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

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Chloro complexes $[RuCl(N\text{-}N)P_3]BPh_4$ (**1**–**3**) [N-N = 2,2′-bipyridine, bpy; 1,10-phenanthroline, phen; 5,5′-dimethyl-2,2′-bipyridine, 5,5′-Me_2bpy; P = $P(OEt)_3$, $PPh(OEt)_2$ and PPh_2OEt] were prepared by allowing the $[RuCl_4(N\text{-}N)]\cdot H_2O$ compounds to react with an excess of phosphite in ethanol. The bis(bipyridine) $[RuCl(bpy)_2\{P(OEt)_3\}]BPh_4$ (**7**) complex was also prepared by reacting $RuCl_2(bpy)_2\cdot 2H_2O$ with phosphite and ethanol. Treatment of the chloro complexes **1**–**3** and **7** with $NaBH_4$ yielded the hydride $[RuH(N\text{-}N)P_3]BPh_4$ (**4**–**6**) and $[RuH(bpy)_2P]BPh_4$ (**8**) derivatives, which were characterized spectroscopically and by the X-ray crystal structure determination of $[RuH(bpy)\{P(OEt)_3\}_3]BPh_4$ (**4a**). Protonation reaction of the new hydrides with Brønsted acid was studied and led to dicationic $[Ru(\eta^2\text{-}H_2)(N\text{-}N)P_3]^{2+}$ (**9**, **10**) and $[Ru(\eta^2\text{-}H_2)(bpy)_2P]^{2+}$ (**11**) dihydrogen derivatives. The presence of the η^2-H_2 ligand was indicated by a short T_{1min} value and by the measurements of the J_{HD} in the $[Ru](\eta^2\text{-}HD)$ isotopomers. From T_{1min} and J_{HD} values the H–H distances of the dihydrogen complexes were also calculated. A series of ruthenium complexes, $[RuL(N\text{-}N)P_3](BPh_4)_2$ and $[RuL(bpy)_2P](BPh_4)_2$ (P = $P(OEt)_3$; L = H_2O, CO, 4-$CH_3C_6H_4NC$, CH_3CN, 4-$CH_3C_6H_4CN$, $PPh(OEt)_2$], was prepared by substituting the labile η^2-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 $[Ru(C_6H_5N{=}NH)(N\text{-}N)P_3](BPh_4)_2$ (**19**, **21**), $[\{Ru(N\text{-}N)P_3\}_2(\mu\text{-}4,4'\text{-}NH{=}NC_6H_4{-}C_6H_4N{=}NH)](BPh_4)_4$ (**20**), and $[Ru(C_6H_5N{=}NH)(bpy)_2P](BPh_4)_2$ (**22**) derivatives. Also the heteroallenes CO_2 and CS_2 reacted with $[RuH(bpy)_2P]BPh_4$, yielding the formato $[Ru\{\eta^1\text{-}OC(H){=}O\}(bpy)_2P]BPh_4$ and dithioformato $[Ru\{\eta^1\text{-}SC(H){=}S\}(bpy)_2P]BPh_4$ derivatives.

Introduction

In the preceding paper of this series[1] we have reported the synthesis and the reactivity of new iron(II) hydride complexes of the $[FeH(N\text{-}N)P_3]BPh_4$ (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 polypyridyl ruthenium hydrides are known and include cationic carbonyls,[2] $[RuH(bpy)(PPh_3)_2(CO)]^+$, neutral[3] $RuHCl(bpy)P_2$ (P = PPh_3, PCy_3), and the bis(2,2′-bipyridine)[4] $[RuH(bpy)_2L]^+$ (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 $RuCl_3 \cdot 3H_2O$ 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 $RuCl_4(bpy) \cdot H_2O$, $RuCl_4(phen) \cdot H_2O$, $RuCl_4(5,5'\text{-}Me_2bpy) \cdot H_2O$, and $RuCl_2(bpy)_2 \cdot 2H_2O$ 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)P$_3$]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 $RuCl_4(bpy) \cdot H_2O$ (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 ≥85%. Anal. Calcd for $C_{52}H_{73}BClN_2O_9P_3Ru$ (**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; $\Lambda_M = 51.7\ \Omega^{-1}\ mol^{-1}\ cm^2$. Anal. Calcd for $C_{64}H_{73}BClN_2O_6P_3Ru$ (**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; $\Lambda_M = 55.6\ \Omega^{-1}\ mol^{-1}\ cm^2$. Anal. Calcd for $C_{76}H_{73}BClN_2O_3P_3Ru$ (**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; $\Lambda_M = 54.8\ \Omega^{-1}\ mol^{-1}\ cm^2$.

[RuCl(phen)P$_3$]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 $RuCl_4(phen) \cdot H_2O$ as a precursor; yield ≥75%. Anal. Calcd for $C_{54}H_{73}BClN_2O_9P_3Ru$ (**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. $\Lambda_M = 55.1\ \Omega^{-1}\ mol^{-1}\ cm^2$. Anal. Calcd for $C_{66}H_{73}BClN_2O_6P_3Ru$ (**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. $\Lambda_M = 57.5\ \Omega^{-1}\ mol^{-1}\ cm^2$. Anal. Calcd for $C_{78}H_{73}BClN_2O_3P_3Ru$ (**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. $\Lambda_M = 58.4\ \Omega^{-1}\ mol^{-1}\ cm^2$.

[RuCl(5,5′-Me$_2$bpy){P(OEt)$_3$}$_3$]BPh$_4$ (3a). Also this complex was prepared following the method used for the related 2,2′-bipyridine derivative **1a**; yield ≥80%. Anal. Calcd for $C_{54}H_{77}BClN_2O_9P_3Ru$: 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. $\Lambda_M = 55.3\ \Omega^{-1}\ mol^{-1}\ cm^2$.

[RuH(bpy)P$_3$]BPh$_4$ (4) [P = P(OEt)$_3$ (a), PPh(OEt)$_2$ (b), PPh$_2$OEt (c)]. To a solution of $RuCl_4(bpy) \cdot H_2O$ (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 $RuCl_4(bpy) \cdot H_2O$ with phosphite to give [RuCl(bpy)P$_3$]BPh$_4$ (**1**) and then treating these complexes with an excess of $NaBH_4$ in ethanol. Anal. Calcd for $C_{52}H_{74}BN_2O_9P_3Ru$ (**4a**): C, 58.05; H, 6.93; N, 2.60. Found: C, 57.94; H, 6.99; N, 2.49. $\Lambda_M = 56.6\ \Omega^{-1}\ mol^{-1}\ cm^2$. Anal. Calcd for $C_{64}H_{74}BN_2O_6P_3Ru$ (**4b**): C, 65.58; H, 6.36; N, 2.39. Found: C, 65.46; H, 6.29; N, 2.28. $\Lambda_M = 54.9\ \Omega^{-1}\ mol^{-1}\ cm^2$. Anal. Calcd for $C_{76}H_{74}BN_2O_3P_3Ru$ (**4c**): C, 71.98; H, 5.88; N, 2.21. Found: C, 71.80; H, 5.76; N, 2.15. $\Lambda_M = 57.8\ \Omega^{-1}\ mol^{-1}\ cm^2$.

[RuH(phen)P$_3$]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 $RuCl_4(phen) \cdot H_2O$ precursor; yield from 65% to 75%. Anal. Calcd for $C_{54}H_{74}BN_2O_9P_3Ru$ (**5a**): C, 58.96; H, 6.78; N, 2.55. Found: C, 58.75; H, 6.84; N, 2.68. $\Lambda_M = 51.2\ \Omega^{-1}\ mol^{-1}\ cm^2$. Anal. Calcd for $C_{66}H_{74}BN_2O_6P_3Ru$ (**5b**): C, 66.27; H, 6.24; N, 2.34. Found: C, 66.17; H, 6.16; N, 2.42. $\Lambda_M = 55.3\ \Omega^{-1}\ mol^{-1}\ cm^2$. Anal. Calcd for $C_{78}H_{74}BN_2O_3P_3Ru$ (**5c**): C, 72.50; H, 5.77; N, 2.17. Found: C, 72.65; H, 5.65; N, 2.05. $\Lambda_M = 57.4\ \Omega^{-1}\ mol^{-1}\ cm^2$.

mer*-[RuH(5,5′-Me$_2$bpy){P(OEt)$_3$}$_3$]BPh$_4$ (6a-*mer*) and *mer*- and *fac*-[RuH(5,5′-Me$_2$bpy){P(OEt)$_3$}$_3$]BPh$_4$ (6a).** This complex was prepared following the method used for the related 2,2′-bipyridine derivative **4** using $RuCl_4(5,5'\text{-}Me_2bpy) \cdot H_2O$ 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 $C_{54}H_{78}BN_2O_9P_3Ru$: C, 58.75; H, 7.12; N, 2.54. Found for **6a-*mer***: C, 58.89; H, 7.15; N, 2.41. $\Lambda_M = 55.7\ \Omega^{-1}\ mol^{-1}\ cm^2$. Found for **6a**: C, 58.58; H, 7.24; N, 2.46. $\Lambda_M = 53.5\ \Omega^{-1}\ mol^{-1}\ cm^2$.

[RuCl(bpy)$_2${P(OEt)$_3$}]BPh$_4$ (7a). An excess of triethyl phosphite (1.16 mmol, 0.19 mL) was added to a solution of $RuCl_2(bpy)_2 \cdot 2H_2O$ (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 ≥75%. Anal. Calcd for $C_{50}H_{51}BClN_4O_3PRu$: 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. $\Lambda_M = 52.6\ \Omega^{-1}\ mol^{-1}\ cm^2$.

[RuH(bpy)$_2$P]BPh$_4$ (8) [P = P(OEt)$_3$ (a), PPh(OEt)$_2$ (b), PPh$_2$OEt (c)]. To a solution of $RuCl_2(bpy)_2 \cdot 2H_2O$ (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 ≥85%. Anal. Calcd for $C_{50}H_{52}BN_4O_3PRu$ (**8a**): C, 66.74; H, 5.82; N, 6.23. Found: C, 66.55; H, 5.88; N, 6.12. $\Lambda_M = 50.8\ \Omega^{-1}\ mol^{-1}\ cm^2$. Anal. Calcd for $C_{54}H_{52}BN_4O_2PRu$ (**8b**): C, 69.60; H, 5.62; N, 6.01. Found: C, 69.44; H, 5.70; N, 5.88. $\Lambda_M = 55.6\ \Omega^{-1}\ mol^{-1}\ cm^2$. Anal. Calcd for $C_{58}H_{52}BN_4OPRu$ (**8c**): C, 72.27; H, 5.44; N, 5.81. Found: C, 72.10; H, 5.37; N, 5.94. $\Lambda_M = 53.1\ \Omega^{-1}\ mol^{-1}\ cm^2$.

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

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Table 1. Selected IR and NMR Data for Ruthenium Complexes

IR[a] (cm^{-1})	assgnt	^1H NMR[b,c] (ppm; *J*, Hz)	assgnt	spin syst	$^{31}P\{^1H\}$ NMR[b,d] (ppm; *J*, Hz)
		[RuCl(bpy){P(OEt$_3$}$_3$]BPh$_4$ (**1a**)			
		4.27 qnt	CH_2	AB_2	δ_A 135.4
		3.72 m			δ_B 116.6
		1.33 t	CH_3		$J_{AB} = 63.2$
		0.88 t			
		[RuCl(bpy){PPh(OEt)$_2$}$_3$]BPh$_4$ (**1b**)			
		4.13 m	CH_2	AB_2	δ_A 168.3
		3.74 m			δ_B 145.3
		1.45 t	CH_3		$J_{AB} = 48.0$
		1.09 t			
		1.00 t			
		[RuCl(bpy){PPh$_2$(OEt)}$_3$]BPh$_4$ (**1c**)			
		3.46 qnt	CH_2	AB_2	δ_A 141.3
		3.20 m			δ_B 116.3
		1.05 t	CH_3		$J_{AB} = 37.2$
		0.85 t			
		[RuCl(phen){P(OEt$_3$}$_3$]BPh$_4$ (**2a**)			
		4.43 qnt	CH_2	AB_2	δ_A 136.0
		3.72 m			δ_B 116.6
		1.47 t	CH_3		$J_{AB} = 64.1$
		0.81 t			
		[RuCl(phen){PPh(OEt)$_2$}$_3$]BPh$_4$ (**2b**)			
		4.25 m	CH_2	AB_2	δ_A 167.4
		3.69 m			δ_B 145.6
		1.54 t	CH_3		$J_{AB} = 50.0$
		1.02 t			
		[RuCl(phen){PPh$_2$(OEt)}$_3$]BPh$_4$ (**2c**)			
		3.49 qnt	CH_2	AB_2	δ_A 141.2
		3.07 m			δ_B 116.8
		1.07 t	CH_3		$J_{AB} = 38.3$
		0.75 t			
		[RuCl(5,5′-Me$_2$bpy){P(OEt$_3$}$_3$]BPh$_4$ (**3a**)			
		4.35 qnt	CH_2	AB_2	δ_A 136.2
		3.80 m			δ_B 117.1
		2.52 s	CH_3		$J_{AB} = 62.5$
		2.35 s			
		1.41 t	CH_3 phos		
		0.96 t			
		[RuH(bpy){P(OEt$_3$}$_3$]BPh$_4$ (**4a**)			
1963 w	ν_{RuH}	4.06 m	CH_2	AB_2	δ_A 150.2
1940 w		3.69 m			δ_B 140.4
		1.32 t	CH_3		$J_{AB} = 64.7$
		1.28 t		A_2B	δ_A 153.6
		0.96 t			δ_B 132.9
		AB_2X spin syst	H^-		$J_{AB} = 37.2$
		(X = H^-)			
		δ_X −6.92			
		$J_{AX} = 148$			
		$J_{BX} = 27$			
		A_2BX spin syst	H^-		
		(X = H^-)			
		δ_X −14.31			
		$J_{AX} = 22$			
		$J_{BX} = 34$			
		[RuH(bpy){PPh(OEt)$_2$}$_3$]BPh$_4$ (**4b**)			
1971 m	ν_{RuH}	4.10 m	CH_2	AB_2	δ_A 178.0
		3.30 m			δ_B 162.9
		1.32 t	CH_3		$J_{AB} = 48.0$
		1.30 t		A_2B	δ_A 176.0
		1.21 t			δ_B 157.6
		0.93 t			$J_{AB} = 24.9$
		AB_2X spin syst	H^-		
		(X = H^-)			
		δ_X −6.72			
		$J_{AX} = 124$			
		$J_{BX} = 24$			
		A_2BX spin syst	H^-		
		(X = H^-)			
		δ_X −13.86			
		$J_{AX} = 20$			
		$J_{BX} = 30$			
		[RuH(bpy){PPh$_2$(OEt)}$_3$]BPh$_4$ (**4c**)			
1965 m	ν_{RuH}	3.43 m	CH_2	AB_2	δ_A 155.9
		3.06 m			δ_B 142.0
		0.72 t	CH_3		$J_{AB} = 40.0$
		0.43 t			
		AB_2X spin syst	H^-		
		(X = H^-)			
		δ_X −12.86			
		$J_{AX} = 32$			
		$J_{BX} = 20$			
		[RuH(phen){P(OEt$_3$}$_3$]BPh$_4$ (**5a**)			
1969 m	ν_{RuH}	4.16 m	CH_2	AB_2	δ_A 151.3
		3.67 m			δ_B 140.7
		1.43 t	CH_3		$J_{AB} = 65.0$
		1.37 t		A_2B	δ_A 153.7
		0.90 t			δ_B 133.1
		0.87 t			$J_{AB} = 37.2$
		AB_2X spin syst	H^-		
		(X = H^-)			
		δ_X −6.73			
		$J_{AX} = 146$			
		$J_{BX} = 27$			
		A_2BX spin syst	H^-		
		(X = H^-)			
		δ_X −13.91			
		$J_{AX} = 24$			
		$J_{BX} = 32$			
		[RuH(phen){PPh(OEt)$_2$}$_3$]BPh$_4$ (**5b**)			
1980 sh	ν_{RuH}	3.98 qnt	CH_2	AB_2	δ_A 179.0
1963 m		3.81 m			δ_B 163.9
		1.35 t	CH_3		$J_{AB} = 46.5$
		0.79 t		A_2B	δ_A 176.4
		AB_2X spin syst	H^-		δ_B 157.8
		(X = H^-)			$J_{AB} = 26.0$
		δ_X −6.35			
		$J_{AX} = 122$			
		$J_{BX} = 24$			
		A_2BX spin syst	H^-		
		(X = H^-)			
		δ_X −13.55			
		$J_{AX} = 20$			
		$J_{BX} = 30$			
		[RuH(phen){PPh$_2$(OEt)}$_3$]BPh$_4$ (**5c**)			
1975 s	ν_{RuH}	3.44 m	CH_2	AB_2	δ_A 156.1
		3.07 m			δ_B 141.9
		0.65 t	CH_3		$J_{AB} = 40.5$
		0.42 t			
		AB_2X spin syst	H^-		
		(X = H^-)			
		δ_X −12.65			
		$J_{AX} = 30$			
		$J_{BX} = 20$			
		fac- and *mer*-[RuH(5,5′-Me$_2$bpy){P(OEt$_3$}$_3$]BPh$_4$ (**6a**)			
1970 w, br	ν_{RuH}	4.07 qnt	CH_2	AB_2	δ_A 151.1
		3.64 m			δ_B 140.7
		2.41 s	CH_3		$J_{AB} = 65.0$
		2.38 s		A_2B	δ_A 153.9
		2.36 s			δ_B 133.4
		1.37 t	CH_3 phos		$J_{AB} = 36.2$
		1.30 t			
		1.20 t			
		0.96 t			
		AB_2X spin syst	H^-		
		(X = H^-)			
		δ_X −14.34			
		$J_{AX} = 32$			
		$J_{BX} = 24$			
		A_2BX spin syst	H^-		
		(X = H^-)			
		δ_X −6.88			
		$J_{AX} = 27$			
		$J_{BX} = 150$			

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)
		mer-[RuH(5,5′-Me_2bpy){P(OEt)$_3$}$_3$]BPh_4 (**6a-*mer***)			
1969 w	ν_{RuH}	4.07 qnt	CH_2	AB_2	δ_A 151.1
		3.63 m			δ_B 140.7
		2.38 s	CH_3		$J_{AB} = 65.0$
		2.36 s			
		1.30 t	CH_3 phos		
		0.96 t			
		AB_2X spin syst	H^-		
		(X = H^-)			
		δ_X −14.34			
		$J_{AX} = 32$			
		$J_{BX} = 24$			
		[RuCl(bpy)$_2${P(OEt)$_3$}]BPh_4 (**7a**)			
		3.98 qnt	CH_2	A	127.7 s
		1.06 t	CH_3		
		[RuH(bpy)$_2${P(OEt)$_3$}]BPh_4 (**8a**)			
1881 m	ν_{RuH}	3.81 qnt	CH_2	A	153.6 s
		1.12 t	CH_3		
		−12.16 d	H^-		
		$J_{PH} = 36$			
		[RuH(bpy)$_2${PPh(OEt)$_2$}]BPh_4 (**8b**)			
1895 m	ν_{RuH}	3.94 qnt	CH_2	A	174.1 s
		1.28 t	CH_3		
		−12.01 d	H^-		
		$J_{PH} = 32$			
		[RuH(bpy)$_2${PPh$_2$(OEt)}]BPh_4 (**8c**)			
1917 m	ν_{RuH}	3.69 qnt	CH_2	A	148.1 s
		1.08 t	CH_3		
		−11.93 d	H^-		
		$J_{PH} = 34$			
		[Ru(η^2-H_2)(bpy){P(OEt)$_3$}$_3$]$^{2+}$ [e] (**9a**)			
		4.15 m	CH_2	AB_2	δ_A 130.7
		3.81 m			δ_B 129.4
		1.39 t	CH_3		$J_{AB} = 80.0$
		1.15 t		AB_2	δ_A 128.2
		1.00 t			δ_B 117.2
		−9.55 br	η^2-H_2		$J_{AB} = 55.3$
		[Ru(η^2-H_2)(bpy){PPh(OEt)$_2$}$_3$]$^{2+}$ (**9b**)			
		3.97 m	CH_2	AB_2	δ_A 155.4
		3.82 m			δ_B 146.9
		3.49 m			$J_{AB} = 44.4$
		1.43 t	CH_3	A_2B	δ_A 162.4
		1.40 t			δ_B 161.3
		1.21 t			$J_{AB} = 62.7$
		0.96 t			
		−9.60 br	η^2-H_2		
		[Ru(η^2-H_2)(bpy){PPh$_2$(OEt)}$_3$]$^{2+}$ [f] (**9c**)			
		3.44 m	CH_2	AB_2	δ_A 140.0
		3.21 qnt			δ_B 129.8
		0.70 t	CH_3		$J_{AB} = 30.5$
		0.52 t			
		−8.0 br	η^2-H_2		
		[Ru(η^2-H_2)(phen){PPh$_2$(OEt)}$_3$]$^{2+}$ [f] (**10c**)			
		3.26 qnt	CH_2	AB_2	δ_A 140.2
		3.23 m			δ_B 130.4
		0.66 t	CH_3		$J_{AB} = 30.4$
		0.54 t			
		−7.8 br	η^2-H_2		
		[Ru(η^2-H_2)(bpy)$_2${P(OEt)$_3$}]$^{2+}$ [g] (**11a**)			
		3.87 qnt	CH_2	A	125.3 s
		1.04 t	CH_3		
		−7.65 br	η^2-H_2		
		[Ru(η^2-H_2)(bpy)$_2${PPh(OEt)$_2$}]$^{2+}$ [h] (**11b**)			
		4.01 m	CH_2	A	159.7
		1.30 t	CH_3		
		−7.55 br	η^2-H_2		
		[Ru(η^2-H_2)(bpy)$_2${PPh$_2$(OEt)}]$^{2+}$ [h] (**11c**)			
		3.65 m	CH_2	A	138.9 s
		1.03 t	CH_3		
		−7.95 br	η^2-H_2		
		[Ru(OH_2)(bpy){P(OEt)$_3$}$_3$](BPh_4)$_2$ (**12a**)			
		4.12 m	CH_2	AB_2	δ_A 129.8
		3.56 m			δ_B 128.8
		2.55 s, br	OH_2		$J_{AB} = 79.6$
		1.37 t	CH_3		
		0.95 t			
		[Ru(CH_3CN)(bpy){P(OEt)$_3$}$_3$](BPh_4)$_2$ (**13a**)			
		4.13 m	CH_2	A_2B	δ_A 129.7
		3.60 qnt			δ_B 125.2
		1.36 t	CH_3		$J_{AB} = 74.9$
		0.94 t			
		0.30 s	CH_3CN		
		[Ru(bpy)(4-$CH_3C_6H_4NC$){P(OEt)$_3$}$_3$](BPh_4)$_2$ (**14a**)			
2158 s	ν_{CN}	4.17 m	CH_2	A_2B	δ_A 129.7
		3.63 m			δ_B 118.4
		2.34 s	CH_3		$J_{AB} = 61.2$
		2.30 s		A_2B	δ_A 128.1
		1.38 t	CH_3 phos		δ_B 115.8
		1.36 t			$J_{AB} = 58.0$
		0.99 t			
		0.97 t			
		[Ru(bpy)(CO){P(OEt)$_3$}$_3$](BPh_4)$_2$ (**15a**)			
2054 s	ν_{CO}	4.18 m	CH_2	A_2B	δ_A 123.2
		3.57 qnt			δ_B 110.0
		1.41 t	CH_3		$J_{AB} = 62.4$
		0.94 t			
		[Ru(bpy){PPh(OEt)$_2$}{P(OEt)$_3$}$_3$](BPh_4)$_2$ (**16a**)			
		4.32 m	CH_2	AB_2C	δ_A 148.7
		4.11 m			δ_B 131.2
		3.95 qnt			δ_C 118.3
		3.50 m			$J_{AB} = 50.9$
		1.48 t	CH_3		$J_{AC} = -534.5$
		1.35 m			$J_{AB} = 58.4$
		0.95 m			
		[Ru(CH_3CN)(bpy)$_2${P(OEt)$_3$}](BPh_4)$_2$ (**17a**)			
		3.80 qnt	CH_2	A	125.5s
		1.66 s	CH_3CN		
		1.01 t	CH_3		
		[Ru(bpy)(4-$CH_3C_6H_4CN$)$_2${P(OEt)$_3$}](BPh_4)$_2$ (**18a**)			
2226 m	ν_{CN}	3.89 qnt	CH_2	A	124.6s
		2.46 s	CH_3		
		1.10 t	CH_3 phos		
		[Ru(C_6H_5N═NH)(bpy){P(OEt)$_3$}$_3$](BPh_4)$_2$ (**19a**)			
		14.16 s, br	NH	AB_2	δ_A 129.4
		13.70 s, br			δ_B 128.4
		4.23 qnt	CH_2		$J_{AB} = 69.2$
		3.67 m		AB_2	δ_A 126.9
		1.39 t	CH_3		δ_B 114.2
		1.37 t			$J_{AB} = 61.0$
		0.99 t			
		0.96 t			

2$CF_3SO_3^-$). These complexes were prepared in solution by reaction with CF_3SO_3H at low temperature. A typical preparation involves the addition of an excess of CF_3SO_3H (0.02 mmol, 1.8 μL) to a solution of the appropriate hydride **4**, **5** (0.01 mmol) in 0.5 mL of CD_2Cl_2 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-H_2)(bpy)$_2$P]$^{2+}$$Y^{2-}$ (11) [P = P(OEt)$_3$ (a), PPh(OEt)$_2$ (b), PPh$_2$OEt (c); Y^{2-} = 2$CF_3SO_3^-$]. These complexes were prepared at low temperature (−80 °C) in an NMR tube by adding an excess of CF_3SO_3H (0.02 mmol, 1.8 μL) to a solution of the appropriate hydride [RuH(bpy)$_2$P]CF_3SO_3 (**8-CF_3SO_3**) (0.01 mmol)

Table 1. Continued

IR[a] (cm^{-1})	assgnt	^1H NMR[b,c] (ppm; *J*, Hz)	assgnt	spin syst	$^{31}P\{^1H\}$ NMR[b,d] (ppm; *J*, Hz)
	$[Ru(C_6H_5N{=}^{15}NH)(bpy)\{P(OEt)_3\}_3](BPh_4)_2$[i] (**19a-^{15}N**)				
		AB_2XY spin syst	NH	AB_2Y	δ_A 126.9
		(X = H, Y = ^{15}N)			δ_B 114.3
		δ_X 14.14			$J_{AB} = 60.7$
		$J_{AX} = 4.7$			$J_{AY} = 5.6$
		$J_{BX} = 2.8$			$J_{BY} = 4.9$
		$J_{AY} = 5.6$		AB_2Y	δ_A 129.0
		$J_{BY} = 4.9$			δ_B 128.4
		$J_{XY} = 67.3$			$J_{AB} = 69.2$
		$J_{AB} = 60.7$			$J_{AY} = -62.5$
		AB_2XY spin syst			$J_{BY} = 4.8$
		(X = H, Y = ^{15}N)			
		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	CH_2		
		3.65 m			
		1.38 t	CH_3		
		1.36 t			
		1.00 t			
		0.96 t			
	$[\{Ru(bpy)[P(OEt)_3]_3\}_2(\mu\text{-}4,4'\text{-}HN{=}NC_6H_4{-}C_6H_4N{=}NH)](BPh_4)_4$ (**20a**)				
		14.16 s, br	NH	AB_2	δ_A 126.3
		14.06 s, br			δ_B 114.1
		4.20 m	CH_2		$J_{AB} = 61.4$
		3.64 m		AB_2	δ_A 130.1
		1.35 t	CH_3		δ_B 115.8
		1.01 t			$J_{AB} = 63.0$
		0.96 t			
		0.92 t			
	$[\{Ru(bpy)[P(OEt)_3]_3\}_2(\mu\text{-}4,4'\text{-}H^{15}N{=}NC_6H_4{-}C_6H_4N{=}^{15}NH)](BPh_4)_4$[j] (**20a-^{15}N**)				
		14.17 d, br	NH	AB_2Y	δ_A 126.7
		$^1J_{^{15}NH} = 64.5$			δ_B 114.2
		14.07 d, br			$J_{AB} = 61.4$
		$^1J_{^{15}NH} = 63.0$			$J_{AY} = 6.3$
		4.21 m	CH_2	AB_2Y	$J_{BY} = 5.0$
		3.65 m			δ_A 130.2
		1.36 t	CH_3		δ_B 115.8
		1.01 t			$J_{AB} = 63.0$
		0.96 t			$J_{AY} = J_{BY} = \leq 1$
		0.93 t			
	$[Ru(C_6H_5N{=}NH)(phen)\{PPh(OEt)_2\}_3](BPh_4)_2$ (**21b**)				
		13.85 s, br	NH	AB_2	δ_A 158.8
		13.26 s, br			δ_B 145.3
		4.34 m	CH_2		$J_{AB} = 46.5$
		3.65 m		AB_2	δ_A 152.0
		1.58 t	CH_3		δ_B 141.1
		1.20 t			$J_{AB} = 43.0$
		1.03 t			
		0.90 t			
	$[Ru(C_6H_5N{=}NH)(bpy)_2\{P(OEt)_3\}](BPh_4)_2$ (**22a**)				
		14.87 d, br	NH	A	123.6 s
		3.89 qnt	CH_2		
		1.13 t	CH_3		
	$[Ru(C_6H_5N{=}^{15}NH)(bpy)_2\{P(OEt)_3\}](BPh_4)_2$[k] (**22a-^{15}N**)				
		14.89 dt	NH	A	124.1 d
		$^1J_{^{15}NH} = 65.5$			$^2J_{^{31}P^{15}N} = 4.7$
		$^3J_{^{31}PH} = 3.5$			
		3.87 m	CH_2		
		1.09 t	CH_3		
	$[Ru\{\eta^1\text{-}SC(H){=}S\}(bpy)_2\{P(OEt)_3\}]BPh_4$ (**23a**)				
1242 m	δ_{HCS}	10.87 s, br	SC(H)=	A	126.8 s
		3.84 br	CH_2		
		1.04 br	CH_3		
	$[Ru\{\eta^1\text{-}SC(H){=}S\}(bpy)_2\{PPh(OEt)_2\}]BPh_4$ (**23b**)				
1256 m	δ_{HCS}	10.94 s	SC(H)=	A	159.1 s
		3.95 qnt	CH_2		
		1.33 t	CH_3		
	$[Ru\{\eta^1\text{-}OC(H){=}O\}(bpy)_2\{P(OEt)_3\}]BPh_4$ (**24a**)				
1601 s	ν_{CO}	7.73 s	OC(H)=	A	128.2 s
		3.85 qnt	CH_2		
		1.04 t	CH_3		
	$[Ru\{\eta^1\text{-}OC(H){=}O\}(bpy)_2\{PPh(OEt)_2\}]BPh_4$ (**24b**)				
1599 s	ν_{CO}	7.48 s	OC(H)=	A	160.9 s
		4.10 qnt	CH_2		
		1.19 t	CH_3		

[a] In KBr pellets. [b] In CD_2Cl_2 at 25 °C. [c] Phenyl and polypyridyl proton resonances omitted; for the OC_2H_5 group of the phosphine $J_{HH} = 7$ Hz. [d] Positive shift downfield from 85% H_3PO_4. [e] At 273 K. [f] At 283 K. [g] At 203 K. [h] At 223 K. [i] $^{15}N\{^1H\}$ NMR, δ (CD_2Cl_2, 25 °C, positive shift downfield from $CH_3{}^{15}NO_2$): AB_2Y spin syst (Y = ^{15}N), δ_Y 0.67, $J_{AY} = 63$, $J_{BY} = 4.8$; AB_2Y spin syst (Y = ^{15}N), δ_Y −5.07, $J_{AY} = 5.6$, $J_{BY} = 4.9$ Hz. [j] $^{15}N\{^1H\}$ NMR, δ: AB_2Y spin syst (Y = ^{15}N), δ_Y −5.97, $J_{AY} = 6.3$, $J_{BY} = 5.0$ Hz; −18.8 (s, br). [k] $^{15}N\{^1H\}$ 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)	$\delta(M{-}H_2)$	T_{1min} (ms)	J_{HD} (Hz)	r_{H-H} (Å)		
9a	$[Ru(\eta^2\text{-}H_2)(bpy)\{P(OEt)_3\}_3]^{2+}$	203	−9.55 br	4.9	29.9	0.99[a]	0.79[b]	0.94[c]
9b	$[Ru(\eta^2\text{-}H_2)(bpy)\{PPh(OEt)_2\}_3]^{2+}$	218	−9.60 br	6.1	30.1	1.03	0.81	0.93
9c	$[Ru(\eta^2\text{-}H_2)(bpy)\{PPh_2(OEt)\}_3]^{2+}$	223	−8.0 br	5.1	28.9	1.00	0.79	0.95
10c	$[Ru(\eta^2\text{-}H_2)(phen)\{PPh_2(OEt)\}_3]^{2+}$	217	−7.80 br	5.9	29.4	1.02	0.81	0.95
11a	$[Ru(\eta^2\text{-}H_2)(bpy)_2\{P(OEt)_3\}]^{2+}$	216	−7.65 br	7.0	32.8	1.05	0.83	0.89
11b	$[Ru(\eta^2\text{-}H_2)(bpy)_2\{PPh(OEt)_2\}]^{2+}$	213	−7.55 br	7.6	31.2	1.07	0.84	0.92
11c	$[Ru(\eta^2\text{-}H_2)(bpy)_2\{PPh_2(OEt)\}]^{2+}$	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	304				
			−14.27 dt	233				

[a,b] The H−H distances were calculated[20] from the T_{1min} values for fast rotation[b] or static regimes[a] of the H_2 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 CD_2Cl_2 following the method used for the related $[Ru(\eta^2\text{-}H_2)(N\text{-}N)P_3]^{2+}$ (**9**, **10**) derivatives.

[RuL(bpy){P(OEt)$_3$}$_3$](BPh$_4$)$_2$ (12−16) [L = H$_2$O (12a), CH$_3$CN (13a), 4-CH$_3$C$_6$H$_4$NC (14a), CO (15a), PPh(OEt)$_2$ (16a)]. These complexes were prepared by substituting the $\eta^2\text{-}H_2$ molecule in $[Ru(\eta^2\text{-}H_2)(bpy)\{P(OEt)_3\}_3]^{2+}$ (**9a**) complex with the appropriate ligand L, by means the following general method. To a solution of $[RuH(bpy)\{P(OEt)_3\}_3]BPh_4$ (0.1 g, 0.093 mmol) in 8 mL of CH_2-

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

$^{13}C\{^1H\}$ NMR[a,b] (ppm; *J*, Hz)	assgnt
[Ru(CH_3CN)(bpy){$P(OEt)_3$}$_3$](BPh_4)$_2$ (**13a**)	
125.4 d	CN
J_{CP} = 22.0	
64.0 t	CH_2
63.7 d	
16.3 t	CH_3
16.0 d	
0.60 s	CH_3CN
[Ru(bpy)(CO){$P(OEt)_3$}$_3$](BPh_4)$_2$ (**15a**)	
190.9 dt	CO
$J_{CP_{cis}}$ = 17.0	
$J_{CP_{trans}}$ = 145	
65.6 t	CH_2
64.7 d	
16.1 m	CH_3
[Ru(CH_3CN)(bpy)$_2${$P(OEt)_3$}](BPh_4)$_2$ (**17a**)	
127.4 d	CN
*J*CP = 16.0	
63.1 d	CH_2
16.3 d	CH_3
3.5 s	CH_3CN
[Ru(η^1−SC(H)═S)(bpy)$_2${$P(OEt)_3$}]BPh_4 (**23a**)	
238.6 s	SC(H)═
62.6 d	CH_2
16.2 d	CH_3
[Ru(η^1-OC(H)═O)(bpy)$_2${$P(OEt)_3$}]BPh_4 (**24a**)	
170.6 s	OC(H)═
62.1 d	CH_2
16.3 d	CH_3
[Ru(η^1-OC(H)═O)(bpy)$_2${$PPh(OEt)_2$}]BPh_4 (**24b**)	
171.3 s	OC(H)═
61.3 d	CH_2
16.8 d	CH_3

[a] In CD_2Cl_2 at 25 °C. [b] Phenyl and polypyridyl carbon resonances are omitted.

Cl_2 cooled to −196 °C was added an excess of CF_3SO_3H (0.36 mmol, 32 μL). 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 $NaBPh_4$ (0.20 mmol, 68 mg). By stirring the resulting solution, a yellow or red solid separated out, which was filtered and crystallized from CH_2Cl_2 and ethanol; yield between 65% and 80%. Anal. Calcd for $C_{76}H_{95}B_2N_2O_{10}P_3Ru$ (**12a**): C, 64.64; H, 6.78; N, 1.98. Found: C, 64.39; H, 6.74; N, 2.05. Λ_M = 118 Ω^{-1} mol^{-1} cm^2. Anal. Calcd for $C_{78}H_{96}B_2N_3O_9P_3Ru$ (**13a**): C, 65.28; H, 6.74; N, 2.93. Found: C, 65.10; H, 6.84; N, 2.79. Λ_M = 112 Ω^{-1} mol^{-1} cm^2. Anal. Calcd for $C_{84}H_{100}B_2N_3O_9P_3Ru$ (**14a**): C, 66.76; H, 6.67; N, 2.78. Found: C, 66.60; H, 6.72; N, 2.69. Λ_M = 116 Ω^{-1} mol^{-1} cm^2. Anal. Calcd for $C_{77}H_{93}B_2N_2O_{10}P_3Ru$ (**15a**): C, 65.03; H, 6.59; N, 1.97. Found: C, 64.85; H, 6.58; N, 2.11. Λ_M = 121 Ω^{-1} mol^{-1} cm^2. Anal. Calcd for $C_{86}H_{108}B_2N_2O_{11}P_4Ru$ (**16a**): C, 64.87; H, 6.84; N, 1.76. Found: C, 64.65; H, 6.94; N, 1.75. Λ_M = 120 Ω^{-1} mol^{-1} cm^2.

[Ru(RCN)(bpy)$_2${P(OEt)$_3$}](BPh$_4$)$_2$ (17a, 18a) [R = CH_3 (17), 4-$CH_3C_6H_4$ (18)]. An excess of HBF_4·Et_2O (0.22 mmol, 32 μL) was added to a solution of [RuH(bpy)$_2${$P(OEt)_3$}]BPh_4 (0.1 g, 0.11 mmol) in 8 mL of CH_2Cl_2 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 $NaBPh_4$ (0.22 mmol, 75 mg). A yellow solid slowly separated out from the resulting solution, which was filtered and crystallized from CH_2Cl_2 and ethanol; yield ≥75%. Anal. Calcd for $C_{76}H_{74}B_2N_5O_3PRu$ (**17a**): C, 72.50; H, 5.92; N, 5.56. Found: C, 72.40; H, 5.98; N, 5.45. Λ_M = 121 Ω^{-1} mol^{-1} cm^2. Anal. Calcd for $C_{82}H_{78}B_2N_5O_3PRu$ (**18a**): C, 73.76; H, 5.89; N, 5.25. Found: C, 73.64; H, 5.82; N, 5.30. Λ_M = 124 Ω^{-1} mol^{-1} cm^2.

[Ru(C_6H_5N═NH)(bpy){P(OEt)$_3$}$_3$](BPh$_4$)$_2$ (19a). In a 25-mL three-necked round-bottomed flask were placed solid samples of [RuH(bpy)P_3]BPh_4 (0.10 mmol) and the [$C_6H_5N_2$]BF_4 aryldiazonium salt (0.2 mmol, 0.38 g). The flask was cooled to −196 °C and CH_2Cl_2 (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 $NaBPh_4$ (0.18 mmol, 62 mg). An orange solid separated out from the resulting solution, which was filtered and crystallized from CH_2Cl_2 and ethanol; yield ≥75%. Anal. Calcd for $C_{82}H_{99}B_2N_4O_9P_3Ru$: C, 65.65; H, 6.65; N, 3.73. Found: C, 65.42; H, 6.77; N, 3.66. Λ_M = 115 Ω^{-1} mol^{-1} cm^2.

[Ru(C_6H_5N═^{15}NH)(bpy){P(OEt)$_3$}$_3$](BPh$_4$)$_2$ (19a-^{15}N). This complex was prepared exactly like the related unlabeled compound **19a**, using the labeled [$C_6H_5N{\equiv}^{15}N$]BF_4 aryldiazonium salt; yield ≥70%.

[{Ru(bpy)[P(OEt)$_3$]$_3$}$_2$(μ-4,4′-NH═NC$_6$H$_4$-C$_6$H$_4$N═NH)](BPh$_4$)$_4$ (20a). In a 25-mL three-necked round-bottomed flask were placed solid samples of [RuH(bpy){$P(OEt)_3$}$_3$]BPh_4 (**4a**) (0.1 g, 0.093 mmol) and of the di-diazonium salt [4,4′-$N_2C_6H_4$−$C_6H_4N_2$]-$(BF_4)_2$ (18 mg, 0.0465 mmol), the flask was cooled to −196 °C, and CH_2Cl_2 (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 $NaBPh_4$ (0.2 mmol, 68 mg). A yellow solid slowly separated out from the resulting solution, which was filtered and crystallized from CH_2Cl_2 and ethanol; yield ≥70%. Anal. Calcd for $C_{164}H_{196}B_4N_8O_{18}P_6Ru_2$: C, 65.69; H, 6.59; N, 3.74. Found: C, 65.48; H, 6.64; N, 3.67. Λ_M = 248 Ω^{-1} mol^{-1} cm^2.

[{Ru(bpy)[P(OEt)$_3$]$_3$}$_2$(μ-4,4′-^{15}NH═NC$_6$H$_4$−C$_6$H$_4$N═^{15}NH)](BPh$_4$)$_4$ (20a-^{15}N). This complex was prepared exactly like the related unlabeled compound **20a** using the [4,4′-$^{15}N{\equiv}NC_6H_4$−$C_6H_4N{\equiv}^{15}N$]$(BF_4)_2$ aryldiazonium salt; yield ≥65%.

[Ru(C_6H_5N═NH)(phen){PPh(OEt)$_2$}$_3$](BPh$_4$)$_2$ (21b). This complex was prepared like the related 2,2′-bipyridine derivative **19a** using [RuH(phen){$PPh(OEt)_2$}$_3$]BPh_4 (**5b**) as a precursor; yield ≥75%. Anal. Calcd for $C_{96}H_{99}B_2N_4O_6P_3Ru$: C, 71.16; H, 6.16; N, 3.46. Found: C, 71.01; H, 6.27; N, 3.40. Λ_M = 117 Ω^{-1} mol^{-1} cm^2.

[Ru(C_6H_5N═NH)(bpy)$_2${P(OEt)$_3$}](BPh$_4$)$_2$ (22a). In a 25-mL three-necked round-bottomed flask were placed solid samples of the appropriate hydride [RuH(bpy)$_2$P]BPh_4 (0.1 mmol) and of the phenyldiazonium salt [$C_6H_5N_2$]BF_4 (0.2 mmol, 38 mg). The flask was cooled to −196 °C and CH_2Cl_2 (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 $NaBPh_4$ (0.2 mmol, 68 mg). An orange solid slowly separated out from the resulting solution, which was filtered and crystallized from CH_2Cl_2 and ethanol; yield ≥75%. Anal. Calcd for $C_{80}H_{77}B_2N_6O_3PRu$: C, 72.56; H, 5.86; N, 6.35. Found: C, 72.38; H, 5.94; N, 6.27. Λ_M = 118 Ω^{-1} mol^{-1} cm^2.

[Ru(C_6H_5N=^{15}NH)(bpy)$_2${P(OEt)$_3$}](BPh$_4$)$_2$ (22a-^{15}N). This compound was prepared exactly like the related unlabeled compound **22a** using [C_6H_5N≡^{15}N]BF_4 as a reagent; yield ≥70%.

[Ru{η^1-SC(H)=S}(bpy)$_2$P]BPh$_4$ (23) [P = P(OEt)$_3$ (a), PPh(OEt)$_2$ (b)]. An excess of carbon disulfide (1 mmol, 61 μL) was added to a solution of the appropriate hydride [RuH(bpy)$_2$P]BPh_4 (0.10 mmol) in 8 mL of CH_2Cl_2 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 $NaBPh_4$ (0.2 mmol, 68 mg). An orange solid separated out from the resulting solution, which was filtered and crystallized from CH_2Cl_2 and ethanol; yield ≥70%. Anal. Calcd for $C_{51}H_{52}BN_4O_3PRuS_2$ (**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. Λ_M = 54.5 Ω^{-1} mol^{-1} cm^2. Anal. Calcd for $C_{55}H_{52}BN_4O_2PRuS_2$ (**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. Λ_M = 56.1 Ω^{-1} mol^{-1} cm^2.

[Ru{η^1-OC(H)=O}(bpy)$_2$P]BPh$_4$ (24) [P = P(OEt)$_3$ (a), PPh(OEt)$_2$ (b)]. A solution of the appropriate hydride [RuH(bpy)$_2$P]BPh_4 (0.10 mmol) in 10 mL of CH_2Cl_2 was stirred at room temperature under a CO_2 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 $NaBPh_4$ (0.2 mmol, 68 mg). A yellow solid slowly separated out from the resulting solution, which was filtered and crystallized from CH_2Cl_2 and ethanol; yield ≥60%. Anal. Calcd for $C_{51}H_{52}BN_4O_5PRu$ (**24a**): C, 64.90; H, 5.55; N, 5.94, Found: C, 64.75; H, 5.48; N, 5.84. Λ_M = 55.7 Ω^{-1} mol^{-1} cm^2. Anal. Calcd for $C_{55}H_{52}BN_4O_4PRu$ (**24b**): C, 67.69; H, 5.37; N, 5.74. Found: C, 67.78; H, 5.30; N, 5.65. Λ_M = 56.3 Ω^{-1} mol^{-1} cm^2.

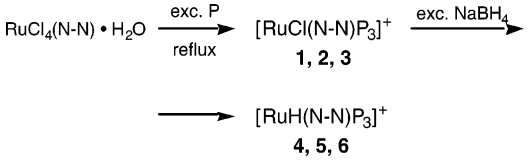
Acidity Measurements. The protonation of complexes [RuH(N-N)P$_3$]CF_3SO_3 (**4c-CF$_3$SO$_3$**, **5c-CF$_3$SO$_3$**) and [RuH(bpy)$_2$P]CF_3SO_3 (**8-CF$_3$SO$_3$**) was studied in CD_2Cl_2 following the method used for the related iron derivatives.[1] Approximately 2.5 equiv of CF_3SO_3H is required to completely generate the [Ru(η^2-H$_2$)(N-N)P$_3$]$^{2+}$ derivatives. Instead, less than 1.5 equiv of CF_3SO_3H is required for the complete formation of the [Ru(η^2-H$_2$)(bpy)$_2$P]$^{2+}$ dicationic species.

X-ray Crystal Structure Determination of [RuH(bpy){P(OEt)$_3$}$_3$]BPh$_4$ (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 Kα radiation (λ = 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°. 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 SADABS[9] procedure (T_{max} = 1.000, T_{min} = 0.8415). The phase problem was solved by direct methods[10] 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 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 Database[13] facilities was made for structure discussion.

Table 4. Crystal Data and Structure Refinement for [RuH(bpy){P(OEt)$_3$}$_3$]BPh$_4$ (**4a**)

empirical formula	$C_{52}H_{73.94}BCl_{0.06}N_2O_9P_3Ru$
structural formula	[Ru($C_{10}H_8N_2$){P(OCH_2CH_3)$_3$}$_3$$H_{0.94}Cl_{0.06}$]-B($C_6H_5$)$_4$
fw	1078.51
temperature	293(2) K
wavelength	0.71069 Å
crystal system	triclinic
space group	$P\bar{1}$
unit cell dimensions	
	a = 11.415(1) Å
	b = 13.980(1) Å
	c = 17.751(1) Å
	α = 90.832(2)°
	β = 91.227(2)°
	γ = 90.481(2)°
volume	2831.7(4) Å^3
Z	2
density (calculated)	1.265 Mg/m^3
absorption coefficient	0.417 mm^{-1}
F(000)	1134
θ range for data collection	1.15−23.26°
index ranges	$-12 \le h \le 12$, $-15 \le k \le 15$, $-19 \le l \le 19$
reflections collected	23523
independent reflections	8030 [R(int) = 0.0280]
refinement method	full-matrix least-squares on F^2
data/restraints/parameters	8030/1/582
GOF on F^2	1.129
final R indices [$I > 2\sigma(I)$]	R1 = 0.0545, wR2 = 0.1156
R indices (all data)	R1 = 0.0729, wR2 = 0.1318
largest ΔF max/min	0.838/−0.765 e Å^{-3}

Scheme 1[a]



[a] N-N = bpy (**1**, **4**); phen (**2**, **5**); 5,5′-(Me)$_2$bpy (**3**, **6**); P = P(OEt)$_3$ (**a**); PPh(OEt)$_2$ (**b**); PPh$_2$OEt (**c**).

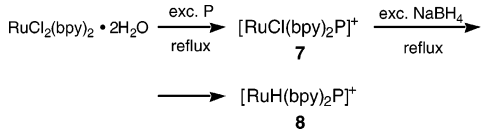
Results and Discussion

Preparation of Hydride Complexes. The synthesis of mixed-ligand hydride complexes [RuH(bpy)P_3]BPh_4 and [RuH(phen)P_3)]BPh_4 was achieved by reacting $RuCl_4$(N-N)·H_2O 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 [RuCl(N-N)P_3]$^+$ (**1**−**3**) intermediates, which can be isolated

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

Scheme 2[a]



[a] P = $P(OEt)_3$ (**a**); $PPh(OEt)_2$ (**b**); PPh_2OEt (**c**).

as BPh_4 salts and characterized, and then the further reaction of this intermediate with $NaBH_4$ affords the final $[ReH(N\text{-}N)P_3]^+$ (**4**−**6**) derivatives. The hydrides can also be prepared in one pot by reacting the $RuCl_4(N\text{-}N)\cdot H_2O$ compounds with an excess of both phosphite and $NaBH_4$ in ethanol.

Bis(2,2′-bipyridine) hydride complexes $[RuH(bpy)_2P]BPh_4$ (**8**) were also prepared by allowing the $RuCl_2(bpy)_2\cdot 2H_2O$ complex to react first with an excess of phosphite and then with $NaBH_4$, as shown in Scheme 2.

The intermediate chloro complex $[RuCl(bpy)_2P]BPh_4$ (**7**) can also be isolated in this case, and their further reaction with $NaBH_4$ allows the final hydride compounds (**8**) to be obtained.

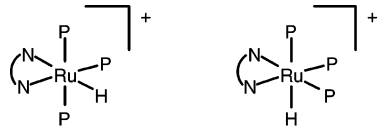
Extensive studies on the reaction of $RuCl_4(N\text{-}N)\cdot H_2O$ with phosphite and $NaBH_4$ showed that the monohydride cations $[RuH(N\text{-}N)P_3]^+$ (**4**, **5**, **6**) were the only hydride species formed in the reaction, and that the change of the experimental conditions and of the ratio 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 $RuH_2(N\text{-}N)P_2$ and $RuHCl(N\text{-}N)P_2$ were not obtained, and even the attempts to synthesize hydride complexes containing exclusively nitrogen-donor ligands such as $RuH_2(N\text{-}N)_2$ or $RuHCl(N\text{-}N)_2$, failed. We also tested the reaction of $RuCl_4(N\text{-}N)\cdot H_2O$ with phosphines such as PPh_3 or $Ph_2PCH_2CH_2PPh_2$ in the presence of $NaBH_4$, 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 $RuCl_4(N\text{-}N)\cdot H_2O$ as a precursor and that the cationic monohydrides $[RuH(N\text{-}N)P_3]^+$ (**4**−**6**), containing the N_2P_3 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 $RuHCl(bpy)(PPh_3)_2$, $[RuH(bpy)(CO)P_2]^+$ (P = PPh_3, PCy_3), and $[RuH(bpy)_2L]^+$ (L = CO, PPh_3) type and were obtained by substituting phosphine ligands with bpy in $RuHCl(PPh_3)_3$ or $RuHCl(CO)P_3$ 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 $[RuH(bpy)\{P(OEt)_3\}_3]BPh_4$ (**4a**) complex (see below).

The ^1H NMR spectra of the chloro complex $[RuCl(N\text{-}N)P_3]^+$ (**4**−**6**) and $[RuCl(bpy)_2P]^+$ (**8**) cations show the characteristic signals of the phosphite and the nitrogenous (bpy and phen) ligands. The $^{31}P\{^1H\}$ NMR spectra, furthermore, appear as AB_2 multiplets for the tris(phosphite) **4**−**6**, 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.

Chart 1



The ^1H and ^{31}P NMR spectra of the hydride cations containing the PPh_2OEt ligand $[RuH(N\text{-}N)(PPh_2OEt)_3]^+$ (**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 $PPh(OEt)_2$ $[RuH(N\text{-}N)P_3]^+$ (**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 AB_2X (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 $^{31}P\{^1H\}$ NMR spectra confirm the hypothesis of the two isomers, showing two AB_2 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 $[RuH(5,5'\text{-}Me_2bpy)\{P(OEt)_3\}_3]BPh_4$ (**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 $[RuH(bpy)\{P(OEt)_3\}_3]BPh_4$ (**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

(14) Geary, W. J. *Coord. Chem. Rev.* **1971**, *7*, 81−122.

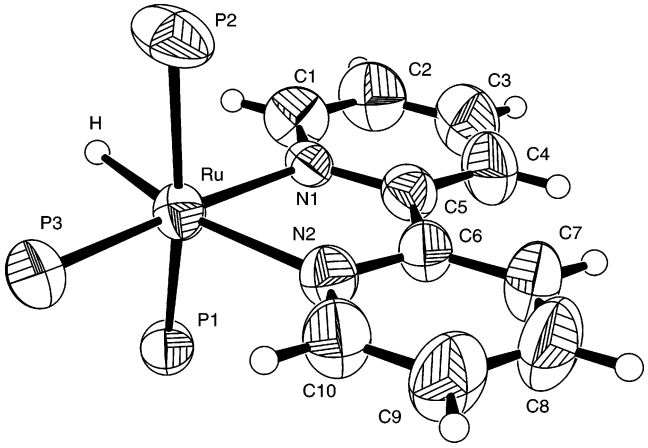


Figure 1. Perspective view of the molecular structure of *mer*-[RuH(bpy)-{P(OEt)$_3$}$_3$]$^+$ (**4a**$^+$). Ethoxy groups are omitted for clarity. The H/Cl substitutional disorder is not shown. Thermal ellipsoids are at the 50% level.

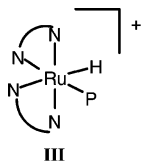
Table 5. Selected Bond Lengths [Å] and Angles [deg] for [RuH(bpy){P(OEt)$_3$}$_3$]BPh$_4$ (**4a**)

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 Ru$_4$ 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 found in **4a** (2.176 and 2.225 Å for [RuH(bpy)$_2$(CO)]$^+$ and [RuH(dmbpy)(CO)$_2$(NCS)]$^+$, respectively).

Chart 2



III

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)$_2$P]BPh$_4$ (**8**) hydride complexes were obtained only with the 2,2′-bipyridine ligand, and their ^{1}H and ^{31}P 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)P$_3$)Y (**4**, **5**) (Y = BPh$_4$, CF$_3$SO$_3$) react with the Brønsted acids CF$_3$SO$_3$H or HBF$_4$ to give the dihydrogen derivatives [Ru(η^2-H$_2$)(N-N)P$_3$]$^{2+}$ (**9**, **10**) as shown in eq 1. The reaction

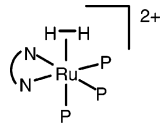
$$\underset{\mathbf{4},\ \mathbf{5}}{[\mathrm{RuH(N\text{-}N)P_3}]^+} \xrightarrow[\text{or } \mathrm{HBF_4}]{\text{excess } \mathrm{CF_3SO_3H}} \underset{\mathbf{9},\ \mathbf{10}}{[\mathrm{Ru}(\eta^2\text{-}\mathrm{H_2})(\mathrm{N\text{-}N})\mathrm{P_3}]^{2+}} \quad (1)$$

N-N = bpy (**4**, **9**), phen (**5**, **10**); P = P(OEt)$_3$ (**a**); PPh(OEt)$_2$ (**b**); PPh$_2$OEt (**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)(PPh$_2$OEt)]$^+$ (**4c**, **5c**) complexes, the addition of the triflic acid CF$_3$SO$_3$H caused the disappearance of the hydride resonances in the ^{1}H 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 η^2-H$_2$ ligand. Measurements of T_{1min} (Table 2) on this signal gave values of 5.1 (**9c**) and 5.9 (**10c**) ms, in agreement[19] with the proposed formulation. The spectra of the isotopomers [Ru(η^2-HD)(N-N)P$_3$]$^{2+}$ 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

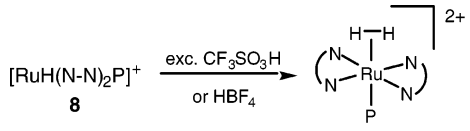
(15) Haasnoot, J. G.; Hinrichs, W.; Weir, O.; Vos, J. G. *Inorg. Chem.* **1986**, *25*, 4140−4143.
(16) Nijhoff, J.; Bakker, M. J.; Hartl, F.; Freeman, G.; Ingham, S. L.; Johnson, B. F. G. *J. Chem. Soc., Dalton Trans.* **1998**, 2625−2634.
(17) Homanen, P.; Haukka, M.; Pakkanen, T. A.; Pursiainen, J.; 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



IV

Scheme 3



11 (V)

for **9c** and 11 Hz for **10c**, suggesting that the H_2 should be in a mutually trans position with one phosphite ligand. Finally, taking into account that the $^{31}P\{^1H\}$ NMR spectra of **9c** and **10c** appear as an AB_2 multiplet, a *fac* geometry **IV** (Chart 3) can be proposed for the observable η^2-H_2 derivatives.

The protonation reaction of the related $PPh(OEt)_2$ and $P(OEt)_3$ $[RuH(N\text{-}N)P_3]^+$ (**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 η^2-H_2 ligand was observed, while two new AB_2 multiplets appeared in the $^{31}P\{^1H\}$ 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 η^2-H_2 derivatives. The presence of only one η^2-H_2 signal observed between -80 and $+10$ °C may be explained, either by a partial overlapping of the signals of the two η^2-H_2 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 η^2-H_2 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 $[Ru(\eta^2\text{-}HD)(N\text{-}N)P_3]^{2+}$ isotopomers (Table 2). The presence of the coupling between the η^2-HD and one phosphite ligand (J_{PH} about 9−10 Hz) also suggests a *fac*-type geometry **IV** for the η^2-H_2 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) $[Ru(\eta^2\text{-}H_2)(N\text{-}N)P_3]^{2+}$ (**9**, **10**) derivatives. The H−H bond length in the H_2 ligand can also be calculated[20] 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 complexes[1] $[Fe(\eta^2\text{-}H_2)(N\text{-}N)P_3]^{2+}$ 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 T_1 method using a static rotation 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 $[M(\eta^2\text{-}H_2)(N\text{-}N)P_3]^{2+}$ 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 $[Ru(\eta^2\text{-}H_2)(PPh_3)_2(bpy)(CO)]^{2+}$ 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 = BPh_4, CF_3SO_3) also react with Brønsted acid in CH_2Cl_2 solution to give the dihydrogen $[Ru(\eta^2\text{-}H_2)(bpy)_2P]^{2+}$ (**11**) cations (Scheme 3), which are stable in solution until 5−10 °C, but lose H_2 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 $^2J_{PH_{HD}}$ of about 7−8 Hz also suggests a mutually trans position of the phosphine and the dihydrogen ligands as in type-**V** geometry.

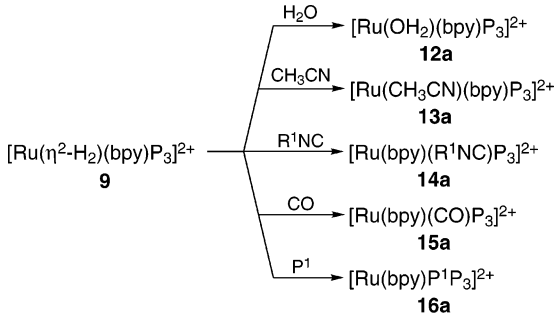
Furthermore, the H−H distances of the dihydrogen ligand were also calculated both from the J_{HD} and the T_{1min} values and are reported in Table 2. Bond H−H lengths of 0.89−0.92 Å were calculated from J_{HD} for $[Ru(\eta^2\text{-}H_2)(bpy)_2P]^{2+}$ (**11**) derivatives and were slightly shorter than the values of the related $[Ru(\eta^2\text{-}H_2)(N\text{-}N)P_3]^{2+}$ (**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) $[Ru(\eta^2\text{-}H_2)(N\text{-}N)P_3]^{2+}$ (**9**, **10**) cations are, as expected, more acidic than the monophosphite $[Ru(\eta^2\text{-}H_2)(bpy)_2P]^{2+}$ (**11**) derivatives. In fact, approximately 2.5 equiv of CF_3SO_3H is required for the complete protonation of $[RuH(N\text{-}N)P_3]^+$, 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 $[Ru(\eta^2\text{-}H_2)(N\text{-}N)(PPh_2OEt)_3]^{2+}$ (**9**, **10**) cations and the related $[Fe(\eta^2\text{-}H_2)(N\text{-}N)(PPh_2OEt)_3]^{2+}$ derivatives[1] 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 $[RuH(N\text{-}N)P_3]^+$ precursors requires less than 2.5 equiv of CF_3SO_3H. The bis(bipyridine) $[Ru(\eta^2\text{-}H_2)(bpy)_2P]^{2+}$

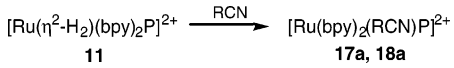
(20) Earl, K. A.; Jia, G.; Maltby, P. A.; Morris, R. H. *J. Am. Chem. Soc.* **1991**, *113*, 3027−3039.
(21) Gusev, D. G.; Kuhlman, R. L.; Renkema, K. B.; Eisenstein, O.; Caulton, K. G. *Inorg. Chem.* **1996**, *35*, 6775−6783.

Scheme 4[a]



[a] P = $P(OEt)_3$; P^1 = $PPh(OEt)_2$; R^1 = 4-$CH_3C_6H_4$.

Scheme 5[a]



[a] R = CH_3 (**17**), 4-$CH_3C_6H_4$ (**18**); P = $P(OEt)_3$.

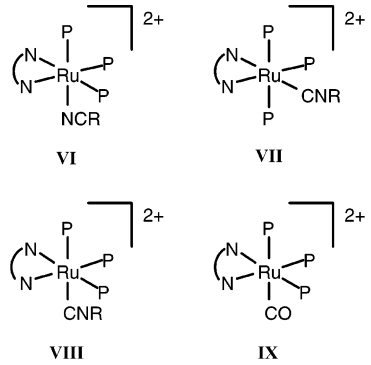
(**11**) derivatives are also, indeed, less acidic than the known dicationic dihydrogen complexes, thus highlighting that the presence of nitrogen-donor ligands such as bpy and phen can delocalize the positive charge of the complexes making the η^2-H_2 ligand relatively less acidic.

Substitution Reactions. Studies on the dihydrogen complexes **9**, **10**, **11** show that the η^2-H_2 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 H_2O and phosphite, however, the deprotonation to give the [RuH(bpy)P_3]$^+$ precursor can be predominant on the substitution of the η^2-H_2 ligand. The preparation of the complexes, therefore, must first involve the loss of H_2 to give, probably, the [Ru(κ^1-OSO_2CF_3)(bpy)P_3]$^+$ 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-H_2 complex in the solid state, due to the presence of traces of H_2O in the solvent. It was also prepared as a yellow solid by adding an excess of H_2O to a solution of the η^2-H_2 complex in CH_2Cl_2. 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 H_2O as a ligand in [Ru(OH_2)(bpy)P_3]-(BPh_4)$_2$ is confirmed by the ^{1}H NMR spectrum, which shows a slightly broad singlet at 2.55 ppm attributed[23] to the H_2O protons. In the spectra the signals of the phosphite and the bpy ligands are also present, while the $^{31}P\{^1H\}$ NMR spectra appear as an AB_2 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 ^{1}H and ^{13}C NMR spectra, however, confirm the presence of the CH_3CN 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 $^{13}C\{^1H\}$ NMR spectrum (Table 3) and were attributed to the CH_3 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 ^{13}C signals at 0.60 ppm (HMQC) and at 125.4 (HMBC) of the CH_3CN 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 ^{31}P spectrum appears as an A_2B 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 $^{31}P\{^1H\}$ NMR spectrum, in fact, shows two A_2B multiplets, while two singlets of the methyl substituent of the 4-$CH_3C_6H_4NC$ 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 ^{13}C spectrum (Table 3) shows the resonance of the carbonyl carbon atom as a doublet of triplets [A_2BY (Y = ^{13}C) 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 $^{31}P\{^1H\}$ NMR spectrum of the carbonyl complex **15a** appears as an A_2B multiplet, and therefore a *fac* geometry of the type **IX** (Chart 4) can be proposed.

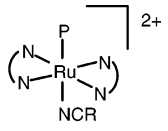
The $^{13}C\{^1H\}$ NMR spectrum of [Ru(CH_3CN)(bpy)$_2$-{$P(OEt)_3$}](BPh$_4$)$_2$ (**17a**) shows one singlet at 3.5 ppm and one doublet at 127.4 ppm (J_{CP} = 16 Hz) attributed to the methyl and CN carbon atoms, respectively, of the CH_3CN

(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



X

Scheme 6

$[RuH(N\text{-}N)P_3]^+ + PhN_2^+ \longrightarrow [Ru(PhN{=}NH)(N\text{-}N)P_3]^{2+}$ **19, 21**

N-N = bpy (**19**), phen (**21**); P = $P(OEt)_3$ (**a**), $PPh(OEt)_2$ (**b**).

$2[RuH(N\text{-}N)P_3]^+ + (N_2Ar\text{-}ArN_2)^{2+} \longrightarrow [\{Ru(N\text{-}N)P_3\}_2(\mu\text{-}NH{=}NAr\text{-}ArN{=}NH)]^{4+}$ **20**

P = $P(OEt)_3$, Ar-Ar = 4,4'-C_6H_4-C_6H_4.

$[RuH(bpy)_2P]^+ + PhN_2^+ \longrightarrow [Ru(PhN{=}NH)(bpy)_2P]^{2+}$ **22**

P = $P(OEt)_3$.

Scheme 7[a]

$[RuH(bpy)_2P]^+ \xrightarrow{\text{exc. } CS_2} [Ru\{\eta^1\text{-}SC(H){=}S\}(bpy)_2P]^+$ **23**

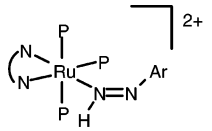
$[RuH(bpy)_2P]^+ \xrightarrow[(1\ atm)]{\text{exc. } CO_2} [Ru\{\eta^1\text{-}OC(H){=}O\}(bpy)_2P]^+$ **24**

[a] P = $P(OEt)_3$ (**a**), $PPh(OEt)_2$ (**b**).

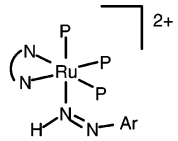
ligand. The HMQC and HMBC experiments confirm these attributions showing a correlation between the methyl proton signal at 1.66 ppm and the carbon signals at 3.5 (HMQC) and 127.4 ppm (HMBC), respectively. Furthermore, the presence of a doublet for the CN carbon resonance with J_{CP} of 16 Hz suggests 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 formato[27] derivatives,

Chart 6



mer



fac

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

The reaction with mono- and bis(aryldiazonium) cations proceeds with both $[RuH(N\text{-}N)P_3]^+$ and $[RuH(bpy)_2P]^+$ 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 $[RuH(bpy)_2P]^+$ (**8**) were the thioformato **23** and formato **24** complexes prepared in pure form. With the tris(phosphite) $[RuH(N\text{-}N)P_3]^+$ (**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 PPh_2OEt 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, ^{31}P, ^{13}C, ^{15}N) data (Tables 1 and 3) support the proposed formulation, and a geometry in solution was also established. The ^{31}P and ^1H NMR spectra of the $[Ru(PhN{=}NH)(N\text{-}N)P_3]^{2+}$ 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 complexes[1] 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 AB_2 multiplets in the ^{31}P, and also two AB_2Y (Y = ^{15}N) multiplets present in the ^{15}N spectra of the ^{15}N-labeled **20a-^{15}N** 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 $[Ru(PhN{=}NH)(bpy)_2P](BPh_4)_2$ (**22**) show only one NH signal, which is split into a doublet in the ^{15}N-labeled complex **22a-^{15}N**, with $J_{^{15}NH}$ of 65.5 Hz, in agreement[28] with the proposed formulation. Furthermore, the ^{31}P spectra show only one singlet suggesting the presence of only one isomer. Finally, the ^{15}N NMR spectra of **22a-^{15}N** appear as a doublet due to

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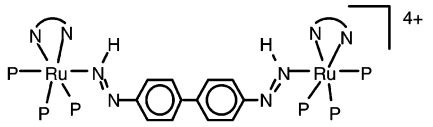
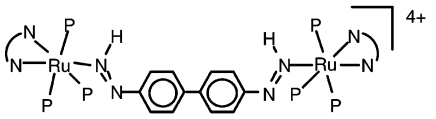
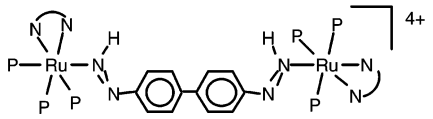
Chart 7



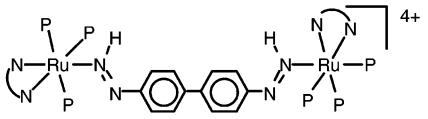
fac-fac



mer-mer

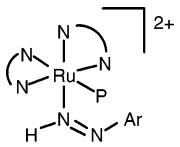


fac-mer



mer-fac

Chart 8



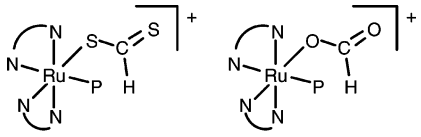
XI

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).

Aryldiazene complexes of ruthenium are known[25] 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 Ru(N-N)P_3 and Ru(bpy)$_2$P are also able to stabilize this class of "diazo" derivatives.

The ^{1}H NMR spectra of the thioformato [Ru{η^1-SC(H)═S}(bpy)P]BPh_4 (**23**) show a singlet at 10.87−10.94 ppm attributed[30] to the CH proton of the SC(H)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 SC(H)S ligand showing the δ_{HCS} as a medium-intensity

Chart 9



XII **XIII**

band at 1242−1256 cm^{-1}. Furthermore, the absence of a measurable coupling constant between the CH proton of SC(H)S ligand and the phosphorus nucleus of the phosphite suggests a mutually cis position of the thioformato and 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 Ru(II) species being rather improbable.

The IR spectra of the formato complexes [Ru{η^1-OC(H)═O}(bpy)$_2$P]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} bands[32] between 1554 and 1585 cm^{-1}.

The ^{13}C spectra confirm the presence of the OC(H)O ligand showing one singlet at 170.6 ppm (**24a**) and at 171.3 (**24b**) due to the formato carbon atom. The ^{1}H 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 OC(H)═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 [Ru{η^1-OC(H)═O}(bpy)$_2$P]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 $[RuH(N\text{-}N)P_3]BPh_4$ and $[RuH(bpy)_2P]BPh_4$ is described. Among the properties shown by these complexes, we can highlight the easy protonation with Brønsted acid to give dicationic dihydrogen $[Ru(\eta^2\text{-}H_2)(N\text{-}N)P_3]^{2+}$ and $[Ru(\eta^2\text{-}H_2)(N\text{-}N)P_3^{2+}$ 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 heteroallene, to give formato $[Ru\{\eta^1\text{-}OC(H)=O\}(bpy)_2P]BPh_4$ and dithioformato $[Ru\{\eta^1\text{-}SC(H)=S\}(bpy)_2P]BPh_4$ 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.

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