 H, H phen.]; 4.36 [m, 24 H, CH₂]; 2.48 [s, 3 H, CH₃ diaz.]; 2.44 [s, 3 H, CH₃ isocy.]; 1.48, 1.45, 1.26 [t, 36 H, CH₃].

cis-[Ru(4-CH₃C₆H₄NC)₂{P(OEt)₃}₄](BPh₄)₂ (**2**). An excess of 4-CH₃C₆H₄NC (1.6 mmol, 0.19 ml) was added to a solution of [Ru(4-CH₃C₆H₄N=NH)₂{P(OEt)₃}₄](BPh₄)₂ (0.4 mmol, 0.66 g) in 30 ml of ClCH₂CH₂Cl and the mixture was refluxed for 3.5 h. Evaporation of the solvent under reduced pressure left an oil, which was triturated with ethanol (15 ml). The white solid obtained contained a small amount (ca. 10% by NMR) of [Ru(ArN=NH)(RNC){P(OEt)₃}₄](BPh₄)₂ which was removed by recrystallization. The crude solid was mixed with 30 ml of ethanol and enough dichloromethane (5–7 ml) to produce a homogeneous solution at 40°C. The solution was cooled very slowly to 4°C to give the white microcrystals of [Ru(4-CH₃C₆H₄NC)₂L₄](BPh₄)₂; yield ≥ 50%.

This bis(isocyanide) complex **2** can also be prepared by treating mono(isocyanide) [Ru(4-CH₃C₆H₄N=NH)(4-CH₃C₆H₄NC)L₄](BPh₄)₂ (**1a**) with *p*-tolyl isocyanide (ratio 1/2) in refluxing 1,2-dichloromethane for 3 h. Anal. Found: C, 64.74; H, 6.95; N, 1.66. **2**, C₇₄H₁₁₄B₂NO₁₂P₄Ru calcd.: C, 64.51; H, 7.01; N, 1.71%. Λ_M 173.6 cm² Ω⁻¹ M⁻¹. ¹H NMR: 7.42, 7.33, 6.87 [m, 48 H, H phen.]; 4.36 [m, 24 H, CH₂]; 2.39 [s, 6 H, CH₃ isocy.]; 1.36, 1.40 [t, 36 H, CH₃].

[Ru(4-CH₃C₆H₄NC)₃{P(OEt)₃}₃](BPh₄)₂ (**3**). An excess of *p*-tolyl isocyanide (2.5 mmol, 0.3 ml) was added to a solution of [Ru(4-CH₃C₆H₄N=NH)₂{P(OEt)₃}₄](BPh₄)₂ (0.5 mmol, 0.82 g) in 30 ml of 1,2-dichloromethane and the mixture was refluxed for 5 h. The solvent was removed and the residual oil treated with ethanol (10 ml) to give a white solid, which was filtered off, and recrystallized from ethanol; yield ≥ 70%. This complex can also be obtained by treating bis(isocyanide) complex **2** with 4-CH₃C₆H₄NC (ratio 1/2) in refluxing 1,2-dichloroethane for 3 h. Anal. Found: C, 67.93; H, 6.90; N, 2.55. **3**, C₇₆H₁₀₆B₂N₂O₉P₃Ru calcd.: C, 68.01; H, 6.72; N, 2.64%. m.p. 183°C dec. Λ_M 165.0 cm² Ω⁻¹ M⁻¹. ¹H NMR: 7.38, 6.88 [m, 52 H, H phen.]; 4.36 [m, 18 H, CH₂]; 2.36 [s, 9 H, CH₃ isocy.]; 1.37 [t, 27 H, CH₃].

$[RuH(4-CH_3C_6H_4N=NH)(4-CH_3C_6H_4NC)\{P(OEt)_3\}_3]BPh_4$ (**4**). An excess of $NaBH_4$ (2.6 mmol, 0.1 g, ratio ca. 1/15) was added to a solution of *cis*- $[Ru(4-CH_3C_6H_4N=NH)(4-CH_3C_6H_4NC)\{P(OEt)_3\}_4](BPh_4)_2$ (0.18 mmol, 0.3 g) in 10 ml of ethanol and the mixture was stirred at room temperature for 24 h. The solution was concentrated to 5 ml and then cooled to $-30^\circ C$. The yellow solid that separated out after 2–3 h was filtered off and recrystallized from CH_2Cl_2 (2 ml)/ethanol (10 ml); yield $\geq 60\%$. Anal. Found: C, 58.86; H, 7.10; N, 3.47. **4**, $C_{57}H_{81}BN_3O_9P_3Ru$ calcd.: C, 59.17; H, 7.06; N, 3.63. m.p. $115^\circ C$ dec. Λ_M $84.6\text{ cm}^2\Omega^{-1}M^{-1}$. 1H NMR (CD_2Cl_2): 14.01 [m, 1 H; $J_{AZ} = 2.0$, $J_{BZ} = 5.5$, $J_{XZ} = 7.5$ Hz; Z part of ABXYZ spectrum for Z = H diazenel]; 7.25, 6.97 [m, 28 H, H phen.]; 4.01 [m, 18 H, CH_2]; 2.39 [s, 3 H, CH_3 diaz.]; 2.37 [s, 3 H, CH_3 isocy.]; 1.28, 1.26, 1.19 [t, 27 H, CH_3]; -7.09 [m, 1 H, H hydride; $J_{AY} = -24.5$, $J_{BY} = -17.0$, $J_{XY} = -1.2$, $J_{YZ} = 0.1$ Hz; Y part of ABXYZ spectrum for Y = H hydride].

$[RuCl(4-CH_3C_6H_4NC)\{P(OEt)_3\}_4]BPh_4$ (**5**). Lithium chloride (1.2 mmol, 0.048 g) was added to a solution of $[Ru(4-CH_3C_6H_4N=NH)(4-CH_3C_6H_4NC)\{P(OEt)_3\}_4](BPh_4)_2$ (0.4 mmol, 0.66 g) in 15 ml of acetone and the mixture was refluxed for 1.5 h. Evaporation of the solvent under reduced pressure left an oil, which was treated with 10 ml of ethanol. The white solid that slowly formed was filtered off and recrystallized from CH_2Cl_2 (3 ml)/ethanol (10 ml); yield $\geq 75\%$. Anal. Found: C, 54.41; H, 7.14; N, 1.04; Cl, 3.01. **5**, $C_{50}H_{84}BClNO_{12}P_4Ru$ calcd.: C, 54.35; H, 7.09; N, 1.13; Cl, 2.86. m.p. $180^\circ C$ dec. Λ_M $85.7\text{ cm}^2\Omega^{-1}M^{-1}$. 1H NMR: 7.27, 6.88 [m, 24 H, H phen.]; 4.31 [m, 24 H, CH_2]; 2.34 [s, 3 H, CH_3 isocy.]; 1.31 [t, 36 H, CH_3].

*X-ray crystallography of $[Ru(4-CH_3C_6H_4N=NH)(4-CH_3C_6H_4NC)\{P(OEt)_3\}_4](PF_6)_2$ (**1f**)*. Diffraction measurements were made at room temperature on a computer-controlled Siemens AED three-circle diffractometer. Ni-filtered $Cu-K_\alpha$ radiation was used, and the choice of this radiation deserves comment. Initially, the data set was collected (on the same crystal) with $Mo-K_\alpha$ radiation (which would usually be expected to be more suitable for a sample of such a chemical composition), but the results were not satisfactory: the data could not be refined below an *R* index of 0.100 and the estimated standard deviations of the atomic coordinates were rather large (ca. 1.5 larger than those later obtained by using $Cu-K_\alpha$ radiation). Because the crystal cell is rather large, these findings can be partly attributed to the fact that the short-wave $Mo-K_\alpha$ radiation as tends to give a worse separation between the reflections. Moreover, the use of $Mo-K_\alpha$ radiation led to a lower number of reflections (no. of data collected: 9201, $\vartheta_{\max} 23.0^\circ$; no. of unique observed data, $I > 2\sigma(I)$: 3996). However, the structural parameters from the two data sets were in full agreement. Peak-search, centering, and indexing procedures led to a primitive monoclinic unit-cell, and gave preliminary lattice constants which were successively refined by least-squares fitting to the diffractometer settings of 15 intense reflections distributed over a wide range of reciprocal space. Crystal parameters are listed in Table 2, together with other information on the data collection and structure refinement. A total of 11244 reflections was measured in the *hkl* and $\bar{h}hl$ octants by the $\vartheta-2\vartheta$ scan technique. Crystals were poor in quality, and although the crystal specimen chosen for data collection was of good size, the reflections with $I \geq 3\sigma(I)$ amounted only to about 43% of all reflections measured. Examination of intensity data revealed systematic absences $h0l$, $h + l$ odd and $0k0$, k odd, showing the space group to be $P2_1/n$. The intensity of a periodically monitored check reflection remained essentially constant throughout the run. Inten-

Table 2

Details of data collection and refinement for $[\text{Ru}(\text{4-CH}_3\text{C}_6\text{H}_4\text{N=NH})(\text{4-CH}_3\text{C}_6\text{H}_4\text{NC})\text{-}\{\text{P}(\text{OEt})_3\}_4](\text{PF}_6)_2$

Formula	$\text{C}_{39}\text{H}_{75}\text{F}_{12}\text{N}_3\text{O}_{12}\text{P}_6\text{Ru}$
<i>fw</i>	1292.93
Crystal system	monoclinic
Color and habit	yellow parallelepipeds
Crystal dimensions (mm)	$0.13 \times 0.26 \times 0.99$
Space group	$P2_1/n^a$
<i>a</i> (Å)	23.527(4)
<i>b</i> (Å)	22.597(3)
<i>c</i> (Å)	11.565(1)
β (deg)	92.78(1)
<i>V</i> (Å ³)	6141(1)
<i>Z</i>	4
Radiation (λ , Å)	Ni-filtered Cu- K_α ($\lambda = 1.54178$ Å)
$d_{\text{calcd.}}$ (g cm ⁻³)	1.398
$\mu(\text{Cu-}K_\alpha)$ (cm ⁻¹)	44.02
Scan method	$\theta - 2\theta$
2θ limits (deg)	6.0–130.0
Standard reflection	one (3 12 3) every 50 reflections
Intensity variation	negligible
No. of reflections measured	11244
No. of independent observed reflections	4812
<i>R</i> _{int}	0.0334
No. of variables	478
Data-to-variable ratio	10.1/1
Max. and min. heights in final ΔF map (e Å ⁻³)	+1.02, -0.51
<i>k</i> , <i>g</i> ($w = k/[\sigma^2(F_o) + gF_o^2]$)	1.7489, 0.003650
<i>R</i> ^b	0.0906
<i>R</i> _w ^c	0.0986
<i>R</i> _g ^d	0.1261
GOF	2.1158

^a A non-standard setting of $P2_1/c$, ⁵*C*_{2h}, No. 14. ^b $R = \Sigma |\Delta F| / \Sigma |F_o|$. ^c $R_w = \Sigma (\Delta F) w^{1/2} / \Sigma w^{1/2} F_o$.

^d $R_g = [\Sigma w(\Delta F)^2 / \Sigma w F_o^2]^{1/2}$.

sities were processed with the peak profile procedure and corrected for Lorentz and polarization effects. Corrections for absorption and extinction were also made by the empirical method of Walker and Stuart [8].

The heavy-atom method was used to solve the structure, with the Patterson map revealing the position of the ruthenium atom. Subsequent alternate structure factor and Fourier difference synthesis calculations yielded the positions of the remaining non-hydrogen atoms. Refinement was performed by full-matrix least-squares techniques, using anisotropic thermal parameters for all atoms except ethyl carbons and fluorines, which were refined isotropically. The function minimized was $\Sigma w(\Delta F)^2$; unit weights were used in the first stages of refinement, while a weighting scheme was then introduced with $w = k[\sigma^2(F_o) + gF_o^2]^{-1}$, the final *k* and *g* values being given in Table 2. In order to reduce the number of variable parameters, the two aromatic rings were treated as rigid bodies of *D*_{6h} symmetry.

The refinement process was complicated by some disorder of the two hexafluorophosphate ions and, to a lesser extent, of the ethyl groups. This disorder,

which is reflected in the large thermal motion shown by all these atoms, probably accounts for the disappointingly high residual R index (0.0906). However, a satisfactory disordered model was found in the case of one of the two PF_6 ions, i.e., that involving P(5), which was refined taking into account two different orientations for the F atoms around a common P site.

Neutral scattering factors were employed and anomalous dispersion corrections were made for Ru and P. The SHELX-76 system [9] was used for most of the

Table 3

Fractional atomic coordinates ($\times 10^5$ for Ru and $\times 10^4$ for P, O, N, C, and F)
(Occupancy 0.6 for F(1)–F(6); occupancy 0.4 for F(1')–F(6'); occupancy 0.75 for F(7)–F(12) efforts to detect a second orientation failed.)

Atom	x	y	z	Atom	x	y	z
Ru	18240(4)	24573(4)	15499(8)	C(19)	2556(11)	2260(11)	4747(24)
P(1)	2260(2)	3052(2)	182(3)	C(20)	2477(12)	2255(13)	5874(28)
P(2)	1018(2)	3026(2)	1622(3)	C(21)	3383(9)	3367(9)	3443(17)
P(3)	1430(2)	1844(2)	91(3)	C(22)	3925(11)	3288(11)	2931(22)
P(4)	2298(2)	3002(2)	3019(3)	C(23)	2177(11)	4012(13)	4209(23)
P(5)	6254(2)	5840(2)	3324(4)	C(24)	1897(12)	4576(13)	4096(24)
P(6)	8740(3)	4234(3)	1850(8)	C(25)	3340(5)	1294(5)	1844(17)
O(1)	1960(5)	3130(5)	–1043(9)	C(26)	3562(5)	1141(5)	788(17)
O(2)	2411(5)	3703(4)	623(9)	C(27)	4086(5)	852(5)	766(17)
O(3)	2851(4)	2761(5)	–108(8)	C(28)	4387(5)	717(5)	1800(17)
O(4)	469(5)	2663(6)	1221(12)	C(29)	4165(5)	869(5)	2856(17)
O(5)	889(5)	3286(6)	2822(11)	C(30)	3642(5)	1158(5)	2878(17)
O(6)	1011(6)	3593(5)	854(12)	C(31)	4948(9)	408(12)	1703(23)
O(7)	1947(5)	1568(6)	–611(11)	C(32)	1476(5)	1950(5)	2733(10)
O(8)	1018(5)	2129(5)	–831(9)	C(33)	930(4)	1336(4)	4133(7)
O(9)	1081(7)	1315(5)	594(13)	C(34)	1197(4)	1001(4)	5016(7)
O(10)	2251(5)	2789(5)	4293(8)	C(35)	872(4)	701(4)	5805(7)
O(11)	2959(4)	3007(4)	2771(8)	C(36)	279(4)	735(4)	5711(7)
O(12)	2117(4)	3669(4)	3149(9)	C(37)	12(4)	1070(4)	4828(7)
N(1)	2548(4)	1929(5)	1568(10)	C(38)	337(4)	1370(4)	4039(7)
N(2)	2736(7)	1562(7)	2134(16)	C(39)	–119(8)	414(8)	6549(15)
N(3)	1257(5)	1662(4)	3375(10)	F(1)	5875(10)	5274(10)	3188(19)
C(1)	1631(15)	3541(16)	–1492(32)	F(2)	6644(10)	5556(10)	4381(20)
C(2)	1668(10)	3702(10)	–2760(22)	F(3)	5873(9)	6062(8)	4367(18)
C(3)	2720(13)	4139(15)	80(27)	F(4)	6722(12)	6322(12)	3457(22)
C(4)	2728(14)	4662(16)	536(28)	F(5)	5826(13)	6165(11)	2528(26)
C(5)	3170(11)	2763(12)	–1127(23)	F(6)	6576(12)	5610(11)	2296(24)
C(6)	3765(11)	2592(10)	–759(22)	F(1')	6136(12)	5109(12)	3291(22)
C(7)	–63(14)	2737(13)	1280(26)	F(2')	6929(20)	5654(20)	3326(43)
C(8)	–482(15)	2480(14)	635(30)	F(3')	6259(16)	5844(15)	4613(27)
C(9)	730(16)	3071(17)	3785(32)	F(4')	6453(13)	6551(13)	3494(25)
C(10)	264(12)	3322(11)	4480(22)	F(5')	5552(17)	6043(18)	3150(40)
C(11)	742(13)	4174(14)	1075(27)	F(6')	6195(15)	5918(14)	1976(25)
C(12)	450(16)	4255(17)	38(38)	F(7)	8188(9)	4278(8)	1200(16)
C(13)	1964(14)	1131(16)	–1457(28)	F(8)	9317(9)	4103(8)	2459(17)
C(14)	2251(18)	666(20)	–1261(34)	F(9)	8505(8)	3741(9)	2545(17)
C(15)	716(18)	1885(20)	–1909(40)	F(10)	8643(9)	4650(9)	2887(19)
C(16)	432(13)	2263(14)	–2584(27)	F(11)	8848(10)	4889(11)	1449(19)
C(17)	739(19)	897(20)	336(39)	F(12)	8906(10)	3922(11)	798(21)
C(18)	702(12)	447(14)	1219(27)				

Table 4

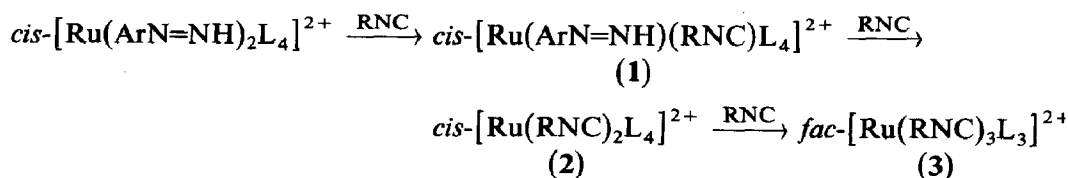
Selected bond distances (Å) and angles (deg).

Ru-P(1)	2.349(4)	Ru-P(2)	2.295(4)	Ru-P(3)	2.340(4)
Ru-P(4)	2.338(4)	Ru-N(1)	2.080(11)	Ru-C(32)	1.992(12)
N(1)-N(2)	1.13(2)	C(32)-N(3)	1.13(2)	N(2)-C(25)	1.59(2)
N(3)-C(33)	1.40(1)				
P(1)-Ru-P(2)	95.3(1)	P(1)-Ru-P(3)	91.4(1)		
P(1)-Ru-P(4)	88.9(1)	P(1)-Ru-N(1)	87.2(3)		
P(1)-Ru-C(32)	178.4(4)	P(2)-Ru-P(3)	93.4(1)		
P(2)-Ru-P(4)	92.5(1)	P(2)-Ru-N(1)	177.2(3)		
P(2)-Ru-C(32)	86.0(4)	P(3)-Ru-P(4)	174.1(1)		
P(3)-Ru-N(1)	87.9(3)	P(3)-Ru-C(32)	89.6(4)		
P(4)-Ru-N(1)	86.2(3)	P(4)-Ru-C(32)	90.1(4)		
N(1)-Ru-C(32)	91.5(5)	Ru-N(1)-N(2)	136.2(12)		
Ru-C(32)-N(3)	177.0(11)	N(1)-N(2)-C(25)	118.9(15)		
C(32)-N(3)-C(33)	173.7(13)				

calculations, which were carried out on a GOULD-SEL 32/77 computer. Other programs used were those of ref. 3. Final atomic coordinates are listed in Table 3; selected bond distances and angles are given in Table 4. Lists of thermal parameters, observed and calculated structure factors, and all bond distances and angles are available from the authors.

Results and discussion

The reaction of the bis(diazeno) complexes $[\text{Ru}(\text{ArN}=\text{NH})_2\text{L}_4]^{2+}$ with an excess of isocyanide in boiling 1,2-dichloroethane first gives the mixed-ligand cations $[\text{Ru}(\text{ArN}=\text{NH})(\text{RNC})\text{L}_4]^{2+}$ (1), which react further with RNC to give the bis(isocyanide) cations $[\text{Ru}(\text{RNC})_2\text{L}_4]^{2+}$ (2) and finally the tris(isocyanide) cations $[\text{Ru}(\text{RNC})_3\text{L}_3]^{2+}$ (3), as shown in Scheme 1. However, at lower temperature (in



(L = P(OEt)₃, Ar = R = 4-CH₃C₆H₄. a: Ar = 4-CH₃C₆H₄ and R = 4-CH₃OC₆H₄, b: Ar = 4-CH₃C₆H₄ and R = C₆H₅, c: Ar = 4-CH₃OC₆H₄ and R = 4-CH₃C₆H₄, d: Ar = 4-FC₆H₄ and R = 4-CH₃C₆H₄, e)

Scheme 1

boiling CH₂Cl₂ instead of 1,2-dichloroethane) only mono(derivative) $[\text{Ru}(\text{ArN}=\text{NH})(\text{RNC})\text{L}_4]^{2+}$ (1) is formed when the bis(diazeno) $[\text{Ru}(\text{ArN}=\text{NH})_2\text{L}_4]^{2+}$ cation is treated with an excess of isocyanide.

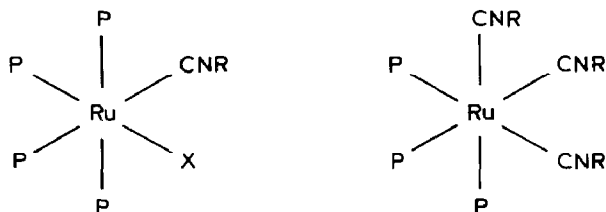
The isolated salts of these cations are stable, white or light-yellow solids, diamagnetic and 1/2 electrolytes; selected data for them are shown in Table 1.

The IR spectra of mono(diazeno) $[\text{Ru}(\text{ArN}=\text{NH})(\text{RNC})\text{L}_4]^{2+}$ derivatives 1 show a strong band at 2168–2174 cm⁻¹ (CH₂Cl₂), attributed to the ν(CN) of the

isocyanide ligand. Furthermore, in the non-aromatic diazene proton region, the ^1H NMR spectra of these compounds show the expected resonance of the $\text{ArN}=\text{NH}$ ligand at δ 13.6–13.8, which appears as a multiplet owing to the coupling between the NH and the four phosphorus nuclei of the phosphite ligand *. In the labeled $[\text{Ru}(\text{ArN}=\text{}^{15}\text{NH})(\text{RNC})\text{L}_4]^{2+}$ compound this NH signal is split into two multiplets ($J(^{15}\text{NH}) = 65$ Hz), confirming the existence of the $\text{ArN}=\text{NH}$ moiety.

In the temperature range $+34$ to -80°C the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of **1** appear as AB_2C multiplets, which can be simulated with the parameters reported in Table 1. The cations thus have *cis*-geometry in solution, as they do in the solid (see below).

Both in the solid state and in CH_2Cl_2 solution, the infrared spectra of bis(isocyanide) complexes **2** show two bands at 2202 – 2165 cm^{-1} attributed to the $\nu(\text{CN})$ of two mutually *cis*-isocyanide ligands. Furthermore, the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra are



A_2B_2 multiplets (Table 1), as expected for a *cis*-geometry (II). On the other hand, a *fac*-geometry (III) can be proposed in solution for the tris(isocyanide) cation **3** on the basis of the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra (singlet at 117.3 ppm) and IR spectra [$\nu(\text{CN})$ at 2204m and 2176s cm^{-1} in CH_2Cl_2].

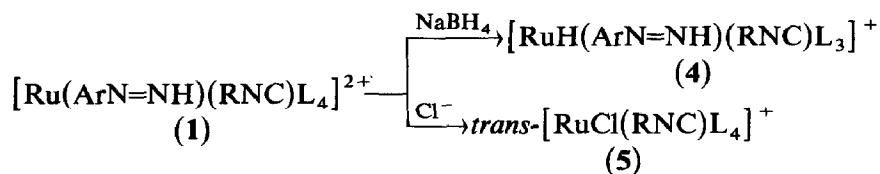
Table 1 shows that $\nu(\text{CN})$ in compounds **1** is not sensitive to the nature of the substituent on the phenyl ring of the isocyanide ligand. Studies of the chemical properties of monodiazenes **1** revealed them to be fairly robust species. The cations **1** can not deprotonated by NEt_3 or KOH to give aryldiazenido derivatives, and this behaviour parallels that previously observed for iron [1] and ruthenium [2] mono(diazeno) $[\text{MH}(\text{ArN}=\text{NH})\text{L}_4]^+$ ($\text{M} = \text{Fe}$ and Ru) derivatives.

Substitution reactions with isocyanide are slow (see above), and there is no reaction when $\text{P}(\text{OEt})_3$. However, refluxing a 1,2-dichloroethane solution of **1** containing an excess of $\text{P}(\text{OEt})_3$ for 6–10 h gives the cation $[\text{RuCl}(\text{RNC})\{\text{P}(\text{OEt})_3\}_4]^+$ (**5**), which is probably formed by replacement of the $\text{ArN}=\text{NH}$ ligand by abstraction of Cl^- from the solvent. Treatment with CO (1 atm) of **1** in boiling $(\text{CH}_3)_2\text{CO}$ or $\text{ClCH}_2\text{CH}_2\text{Cl}$ gives rise to a slow carbonylation reaction, to form an oily product whose IR and NMR spectra indicate that it is a mixture.

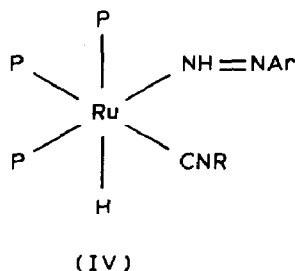
Diazeno complexes **1** react at room temperature with an excess of NaBH_4 in ethanol (Scheme 2) to afford the new hydridic species, $[\text{RuH}(\text{ArN}=\text{NH})(\text{RNC})\text{L}_3]^+$

* In the case of the cation *cis*- $[\text{Ru}(4\text{-CH}_3\text{C}_6\text{H}_4\text{N}=\text{NH})(\text{C}_6\text{H}_5\text{NC})\text{L}_4]^{2+}$ (**1c**), in view of the fact that the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum is an AB_2C multiplet (see Table 1), the NH pattern at δ 13.63 can be simulated as the X part of an AB_2CX system ($\text{X} = \text{H}$ diazene) with the following parameters: $J_{\text{AX}} = 9.5$; $J_{\text{BX}} = 1.29$; $J_{\text{CX}} = 2.5$ Hz. A similar coupling between the non-aromatic diazene hydrogen atom and the P nuclei of the phosphite was observed for the bis(diazeno) $[\text{Ru}(\text{ArN}=\text{NH})_2\text{L}_4]^{2+}$ derivatives (ref. 2).

(4), the tetraphenylborate salt of which was isolated as a yellow solid, which was diamagnetic and a 1/1 electrolyte. It gives a $\nu(\text{CN})$ band at 2137 cm^{-1} (CH_2Cl_2), and the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra appear as an ABX multiplet (Table 1), in agreement with a *fac*-structure (IV). Chloride ion does not react with 1 at room temperature, but in boiling acetone substitution of the diazene ligand is observed, and gives the cation *trans*- $[\text{RuCl}(\text{RNC})\text{L}_4]^+$ (5).



Scheme 2



We also studied the reactions of these derivatives with alkoxide ions and amines in an attempt to obtain carbene complexes. However, no reaction was observed when the cations 1, 2, and 3 were treated with either of these reagents, indicating that the RNC ligand is not susceptible to nucleophilic attack.

Figure 1 gives a perspective view of the complex cation 1f and shows the atom-labeling scheme used. The salt $[\text{Ru}(4\text{-CH}_3\text{C}_6\text{H}_4\text{N=NH})(4\text{-CH}_3\text{C}_6\text{H}_4\text{NC})\{\text{P}(\text{OEt})_3\}_4](\text{PF}_6)_2$ crystallized with four cations and eight anions in the unit cell. The ruthenium atom is in a hexacoordinate octahedral environment formed by four phosphite groups, one diazene ligand, and one isocyanide ligand, with the latter two ligands in mutually *cis*-position. The arrangement of the six coordinating atoms around ruthenium is not far removed from a regular octahedral, as indicated by the angles, all very near 90° or 180° , and by least-squares calculations which show that the set of four ligand atoms forming the coordination planes of the octahedron are satisfactorily planar, deviating at most by $0.15\text{ \AA}$ from their plane of best fit (mean deviation: $0.02\text{ \AA}$, metal atom not included in calculations).

The Ru–P distances are $2.349(4)$, $2.295(4)$, $2.340(4)$, and $2.338(4)\text{ \AA}$, the shortest distance being for the bond *trans* to the diazene ligand, reflecting the very small *trans*-influence of diazene, a feature which was also found in the bis(diazene) complex. These distances fall within the range of $2.21\text{--}2.35\text{ \AA}$ observed for other phosphite-ruthenium(II) complexes [10].

The tetrahedral coordination around the P atoms is considerably distorted, as expected for coordinated phosphite ligands with Ru–P–O angles larger (mean 113.8°) than the tetrahedral value and O–P–O angles smaller (mean 104.8°). The P–O distances range from $1.55(1)$ to $1.62(1)\text{ \AA}$.

The Ru–N distance at $2.080(11)\text{ \AA}$ is in fair agreement with the corresponding distances in $[\text{RuCl}(\text{CO})_2(\text{HN}_2\text{C}_6\text{H}_5)(\text{PPh}_3)_2][\text{ClO}_4] \cdot \text{CH}_2\text{Cl}_2$ [11] ($2.086(5)\text{ \AA}$) and

Table 5
Structural parameters for ruthenium-isocyanide complexes (distance in Å, angles in deg)

Compound	Ru-C	C-N	N-C	Ru-C-N	C-N-C
$\text{RuI}_2[\text{CHNMe}(p\text{-MeC}_6\text{H}_4)(\text{CO})(p\text{-MeC}_6\text{H}_4\text{NC}(\text{PPh}_3) \cdot \text{H}_2\text{O})]_{12}$	1.998(16)	1.155(22)	1.420(22)	177.1(7)	170.9(10)
$\text{Ru}(\text{t-BuNC})_4(\text{PPh}_3) [4b]$	2.00(3)	1.17(4)	1.42(5)	176(2)	167(2)
	1.86(2)	1.22(3)	1.51(4)	177(2)	131(2)
	1.94(2)	1.14(3)	1.34(3)	176(2)	165(2)
$\text{RuCl}_2(\text{CO})(p\text{-ClC}_6\text{H}_4\text{NC}(\text{PPh}_3)_2 \cdot \text{C}_2\text{H}_5\text{OH}) [13]$	2.004(15)	1.199(19)	1.455(18)	173.1(10)	176.9(12)
$\text{Ru}(\text{Ph})(\text{CO})(\text{PhCO})(\text{t-BuNC})(\text{PMe}_2\text{Ph})_2 [14]$	2.013(9)	1.143(12)	1.458(13)	171.6(8)	169.7(9)
$\text{RuCl}(\text{Ph})(\text{CO})(\text{t-BuNC})(\text{PMe}_2\text{Ph})_2 [15]$	1.992(12)	1.13(2)	1.40(1)	177.0(11)	173.7(13)
$[\text{Ru}(p\text{-MeC}_6\text{H}_4\text{N}=\text{NH})(p\text{-MeC}_6\text{H}_4\text{NC})(\text{P}(\text{OEt})_3)_4](\text{PF}_6)_2^a$					

^a Compound 1f.

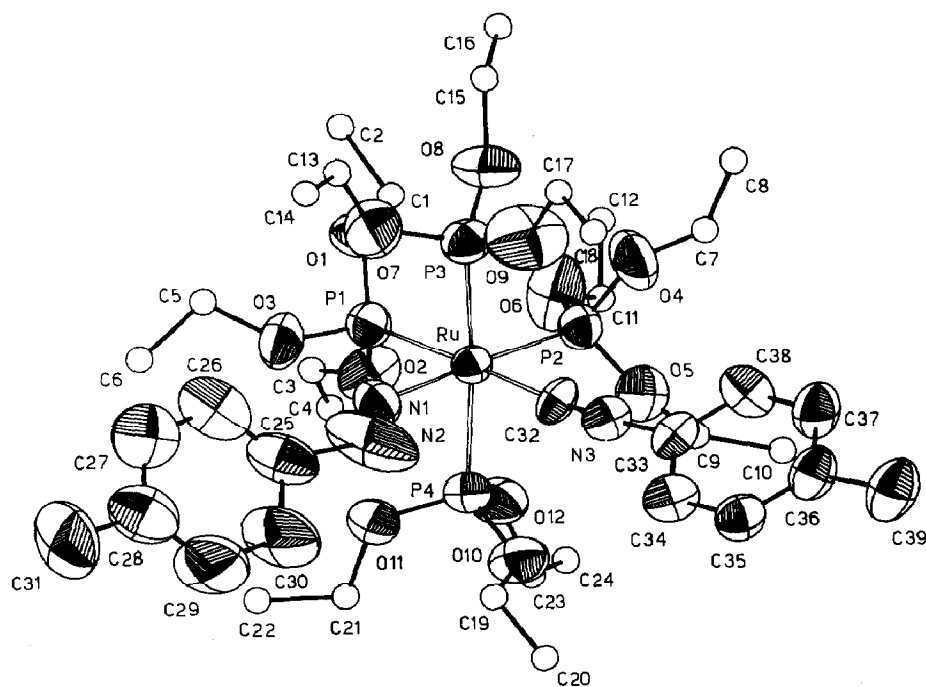


Fig. 1. ORTEP diagram and atom labeling scheme for the $[\text{Ru}(4\text{-CH}_3\text{C}_6\text{H}_4\text{N=NH})(4\text{-CH}_3\text{C}_6\text{H}_4\text{NC})(\text{P}(\text{OEt})_3)_4]^{2+}$ cation. Thermal ellipsoids are drawn at the 40% probability level. Anisotropic parameters were used only for shaded atoms. Ethyl carbon atoms are shown artificially small.

$[\text{Ru}(4\text{-CH}_3\text{C}_6\text{H}_4\text{N=NH})_2\{\text{P}(\text{OEt})_3\}_4](\text{PF}_6)_2$ [2] (2.09(1) and 2.12(1) Å), the only two other comparable species containing Ru–N diazene linkages for which structural data are available. When comparison is made with the structural parameters found for these ruthenium compounds, the N–N distance in **1f** is seen to be significantly shorter, and the N–C distance longer, but little more can be said of them in view of the relatively high standard deviations for the position of the N(2) atom and the rather large value of its thermal parameters.

The isocyanide moiety bonds to ruthenium in an essentially linear manner, the Ru–C–N–C sequence showing a bend of 3.0° at the C atom and 6.3° at the N atom. The structural parameters agree closely with those for other ruthenium-isocyanide complexes (Table 5).

There are several intermolecular contacts in the structure, the shortest of which (3.0 Å) are between the ethyl carbon and fluorine atoms.

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