

Preparation and Reactivity of Mixed-Ligand Ruthenium(II) Hydride Complexes with Phosphites and Polypyridyls

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Chloro complexes $[\text{RuCl}(\text{N-N})\text{P}_3]\text{BPh}_4$ (**1–3**) [N-N = 2,2'-bipyridine, bpy; 1,10-phenanthroline, phen; 5,5'-dimethyl-2,2'-bipyridine, 5,5'-Me₂bpy; P = $\text{P}(\text{OEt})_3$, $\text{PPh}(\text{OEt})_2$ and PPh_2OEt] were prepared by allowing the $[\text{RuCl}_4(\text{N-N})]\cdot\text{H}_2\text{O}$ compounds to react with an excess of phosphite in ethanol. The bis(bipyridine) $[\text{RuCl}(\text{bpy})_2\{\text{P}(\text{OEt})_3\}]\text{BPh}_4$ (**7**) complex was also prepared by reacting $\text{RuCl}_2(\text{bpy})_2\cdot 2\text{H}_2\text{O}$ with phosphite and ethanol. Treatment of the chloro complexes **1–3** and **7** with NaBH_4 yielded the hydride $[\text{RuH}(\text{N-N})\text{P}_3]\text{BPh}_4$ (**4–6**) and $[\text{RuH}(\text{bpy})_2\text{P}]\text{BPh}_4$ (**8**) derivatives, which were characterized spectroscopically and by the X-ray crystal structure determination of $[\text{RuH}(\text{bpy})\{\text{P}(\text{OEt})_3\}_3]\text{BPh}_4$ (**4a**). Protonation reaction of the new hydrides with Brønsted acid was studied and led to dicationic $[\text{Ru}(\eta^2\text{-H}_2)(\text{N-N})\text{P}_3]^{2+}$ (**9**, **10**) and $[\text{Ru}(\eta^2\text{-H}_2)(\text{bpy})_2\text{P}]^{2+}$ (**11**) dihydrogen derivatives. The presence of the $\eta^2\text{-H}_2$ ligand was indicated by a short $T_{1\text{min}}$ value and by the measurements of the J_{HD} in the $[\text{Ru}](\eta^2\text{-HD})$ isotopomers. From $T_{1\text{min}}$ and J_{HD} values the H–H distances of the dihydrogen complexes were also calculated. A series of ruthenium complexes, $[\text{RuL}(\text{N-N})\text{P}_3](\text{BPh}_4)_2$ and $[\text{RuL}(\text{bpy})_2\text{P}](\text{BPh}_4)_2$ (P = $\text{P}(\text{OEt})_3$; L = H_2O , CO , 4- $\text{CH}_3\text{C}_6\text{H}_4\text{NC}$, CH_3CN , 4- $\text{CH}_3\text{C}_6\text{H}_4\text{CN}$, $\text{PPh}(\text{OEt})_2$), was prepared by substituting the labile $\eta^2\text{-H}_2$ ligand in the **9**, **10**, **11** derivatives. The reactions of the new hydrides **4–6** and **8** with both mono- and bis(aryldiazonium) cations were studied and led to aryldiazene $[\text{Ru}(\text{C}_6\text{H}_5\text{N}=\text{NH})(\text{N-N})\text{P}_3](\text{BPh}_4)_2$ (**19**, **21**), $[\{\text{Ru}(\text{N-N})\text{P}_3\}_2(\mu\text{-4,4'}\text{-NH}=\text{NC}_6\text{H}_4\text{-C}_6\text{H}_4\text{N}=\text{NH})](\text{BPh}_4)_4$ (**20**), and $[\text{Ru}(\text{C}_6\text{H}_5\text{N}=\text{NH})(\text{bpy})_2\text{P}](\text{BPh}_4)_2$ (**22**) derivatives. Also the heteroallenes CO_2 and CS_2 reacted with $[\text{RuH}(\text{bpy})_2\text{P}]\text{BPh}_4$, yielding the formate $[\text{Ru}\{\eta^1\text{-OC(H)=O}\}(\text{bpy})_2\text{P}]\text{BPh}_4$ and dithioformate $[\text{Ru}\{\eta^1\text{-SC(H)=S}\}(\text{bpy})_2\text{P}]\text{BPh}_4$ derivatives.

Introduction

In the preceding paper of this series¹ we have reported the synthesis and the reactivity of new iron(II) hydride complexes of the $[\text{FeH}(\text{N-N})\text{P}_3]\text{BPh}_4$ (N-N = 2,2'-bipyridine and 1,10-phenanthroline; P = phosphite) type containing mixed phosphite and polypyridyl as supporting ligands. We have now extended these studies to ruthenium with the aim first to test whether similar complexes can be prepared and then to compare the properties of the complexes through the two metals, mainly toward the protonation reaction and the insertion into the M–H bonds. A glance through the literature shows that, in contrast with iron, some examples of poly-

pyridyl ruthenium hydrides are known and include cationic carbonyls,² $[\text{RuH}(\text{bpy})(\text{PPh}_3)_2(\text{CO})]^+$, neutral³ $\text{RuHCl}(\text{bpy})\text{-P}_2$ (P = PPh_3 , PCy_3), and the bis(2,2'-bipyridine)⁴ $[\text{RuH}(\text{bpy})_2\text{L}]^+$ (L = CO , PPh_3) derivatives. No examples, however, of ruthenium hydride complexes containing either the N_2P_3 donor set or the mixed-ligand phosphite–polypyridyl have been reported. In this paper we describe the development of a new synthetic route to new ruthenium hydrides containing both phosphite and polypyridyl as

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supporting ligands as well as some reactivity, including the protonation and the insertion reaction of the new hydrides.

Experimental Section

The general procedures have been previously reported.¹ The $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ was a Pressure Chem. (U.S.A.) product, used as received. *p*-Tolyl isocyanide was obtained by the method of Ziehn et al.⁵

Synthesis of Complexes. The complexes $\text{RuCl}_4(\text{bpy}) \cdot \text{H}_2\text{O}$, $\text{RuCl}_4(\text{phen}) \cdot \text{H}_2\text{O}$, $\text{RuCl}_4(5,5'\text{-Me}_2\text{bpy}) \cdot \text{H}_2\text{O}$, and $\text{RuCl}_2(\text{bpy})_2 \cdot 2\text{H}_2\text{O}$ were prepared following the method previously reported.^{6,7} The spectroscopic data (IR and NMR) of the new complexes are reported in Tables 1, 2, and 3.

[RuCl(bpy) $_3$]BPh $_4$ (1) [P = P(OEt) $_3$ (a), PPh(OEt) $_2$ (b), PPh $_2$ OEt (c)]. An excess of the appropriate phosphite (3.75 mmol) was added to a solution of $\text{RuCl}_4(\text{bpy}) \cdot \text{H}_2\text{O}$ (0.30 g, 0.72 mmol) in 10 mL of ethanol, and the reaction mixture was refluxed for 3 h. After filtration, the solution was concentrated to about 5 mL and an excess of NaBPh $_4$ (1.5 mmol, 0.513 g) in 3 mL of ethanol was added. A red-brown solid slowly separated out from the resulting solution, which was filtered and crystallized from CH_2Cl_2 and ethanol; yield $\geq 85\%$. Anal. Calcd for $\text{C}_{52}\text{H}_{73}\text{BClN}_2\text{O}_9\text{P}_3\text{Ru}$ (1a): C, 56.25; H, 6.63; N, 2.52; Cl, 3.19. Found: C, 56.12; H, 6.74; N, 2.40; Cl, 3.41; $\Lambda_M = 51.7 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$. Anal. Calcd for $\text{C}_{64}\text{H}_{73}\text{BClN}_2\text{O}_6\text{P}_3\text{Ru}$ (1b): C, 63.71; H, 6.10; N, 2.32; Cl, 2.94. Found: C, 63.48; H, 6.05; N, 2.25; Cl, 3.13; $\Lambda_M = 55.6 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$. Anal. Calcd for $\text{C}_{76}\text{H}_{73}\text{BClN}_2\text{O}_3\text{P}_3\text{Ru}$ (1c): C, 70.07; H, 5.65; N, 2.15; Cl, 2.72. Found: C, 70.29; H, 5.52; N, 2.02; Cl, 2.59; $\Lambda_M = 54.8 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$.

[RuCl(phen) $_3$]BPh $_4$ (2) [P = P(OEt) $_3$ (a), PPh(OEt) $_2$ (b), PPh $_2$ OEt (c)]. These complexes were prepared like the related 2,2'-bipyridine derivatives 1, using $\text{RuCl}_4(\text{phen}) \cdot \text{H}_2\text{O}$ as a precursor; yield $\geq 75\%$. Anal. Calcd for $\text{C}_{54}\text{H}_{73}\text{BClN}_2\text{O}_9\text{P}_3\text{Ru}$ (2a): C, 57.17; H, 6.49; N, 2.47; Cl, 3.13. Found: C, 56.95; H, 6.34; N, 2.32; Cl, 2.95. $\Lambda_M = 55.1 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$. Anal. Calcd for $\text{C}_{66}\text{H}_{73}\text{BClN}_2\text{O}_6\text{P}_3\text{Ru}$ (2b): C, 64.42; H, 5.98; N, 2.28; Cl, 2.88. Found: C, 64.18; H, 5.84; N, 2.20; Cl, 2.63. $\Lambda_M = 57.5 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$. Anal. Calcd for $\text{C}_{78}\text{H}_{73}\text{BClN}_2\text{O}_3\text{P}_3\text{Ru}$ (2c): C, 70.62; H, 5.55; N, 2.11; Cl, 2.67. Found: C, 70.45; H, 5.45; N, 2.08; Cl, 2.86. $\Lambda_M = 58.4 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$.

[RuCl(5,5'-Me $_2$ bpy) $_3$]BPh $_4$ (3a). Also this complex was prepared following the method used for the related 2,2'-bipyridine derivative 1a; yield $\geq 80\%$. Anal. Calcd for $\text{C}_{54}\text{H}_{77}\text{BClN}_2\text{O}_9\text{P}_3\text{Ru}$: C, 56.97; H, 6.82; N, 2.46; Cl, 3.11. Found: C, 57.07; H, 6.80; N, 2.32; Cl, 3.01. $\Lambda_M = 55.3 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$.

[RuH(bpy) $_3$]BPh $_4$ (4) [P = P(OEt) $_3$ (a), PPh(OEt) $_2$ (b), PPh $_2$ OEt (c)]. To a solution of $\text{RuCl}_4(\text{bpy}) \cdot \text{H}_2\text{O}$ (0.5 g, about 1.20 mmol) in 10 mL of ethanol was added first an excess of the appropriate phosphite (6.25 mmol) and then an excess of NaBH $_4$ (0.47 g, 12.5 mmol) in 20 mL of ethanol. The reaction mixture was stirred at room temperature for 3 h and filtered, and then an excess of NaBPh $_4$ (0.86 g, 2.5 mmol) in 5 mL of ethanol was added. The resulting solution was concentrated to about half volume and then cooled to -25°C . A red-brown solid separated out, which was filtered and crystallized from CH_2Cl_2 and ethanol. Crystals were obtained by cooling to -25°C a saturated solution prepared

at room temperature by treating the solid with ethanol (10 mL) and enough CH_2Cl_2 to obtain a saturated solution; yield from 65% to 80%.

These complexes can also be prepared in two steps by reacting $\text{RuCl}_4(\text{bpy}) \cdot \text{H}_2\text{O}$ with phosphite to give $[\text{RuCl}(\text{bpy})\text{P}_3]\text{BPh}_4$ (1) and then treating these complexes with an excess of NaBH $_4$ in ethanol. Anal. Calcd for $\text{C}_{52}\text{H}_{74}\text{BN}_2\text{O}_9\text{P}_3\text{Ru}$ (4a): C, 58.05; H, 6.93; N, 2.60. Found: C, 57.94; H, 6.99; N, 2.49. $\Lambda_M = 56.6 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$. Anal. Calcd for $\text{C}_{64}\text{H}_{74}\text{BN}_2\text{O}_6\text{P}_3\text{Ru}$ (4b): C, 65.58; H, 6.36; N, 2.39. Found: C, 65.46; H, 6.29; N, 2.28. $\Lambda_M = 54.9 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$. Anal. Calcd for $\text{C}_{76}\text{H}_{74}\text{BN}_2\text{O}_3\text{P}_3\text{Ru}$ (4c): C, 71.98; H, 5.88; N, 2.21. Found: C, 71.80; H, 5.76; N, 2.15. $\Lambda_M = 57.8 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$.

[RuH(phen) $_3$]BPh $_4$ (5) [P = P(OEt) $_3$ (a), PPh(OEt) $_2$ (b), PPh $_2$ OEt (c)]. These complexes were prepared, as red solids, exactly like the related 2,2'-bipyridine derivatives 4, starting from the $\text{RuCl}_4(\text{phen}) \cdot \text{H}_2\text{O}$ precursor; yield from 65% to 75%. Anal. Calcd for $\text{C}_{54}\text{H}_{74}\text{BN}_2\text{O}_9\text{P}_3\text{Ru}$ (5a): C, 58.96; H, 6.78; N, 2.55. Found: C, 58.75; H, 6.84; N, 2.68. $\Lambda_M = 51.2 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$. Anal. Calcd for $\text{C}_{66}\text{H}_{74}\text{BN}_2\text{O}_6\text{P}_3\text{Ru}$ (5b): C, 66.27; H, 6.24; N, 2.34. Found: C, 66.17; H, 6.16; N, 2.42. $\Lambda_M = 55.3 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$. Anal. Calcd for $\text{C}_{78}\text{H}_{74}\text{BN}_2\text{O}_3\text{P}_3\text{Ru}$ (5c): C, 72.50; H, 5.77; N, 2.17. Found: C, 72.65; H, 5.65; N, 2.05. $\Lambda_M = 57.4 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$.

mer-[RuH(5,5'-Me $_2$ bpy) $_3$]BPh $_4$ (6a-mer) and mer- and fac-[RuH(5,5'-Me $_2$ bpy) $_3$]BPh $_4$ (6a). This complex was prepared following the method used for the related 2,2'-bipyridine derivative 4 using $\text{RuCl}_4(5,5'\text{-Me}_2\text{bpy}) \cdot \text{H}_2\text{O}$ as a precursor. In this case, however, the addition of NaBPh $_4$ to the reaction mixture caused the separation of the *mer* isomer 6a-mer as a red-brown microcrystalline solid in about 45% yield. By cooling to -25°C of the mother solution, a further amount of solid separated out, which resulted to be a mixture of *fac* and *mer* isomers (6a) with yield of about 15%. Anal. Calcd for $\text{C}_{54}\text{H}_{78}\text{BN}_2\text{O}_9\text{P}_3\text{Ru}$: C, 58.75; H, 7.12; N, 2.54. Found for 6a-mer: C, 58.89; H, 7.15; N, 2.41. $\Lambda_M = 55.7 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$. Found for 6a: C, 58.58; H, 7.24; N, 2.46. $\Lambda_M = 53.5 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$.

[RuCl(bpy) $_2$]BPh $_4$ (7a). An excess of triethyl phosphite (1.16 mmol, 0.19 mL) was added to a solution of $\text{RuCl}_2(\text{bpy})_2 \cdot 2\text{H}_2\text{O}$ (0.30 g, 0.58 mmol) in 10 mL of ethanol, and the reaction mixture was refluxed for 2 h. After filtration, the resulting solution was concentrated to about half volume and an excess of NaBPh $_4$ (0.4 g, 1.16 mmol) in 3 mL of ethanol was added. A red-brown solid slowly separated out, which was filtered and crystallized from CH_2Cl_2 and ethanol; yield $\geq 75\%$. Anal. Calcd for $\text{C}_{50}\text{H}_{51}\text{BClN}_4\text{O}_3\text{PRu}$: C, 64.28; H, 5.50; N, 6.00; Cl, 3.79. Found: C, 64.04; H, 5.41; N, 5.89; Cl, 3.60. $\Lambda_M = 52.6 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$.

[RuH(bpy) $_2$]BPh $_4$ (8) [P = P(OEt) $_3$ (a), PPh(OEt) $_2$ (b), PPh $_2$ OEt (c)]. To a solution of $\text{RuCl}_2(\text{bpy})_2 \cdot 2\text{H}_2\text{O}$ (0.5 g, 0.96 mmol) in 15 mL of ethanol was added first an excess of the appropriate phosphite (1.9 mmol) and then an excess of NaBH $_4$ (0.36 g, 9.6 mmol) in 15 mL of ethanol. The reaction mixture was refluxed for 30 min, concentrated to about 15 mL, and then filtered. The addition of an excess of NaBPh $_4$ (0.68 g, 2 mmol) caused the separation of a red-brown solid, which was filtered and crystallized from CH_2Cl_2 and ethanol; yield $\geq 85\%$. Anal. Calcd for $\text{C}_{50}\text{H}_{52}\text{BN}_4\text{O}_3\text{PRu}$ (8a): C, 66.74; H, 5.82; N, 6.23. Found: C, 66.55; H, 5.88; N, 6.12. $\Lambda_M = 50.8 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$. Anal. Calcd for $\text{C}_{54}\text{H}_{52}\text{BN}_4\text{O}_2\text{PRu}$ (8b): C, 69.60; H, 5.62; N, 6.01. Found: C, 69.44; H, 5.70; N, 5.88. $\Lambda_M = 55.6 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$. Anal. Calcd for $\text{C}_{58}\text{H}_{52}\text{BN}_4\text{OPRu}$ (8c): C, 72.27; H, 5.44; N, 5.81. Found: C, 72.10; H, 5.37; N, 5.94. $\Lambda_M = 53.1 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$.

[Ru($\eta^2\text{-H}_2$)(bpy) $_3$] $^{2+}\text{Y}^{2-}$ (9) [P = P(OEt) $_3$ (a), PPh(OEt) $_2$ (b); $\text{Y}^{2-} = \text{BPh}_4$ and CF_3SO_3^-], [Ru($\eta^2\text{-H}_2$)(bpy)(PPh $_2$ OEt) $_3$] $^{2+}\text{Y}^{2-}$ (9c) and [Ru($\eta^2\text{-H}_2$)(phen)(PPh $_2$ OEt) $_3$] $^{2+}\text{Y}^{2-}$ (10c) ($\text{Y}^{2-} =$

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Table 1. Selected IR and NMR Data for Ruthenium Complexes

IR ^a (cm ⁻¹)	assgnt	¹ H NMR ^{b,c} (ppm; J, Hz)	assgnt	spin syst	³¹ P{ ¹ H} NMR ^{b,d} (ppm; J, Hz)	IR ^a (cm ⁻¹)	assgnt	¹ H NMR ^{b,c} (ppm; J, Hz)	assgnt	spin syst	³¹ P{ ¹ H} NMR ^{b,d} (ppm; J, Hz)
		[RuCl(bpy){P(OEt) ₃] ₃]BPh ₄ (1a)						[RuH(bpy){PPh ₂ (OEt) ₃] ₃]BPh ₄ (4c)			
		4.27 qnt	CH ₂	AB ₂	δ _A 135.4	1965 m	ν _{RuH}	3.43 m	CH ₂	AB ₂	δ _A 155.9
		3.72 m			δ _B 116.6			3.06 m			δ _B 142.0
		1.33 t	CH ₃		J _{AB} = 63.2			0.72 t	CH ₃		J _{AB} = 40.0
		0.88 t						0.43 t			
		[RuCl(bpy){PPh(OEt) ₂] ₃]BPh ₄ (1b)						AB ₂ X spin syst	H ⁻		
		4.13 m	CH ₂	AB ₂	δ _A 168.3			(X = H ⁻)			
		3.74 m			δ _B 145.3			δ _X -12.86			
		1.45 t	CH ₃		J _{AB} = 48.0			J _{AX} = 32			
		1.09 t						J _{BX} = 20			
		1.00 t						[RuH(phen){P(OEt) ₃] ₃]BPh ₄ (5a)			
		[RuCl(bpy){PPh ₂ (OEt) ₃] ₃]BPh ₄ (1c)				1969 m	ν _{RuH}	4.16 m	CH ₂	AB ₂	δ _A 151.3
		3.46 qnt	CH ₂	AB ₂	δ _A 141.3			3.67 m			δ _B 140.7
		3.20 m			δ _B 116.3			1.43 t	CH ₃		J _{AB} = 65.0
		1.05 t	CH ₃		J _{AB} = 37.2			1.37 t		A ₂ B	δ _A 153.7
		0.85 t						0.90 t			δ _B 133.1
		[RuCl(phen){P(OEt) ₃] ₃]BPh ₄ (2a)						0.87 t			J _{AB} = 37.2
		4.43 qnt	CH ₂	AB ₂	δ _A 136.0			AB ₂ X spin syst	H ⁻		
		3.72 m			δ _B 116.6			(X = H ⁻)			
		1.47 t	CH ₃		J _{AB} = 64.1			δ _X -6.73			
		0.81 t						J _{AX} = 146			
		[RuCl(phen){PPh(OEt) ₂] ₃]BPh ₄ (2b)						J _{BX} = 27			
		4.25 m	CH ₂	AB ₂	δ _A 167.4			A ₂ BX spin syst	H ⁻		
		3.69 m			δ _B 145.6			(X = H ⁻)			
		1.54 t	CH ₃		J _{AB} = 50.0			δ _X -13.91			
		1.02 t						J _{AX} = 24			
		[RuCl(phen){PPh ₂ (OEt) ₃] ₃]BPh ₄ (2c)						J _{BX} = 32			
		3.49 qnt	CH ₂	AB ₂	δ _A 141.2			[RuH(phen){PPh(OEt) ₂] ₃]BPh ₄ (5b)			
		3.07 m			δ _B 116.8	1980 sh	ν _{RuH}	3.98 qnt	CH ₂	AB ₂	δ _A 179.0
		1.07 t	CH ₃		J _{AB} = 38.3	1963 m		3.81 m			δ _B 163.9
		0.75 t						1.35 t	CH ₃		J _{AB} = 46.5
		[RuCl(5,5'-Me ₂ bpy){P(OEt) ₃] ₃]BPh ₄ (3a)						0.79 t		A ₂ B	δ _A 176.4
		4.35 qnt	CH ₂	AB ₂	δ _A 136.2			AB ₂ X spin syst	H ⁻		δ _B 157.8
		3.80 m			δ _B 117.1			(X = H ⁻)			J _{AB} = 26.0
		2.52 s	CH ₃		J _{AB} = 62.5			δ _X -6.35			
		2.35 s						J _{AX} = 122			
		1.41 t	CH ₃ phos					J _{BX} = 24			
		0.96 t						A ₂ BX spin syst	H ⁻		
		[RuH(bpy){P(OEt) ₃] ₃]BPh ₄ (4a)						(X = H ⁻)			
1963 w	ν _{RuH}	4.06 m	CH ₂	AB ₂	δ _A 150.2			δ _X -13.55			
1940 w		3.69 m			δ _B 140.4			J _{AX} = 20			
		1.32 t	CH ₃		J _{AB} = 64.7			J _{BX} = 30			
		1.28 t		A ₂ B	δ _A 153.6			[RuH(phen){PPh ₂ (OEt) ₃] ₃]BPh ₄ (5c)			
		0.96 t			δ _B 132.9	1975 s	ν _{RuH}	3.44 m	CH ₂	AB ₂	δ _A 156.1
		AB ₂ X spin syst	H ⁻		J _{AB} = 37.2			3.07 m			δ _B 141.9
		(X = H ⁻)						0.65 t	CH ₃		J _{AB} = 40.5
		δ _X -6.92						0.42 t			
		J _{AX} = 148						AB ₂ X spin syst	H ⁻		
		J _{BX} = 27						(X = H ⁻)			
		A ₂ BX spin syst	H ⁻					δ _X -12.65			
		(X = H ⁻)						J _{AX} = 30			
		δ _X -14.31						J _{BX} = 20			
		J _{AX} = 22						<i>fac</i> - and <i>mer</i> -[RuH(5,5'-Me ₂ bpy){P(OEt) ₃] ₃]BPh ₄ (6a)			
		J _{BX} = 34				1970 w, br	ν _{RuH}	4.07 qnt	CH ₂	AB ₂	δ _A 151.1
		[RuH(bpy){PPh(OEt) ₂] ₃]BPh ₄ (4b)						3.64 m			δ _B 140.7
1971 m	ν _{RuH}	4.10 m	CH ₂	AB ₂	δ _A 178.0			2.41 s	CH ₃		J _{AB} = 65.0
		3.30 m			δ _B 162.9			2.38 s		A ₂ B	δ _A 153.9
		1.32 t	CH ₃		J _{AB} = 48.0			2.36 s			δ _B 133.4
		1.30 t		A ₂ B	δ _A 176.0			1.37 t	CH ₃ phos		J _{AB} = 36.2
		1.21 t			δ _B 157.6			1.30 t			
		0.93 t			J _{AB} = 24.9			1.20 t			
		AB ₂ X spin syst	H ⁻					0.96 t			
		(X = H ⁻)						AB ₂ X spin syst	H ⁻		
		δ _X -6.72						(X = H ⁻)			
		J _{AX} = 124						δ _X -14.34			
		J _{BX} = 24						J _{AX} = 32			
		A ₂ BX spin syst	H ⁻					J _{BX} = 24			
		(X = H ⁻)						A ₂ BX spin syst	H ⁻		
		δ _X -13.86						(X = H ⁻)			
		J _{AX} = 20						δ _X -6.88			
		J _{BX} = 30						J _{AX} = 27			
								J _{BX} = 150			

Table 1. Continued

IR ^a (cm ⁻¹)	assgnt	¹ H NMR ^{b,c} (ppm; J, Hz)	assgnt	spin syst	³¹ P{ ¹ H} NMR ^{b,d} (ppm; J, Hz)	IR ^a (cm ⁻¹)	assgnt	¹ H NMR ^{b,c} (ppm; J, Hz)	assgnt	spin syst	³¹ P{ ¹ H} NMR ^{b,d} (ppm; J, Hz)
1969 w	ν_{RuH}	<i>mer</i> -[RuH(5,5'-Me ₂ bpy){P(OEt) ₃] ₃]BPh ₄ (6a-mer)					[Ru(η^2 -H ₂)(bpy) ₂ {PPh(OEt) ₂ }] ^{2+ h} (11b)				
		4.07 qnt	CH ₂	AB ₂	δ_{A} 151.1	4.01 m	CH ₂	A	159.7		
		3.63 m			δ_{B} 140.7	1.30 t	CH ₃				
		2.38 s	CH ₃		$J_{\text{AB}} = 65.0$	-7.55 br	η^2 -H ₂				
		2.36 s				[Ru(η^2 -H ₂)(bpy) ₂ {PPh ₂ (OEt)}] ^{2+ h} (11c)					
		1.30 t	CH ₃ phos			3.65 m	CH ₂	A	138.9 s		
		0.96 t				1.03 t	CH ₃				
		AB ₂ X spin syst	H ⁻			-7.95 br	η^2 -H ₂				
		(X = H ⁻)				[Ru(OH ₂)(bpy){P(OEt) ₃] ₃](BPh ₄) ₂ (12a)					
		$\delta_{\text{X}} -14.34$				4.12 m	CH ₂	AB ₂	δ_{A} 129.8		
1881 m	ν_{RuH}	$J_{\text{AX}} = 32$				3.56 m			δ_{B} 128.8		
		$J_{\text{BX}} = 24$				2.55 s, br	OH ₂		$J_{\text{AB}} = 79.6$		
		[RuCl(bpy) ₂ {P(OEt) ₃ }]BPh ₄ (7a)				1.37 t	CH ₃				
		3.98 qnt	CH ₂	A	127.7 s	0.95 t					
		1.06 t	CH ₃			[Ru(CH ₃ CN)(bpy){P(OEt) ₃] ₃](BPh ₄) ₂ (13a)					
		[RuH(bpy) ₂ {P(OEt) ₃ }]BPh ₄ (8a)				4.13 m	CH ₂	A ₂ B	δ_{A} 129.7		
		3.81 qnt	CH ₂	A	153.6 s	3.60 qnt			δ_{B} 125.2		
		1.12 t	CH ₃			1.36 t	CH ₃		$J_{\text{AB}} = 74.9$		
		-12.16 d	H ⁻			0.94 t					
		$J_{\text{PH}} = 36$				0.30 s	CH ₃ CN				
1895 m	ν_{RuH}	[RuH(bpy) ₂ {PPh(OEt) ₂ }]BPh ₄ (8b)				[Ru(bpy)(4-CH ₃ C ₆ H ₄ CN){P(OEt) ₃] ₃](BPh ₄) ₂ (14a)					
		3.94 qnt	CH ₂	A	174.1 s	4.17 m	CH ₂	A ₂ B	δ_{A} 129.7		
		1.28 t	CH ₃			3.63 m			δ_{B} 118.4		
		-12.01 d	H ⁻			2.34 s	CH ₃		$J_{\text{AB}} = 61.2$		
		$J_{\text{PH}} = 32$				2.30 s		A ₂ B	δ_{A} 128.1		
		[RuH(bpy) ₂ {PPh ₂ (OEt)}]BPh ₄ (8c)				1.38 t	CH ₃ phos		δ_{B} 115.8		
		3.69 qnt	CH ₂	A	148.1 s	1.36 t			$J_{\text{AB}} = 58.0$		
		1.08 t	CH ₃			0.99 t					
		-11.93 d	H ⁻			0.97 t					
		$J_{\text{PH}} = 34$				[Ru(bpy)(CO){P(OEt) ₃] ₃](BPh ₄) ₂ (15a)					
1917 m	ν_{RuH}	[Ru(η^2 -H ₂)(bpy){P(OEt) ₃ }] ^{2+ e} (9a)				2054 s	ν_{CO}	4.18 m	CH ₂	A ₂ B	δ_{A} 123.2
		4.15 m	CH ₂	AB ₂	δ_{A} 130.7	3.57 qnt			δ_{B} 110.0		
		3.81 m			δ_{B} 129.4	1.41 t	CH ₃		$J_{\text{AB}} = 62.4$		
		1.39 t	CH ₃		$J_{\text{AB}} = 80.0$	0.94 t					
		1.15 t		AB ₂	δ_{A} 128.2	[Ru(bpy){PPh(OEt) ₂ }{P(OEt) ₃] ₃](BPh ₄) ₂ (16a)					
		1.00 t			δ_{B} 117.2	4.32 m	CH ₂	AB ₂ C	δ_{A} 148.7		
		-9.55 br	η^2 -H ₂		$J_{\text{AB}} = 55.3$	4.11 m			δ_{B} 131.2		
		[Ru(η^2 -H ₂)(bpy){PPh(OEt) ₂ }] ^{2+ f} (9b)				3.95 qnt			δ_{C} 118.3		
		3.97 m	CH ₂	AB ₂	δ_{A} 155.4	3.50 m			$J_{\text{AB}} = 50.9$		
		3.82 m			δ_{B} 146.9	1.48 t	CH ₃		$J_{\text{AC}} = -534.5$		
		3.49 m			$J_{\text{AB}} = 44.4$	1.35 m			$J_{\text{AB}} = 58.4$		
		1.43 t	CH ₃	A ₂ B	δ_{A} 162.4	0.95 m					
		1.40 t			δ_{B} 161.3	[Ru(CH ₃ CN)(bpy) ₂ {P(OEt) ₃] ₃](BPh ₄) ₂ (17a)					
		1.21 t			$J_{\text{AB}} = 62.7$	3.80 qnt	CH ₂	A	125.5s		
		0.96 t				1.66 s	CH ₃ CN				
		-9.60 br	η^2 -H ₂			1.01 t	CH ₃				
		[Ru(η^2 -H ₂)(bpy){PPh ₂ (OEt)}] ^{2+ f} (9c)				[Ru(bpy)(4-CH ₃ C ₆ H ₄ CN) ₂ {P(OEt) ₃] ₃](BPh ₄) ₂ (18a)					
		3.44 m	CH ₂	AB ₂	δ_{A} 140.0	3.89 qnt	CH ₂	A	124.6s		
		3.21 qnt			δ_{B} 129.8	2.46 s	CH ₃				
		0.70 t	CH ₃		$J_{\text{AB}} = 30.5$	1.10 t	CH ₃ phos				
		0.52 t				[Ru(C ₆ H ₅ N=NH)(bpy){P(OEt) ₃] ₃](BPh ₄) ₂ (19a)					
		-8.0 br	η^2 -H ₂			14.16 s, br	NH	AB ₂	δ_{A} 129.4		
		[Ru(η^2 -H ₂)(phen){PPh ₂ (OEt)}] ^{2+ f} (10c)				13.70 s, br			δ_{B} 128.4		
		3.26 qnt	CH ₂	AB ₂	δ_{A} 140.2	4.23 qnt	CH ₂		$J_{\text{AB}} = 69.2$		
		3.23 m			δ_{B} 130.4	3.67 m		AB ₂	δ_{A} 126.9		
		0.66 t	CH ₃		$J_{\text{AB}} = 30.4$	1.39 t	CH ₃		δ_{B} 114.2		
		0.54 t				1.37 t			$J_{\text{AB}} = 61.0$		
		-7.8 br	η^2 -H ₂			0.99 t					
		[Ru(η^2 -H ₂)(bpy) ₂ {P(OEt) ₃ }] ^{2+ g} (11a)				0.96 t					
		3.87 qnt	CH ₂	A	125.3 s						
		1.04 t	CH ₃								
		-7.65 br	η^2 -H ₂								

2CF₃SO₃⁻). These complexes were prepared in solution by reaction with CF₃SO₃H at low temperature. A typical preparation involves the addition of an excess of CF₃SO₃H (0.02 mmol, 1.8 μ L) to a solution of the appropriate hydride **4**, **5** (0.01 mmol) in 0.5 mL of CD₂Cl₂ placed in a 5-mm NMR tube and cooled to -80 °C. The tube was rapidly transferred into the probe, precooled to -80 °C, of the NMR spectrometer, and the spectrum was recorded. The

temperature was also increased until 30 °C and the progress of the reaction detected.

[Ru(η^2 -H₂)(bpy)₂P]²⁺Y²⁻ (**11**) [P = P(OEt)₃ (**a**), PPh(OEt)₂ (**b**), PPh₂OEt (**c**); Y²⁻ = 2CF₃SO₃⁻]. These complexes were prepared at low temperature (-80 °C) in an NMR tube by adding an excess of CF₃SO₃H (0.02 mmol, 1.8 μ L) to a solution of the appropriate hydride [RuH(bpy)₂P]CF₃SO₃ (**8**-CF₃SO₃) (0.01 mmol)

Table 1. Continued

IR ^a (cm ⁻¹)	assgnt	¹ H NMR ^{b,c} (ppm; J, Hz)	assgnt	spin syst	³¹ P{ ¹ H} NMR ^{b,d} (ppm; J, Hz)	IR ^a (cm ⁻¹)	assgnt	¹ H NMR ^{b,c} (ppm; J, Hz)	assgnt	spin syst	³¹ P{ ¹ H} NMR ^{b,d} (ppm; J, Hz)
[Ru(C ₆ H ₅ N= ¹⁵ NH)(bpy){P(OEt) ₃ }] ₃ (BPh ₄) ₂ ⁱ (19a-¹⁵N)						[Ru(C ₆ H ₅ N=NH)(phen){PPh(OEt) ₂ }] ₃ (BPh ₄) ₂ (21b)					
		AB ₂ XY spin syst (X = H, Y = ¹⁵ N)	NH	AB ₂ Y	δ _A 126.9 δ _B 114.3 J _{AB} = 60.7 J _{AY} = 5.6 J _{BY} = 4.9			13.85 s, br 13.26 s, br 4.34 m 3.65 m 1.58 t 1.20 t 1.03 t 0.90 t		AB ₂	δ _A 158.8 δ _B 145.3 J _{AB} = 46.5 δ _A 152.0 δ _B 141.1 J _{AB} = 43.0
		J _{AX} = 4.7 J _{BX} = 2.8 J _{AY} = 5.6 J _{BY} = 4.9 J _{XY} = 67.3 J _{AB} = 60.7 AB ₂ XY spin syst (X = H, Y = ¹⁵ N)		AB ₂ Y	δ _A 129.0 δ _B 128.4 J _{AB} = 69.2 J _{AY} = -62.5 J _{BY} = 4.8					AB ₂	
		δ _X 13.69 J _{AX} = -8.0 J _{BX} = -2.97 J _{AY} = -62.5 J _{BY} = 4.8 J _{XY} = -63.96 J _{AB} = 69.2 4.21 m 3.65 m 1.38 t 1.36 t 1.00 t 0.96 t	CH ₂ CH ₃								
[[Ru(bpy)[P(OEt) ₃]] ₂ (μ-4,4'-HN=NC ₆ H ₄ -C ₆ H ₄ N=NH)](BPh ₄) ₄ (20a)						[Ru(C ₆ H ₅ N=NH)(bpy) ₂ {P(OEt) ₃ }] ₃ (BPh ₄) ₂ (22a)					
		14.16 s, br 14.06 s, br 4.20 m 3.64 m 1.35 t 1.01 t 0.96 t 0.92 t	NH CH ₂ CH ₃	AB ₂ AB ₂	δ _A 126.3 δ _B 114.1 J _{AB} = 61.4 δ _A 130.1 δ _B 115.8 J _{AB} = 63.0			14.87 d, br 3.89 qnt 1.13 t 1.13 t 14.89 dt ¹ J _{NH} = 65.5 ³ J _{PH} = 3.5 3.87 m 1.09 t		A	123.6 s
[[Ru(bpy)[P(OEt) ₃]] ₂ (μ-4,4'-H ¹⁵ N=NC ₆ H ₄ -C ₆ H ₄ N= ¹⁵ NH)](BPh ₄) ₄ ⁱ (20a-¹⁵N)						[Ru(C ₆ H ₅ N= ¹⁵ NH)(bpy) ₂ {P(OEt) ₃ }] ₃ (BPh ₄) ₂ ^k (22a-¹⁵N)					
		14.17 d, br ¹ J _{NH} = 64.5 14.07 d, br ¹ J _{NH} = 63.0 4.21 m 3.65 m 1.36 t 1.01 t 0.96 t 0.93 t	NH CH ₂ CH ₃	AB ₂ Y AB ₂ Y	δ _A 126.7 δ _B 114.2 J _{AB} = 61.4 J _{AY} = 6.3 J _{BY} = 5.0 δ _A 130.2 δ _B 115.8 J _{AB} = 63.0 J _{AY} = J _{BY} = ≤ 1			1.13 t CH ₂ CH ₃ 10.87 s, br 3.84 br 1.04 br 10.94 s 3.95 qnt 1.33 t 7.73 s 3.85 qnt 1.04 t 7.48 s 4.10 qnt 1.19 t		A	124.1 d ² J _{P¹⁵N} = 4.7 126.8 s 159.1 s 128.2 s 160.9 s
						[Ru{η ¹ -SC(H)=S}(bpy) ₂ {P(OEt) ₃ }]BPh ₄ (23a)					
						[Ru{η ¹ -SC(H)=S}(bpy) ₂ {PPh(OEt) ₂ }]BPh ₄ (23b)					
						[Ru{η ¹ -OC(H)=O}(bpy) ₂ {P(OEt) ₃ }]BPh ₄ (24a)					
						[Ru{η ¹ -OC(H)=O}(bpy) ₂ {PPh(OEt) ₂ }]BPh ₄ (24b)					

^a In KBr pellets. ^b In CD₂Cl₂ at 25 °C. ^c Phenyl and polypyridyl proton resonances omitted; for the OC₂H₅ group of the phosphine J_{HH} = 7 Hz. ^d Positive shift downfield from 85% H₃PO₄. ^e At 273 K. ^f At 283 K. ^g At 203 K. ^h At 223 K. ⁱ ¹⁵N{¹H} NMR, δ (CD₂Cl₂, 25 °C, positive shift downfield from CH₃¹⁵NO₂): AB₂Y spin syst (Y = ¹⁵N), δ_Y 0.67, J_{AY} = 63, J_{BY} = 4.8; AB₂Y spin syst (Y = ¹⁵N), δ_Y -5.07, J_{AY} = 5.6, J_{BY} = 4.9 Hz. ^j ¹⁵N{¹H} NMR, δ: AB₂Y spin syst (Y = ¹⁵N), δ_Y -5.97, J_{AY} = 6.3, J_{BY} = 5.0 Hz; -18.8 (s, br). ^k ¹⁵N{¹H} NMR, δ: 0.23 (d, J_{NP} = 4.7 Hz).

Table 2. T_{1min} (200 MHz) and J_{HD} NMR Data for Some Dihydrogen and Hydride Complexes and Calculated H–H Distances

no.	compound	T (K)	δ(M–H ₂)	T _{1min} (ms)	J _{HD} (Hz)	r _{H–H} (Å)		
9a	[Ru(η ² -H ₂)(bpy){P(OEt) ₃ }] ₃ ²⁺	203	-9.55 br	4.9	29.9	0.99 ^a	0.79 ^b	0.94 ^c
9b	[Ru(η ² -H ₂)(bpy){PPh(OEt) ₂ }] ₃ ²⁺	218	-9.60 br	6.1	30.1	1.03	0.81	0.93
9c	[Ru(η ² -H ₂)(bpy){PPh ₂ (OEt) ₃ }] ₃ ²⁺	223	-8.0 br	5.1	28.9	1.00	0.79	0.95
10c	[Ru(η ² -H ₂)(phen){PPh ₂ (OEt) ₃ }] ₃ ²⁺	217	-7.80 br	5.9	29.4	1.02	0.81	0.95
11a	[Ru(η ² -H ₂)(bpy) ₂ {P(OEt) ₃ }] ₃ ²⁺	216	-7.65 br	7.0	32.8	1.05	0.83	0.89
11b	[Ru(η ² -H ₂)(bpy) ₂ {PPh(OEt) ₂ }] ₃ ²⁺	213	-7.55 br	7.6	31.2	1.07	0.84	0.92
11c	[Ru(η ² -H ₂)(bpy) ₂ {PPh ₂ (OEt) ₃ }] ₃ ²⁺	218	-7.95 br	7.2	31.7	1.06	0.84	0.91
4a	[RuH(bpy){P(OEt) ₃ }] ₃ BPh ₄	200	-6.99 dt -14.27 dt	304 233				

^{a,b} The H–H distances were calculated²⁰ from the T_{1min} values for fast rotation^b or static regimes^a of the H₂ ligand. ^c The H–H distances were calculated from the J_{HD} values of the HD complexes using the equation^{2b} r_{H–H} = 1.44–0.0168 (J_{HD}).

in 0.5 mL of CD₂Cl₂ following the method used for the related [Ru(η²-H₂)(N–N)P₃]₃²⁺ (**9**, **10**) derivatives.

[RuL(bpy){P(OEt)₃}]₃(BPh₄)₂ (**12–16**) [L = H₂O (**12a**), CH₃CN (**13a**), 4-CH₃C₆H₄CN (**14a**), CO (**15a**), PPh(OEt)₂ (**16a**)].

These complexes were prepared by substituting the η²-H₂ molecule in [Ru(η²-H₂)(bpy){P(OEt)₃}]₃²⁺ (**9a**) complex with the appropriate ligand L, by means the following general method. To a solution of [RuH(bpy){P(OEt)₃}]₃BPh₄ (0.1 g, 0.093 mmol) in 8 mL of CH₂-

Table 3. $^{13}\text{C}\{^1\text{H}\}$ NMR Data for Selected Complexes

$^{13}\text{C}\{^1\text{H}\}$ NMR ^{a,b} (ppm; J, Hz)	assgnt
[Ru(CH₃CN)(bpy){P(OEt)₃]₃(BPh₄)₂ (13a)	
125.4 d	CN
$J_{\text{CP}} = 22.0$	
64.0 t	CH ₂
63.7 d	
16.3 t	CH ₃
16.0 d	
0.60 s	CH ₃ CN
[Ru(bpy)(CO){P(OEt)₃]₃(BPh₄)₂ (15a)	
190.9 dt	CO
$J_{\text{CP}_{\text{cis}}} = 17.0$	
$J_{\text{CP}_{\text{trans}}} = 145$	
65.6 t	CH ₂
64.7 d	
16.1 m	CH ₃
[Ru(CH₃CN)(bpy)₂{P(OEt)₃]₃(BPh₄)₂ (17a)	
127.4 d	CN
$J_{\text{CP}} = 16.0$	
63.1 d	CH ₂
16.3 d	CH ₃
3.5 s	CH ₃ CN
[Ru(η^1-SC(H)=S)(bpy)₂{P(OEt)₃]₃BPh₄ (23a)	
238.6 s	SC(H)=
62.6 d	CH ₂
16.2 d	CH ₃
[Ru(η^1-OC(H)=O)(bpy)₂{P(OEt)₃]₃BPh₄ (24a)	
170.6 s	OC(H)=
62.1 d	CH ₂
16.3 d	CH ₃
[Ru(η^1-OC(H)=O)(bpy)₂{PPh(OEt)₂]₃BPh₄ (24b)	
171.3 s	OC(H)=
61.3 d	CH ₂
16.8 d	CH ₃

^a In CD₂Cl₂ at 25 °C. ^b Phenyl and polypyridyl carbon resonances are omitted.

Cl₂ cooled to -196 °C was added an excess of CF₃SO₃H (0.36 mmol, 32 μ L). The reaction mixture was brought to 0 °C and stirred for 10 min, and then an excess (1.1 mmol) of the appropriate ligand molecule L was added. In the case of CO, the reaction mixture was allowed to stand under a CO atmosphere (1 atm). The resulting solution was brought to room temperature and stirred for 30 min, and then the solvent was removed under reduced pressure. The oil obtained was treated with ethanol (2 mL) containing an excess of NaBPh₄ (0.20 mmol, 68 mg). By stirring the resulting solution, a yellow or red solid separated out, which was filtered and crystallized from CH₂Cl₂ and ethanol; yield between 65% and 80%. Anal. Calcd for C₇₆H₉₅B₂N₂O₁₀P₃Ru (12a): C, 64.64; H, 6.78; N, 1.98. Found: C, 64.39; H, 6.74; N, 2.05. $\Lambda_{\text{M}} = 118 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$. Anal. Calcd for C₇₈H₉₆B₂N₃O₉P₃Ru (13a): C, 65.28; H, 6.74; N, 2.93. Found: C, 65.10; H, 6.84; N, 2.79. $\Lambda_{\text{M}} = 112 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$. Anal. Calcd for C₈₄H₁₀₀B₂N₃O₉P₃Ru (14a): C, 66.76; H, 6.67; N, 2.78. Found: C, 66.60; H, 6.72; N, 2.69. $\Lambda_{\text{M}} = 116 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$. Anal. Calcd for C₇₇H₉₃B₂N₂O₁₀P₃Ru (15a): C, 65.03; H, 6.59; N, 1.97. Found: C, 64.85; H, 6.58; N, 2.11. $\Lambda_{\text{M}} = 121 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$. Anal. Calcd for C₈₆H₁₀₈B₂N₂O₁₁P₄Ru (16a): C, 64.87; H, 6.84; N, 1.76. Found: C, 64.65; H, 6.94; N, 1.75. $\Lambda_{\text{M}} = 120 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$.

[Ru(RCN)(bpy)₂{P(OEt)₃]₃(BPh₄)₂ (17a, 18a) [R = CH₃ (17), 4-CH₃C₆H₄ (18)]. An excess of HBF₄·Et₂O (0.22 mmol, 32 μ L) was added to a solution of [RuH(bpy)₂{P(OEt)₃]₃BPh₄ (0.1 g, 0.11 mmol) in 8 mL of CH₂Cl₂ cooled to -196 °C, and the reaction mixture, brought to 0 °C, was stirred for 10 min. An excess of the appropriate nitrile (1.1 mmol) was added and the resulting solution, brought to room temperature, stirred for 1 h. The solvent was removed under reduced pressure to give an oil, which was triturated

with ethanol containing an excess of NaBPh₄ (0.22 mmol, 75 mg). A yellow solid slowly separated out from the resulting solution, which was filtered and crystallized from CH₂Cl₂ and ethanol; yield $\geq 75\%$. Anal. Calcd for C₇₆H₇₄B₂N₅O₃PRu (17a): C, 72.50; H, 5.92; N, 5.56. Found: C, 72.40; H, 5.98; N, 5.45. $\Lambda_{\text{M}} = 121 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$. Anal. Calcd for C₈₂H₇₈B₂N₅O₃PRu (18a): C, 73.76; H, 5.89; N, 5.25. Found: C, 73.64; H, 5.82; N, 5.30. $\Lambda_{\text{M}} = 124 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$.

[Ru(C₆H₅N=NH)(bpy){P(OEt)₃]₃(BPh₄)₂ (19a). In a 25-mL three-necked round-bottomed flask were placed solid samples of [RuH(bpy)₃]BPh₄ (0.10 mmol) and the [C₆H₅N₂]BF₄ aryldiazonium salt (0.2 mmol, 0.38 g). The flask was cooled to -196 °C and CH₂Cl₂ (8 mL) added. The reaction mixture was brought to room temperature, stirred for 3 h, and then evaporated to dryness under reduced pressure. The oil obtained was triturated with ethanol containing an excess of NaBPh₄ (0.18 mmol, 62 mg). An orange solid separated out from the resulting solution, which was filtered and crystallized from CH₂Cl₂ and ethanol; yield $\geq 75\%$. Anal. Calcd for C₈₂H₉₉B₂N₄O₉P₃Ru: C, 65.65; H, 6.65; N, 3.73. Found: C, 65.42; H, 6.77; N, 3.66. $\Lambda_{\text{M}} = 115 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$.

[Ru(C₆H₅N=¹⁵NH)(bpy){P(OEt)₃]₃(BPh₄)₂ (19a-¹⁵N). This complex was prepared exactly like the related unlabeled compound 19a, using the labeled [C₆H₅N=¹⁵N]BF₄ aryldiazonium salt; yield $\geq 70\%$.

[{Ru(bpy)[P(OEt)₃]₃}(μ -4,4'-NH=NC₆H₄-C₆H₄N=NH)]-(BPh₄)₄ (20a). In a 25-mL three-necked round-bottomed flask were placed solid samples of [RuH(bpy){P(OEt)₃]₃BPh₄ (4a) (0.1 g, 0.093 mmol) and of the di-diazonium salt [4,4'-N₂C₆H₄-C₆H₄N₂](BF₄)₂ (18 mg, 0.0465 mmol), the flask was cooled to -196 °C, and CH₂Cl₂ (18 mL) was added. The reaction mixture was brought to room temperature and stirred for about 10 h, and then the solvent was removed under reduced pressure. The oil obtained was triturated with ethanol (2 mL) containing an excess of NaBPh₄ (0.2 mmol, 68 mg). A yellow solid slowly separated out from the resulting solution, which was filtered and crystallized from CH₂Cl₂ and ethanol; yield $\geq 70\%$. Anal. Calcd for C₁₆₄H₁₉₆B₄N₈O₁₈P₆Ru₂: C, 65.69; H, 6.59; N, 3.74. Found: C, 65.48; H, 6.64; N, 3.67. $\Lambda_{\text{M}} = 248 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$.

[{Ru(bpy)[P(OEt)₃]₃}(μ -4,4'-¹⁵NH=NC₆H₄-C₆H₄N=¹⁵NH)]-(BPh₄)₄ (20a-¹⁵N). This complex was prepared exactly like the related unlabeled compound 20a using the [4,4'-¹⁵N≡NC₆H₄-C₆H₄N=¹⁵N](BF₄)₂ aryldiazonium salt; yield $\geq 65\%$.

[Ru(C₆H₅N=NH)(phen){PPh(OEt)₂]₃(BPh₄)₂ (21b). This complex was prepared like the related 2,2'-bipyridine derivative 19a using [RuH(phen){PPh(OEt)₂]₃BPh₄ (5b) as a precursor; yield $\geq 75\%$. Anal. Calcd for C₉₆H₉₉B₂N₄O₆P₃Ru: C, 71.16; H, 6.16; N, 3.46. Found: C, 71.01; H, 6.27; N, 3.40. $\Lambda_{\text{M}} = 117 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$.

[Ru(C₆H₅N=NH)(bpy)₂{P(OEt)₃]₃(BPh₄)₂ (22a). In a 25-mL three-necked round-bottomed flask were placed solid samples of the appropriate hydride [RuH(bpy)₂]BPh₄ (0.1 mmol) and of the phenyldiazonium salt [C₆H₅N₂]BF₄ (0.2 mmol, 38 mg). The flask was cooled to -196 °C and CH₂Cl₂ (5 mL) added. The reaction mixture was brought to 0 °C with an ice bath, stirred for 1 h, and then evaporated to dryness under reduced pressure. The oil obtained was triturated with ethanol (3 mL) containing an excess of NaBPh₄ (0.2 mmol, 68 mg). An orange solid slowly separated out from the resulting solution, which was filtered and crystallized from CH₂-Cl₂ and ethanol; yield $\geq 75\%$. Anal. Calcd for C₈₀H₇₇B₂N₆O₃PRu: C, 72.56; H, 5.86; N, 6.35. Found: C, 72.38; H, 5.94; N, 6.27. $\Lambda_{\text{M}} = 118 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$.

[Ru(C₆H₅N=15NH)(bpy)₂(P(OEt)₃)](BPh₄)₂ (22a-15N). This compound was prepared exactly like the related unlabeled compound **22a** using [C₆H₅N≡15N]BF₄ as a reagent; yield ≥70%.

[Ru(η^1 -SC(H)=S)(bpy)₂]P[BPh₄] (**23**) [P = P(OEt)₃ (**a**), PPh₃(OEt)₂ (**b**)]. An excess of carbon disulfide (1 mmol, 61 μ L) was added to a solution of the appropriate hydride [RuH(bpy)₂]P[BPh₄] (0.10 mmol) in 8 mL of CH₂Cl₂ and the reaction mixture stirred for 2 h. The solvent was removed under reduced pressure to give an oil, which was triturated with ethanol (3 mL) containing an excess of NaBPh₄ (0.2 mmol, 68 mg). An orange solid separated out from the resulting solution, which was filtered and crystallized from CH₂Cl₂ and ethanol; yield $\geq 70\%$. Anal. Calcd for C₅₁H₅₂BN₄O₃PRuS₂ (**23a**): C, 62.76; H, 5.37; N, 5.74; S, 6.57. Found: C, 62.59; H, 5.46; N, 5.62; S, 6.40. $\Lambda_M = 54.5 \text{ } \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$. Anal. Calcd for C₅₅H₅₂BN₄O₂PRuS₂ (**23b**): C, 65.54; H, 5.20; N, 5.56; S, 6.36. Found: C, 65.30; H, 5.27; N, 5.45; S, 6.18. $\Lambda_M = 56.1 \text{ } \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$.

[Ru(η^1 -OC(H)=O)(bpy)₂P]BPh₄ (**24**) [P = P(OEt)₃ (**a**), PPh-(OEt)₂ (**b**)]. A solution of the appropriate hydride [RuH(bpy)₂P]-BPh₄ (0.10 mmol) in 10 mL of CH₂Cl₂ was stirred at room temperature under a CO₂ atmosphere (1 atm) for 24 h. The solvent was removed under reduced pressure to give an oil, which was triturated with ethanol (3 mL) containing an excess of NaBPh₄ (0.2 mmol, 68 mg). A yellow solid slowly separated out from the resulting solution, which was filtered and crystallized from CH₂-Cl₂ and ethanol; yield $\geq 60\%$. Anal. Calcd for C₅₁H₅₂N₄O₅PRu (**24a**): C, 64.90; H, 5.55; N, 5.94. Found: C, 64.75; H, 5.48; N, 5.84. $\Lambda_M = 55.7 \text{ } \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$. Anal. Calcd for C₅₅H₅₂N₄O₄-PRu (**24b**): C, 67.69; H, 5.37; N, 5.74. Found: C, 67.78; H, 5.30; N, 5.65. $\Lambda_M = 56.3 \text{ } \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$.

Acidity Measurements. The protonation of complexes [RuH-(N-N)P₃]CF₃SO₃ (**4c-CF₃SO₃**, **5c-CF₃SO₃**) and [RuH(bpy)₂P]CF₃SO₃ (**8-CF₃SO₃**) was studied in CD₂Cl₂ following the method used for the related iron derivatives.¹ Approximately 2.5 equiv of CF₃SO₃H is required to completely generate the [Ru(η²-H₂)(N-N)P₃]²⁺ derivatives. Instead, less than 1.5 equiv of CF₃SO₃H is required for the complete formation of the [Ru(η²-H₂)(bpy)₂P]²⁺ dicationic species.

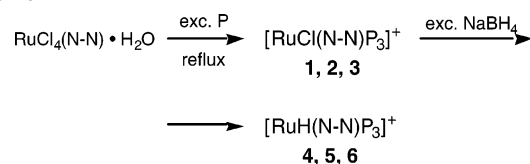
X-ray Crystal Structure Determination of [RuH(bpy)-{P(OEt)₃}₃]BPPh₄ (4a). A large orange prism single crystal was mounted on a glass fiber, and X-ray diffraction data were collected on a Bruker-Siemens SMART AXS 1000 equipped with CCD detector, using graphite monochromated Mo K α radiation ($\lambda = 0.71069$ Å). Data collection details: crystal to detector distance = 5.0 cm, 2424 frames collected (complete sphere mode), time per frame = 30 s, oscillation $\Delta\omega = 0.300^\circ$. Crystal decay resulted negligible. Data reduction was performed up to $d = 0.90$ Å by the SAINT package,⁸ and data were corrected for absorption effects by the SADABS⁹ procedure ($T_{\text{max}} = 1.000$, $T_{\text{min}} = 0.8415$). The phase problem was solved by direct methods¹⁰ and refined by full matrix least squares on all F^2 ,¹¹ implemented in the WinGX package.¹² Anisotropic displacement parameters were refined for all non-hydrogen atoms, while hydrogen atoms were introduced in

Table 4. Crystal Data and Structure Refinement for [RuH(bpy){P(OEt)₃}₃]BPh₄ (**4a**)

empirical formula	C ₅₂ H _{73.94} BCl _{0.06} N ₂ O ₉ P ₃ Ru
structural formula	[Ru(C ₁₀ H ₈ N ₂) ₃ {P(OCH ₂ CH ₃) ₃ } ₃ H _{0.94} Cl _{0.06}]- B(C ₆ H ₅) ₄
fw	1078.51
temperature	293(2) K
wavelength	0.71069 Å
crystal system	triclinic
space group	<i>P</i> 1
unit cell dimensions	<i>a</i> = 11.415(1) Å <i>b</i> = 13.980(1) Å <i>c</i> = 17.751(1) Å α = 90.832(2) $^\circ$ β = 91.227(2) $^\circ$ γ = 90.481(2) $^\circ$
volume	2831.7(4) Å ³
<i>Z</i>	2
density (calculated)	1.265 Mg/m ³
absorption coefficient	0.417 mm ⁻¹
<i>F</i> (000)	1134
θ range for data collection	1.15–23.26 $^\circ$
index ranges	−12 ≤ <i>h</i> ≤ 12, −15 ≤ <i>k</i> ≤ 15, −19 ≤ <i>l</i> ≤ 19
reflections collected	23523
independent reflections	8030 [<i>R</i> (int) = 0.0280]
refinement method	full-matrix least-squares on <i>F</i> ²
data/restraints/parameters	8030/1/582
GOF on <i>F</i> ²	1.129
final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0545, <i>wR</i> 2 = 0.1156
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0729, <i>wR</i> 2 = 0.1318
largest Δ <i>F</i> max/min	0.838/−0.765 e Å ^{−3}

calculated positions, with the exception of hydride, which was located on the Fourier map at about 1.7 Å from the metal, and was initially refined isotropically. A significant peak appearing in the difference map suggested consideration of a model of H/Cl substitution, giving a refined occupancy of about 6% for the chloride, obtained by restraining similar thermal parameters for the two anions. The refinement of a full chloride atom gave inconsistent results. The final model, retaining the restraint on the Ru–H distance, gave good geometric and thermal parameters for both anions, and revealed a large prevalence of the hydride anion in the crystal composition (94%). The final difference map was featureless. Data collection and refinement results are summarized in Table 4. Use of the Cambridge Crystallographic Database¹³ facilities was made for structure discussion.

Scheme 1^a



^a N-N = bpy (**1**, **4**); phen (**2**, **5**); 5,5'-(Me)₂bpy (**3**, **6**); P = P(OEt)₃ (**a**); PPh(OEt)₂ (**b**); PPh₂OEt (**c**).

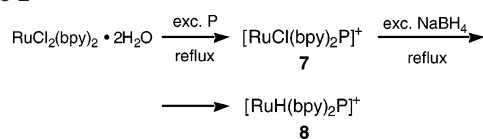
Results and Discussion

Preparation of Hydride Complexes. The synthesis of mixed-ligand hydride complexes $[\text{RuH}(\text{bpy})\text{P}_3]\text{BPh}_4$ and $[\text{RuH}(\text{phen})\text{P}_3]\text{BPh}_4$ was achieved by reacting $\text{RuCl}_4(\text{N-N})\cdot\text{H}_2\text{O}$ species first with an excess of phosphite and then of NaBH_4 , as shown in Scheme 1.

The reaction proceeds to give first the chloro complex $[\text{RuCl}(\text{N-N})\text{P}_3]^+$ (**1-3**) intermediates, which can be isolated

(13) Allen, F. H.; Kennard, O.; Taylor, R. *Acc. Chem. Res.* **1983**, *16*, 146–153.

- (8) SAINT: SAX, Area Detector Integration; Siemens Analytical instruments Inc., Madison, WI, Bruker AXS Copyright 1997–1999.
- (9) Sheldrick, G. SADABS: *Siemens Area Detector Absorption Correction Software*; University of Göttingen: Göttingen, Germany, 1996.
- (10) Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G.; Polidori, G.; Spagna R. *Sir97: A New Program For Solving And Refining Crystal Structures*; Istituto di Ricerca per lo Sviluppo di Metodologie Cristallografiche CNR: Bari, Italy, 1997.
- (11) Sheldrick, G. *Shelxl97. Program for structure refinement*; University of Göttingen: Göttingen, Germany, 1997.
- (12) Farrugia, L. J. *J. Appl. Crystallogr.* **1999**, 32, 837–838.

Scheme 2^a

^a P = P(OEt)₃ (a); PPh(OEt)₂ (b); PPh₂OEt (c).

as BPh₄ salts and characterized, and then the further reaction of this intermediate with NaBH₄ affords the final [RuH(N-N)P₃]⁺ (4–6) derivatives. The hydrides can also be prepared in one pot by reacting the RuCl₄(N-N)·H₂O compounds with an excess of both phosphite and NaBH₄ in ethanol.

Bis(2,2'-bipyridine) hydride complexes [RuH(bpy)₂P]BPh₄ (8) were also prepared by allowing the RuCl₂(bpy)₂·2H₂O complex to react first with an excess of phosphite and then with NaBH₄, as shown in Scheme 2.

The intermediate chloro complex [RuCl(bpy)₂P]BPh₄ (7) can also be isolated in this case, and their further reaction with NaBH₄ allows the final hydride compounds (8) to be obtained.

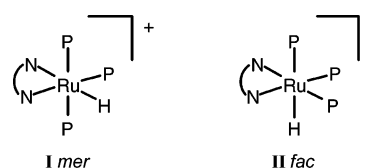
Extensive studies on the reaction of RuCl₄(N-N)·H₂O with phosphite and NaBH₄ showed that the monohydride cations [RuH(N-N)P₃]⁺ (4, 5, 6) were the only hydride species formed in the reaction, and that the change of the experimental conditions and of the ratio between the reagents only gave a lowering in the yields of 4, 5, or 6 due to the formation of decomposition products. Neutral hydride species such as RuH₂(N-N)P₂ and RuHCl(N-N)P₂ were not obtained, and even the attempts to synthesize hydride complexes containing exclusively nitrogen-donor ligands such as RuH₂(N-N)₂ or RuHCl(N-N)₂, failed. We also tested the reaction of RuCl₄(N-N)·H₂O with phosphines such as PPh₃ or Ph₂PCH₂CH₂-PPh₂ in the presence of NaBH₄, but no hydride was obtained under any attempted condition. It seems, therefore, that the synthesis of hydride species can only be obtained with phosphites using RuCl₄(N-N)·H₂O as a precursor and that the cationic monohydrides [RuH(N-N)P₃]⁺ (4–6), containing the N₂P₃ donor atoms set, are the only stable species formed in the reaction. It can also be noted that the known^{2–4} mixed-ligand hydride complexes of ruthenium with polypyridyl are of the RuHCl(bpy)(PPh₃)₂, [RuH(bpy)(CO)P₂]⁺ (P = PPh₃, PCy₃), and [RuH(bpy)₂L]⁺ (L = CO, PPh₃) type and were obtained by substituting phosphine ligands with bpy in RuHCl(PPh₃)₃ or RuHCl(CO)P₃ precursors.

Good analytical data were obtained for both chloro (1, 2, 3, 7) and hydrido (4, 5, 6, 8) complexes which are orange or red-brown solids stable in air and in a solution of polar organic solvents, in which they behave as 1:1 electrolytes.¹⁴

The IR and NMR data (Table 1) support the proposed formulation, which is further confirmed by an X-ray analysis of the [RuH(bpy){P(OEt)₃}₃]BPh₄ (4a) complex (see below).

The ¹H NMR spectra of the chloro complex [RuCl(N-N)P₃]⁺ (4–6) and [RuCl(bpy)₂P]⁺ (8) cations show the characteristic signals of the phosphite and the nitrogenous (bpy and phen) ligands. The ³¹P{¹H} NMR spectra, furthermore, appear as AB₂ multiplets for the tris(phosphite) 4–6,

Chart 1



while only one singlet is observed for the monophosphite complex 8. These data, however, do not give any conclusive information on the geometry of the chloro derivatives.

The ¹H and ³¹P NMR spectra of the hydride cations containing the PPh₂OEt ligand [RuH(N-N)(PPh₂OEt)₃]⁺ (4c, 5c) are strictly comparable with those of the related iron complexes and suggest the presence in solution of a *mer* geometry I (Chart 1).

The ¹H NMR spectra of the related P(OEt)₃ and PPh(OEt)₂ [RuH(N-N)P₃]⁺ (4a, 4b, 5a, 5b) complexes, instead, show two sets of signals in the hydride region. Each of these appears as a doublet of triplets due to the coupling of H⁻ with the phosphorus nuclei, and they were easily simulated using an AB₂X (X = H) model (Table 1). The two coupling constants *J*_{PH} of the two multiplets show different values, and, whereas in the multiplet near -7 ppm the two *J*_{PH} have comparable values of 20–30 Hz, in those at -14 ppm one constant (120–150 Hz) is far greater than the other (20–30 Hz), suggesting that one phosphite is in a *trans* geometry with respect to the hydride ligand. These results may be interpreted on the basis of the presence of two isomers, in one of which the hydride ligand is in a mutually *cis* position with all the phosphites, while in the other the hydride is *trans* with respect to one phosphite and *cis* with respect to the other two. The ³¹P{¹H} NMR spectra confirm the hypothesis of the two isomers, showing two AB₂ multiplets which can be simulated with the parameters reported in Table 1. On the basis of these data we propose the two geometries, *mer* I and *fac* II, for the two isomers (Chart 1). Spectroscopic data also indicated that the *mer* isomer is present in major amounts (between 70% and 80%), but the attempts to separate the two isomers in pure form by fractional crystallization failed. Only in one case the *mer* isomer of [RuH-(5,5'-Me₂bpy){P(OEt)₃}₃]BPh₄ (6a-*mer*) was obtained in pure form, while in the other cases only mixtures enriched in one isomer were always obtained.

Instead, suitable crystals for the X-ray crystal structure determination of the *mer* isomer of the [RuH(bpy){P(OEt)₃}₃]BPh₄ (4a) complex were separated by Pasteur method, and the crystal structure is shown in Figure 1, which also reports the atom numbering. Table 5 lists the most relevant geometric parameters of the ruthenium coordination.

The metal coordination is octahedral, and the hydride ligand is *trans* to one bipyridyl nitrogen, resulting in a *mer* geometry for the complex. As reported in the Experimental Section, the hydride is partially substituted by a chloride anion in the solid state (H:Cl ≈ 94:6), hence the final Ru–H distance is biased by the restraints applied in the refinement and we are not considering it in this discussion. Nevertheless, we can investigate the effect of hydride coordination on the bipyridyl ligand, by comparing the different local bonding

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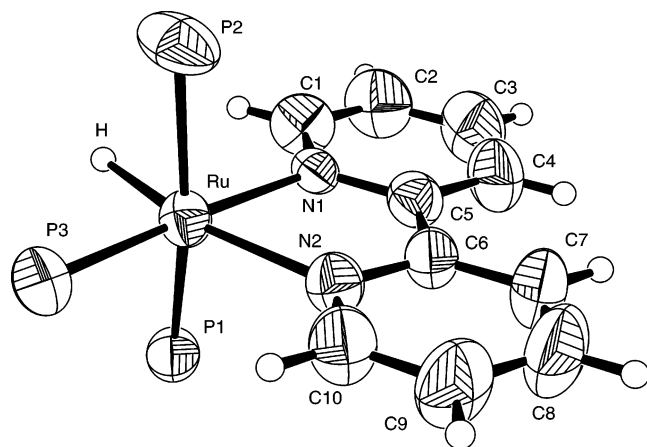


Figure 1. Perspective view of the molecular structure of *mer*-[RuH(bpy)-{P(OEt)₃}₃]⁺ (**4a**⁺). Ethoxy groups are omitted for clarity. The H/Cl substitutional disorder is not shown. Thermal ellipsoids are at the 50% level.

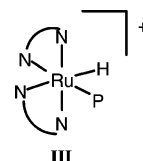
Table 5. Selected Bond Lengths [Å] and Angles [deg] for [RuH(bpy){P(OEt)₃}₃]BPh₄ (**4a**)

Ru–N1	2.151(3)	Ru–P1	2.291(1)
Ru–N2	2.178(4)	Ru–Cl	2.42(3)
Ru–P3	2.222(1)	Ru–H	1.67(4)
Ru–P2	2.280(2)	Ru–Cl (6%)	2.42(3)
N1–Ru–N2	76.6(1)	P3–Ru–P1	94.43(5)
N1–Ru–P3	176.6(1)	P2–Ru–P1	164.07(6)
N2–Ru–P3	100.1(1)	P1–Ru–H	84(1)
N1–Ru–P2	90.0(1)	P2–Ru–H	80(2)
N2–Ru–P2	98.3(1)	P3–Ru–H	95(2)
P3–Ru–P2	91.24(6)	H–Ru–N1	89(2)
N1–Ru–P1	85.2(1)	H–Ru–N2	165(2)
N2–Ru–P1	95.3(1)		

geometry of the two nitrogen donors, N1 trans to P3 (Ru–N1 = 2.151(3) Å), and N2 trans to H (Ru–N2 = 2.178(4) Å).

As for the Ru–N1 bond, this is the first structural determination of a ruthenium complex containing a phosphite ligand trans to a bipyridyl; we note that the bond length is only slightly longer than the average Ru–N distance found for bipyridyl nitrogens trans to a generic P donor (2.12 Å). The larger value of Ru–N2 (trans to hydride) compared to Ru–N1 could be due to electronic effects, but also to steric reasons: N2 is cis to the bulky phosphite at P3, whereas N1 is adjacent to the small hydride ion, and can get closer to the metal. To elucidate the role of the electronic effects we carried out a search in the Cambridge Structural Database (version 5.24, November 2002), which has shown that only four other ruthenium hydride bipyridyl complexes^{15–18} are structurally known, one of these being a Ru₄ cluster with bridging H[–],¹⁶ and one containing the 6,6′-dimethyl-2,2′-bipyridine ligand (dmbpy).¹⁷ Focusing on the mononuclear complexes, only two of these are *mer* isomers,^{15,17} and the Ru–N bonds trans to the hydride are comparable to those

Chart 2

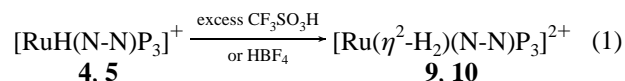


found in **4a** (2.176 and 2.225 Å for [RuH(bpy)₂(CO)]⁺ and [RuH(dmbpy)(CO)₂(NCS)]⁺, respectively).

As concerns the phosphite ligands, the Ru–P3 bond is remarkably shorter (2.222(1) Å) than the Ru–P1 (2.291(1) Å) and Ru–P2 (2.279(2) Å) ones, which are trans each other, and which are closer to the average found for Ru–P(OEt)₃ bond lengths (2.30 Å). The shortening of the Ru–P1 distance could be favored by the lower steric hindrance exerted by the bpy and the hydride ligands in the equatorial plane, due to the small radius of H[–] and to the tight bite angle of bpy (N1–Ru–N2 = 76.6(1)°), which allows more room for the phosphite ligand (P3–Ru–N2 = 100.1(1)°).

Monophosphite [RuH(bpy)₂P]BPh₄ (**8**) hydride complexes were obtained only with the 2,2′-bipyridine ligand, and their ¹H and ³¹P NMR spectra suggest, in contrast to the related iron complexes, a cis geometry of type **III** (Chart 2) for these derivatives. The value of 32–36 Hz found for the *J*_{HP} of the hydride ligand, in fact, indicates a mutually cis position of the hydride and phosphite ligands by comparison with the values of the related **4**, **5**, and **6** derivatives.

Protonation Reactions. Hydride complexes [RuH(N–N)–P₃Y] (**4**, **5**) (Y = BPh₄, CF₃SO₃) react with the Brønsted acids CF₃SO₃H or HBF₄ to give the dihydrogen derivatives [Ru(η²-H₂)(N–N)P₃]²⁺ (**9**, **10**) as shown in eq 1. The reaction



N–N = bpy (**4**, **9**), phen (**5**, **10**); P = P(OEt)₃ (**a**);

PPh(OEt)₂ (**b**); PPh₂OEt (**c**) (1)

was studied in an NMR tube at temperatures varying between –80 and +20 °C and showed that, in the case of the [RuH(N–N)(PPh₂OEt)]⁺ (**4c**, **5c**) complexes, the addition of the triflic acid CF₃SO₃H caused the disappearance of the hydride resonances in the ¹H NMR spectra and the appearance of one broad signal (half-height width of about 180 Hz at –80 °C) at –8.0 to –7.8 ppm respectively, attributed to the η²-H₂ ligand. Measurements of *T*_{1min} (Table 2) on this signal gave values of 5.1 (**9c**) and 5.9 (**10c**) ms, in agreement¹⁹ with the proposed formulation. The spectra of the isotopomers [Ru(η²-HD)(N–N)P₃]²⁺ derivatives appear as a triplet of doublets from which a *J*_{HD} value of 28.9 (**9c**) and 29.4 Hz (**10c**) was measured, which further confirms the formation of the dihydrogen derivatives. Furthermore, the split of each peak of the triplet is attributable to the coupling with the phosphorus nuclei of a phosphite, with *J*_{PH} of about 9 Hz

(15) Haasnoot, J. G.; Hinrichs, W.; Weir, O.; Vos, J. G. *Inorg. Chem.* **1986**, 25, 4140–4143.

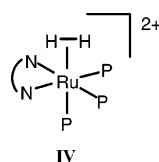
(16) Nijhoff, J.; Bakker, M. J.; Hartl, F.; Freeman, G.; Ingham, S. L.; Johnson, B. F. G. *J. Chem. Soc., Dalton Trans.* **1998**, 2625–2634.

(17) Homanen, P.; Haukka, M.; Pakkanen, T. A.; Pursiainen, J.; Laitinen, R. H. *Organometallics* **1996**, 15, 4081–4084.

(18) Haukka, M.; Hirva, P.; Luukkanen, S.; Kallinen, M.; Ahlgrén, M.; Pakkanen, T. A. *Inorg. Chem.* **1999**, 38, 3182–3189.

(19) (a) Hamilton, D. G.; Crabtree, R. H. *J. Am. Chem. Soc.* **1988**, 110, 4126–4136. (b) Bautista, M. T.; Earl, K. A.; Maltby, P. A.; Morris, R. H.; Schweitzer, C. T.; Sella, A. J. *Am. Chem. Soc.* **1988**, 110, 7031–7036. (c) Desrosiers, P. J.; Cai, L.; Lin, Z.; Richards, R.; Halpern, J. *J. Am. Chem. Soc.* **1991**, 113, 4173–4184.

Chart 3



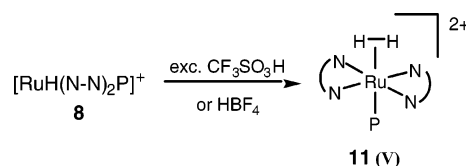
for **9c** and 11 Hz for **10c**, suggesting that the H₂ should be in a mutually trans position with one phosphite ligand. Finally, taking into account that the ³¹P{¹H} NMR spectra of **9c** and **10c** appear as an AB₂ multiplet, a *fac* geometry **IV** (Chart 3) can be proposed for the observable η²-H₂ derivatives.

The protonation reaction of the related PPh(OEt)₂ and P(OEt)₃ [RuH(N-N)P₃]⁺ (**4a**, **5a**, **4b**, **5b**) derivatives containing both the *mer* and *fac* isomers was also studied. The ¹H NMR spectra, in fact, showed that the addition of the triflic acid caused the disappearance of both the ¹H multiplet at -7 and at -14 ppm of the hydrides of the two isomers. However, only one broad signal between -9 and -10 ppm attributable to the η²-H₂ ligand was observed, while two new AB₂ multiplets appeared in the ³¹P{¹H} NMR spectra concurrent with the disappearance of those of the hydride precursors, in agreement with the reaction of both the isomers of the hydrides giving η²-H₂ derivatives. The presence of only one η²-H₂ signal observed between -80 and +10 °C may be explained, either by a partial overlapping of the signals of the two η²-H₂ isomers formed, or by the large broadness of the signal of the isomer present in minor amount. The loss of dihydrogen even at -80 °C cannot be excluded. In every case the formation of at least one η²-H₂ complex was observed, which was confirmed both by T_{1min} measurements on this broad signal and by determination of the J_{HD} values of the related [Ru(η²-HD)(N-N)P₃]²⁺ isotopomers (Table 2). The presence of the coupling between the η²-HD and one phosphite ligand (J_{PH} about 9–10 Hz) also suggests a *fac*-type geometry **IV** for the η²-H₂ derivatives.

From the J_{HD} values the H–H distances were calculated,^{2b} and they are reported in Table 2. Values between 0.93 and 0.95 Å were observed for the tris(phosphite) [Ru(η²-H₂)(N-N)P₃]²⁺ (**9**, **10**) derivatives. The H–H bond length in the H₂ ligand can also be calculated²⁰ by the T_{1min} values. The results for the ruthenium complexes are reported in Table 2 for both a slow and a fast rotation model and, unexpectedly,²¹ do not result comparable with those calculated from the J_{HD} values. In fact, a H–H distance of 0.93–0.95 Å from the J_{HD} values, which is intermediate between the two possible values of 0.99–1.03 Å (slow rotation) and 0.79–0.81 Å (fast rotation) for the H–H bond length calculated for the T_{1min} values, has been calculated.

In the related iron complexes¹ [Fe(η²-H₂)(N-N)P₃]²⁺ values for the H–H distances of 0.92–0.94 Å were deduced for the J_{HD} values, which showed a good agreement with the distances calculated by the T₁ method using a static rotation

Scheme 3



model. These values are also strictly comparable with those calculated from J_{HD} of the ruthenium complexes and seem to indicate that the H–H distances (from J_{HD}) in mixed-ligand [M(η²-H₂)(N-N)P₃]²⁺ complexes are not influenced by the nature of the central metal. A comparable value of 0.92 Å for r_{H–H} was in fact calculated for the 2,2'-bipyridine [Ru(η²-H₂)(PPh₃)₂(bpy)(CO)]²⁺ derivative.^{2b}

Variable temperature NMR studies also indicated that the dihydrogen complexes are rather stable and the loss of hydrogen begins over 5–10 °C. However, as for the related iron complexes, no solid sample was isolated.

Monophosphite complexes [RuH(bpy)₂P]Y (**8**) (Y = BPh₄, CF₃SO₃) also react with Brønsted acid in CH₂Cl₂ solution to give the dihydrogen [Ru(η²-H₂)(bpy)₂P]²⁺ (**11**) cations (Scheme 3), which are stable in solution until 5–10 °C, but lose H₂ if attempts of separation in a solid state are made.

Measurements of T_{1min} (7.2–7.6 ms) and J_{HD} (31.2–32.8 Hz) values (Table 2) strongly support the formulation of **11** as dihydrogen derivatives. The observed value for ²J_{PHD} of about 7–8 Hz also suggests a mutually trans position of the phosphine and the dihydrogen ligands as in type-V geometry.

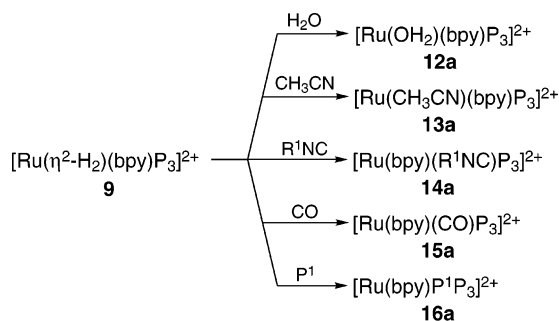
Furthermore, the H–H distances of the dihydrogen ligand were also calculated both from the J_{HD} and the T_{1min} values and are reported in Table 2. Bond H–H lengths of 0.89–0.92 Å were calculated from J_{HD} for [Ru(η²-H₂)(bpy)₂P]²⁺ (**11**) derivatives and were slightly shorter than the values of the related [Ru(η²-H₂)(N-N)P₃]²⁺ (**9**, **10**) cations. In the monophosphites **11**, however, the H–H distances deduced from J_{HD} could not be correlated with those deduced from T_{1min} values, using either a fast rotation model or with those using a slow rotation one, the calculated H–H distance being an intermediate value between the two.

Studies on the protonation of the hydride complexes **4**, **5**, and **8** reveal that the tris(phosphite) [Ru(η²-H₂)(N-N)P₃]²⁺ (**9**, **10**) cations are, as expected, more acidic than the monophosphite [Ru(η²-H₂)(bpy)₂P]²⁺ (**11**) derivatives. In fact, approximately 2.5 equiv of CF₃SO₃H is required for the complete protonation of [RuH(N-N)P₃]⁺, while less than 1.5 equiv is required for the monophosphite [RuH(bpy)₂P]⁺ hydride cations.

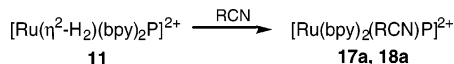
A qualitative comparison between the acidity of the ruthenium [Ru(η²-H₂)(N-N)(PPh₂OEt)₃]²⁺ (**9**, **10**) cations and the related [Fe(η²-H₂)(N-N)(PPh₂OEt)₃]²⁺ derivatives¹ can also be made, and shows that the ruthenium complexes **9**, **10** are slightly more acidic than the related iron compounds. However, although more acidic than those of iron, the ruthenium complexes **9**, **10** are the least acidic among the known dicationic derivatives,²² whose complete formation from the [RuH(N-N)P₃]⁺ precursors requires less than 2.5 equiv of CF₃SO₃H. The bis(bipyridine) [Ru(η²-H₂)(bpy)₂P]²⁺

(20) Earl, K. A.; Jia, G.; Maltby, P. A.; Morris, R. H. *J. Am. Chem. Soc.* **1991**, *113*, 3027–3039.

(21) Gusev, D. G.; Kuhlman, R. L.; Renkema, K. B.; Eisenstein, O.; Caulton, K. G. *Inorg. Chem.* **1996**, *35*, 6775–6783.

Scheme 4^a

^a P = P(OEt)₃; P¹ = PPh(OEt)₂; R¹ = 4-CH₃C₆H₄.

Scheme 5^a

^a R = CH₃ (17), 4-CH₃C₆H₄ (18); P = P(OEt)₃.

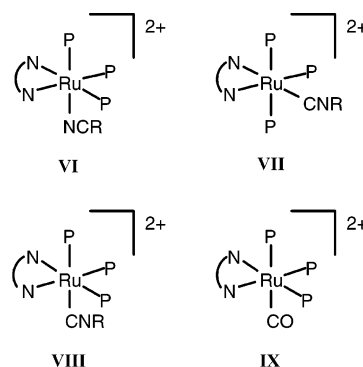
(11) derivatives are also, indeed, less acidic than the known dicationic dihydrogen complexes, thus highlighting that the presence of nitrogen-donor ligands such as bpy and phen can delocalize the positive charge of the complexes making the η^2 -H₂ ligand relatively less acidic.

Substitution Reactions. Studies on the dihydrogen complexes **9**, **10**, **11** show that the η^2 -H₂ ligand is labile and can be easily substituted by several molecules allowing new ruthenium complexes to be prepared. Some examples are reported in Schemes 4 and 5. With molecules such as H₂O and phosphite, however, the deprotonation to give the [RuH-(bpy)P₃]⁺ precursor can be predominant on the substitution of the η^2 -H₂ ligand. The preparation of the complexes, therefore, must first involve the loss of H₂ to give, probably, the [Ru(κ^1 -OSO₂CF₃)(bpy)P₃]⁺ intermediate which, by substitution of the triflate, yields the final complexes.

At first, the aquo complex **12a** was obtained in an attempt to isolate the η^2 -H₂ complex in the solid state, due to the presence of traces of H₂O in the solvent. It was also prepared as a yellow solid by adding an excess of H₂O to a solution of the η^2 -H₂ complex in CH₂Cl₂. Nitrile, isonitrile, carbonyl, and mixed-phosphite derivatives **13**–**16** were also prepared and are yellow or red-orange solids stable in air and in a solution of polar organic solvents, diamagnetic and 1:2 electrolyte.¹⁴ Analytical and spectroscopic data (Table 1) support the proposed formulation.

The presence of H₂O as a ligand in [Ru(OH₂)(bpy)P₃](BPh₄)₂ is confirmed by the ¹H NMR spectrum, which shows a slightly broad singlet at 2.55 ppm attributed²³ to the H₂O protons. In the spectra the signals of the phosphite and the bpy ligands are also present, while the ³¹P{¹H} NMR spectra appear as an AB₂ multiplet. Unfortunately, these data do not allow us to distinguish between a *mer* or *fac* geometry.

Chart 4



The IR spectrum of the nitrile complex **13a** does not show any absorption attributable to the ν_{CN} probably due to its low intensity.²⁴ The ¹H and ¹³C NMR spectra, however, confirm the presence of the CH₃CN ligand showing a singlet at 0.30 ppm of the methyl group in the proton spectrum, while a singlet at 0.60 ppm and a doublet at 125.4 ppm (J_{CP} = 22 Hz) appear in the ¹³C{¹H} NMR spectrum (Table 3) and were attributed to the CH₃ and the CN carbon atoms of the acetonitrile ligands, respectively. The HMQC and HMBC experiments confirm the attributions, showing the correlation between the methyl proton signal at 0.30 ppm with the ¹³C signals at 0.60 ppm (HMQC) and at 125.4 (HMBC) of the CH₃CN ligand. Furthermore, the presence of a doublet for the CN carbon resonance with J_{CP} of 22 Hz suggests that the nitrile ligand should be in a *trans* position with one phosphorus nucleus of the phosphite ligands. Taking into account that the ³¹P spectrum appears as an A₂B multiplet, a *fac* geometry (VI) can be reasonably proposed for the nitrile complex **13a**.

The isocyanide derivative **14a** was obtained as a mixture of two isomers, probably with a *mer* (VII) and *fac* (VIII) geometry (Chart 4). The ³¹P{¹H} NMR spectrum, in fact, shows two A₂B multiplets, while two singlets of the methyl substituent of the 4-CH₃C₆H₄NC ligand were observed in the proton spectra. The presence of the isocyanide was confirmed by the IR spectrum, which shows the ν_{CN} bond as a strong, slightly broad absorption at 2158 cm⁻¹.

One strong ν_{CO} band at 2054 cm⁻¹ was observed in the IR spectrum of the carbonyl complex **15a**, whose ¹³C spectrum (Table 3) shows the resonance of the carbonyl carbon atom as a doublet of triplets [A₂BY (Y = ¹³C) multiplet] at 190.9 ppm, with values for the two J_{CP} of 17.0 and 245 Hz. The different values for the two J_{CP} suggest that the carbonyl ligand should be in a mutually *trans* position with one phosphite and *cis* with the other two. The ³¹P{¹H} NMR spectrum of the carbonyl complex **15a** appears as an A₂B multiplet, and therefore a *fac* geometry of the type IX (Chart 4) can be proposed.

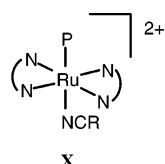
The ¹³C{¹H} NMR spectrum of [Ru(CH₃CN)(bpy)₂-{P(OEt)₃}] (BPh₄)₂ (**17a**) shows one singlet at 3.5 ppm and one doublet at 127.4 ppm (J_{CP} = 16 Hz) attributed to the methyl and CN carbon atoms, respectively, of the CH₃CN

(22) (a) Schlaf, M.; Lough, A. J.; Maltby, P. A.; Morris, R. H. *Organometallics* **1996**, *15*, 2270–2278. (b) Rocchini, E.; Mezzetti, A.; Rüegger, H.; Burckhardt, U.; Gramlich, V.; Del Zotto, A.; Martinuzzi, P.; Rigo, P. *Inorg. Chem.* **1997**, *36*, 711–720. (c) Forde, C. E.; Landau, S. E.; Morris, R. H. *J. Chem. Soc., Dalton Trans.* **1997**, 1663–1664. (d) Landau, S. E.; Morris, R. H.; Lough, A. J. *Inorg. Chem.* **1999**, *38*, 6060–6068. (e) Smith, K. T.; Tilset, M.; Kuhlman, R.; Caulton, K. G. *J. Am. Chem. Soc.* **1995**, *117*, 9473–9480.

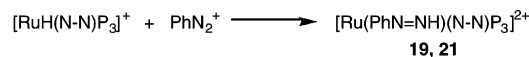
(23) Albertin, G.; Antoniutti, S.; Bacchi, A.; Boato, M.; Pelizzi, G. *J. Chem. Soc., Dalton Trans.* **2002**, 3313–3320.

(24) The low intensity or even absence of ν_{CN} in acetonitrile complexes is a feature that has already been observed: Rouschias, G.; Wilkinson, G. *J. Chem. Soc. A* **1967**, 993–1000.

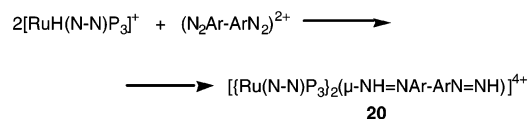
Chart 5



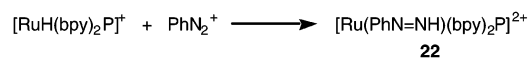
Scheme 6



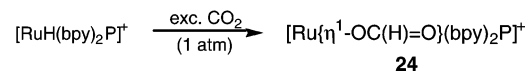
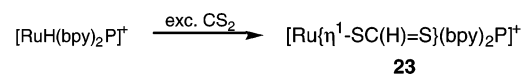
N-N = bpy (19), phen (21); P = P(OEt)₃ (a), PPh(OEt)₂ (b).



P = P(OEt)₃, Ar-Ar = 4,4'-C₆H₄-C₆H₄.



P = P(OEt)₃.

Scheme 7^a

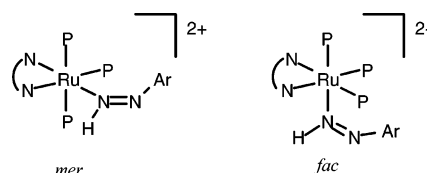
^a P = P(OEt)₃ (a), PPh(OEt)₂ (b).

ligand. The HMQC and HMBC experiments confirm these attributions showing a correlation between the methyl proton signal at 1.66 ppm and the carbon signals at 3.5 (HMQC) and 127.4 ppm (HMBC), respectively. Furthermore, the presence of a doublet for the CN carbon resonance with J_{CP} of 16 Hz suggests a mutually trans position of the nitrile and the phosphine ligand as in type-X geometry (Chart 5).

Insertion Reactions: Preparation of Aryldiazene and Formato Derivatives. Insertion reactions into the Ru-H bond of the new mixed-ligand hydride complexes **4**, **5**, **6**, **8** were studied extensively with several unsaturated molecules, and the results are summarized in Schemes 6 and 7. Aryldiazonium cation (ArN_2^+) and heteroallenes (CS_2 and CO_2) quickly react with the ruthenium hydride to give aryldiazene,^{25,26} thioformato, and formato²⁷ derivatives,

- (25) For aryldiazene complexes see: (a) Sutton, D. *Chem. Rev.* **1993**, 93, 995–1022. (b) Kisch, H.; Holzmeier, P. *Adv. Organomet. Chem.* **1992**, 34, 67–109. (c) Zollinger, H. *Diazo Chemistry II*; VCH: Weinheim, Germany, 1995.
- (26) Albertin, G.; Antoniutti, S.; Bacchi, A.; Ballico, G. B.; Bordignon, E.; Pelizzi, G.; Ranieri, M.; Ugo, P. *Inorg. Chem.* **2000**, 39, 3265–3279 and references therein.
- (27) (a) Aresta, M.; Quaranta, E.; Tommasi, I. *New J. Chem.* **1994**, 18, 133–142. (b) Pandey, K. K. *Coord. Chem. Rev.* **1995**, 140, 37–114. (c) Leitner, W. *Coord. Chem. Rev.* **1996**, 153, 257–284. (d) Yin, X.; Moss, J. R. *Coord. Chem. Rev.* **1999**, 181, 27–59. (e) Field, L. D.; Lawrenz, E. T.; Shaw, W. J.; Turner, P. *Inorg. Chem.* **2000**, 39, 5632–5638. (f) Field, L. D.; Shaw, W. J.; Turner, P. *Organometallics* **2001**, 20, 3491–3499. (g) Gandhi, T.; Nethaji, M.; Jagirdar, B. R. *Inorg. Chem.* **2003**, 42, 667–669.

Chart 6



whereas no reaction was observed with CO, alkenes, and terminal alkynes.

The reaction with mono- and bis(aryldiazonium) cations proceeds with both $[\text{RuH}(\text{N-N})\text{P}_3]^+$ and $[\text{RuH}(\text{bpy})_2\text{P}]^+$ complexes yielding mononuclear **19**, **21**, **22** and binuclear **20** aryldiazene derivatives.

Carbon disulfide and carbon dioxide also react with all the hydrides **4–8**, but only with the bis(bipyridine) derivatives $[\text{RuH}(\text{bpy})_2\text{P}]^+$ (**8**) were the thioformato **23** and formato **24** complexes prepared in pure form. With the tris(phosphite) $[\text{RuH}(\text{N-N})\text{P}_3]^+$ (**4–6**) cations, instead, the reaction with CS_2 is very slow at room temperature, while CO_2 does not react. The use of reflux conditions, however, causes some decomposition, which prevents the separation of pure samples of the thioformato derivative. It can also be noted that only the hydrides with P(OEt)₃ and PPh(OEt)₂ undergo a fast insertion reaction which allows the isolation of the final products, while the related PPh₂OEt hydride derivative reacts so slowly as to prevent the separation of the product in pure form.

Good analytical data were obtained for the new complexes **19–24**, which are yellow or orange solids stable in the air and in solution of polar organic solvents, in which they behave as 1:1 (**23**, **24**), 2:1 (**19**, **21**, **22**), or 4:1 (**20**) electrolytes.¹⁴ Infrared and NMR (¹H, ³¹P, ¹³C, ¹⁵N) data (Tables 1 and 3) support the proposed formulation, and a geometry in solution was also established. The ³¹P and ¹H NMR spectra of the $[\text{Ru}(\text{PhN}=\text{NH})(\text{N-N})\text{P}_3]^{2+}$ complexes **19**, **21** indicate the presence of two isomers, as had been observed in the hydride **4–5** precursors. Furthermore, a comparison of the spectroscopic data (Table 1) with those of the related iron complexes¹ suggests that their geometries should be of the *fac*- and *mer*-types of Chart 6.

The NMR spectra of the binuclear complex **20a** show two NH signals in the proton spectra, two AB₂ multiplets in the ³¹P, and also two AB₂Y (Y = ¹⁵N) multiplets present in the ¹⁵N spectra of the ¹⁵N-labeled **20a**-¹⁵N derivative. These data may suggest, in this case as well, the presence of the two isomers. However, because the complex is binuclear, a total of four isomers (two of which are equivalent) should be formed, of the type shown in Chart 7.

The ¹H NMR spectra of the monophosphite $[\text{Ru}(\text{PhN}=\text{NH})(\text{bpy})_2\text{P}](\text{BPh}_4)_2$ (**22**) show only one NH signal, which is split into a doublet in the ¹⁵N-labeled complex **22a**-¹⁵N, with J_{NH} of 65.5 Hz, in agreement²⁸ with the proposed formulation. Furthermore, the ³¹P spectra show only one singlet suggesting the presence of only one isomer. Finally, the ¹⁵N NMR spectra of **22a**-¹⁵N appear as a doublet due to

- (28) (a) Laing, K. R.; Robinson, S. D.; Uttley, M. F. *J. Chem. Soc., Dalton Trans.* **1973**, 2713–2722. (b) Carroll, J. A.; Sutton, D.; Xiaoheng, Z. *J. Organomet. Chem.* **1983**, 244, 73–86.

Chart 7

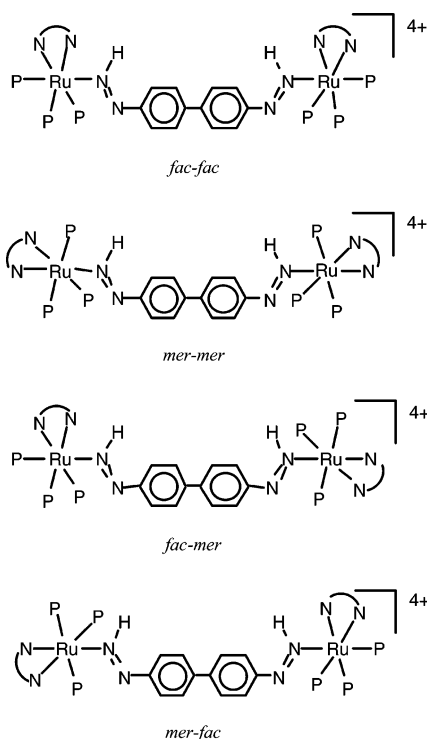
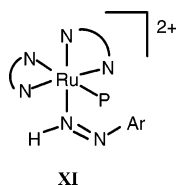


Chart 8

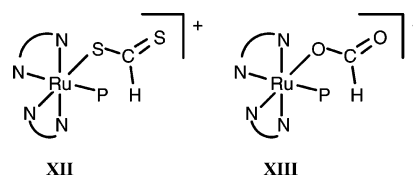


the coupling with the phosphorus nucleus. The value of J_{NP} of 4.7 Hz also suggests, by comparison with the values of the related **19a**- ^{15}N and **20a**- ^{15}N compounds, a mutually cis position of the diazene and the phosphite ligand, as in a type-**XI** geometry (Chart 8).

Aryldiazenes complexes of ruthenium are known²⁵ and are generally stabilized^{25a,29} by phosphine and/or carbonyl as supporting ligands. The preparation of our derivatives **19**–**22** shows how bipyridine or phenanthroline in the mixed-ligand fragments $\text{Ru}(\text{N}-\text{N})\text{P}_3$ and $\text{Ru}(\text{bpy})_2\text{P}$ are also able to stabilize this class of “diazo” derivatives.

The ^1H NMR spectra of the thioformato $[\text{Ru}\{\eta^1\text{-SC}(\text{H})=\text{S}\}(\text{bpy})\text{P}]\text{BPh}_4$ (**23**) show a singlet at 10.87–10.94 ppm attributed³⁰ to the CH proton of the $\text{SC}(\text{H})\text{S}$ ligand. In the ^{13}C spectra of **23a** the carbon signal of this ligand appears as a singlet at 238.6 ppm, and the attribution is confirmed by a HMQC experiment, which shows the correlation between this signal at 238.6 ppm and those in the proton NMR spectra at 10.87 ppm, in agreement with the presence of the thioformato ligand. The IR spectra also confirm the presence of the $\text{SC}(\text{H})\text{S}$ ligand showing the δ_{HCS} as a medium-intensity

Chart 9



band at 1242–1256 cm^{-1} . Furthermore, the absence of a measurable coupling constant between the CH proton of $\text{SC}(\text{H})\text{S}$ ligand and the phosphorus nucleus of the phosphite as in a type-**XII** geometry (Chart 9). Finally, the thioformate ligand should act as monodentate in our ruthenium complexes **23**, a heptacoordinate $\text{Ru}(\text{II})$ species being rather improbable.

The IR spectra of the formato complexes $[\text{Ru}\{\eta^1\text{-OC}(\text{H})=\text{O}\}(\text{bpy})_2\text{P}]\text{BPh}_4$ (**24**) show a strong absorption at 1601–1599 cm^{-1} attributed to ν_{asymCO_2} of the η^1 -formato ligand. Other η^1 -formato complexes show ν_{asymCO_2} bands in the 1603–1667 cm^{-1} range,³¹ whereas η^2 -formates generally show ν_{asymCO_2} bands³² between 1554 and 1585 cm^{-1} .

The ^{13}C spectra confirm the presence of the $\text{OC}(\text{H})\text{O}$ ligand showing one singlet at 170.6 ppm (**24a**) and at 171.3 ppm (**24b**) due to the formato carbon atom. The ^1H NMR spectra do not allow us to clearly assign the formyl CH resonance, due to the superimposing with the phenyl proton signals. However, a HMQC experiment clearly shows the correlation between one singlet at 7.73 (**24a**) and at 7.48 (**24b**) ppm in the proton NMR spectra and the singlet due to the ^{13}C formyl carbon resonance at 170–171 ppm, in agreement with the presence of the formato ligand. The absence of a measurable coupling constant between the CH proton of $\text{OC}(\text{H})=\text{O}$ and the phosphorus nucleus of the phosphite may suggest a mutually cis position of the formato with the phosphite as in type-**XIII** geometry (Chart 9) in this case as well.

Formato complexes obtained by insertion of CO_2 into the metal–hydride bond are of interest as an important chemical step in functionalizing this molecule,²⁷ and the preparation of $[\text{Ru}\{\eta^1\text{-OC}(\text{H})=\text{O}\}(\text{bpy})_2\text{P}]\text{BPh}_4$ complexes constitutes a new example for the ruthenium central metal with nitrogen donor and phosphite as supporting ligands.

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Conclusions

In this paper the synthesis of a new series of mixed-ligand hydride complexes of ruthenium(II) with phosphite and polypyridine of the type $[\text{RuH}(\text{N-N})\text{P}_3]\text{BPh}_4$ and $[\text{RuH}(\text{bpy})_2\text{P}]\text{BPh}_4$ is described. Among the properties shown by these complexes, we can highlight the easy protonation with Brønsted acid to give dicationic dihydrogen $[\text{Ru}(\eta^2\text{-H}_2)(\text{N-N})\text{P}_3]^{2+}$ and $[\text{Ru}(\eta^2\text{-H}_2)(\text{N-N})\text{P}_3]^{2+}$ derivatives. Acidity studies of these $\eta^2\text{-H}_2$ complexes were also carried out and compared with other dicationic dihydrogen derivatives. The Ru–H bond of the mixed-ligand hydride can undergo insertion of both aryldiazonium cation, to give aryldiazene, and heteroal-

lene, to give formate $[\text{Ru}\{\eta^1\text{-OC(H)=O}\}(\text{bpy})_2\text{P}]\text{BPh}_4$ and dithioformate $[\text{Ru}\{\eta^1\text{-SC(H)=S}\}(\text{bpy})_2\text{P}]\text{BPh}_4$ derivatives.

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Supporting Information Available: Crystallographic data in CIF format. Experimental details and spectroscopic data (IR, NMR) of compounds **4c**- CF_3SO_3 , **5c**- CF_3SO_3 , and **8**- CF_3SO_3 . This material is available free of charge via the Internet at <http://pubs.acs.org>. IC034820Z