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The Chemistry of Cyclopentadienyl–Ruthenium and –Osmium Complexes. 5. The Systematic Synthesis of Novel Bridged Diruthenium Cations Containing Cyclopentadienyl and Bidentate Amine Ligands. The Crystal and Molecular Structure of $[\{(\eta^5\text{-}C_5H_5)Ru(1,10\text{-phen})\}_2(\mu\text{-dppm})](PF_6)_2\cdot CH_2Cl_2$ [dppm = bis(diphenylphosphino)methane; phen = phenanthroline]

Michel O. Albers, David C. Liles, David J. Robinson, and Eric Singleton*

National Chemical Research Laboratory, Council for Scientific and Industrial Research, P.O. Box 395, Pretoria 0001, Republic of South Africa

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The electron-rich complexes $[(\eta^5\text{-}C_5H_5)Ru(\text{diamine})Cl]$ (diamine = 1,10-phenanthroline, 2,2′-bipyridine, and substituted derivatives thereof) undergo facile chloro ligand labilization in alcohol solvents. In the presence of donor ligands L [CO, PPh_3, PPh_2H, $P(CH{=}CH_2)Ph_2$, $P(OEt)Ph_2$, $P(O\text{-}i\text{-}Pr)_3$, $AsMePh_2$, $SbPh_3$, $2,6\text{-}Me_2C_6H_3NC$, Bu-*t*-NC] the novel cationic cyclopentadienyl–ruthenium(II) complexes $[(\eta^5\text{-}C_5H_5)Ru(\text{diamine})(L)]^+$ are isolated by the addition of suitable counterions. The analogous reaction with a half-molar equivalent of bidentate donor ligands L_2 [bis(dimethylphosphino)methane, bis(diphenylphosphino)methane, 1,2-bis(dimethylphosphino)ethane, 1,2-bis(diethylphosphino)ethane, 1,2-bis(diphenylphosphino)ethane, 1-(diphenylphosphino)-2-(diphenylarsino)ethane, 1,5-bis(diphenylphosphino)pentane, 1,6-diisocyanohexane] yields the corresponding bimetallic complexes $[\{(\eta^5\text{-}C_5H_5)Ru(\text{diamine})\}_2(\mu\text{-}L_2)](PF_6)_2$. The reactions proceed via the intermediacy of the labile solvolyzed ruthenium(II) cations $[(\eta^5\text{-}C_5H_5)Ru(\text{diamine})(EtOH)]^+$ (EtOH = ethanol) and, in the case of the bimetallic products, also via the reactive mononuclear species $[(\eta^5\text{-}C_5H_5)Ru(\text{diamine})(\eta^1\text{-}L_2)]^+$. The ethanol cation $[(\eta^5\text{-}C_5H_5)Ru(1,10\text{-phen})(EtOH)]^+$ (phen = phenanthroline) has been isolated as the hexafluorophosphate salt, while the mononuclear species containing $\eta^1\text{-}L_2$ ligand systems $[(\eta^5\text{-}C_5H_5)Ru(1,10\text{-phen})(\eta^1\text{-}L_2)]PF_6$ [L_2 = bis(diphenylphosphino)methane, 1,2-bis(dimethylphosphino)ethane, 1,5-bis(diphenylphosphino)pentane] have been isolated in high yield when the substitution reactions are performed under mild conditions. The latter complexes react with $[(\eta^5\text{-}C_5H_5)Ru(1,10\text{-phen})Cl]$ to give the expected symmetrical bimetallic complexes $[\{(\eta^5\text{-}C_5H_5)Ru(1,10\text{-phen})\}_2(\mu\text{-}L_2)](PF_6)_2$ and with $[(\eta^5\text{-}C_5H_5)Ru(2,2'\text{-bpy})Cl]$ (bpy = bipyridine) to give the unsymmetrical bimetallic complexes $[\{(\eta^5\text{-}C_5H_5)Ru(1,10\text{-phen})\}\{(\eta^5\text{-}C_5H_5)Ru(2,2'\text{-bpy})\}(\mu\text{-}L_2)](PF_6)_2$ [L_2 = bis(diphenylphosphino)methane, 1,5-bis(diphenylphosphino)pentane]. Reaction of $[(\eta^5\text{-}C_5H_5)Ru(1,10\text{-phen})Cl]$ with the complexes $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)(\eta^1\text{-dppm})Cl]$ and $[(\eta^5\text{-}C_5H_5)Ru(\text{dppm})(\eta^1\text{-dppm})]PF_6$ in ethanol solution gives, following anion exchange with NH_4PF_6, high yields of the novel unsymmetrical diruthenium complexes $[\{(\eta^5\text{-}C_5H_5)Ru(PPh_3)Cl\}\{(\eta^5\text{-}C_5H_5)Ru(1,10\text{-phen})\}(\mu\text{-dppm})]PF_6$ and $[\{(\eta^5\text{-}C_5H_5)Ru(\text{dppm})\}\{(\eta^5\text{-}C_5H_5)Ru(1,10\text{-phen})\}(\mu\text{-dppm})](PF_6)_2$, respectively. The new cyclopentadienyl–ruthenium(II) complexes have been characterized by elemental analysis and by spectroscopic (IR, UV-visible, ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR) techniques. The crystal and molecular structure of $[\{(\eta^5\text{-}C_5H_5)Ru(1,10\text{-phen})\}_2(\mu\text{-dppm})](PF_6)_2\cdot CH_2Cl_2$ has been determined by single-crystal X-ray diffraction. Crystals were obtained from a dichloromethane–ethanol solution and found to be triclinic, space group $P\bar{1}$, with a = 10.439 (5) Å, b = 15.614 (4) Å, c = 18.990 (2) Å, α = 68.21 (1)°, β = 81.86 (2)°, γ = 87.79 (3)°, and Z = 2. The most salient features of the cation include the very long Ru···Ru internuclear distance of 6.445 (1) Å and the relatively large P–C–P angle of 133.1 (3)° subtended by the bridging dppm ligand. Both features reflect the accommodation within the cation of the steric requirements of the two ruthenium atoms and their associated ligands.

Introduction

One of the potentially most attractive synthetic routes for the rational synthesis of bimetallic transition-metal complexes is based upon the use of pendant functionality and incipient pendant functionality to draw the two metal centers together. The most common illustration of the first method involves the use of monodentate diphosphine ligands, most particularly bis(diphenylphosphino)methane (dppm),[1,2] while the best example of the second is provided by chelate dppm ligands which under certain circumstances would thermodynamically prefer to bridge two metal centers.[3-5] However, there are shortcomings associated with this strategy, and these relate primarily to the paucity of available complexes containing suitable uncoordinated functionality[1,6] and also to the limited number of suitable receptor complexes which must, by definition, have built in potential coordinative unsaturation.

We recently reported the synthesis of several general classes of new cyclopentadienyl–ruthenium(II) complexes including $[(\eta^5\text{-}C_5H_5)Ru(\eta^4\text{-diene})X]$ (diene = typically cycloocta-1,5-diene; X = H, halide)[7] and $[(\eta^5\text{-}C_5H_5)Ru(\text{diamine})X]$ (diamine = 1,10-phenanthroline, 2,2′-bipyridine, and substituted derivatives thereof; X = halide).[8] We are currently investigating certain aspects of the syn-

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Table I. Physical and Microanalytical Data for the New Complexes

	complex	color	yield, %	mp[a]	microanal.[b] found		
					C	H	N
1	[(η^5-C_5H_5)Ru(1,10-phen)(CO)]BPh_4[c]	yellow	87	225–227	72.55 (72.73)	4.65 (4.80)	4.01 (4.04)
2	[(η^5-C_5H_5)Ru(1,10-phen)(PPh_3)]PF_6	orange	76	>250	55.70 (55.78)	3.65 (3.74)	3.75 (3.72)
3	[(η^5-C_5H_5)Ru(1,10-phen)(PPh_2H)]PF_6	orange	92	223–224	51.06 (51.41)	3.17 (3.57)	4.22 (4.13)
4	[(η^5-C_5H_5)Ru(1,10-phen)($PPh_2CH{=}CH_2$)]PF_6	orange	95	121–123	52.38 (52.92)	3.72 (3.73)	3.98 (3.98)
5	[(η^5-C_5H_5)Ru(1,10-phen)(PPh_2OEt)]PF_6	orange	74	244–245	51.64 (51.60)	4.00 (3.91)	4.01 (3.88)
6	[(η^5-C_5H_5)Ru(1,10-phen){P(O-*i*-Pr)$_3$}]PF_6	orange	72	246–248	44.56 (44.64)	4.98 (4.90)	3.99 (4.00)
7	[(η^5-C_5H_5)Ru(1,10-phen)($AsMePh_2$)]PF_6	red-orange	85	211–213	48.95 (48.99)	3.45 (3.56)	3.82 (3.81)
8	[(η^5-C_5H_5)Ru(1,10-phen)($SbPh_3$)]PF_6	orange	86	>250	49.55 (49.78)	3.11 (3.45)	3.46 (3.32)
9	[(η^5-C_5H_5)Ru(1,10-phen)($CNC_6H_3Me_2$-2,6)]PF_6[d]	orange	67	230–231	50.04 (50.16)	3.54 (3.56)	6.51 (6.75)
10	[(η^5-C_5H_5)Ru(5-NO_2-1,10-phen)(CN-*t*-Bu)]PF_6[e]	red-purple	77	217–219	42.96 (42.65)	3.59 (3.42)	9.12 (9.04)
11	[(η^5-C_5H_5)Ru(4,4′-Me_2-2,2′-bpy)(PPh_3)]PF_6	orange	88	>250	55.34 (55.47)	4.34 (4.26)	3.66 (3.69)
12	[{(η^5-C_5H_5)Ru(1,10-phen)}$_2$(μ-dmpm)]$(PF_6)_2$	red-orange	94	>250	42.53 (41.87)	3.56 (3.60)	4.84 (5.08)
13	[{(η^5-C_5H_5)Ru(1,10-phen)}$_2$(μ-dppm)]$(PF_6)_2$	orange	84	169–171	51.68 (51.83)	3.63 (3.54)	3.90 (4.10)
14	[{(η^5-C_5H_5)Ru(1,10-phen)}$_2$(μ-dmpe)]$(PF_6)_2$	orange	98	>250	41.65 (42.40)	3.73 (3.74)	5.01 (4.95)
15	[{(η^5-C_5H_5)Ru(1,10-phen)}$_2$(μ-depe)]$(PF_6)_2$	orange	97	>250	44.16 (44.45)	4.08 (4.24)	4.80 (4.71)
16	[{(η^5-C_5H_5)Ru(1,10-phen)}$_2$(μ-dppe)]$(PF_6)_2$	orange	90	192–195	52.34 (52.18)	3.70 (3.65)	4.15 (4.06)
17	[{(η^5-C_5H_5)Ru(1,10-phen)}$_2$(μ-dppam)]$(PF_6)_2$	orange	98	>250	50.71 (50.57)	3.50 (3.54)	3.83 (3.93)
18	[{(η^5-C_5H_5)Ru(1,10-phen)}$_2$(μ-dppp)]$(PF_6)_2$	orange	98	>250	52.33 (53.17)	3.99 (3.97)	4.02 (3.94)
19	[{(η^5-C_5H_5)Ru(1,10-phen)}$_2${μ-$CN(CH_2)_6NC$}]$(PF_6)_2$[f]	orange	97	>250	44.87 (45.09)	3.35 (3.42)	7.44 (7.51)
20	[(η^5-C_5H_5)Ru(1,10-phen)(EtOH)]PF_6	orange	48	*g*	41.85 (42.46)	3.32 (3.56)	4.95 (5.21)
21	[(η^5-C_5H_5)Ru(1,10-phen)(η^1-dppm)]PF_6	orange	95	144–146	57.91 (57.60)	4.22 (4.03)	3.30 (3.20)
22	[(η^5-C_5H_5)Ru(1,10-phen)(η^1-dmpe)]PF_6	red-orange	86	155–156	42.62 (43.06)	4.15 (4.56)	4.46 (4.37)
23	[(η^5-C_5H_5)Ru(1,10-phen)(η^1-dppp)]PF_6	orange	96	159–161	58.79 (59.29)	4.59 (4.65)	3.01 (3.01)
24	[{(η^5-C_5H_5)Ru(1,10-phen)}{(η^5-C_5H_5)Ru(2,2′-bpy)}(μ-dppm)]$(PF_6)_2$	orange	92	207–210	51.17 (50.97)	3.50 (3.60)	4.39 (4.17)
25	[{(η^5-C_5H_5)Ru(1,10-phen)}{(η^5-C_5H_5)Ru(2,2′-bpy)}(μ-dppp)]$(PF_6)_2$	orange	90	>250	51.62 (52.36)	3.60 (4.03)	3.94 (4.00)
26	[{(η^5-C_5H_5)Ru(1,10-phen)}{(η^5-C_5H_5)Ru(PPh_3)Cl}(μ-dppm)]PF_6[h]	orange	69	162–164	52.60 (52.55)	3.69 (3.73)	2.22 (1.88)
27	[{(η^5-C_5H_5)Ru(1,10-phen)}{(η^5-C_5H_5)Ru(dppm)}(μ-dppm)]$(PF_6)_2$	yellow-orange	70	>250	54.68 (55.04)	3.87 (3.98)	2.11 (1.78)

[a] Uncorrected (°C). [b] Calculated values in parentheses. [c] $\nu(CO) = 1948\ cm^{-1}$. [d] $\nu(NC) = 2070\ cm^{-1}$. [e] $\nu(NC) = 2140\ cm^{-1}$. [f] $\nu(NC) = 2155\ cm^{-1}$. [g] Decomposes on heating >150 °C. [h] Found: Cl, 2.19. Calcd: Cl, 2.38.

thesis of bimetallic transition-metal complexes utilizing cyclopentadienyl–ruthenium precursors. Herein we wish to report model studies featuring one of our series of compounds, [(η^5-C_5H_5)Ru(diamine)X],[8] which lead to a rare example[2] of the systematic synthesis of bimetallic complexes containing single bringing diphosphine ligands. These reactions proceed via the intermediacy of the novel, highly reactive receptor and pendant functionality systems [(η^5-C_5H_5)Ru(diamine)(EtOH)]$^+$ and [(η^5-C_5H_5)Ru(diamine)(η^1-diphosphine)]$^+$. A preliminary account of some of this work has appeared.[9]

Experimental Section

All reactions were routinely performed under an inert atmosphere of either nitrogen or argon by using Schlenk techniques and dry and deoxygenated solvents. Recrystallizations were all performed in air. Triphenylstibine, 2,6-dimethylphenyl isocyanide, *tert*-butyl isocyanide, 1,6-diisocyanohexane (Fluka AG, Switzerland), tri-*iso*-propyl phosphite (K and K Laboratories Inc.), and other mono- and bidentate phosphorus and arsenic donor ligands (Strem Chemicals Inc.) were all used as purchased. The complexes [(η^5-C_5H_5)Ru(diamine)Cl] (diamine = 1,10-phenanthroline, 5-nitro-1,10-phenanthroline, 2,2′-bipyridine, 4,4′-dimethyl-2,2′-bipyridine),[8] [(η^5-C_5H_5)Ru(PPh_3)(η^1-dppm)Cl],[10] and [(η-C_5H_5)Ru(dppm)(η^1-dppm)]PF_6[10] were all prepared by the published procedures. ^1H NMR spectra were recorded at 500.13 MHz and $^{13}C\{^1H\}$ NMR spectra at 125.76 MHz in both cases by using a Bruker WM500 (500 MHz) instrument. $^{31}P\{^1H\}$ NMR spectra were recorded at 121.50 MHz by using a Bruker AM300 (300 MHz) instrument. All NMR spectra were recorded at 303 K. Infrared spectra were recorded as Nujol mulls by using a Bruker IFS85 FT-IR spectrometer. Visible spectra were recorded by using a Cary 210 spectrophotometer with a thermostated (298 K) cell compartment. Melting points were determined by using a Kofler micro-hotstage apparatus and are uncorrected. Elemental analyses were all performed by the microanalytical section of the Analytical Division of the NCRL. Physical, microanalytical, NMR, and visible spectral data for all new complexes are given in Tables I-V.

(a) Synthesis of [(η^5-C_5H_5)Ru(1,10-phen)(CO)]BPh_4 (1; phen = phenanthroline). A suspension of [(η^5-C_5H_5)Ru(1,10-phen)Cl] (0.38 g, 1.0 mmol) in ethanol (25 mL) was heated under reflux. A stream of CO was bubbled through the solution for 20 min. The resulting orange solution was filtered while still hot and after being cooled to room temperature was treated with a filtered solution of $NaBPh_4$ (0.34 g, 1.0 mmol) in ethanol (10 mL). The resultant yellow crystalline solid was collected by filtration, washed with diethyl ether (20 mL), and dried under vacuum. The yield of [(η^5-C_5H_5)Ru(1,10-phen)(CO)]BPh_4 was 0.6 g (0.87 mmol, 87%).

(b) Synthesis of [(η^5-C_5H_5)Ru(1,10-phen)(L)]PF_6 [2–9; L = PPh_3, PPh_2H, P(CH=CH_2)Ph_2, P(OEt)Ph_2, P(O-*i*-Pr)$_3$, $AsMePh_2$, $SbPh_3$, 2,6-$Me_2C_6H_3NC$]. A suspension of [(η^5-C_5H_5)Ru(1,10-phen)Cl] (0.38 g, 1.0 mmol) in ethanol (40 mL) was treated with a solution of the ligand (1.05 mmol) in ethanol (5 mL) and the resultant mixture heated under reflux for 20 min. After filtration and cooling to room temperature, a solution of NH_4PF_6 (0.18 g, 1.1 mmol) in ethanol (5 mL) was added with stirring. The resultant precipitate was filtered and washed with diethyl ether (20 mL). The products [(η^5-C_5H_5)Ru(1,10-phen)(L)]PF_6 (2–9), all orange to orange-red crystalline solids, were isolated in high (67–86%) yield.

(c) Synthesis of the Complexes [(η^5-C_5H_5)Ru(diamine)(L)]PF_6 [10, Diamine = 5-Nitro-1,10-phenanthroline, L = Bu-*t*-NC; 11, Diamine = 4,4′-dimethyl-2,2′-bipyridine, L = PPh_3]. In a procedure similar to that described above in (b) the products were obtained as red (**10**) and orange (**11**) crystalline solids. Yield: **10**, 0.48 g (0.77 mmol, 77%); **11**, 0.61 g (0.88 mmol, 88%).

(d) Synthesis of the Complexes [{(η^5-C_5H_5)Ru(1,10-phen)}$_2$(μ-L_2)]$(PF_6)_2$ (12–19; L_2 = dmpm, dppm, dmpe, depe,

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dppe, dppae, dppp, $CN(CH_2)_6NC$). With use of a procedure similar to that described in (b) above, [(η^5-C_5H_5)Ru(1,10-phen)Cl] (0.38 g, 1.0 mmol) was treated with the respective ligand (0.5 mmol). The crystalline, orange to red products were isolated in a similar manner to that described in (b); yields 84–98%.

(e) Synthesis of [(η^5-C_5H_5)Ru(1,10-phen)(EtOH)]PF_6 (20). A suspension of [(η^5-C_5H_5)Ru(1,10-phen)Cl] (0.38 g, 1.0 mmol) in ethanol (30 mL) was heated under reflux for 20 min. After filtration of the orange solution, cooling to room temperature, and the reduction of the solvent volume by 15 mL under vacuum, a solution of NH_4PF_6 (0.18 g, 1.1 mmol) in ethanol (5 mL) was added with stirring. The resultant orange precipitate was collected by filtration and washed with diethyl ether (20 mL) and vacuum dried; yield 0.26 g (0.48 mmol, 48%).

(f) Alternative Synthesis of 1–19 from [(η^5-C_5H_5)Ru(diamine)(ethanol)]$^+$ (Diamine = 1,10-Phenanthroline, 5-Nitro-1,10-phenanthroline, 4,4′-Dimethyl-2,2′-bipyridine). (i) A suspension of [(η^5-C_5H_5)Ru(diamine)Cl] (1.0 mmol) in ethanol (40 mL) was heated under reflux for 20 min generating the solvolyzed cation [(η^5-C_5H_5)Ru(diamine)(ethanol)]$^+$. After treatment of the orange solution with the required amount of the respective ligand [(a)–(d) above], the mixture was gently refluxed for 5 min. Workup procedures were as detailed for 1–19 above.

(ii) Alternatively, isolated [(η^5-C_5H_5)Ru(1,10-phen)(EtOH)]PF_6 (**20**) may be reacted in warm ethanol with the required amount of ligand giving, following workup as detailed above **1–9** and **12–19** in high yield.

(g) Synthesis of [(η^5-C_5H_5)Ru(1,10-phen)(η^1-L_2)]PF_6 (21, L_2 = dppm; 22, L_2 = dmpe; 23, L_2 = dppp). A suspension of [(η^5-C_5H_5)Ru(1,10-phen)Cl] (0.38 g, 1.0 mmol) in ethanol (100 mL) at 0 °C was treated with a solution of the ligand (1.05 mmol) in ethanol (20 mL) and the resultant mixture stirred at 0 °C for 1 h. After filtration and solvent reduction of 50 mL under vacuum, a solution of NH_4PF_6 (0.18 g, 1.1 mmol) in ethanol (5 mL) was added with stirring. The resultant orange precipitate was isolated by filtration and washed with diethyl ether (20 mL). Yield: **21**, 0.83 g (0.95 mmol, 95%); **22**, 0.55 g (0.86 mmol, 86%); **23**, 0.89 g (0.96 mmol, 96%).

(h) Synthesis of the Complexes [{(η^5-C_5H_5)Ru(1,10-phen)}{(η^5-C_5H_5)Ru(2,2′-bpy)}(μ-L_2)]$(PF_6)_2$ (24, L_2 = dppm; 25, L_2 = dppp). A suspension of [(η^5-C_5H_5)Ru(2,2′-bpy)Cl] (0.18 g, 0.5 mmol) and [(η^5-C_5H_5)Ru(1,10-phen)(η^1-L_2)]PF_6 (0.5 mmol; L_2 = dppm, dppp) in ethanol (30 mL) was heated under reflux for 20 min. After being cooled to room temperature, the orange suspension was collected by filtration and washed with diethyl ether (20 mL). Treatment of the filtrate with NH_4PF_6 (0.09 g, 0.55 mmol) in ethanol (3 mL) with stirring gives a second crop of the product, isolated in a similar manner to the first. Combined yield: **24**, 0.62 g (0.46 mmol, 92%); **25**, 0.63 g (0.45 mmol, 90%).

(i) Synthesis of [{(η^5-C_5H_5)Ru(PPh_3)Cl}{(η^5-C_5H_5)Ru(1,10-phen)}(μ-dppm)]PF_6 (26). A suspension of [(η^5-C_5H_5)Ru(1,10-phen)Cl] (0.19 g, 0.5 mmol) and [(η^5-C_5H_5)Ru(PPh_3)(η^1-dppm)Cl][10] (0.42 g, 0.5 mmol) in ethanol (40 mL) was heated under reflux for 25 min. The reaction solution was filtered hot, and NH_4PF_6 (0.09 g, 0.5 mmol) in ethanol (5 mL) was added. The orange crystalline precipitate was separated by filtration, washed with diethyl ether, and vacuum dried; yield 0.46 g (0.35 mmol, 69%).

(j) Synthesis of [{(η^5-C_5H_5)Ru(dppm)}{(η^5-C_5H_5)Ru(1,10-phen)}(μ-dppm)]$(PF_6)_2$ (27). A suspension of [(η^5-C_5H_5)Ru(1,10-phen)Cl] (0.19 g, 0.5 mmol) and [(η^5-C_5H_5)Ru(dppm)(η^1-dppm)]PF_6[10] (0.54 g, 0.5 mmol) in ethanol (40 mL) was heated under reflux for 25 min. After filtration and cooling to room temperature, the yellow-orange precipitate was collected by filtration and washed with diethyl ether (10 mL). The mother liquors were treated with NH_4PF_6 (0.09 g, 0.5 mmol) in ethanol (5 mL) yielding a second crop of the product; combined yield 0.55 g (0.35 mmol, 70%).

X-ray Data Collection, Solution, and Refinement of [{(η^5-C_5H_5)Ru(1,10-phen)}$_2$(μ-dppm)]$(PF_6)_2$·CH_2Cl_2 [13; phen = phenanthroline; dppm = bis(diphenylphosphino)methane]. Crystals were obtained as orange-red plates from a dichloromethane–ethanol solution. A crystal of dimensions 0.41 × 0.25 × 0.06 mm was used for the determination of cell parameters and data collection.

Crystal data: $C_{60}H_{50}Cl_2F_{12}N_4P_4Ru_2$, $M_r = 1452.01$; triclinic, space group $P\bar{1}$, $a = 10.439$ (5) Å, $b = 15.614$ (4) Å, $c = 18.990$ (2) Å, $\alpha = 68.21$ (1)°, $\beta = 81.86$ (2)°, $\gamma = 87.79$ (3)°; $U = 2844.6$ Å^3; $Z = 2$, $D_{\text{calcd}} = 1.695$ Mg m^{-3}; $F(000) = 1456$; $\lambda = 0.71069$ Å; μ(Mo $K\alpha$) = 0.728 mm^{-1}.

Unit-cell parameters were determined, and intensity data were measured on an Enraf-Nonius CAD4F diffractometer using graphite-crystal-monochromatized Mo $K\alpha$ radiation. A total of 9824 reflections with $3 \le \theta \le 25°$ (h, 0–12; k, −18 to 18; l, −22 to 22) were measured by the ω–2θ scan method with a scan width of (0.58 + 0.50 tan θ)° in ω, a variable scan speed (maximum 0.0915° s^{-1}, maximum time 50 s/reflection), and a detector aperture of (1.80 + 1.27 tan θ)-mm horizontal by 4.0-mm vertical. Three orientation control reflections were centered every 200 reflections. Three intensity control reflections were measured every hour and showed no significant change in their intensities over the 78.6-h X-ray exposure time. No absorption corrections were applied to the data.

The structure was solved by Patterson and difference-Fourier methods and was refined by using SHELX.[11] The fluorine atoms of the anions were found to be disordered, and two positions, each with an occupancy of 0.5 and an individual isotropic temperature factor, were refined for each fluorine atom. All hydrogen atoms were added in calculated positions and were allowed to ride on the atoms to which they were bonded with $d_{\text{C-H}}$ fixed at 0.95 Å.[12] Eight common isotropic temperature factors were refined for the hydrogen atoms. Anisotropic temperature factors were used for all atoms except the fluorine and hydrogen atoms. Blocked-matrix least-squares refinement (three blocks), with the function $\sum|\Delta F|^2$ minimized and unit weights, converged with $R = 0.0583$ for 7530 unique reflections with $F_o \ge 4\sigma(F_o)$. In the final cycles 753 parameters were refined. The largest shifts/error were 0.097 for the cation and 1.044 for the anions. A final difference map showed no significant residual features: the maximum and minimum residual electron density were 1.210 (close to an anion) and −0.729 e Å^{-3}, respectively. Complex neutral-atom scattering factors[13] were used for all atoms.

Final atomic coordinates are given in Table VI. Tables of observed and calculated structure factors, anisotropic temperature factors, hydrogen atom coordinates, and bond lengths and angles are available as supplementary material.

Results and Discussion

Amine complexes form one of the cornerstones of the coordination chemistry of ruthenium.[14] It is thus surprising that there are relatively few organometallic complexes of ruthenium-containing amine ligands,[15] and in particular there are only a handful of reports dealing to any significant extent with cyclopentadienyl– (or related η^5-dienyl–) ruthenium amine complexes.[16]

Recently, the cationic complexes [(η^5-C_5H_5)Ru(diamine)(PPh_3)]$^+$ and [(η^5-C_9H_7)Ru(diamine)(PPh_3)]$^+$ (C_9H_7 = indenyl; diamine includes 2,2′-bipyridine and 1,10-phenanthroline[17,18]) were obtained by the treatment of the neutral complexes [(η^5-C_5H_5)Ru$(PPh_3)_2$Cl] and [(η^5-C_9H_7)Ru$(PPh_3)_2$Cl] with diamine ligands in alcohol sol-

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Table II. ^{1}H NMR Data for the New Complexes[a]

complex	
1	9.50 [2 H, dd, $J(H_AH_B)$ = 5.1, $J(H_AH_C)$ = 1.3, H_A], 8.81 [2 H, dd, $J(H_CH_B)$ 8.2, $J(H_CH_A)$ = 1.3, H_C], 8.22 (2 H, s, H_D), 7.94 [2 H, dd, $J(H_BH_C)$ = 8.2, $J(H_BH_A)$ = 5.1, H_B], 7.34 (8 H, m, Ph), 6.90 (8 H, m, Ph), 6.75 (4 H, m, Ph), 5.48 (5 H, s, C_5H_5)
2	9.81 [2 H, dd, $J(H_AH_B)$ = 5.4, $J(H_AH_C)$ = 1.1, H_A], 8.46 [2 H, dd, $J(H_CH_B)$ = 8.1, $J(H_CH_A)$ = 1.1, H_C], 7.98 (2 H, s, H_D), 7.70 [2 H, dd, $J(H_BH_C)$ = 8.1, $J(H_BH_A)$ = 5.4, H_B], 7.27 (3 H, m, Ph), 7.15 (6 H, m, Ph), 6.98 (6 H, m, Ph), 4.98 (5 H, s, C_5H_5)
3	9.74 [2 H, dd, $J(H_AH_B)$ = 5.2, $J(H_AH_C)$ = 1.1, H_A], 8.52 [2 H, dd, $J(H_CH_B)$ = 8.2, $J(H_CH_A)$ = 1.1, H_C], 7.98 (2 H, s, H_D), 7.81 [2 H, dd, $J(H_BH_C)$ = 8.2, $J(H_BH_A)$ = 5.2, H_B], 7.14 (3 H, m, Ph), 7.02 (6 H, m, Ph), 6.95 (6 H, m, Ph), 6.91 (1 H, d, J = 359.1, PH), 5.01 (5 H, s, C_5H_5)
4	9.78 [2 H, dd, $J(H_AH_B)$ = 5.3, $J(H_AH_C)$ = 1.0, H_A], 8.46 [2 H, dd, $J(H_CH_B)$ = 8.1, $J(H_CH_A)$ = 1.0, H_C], 7.92 (2 H, s, H_D), 7.78 [2 H, dd, $J(H_BH_C)$ = 8.1, $J(H_BH_A)$ = 5.3, H_B], 7.12 (2 H, m, Ph), 6.96 (4 H, m, Ph), 6.77 (4 H, m, Ph), 6.11 (1 H, m, CH), 5.76 (1 H, m, CH_2), 5.72 (1 H, m, CH_2), 5.04 (5 H, s, C_5H_5)
5	9.73 [2 H, dd, $J(H_AH_B)$ = 5.3, $J(H_AH_C)$ = 0.9, H_A], 8.51 [2 H, dd, $J(H_CH_B)$ = 8.1 $J(H_CH_A)$ = 0.9, H_C], 7.93 (2 H, s, H_D), 7.82 [2 H, dd, $J(H_BH_C)$ = 8.1, $J(H_BH_A)$ = 5.3, H_B], 7.12 (2 H, m, Ph), 6.99 (4 H, m, Ph), 6.86 (4 H, m, Ph), 5.15 (5 H, s, C_5H_5), 4.03 (2 H, dq, J(POCH) = 14.4, J = 6.9, CH_2), 1.27 (3 H, t, J = 6.9, Me)
6	9.75 [2 H, d, $J(H_AH_B)$ = 5.2, H_A], 8.71 [2 H, d, $J(H_CH_B)$ = 8.2, H_C], 8.22 (2 H, s, H_D), 7.90 [2 H, dd, $J(H_BH_C)$ = 8.2, $J(H_BH_A)$ = 5.2, H_B], 5.13 (5 H, s, C_5H_5), 4.58 [3 H, m, J(POCH) = 9.0, CH], 0.85 (18 H, d, J = 6.1, Me)
7	9.88 [2 H, dd, $J(H_AH_B)$ = 5.2, $J(H_AH_C)$ = 1.3, H_A], 8.45 [2 H, dd, $J(H_CH_B)$ = 8.2, $J(H_CH_A)$ = 1.3, H_C], 7.90 (2 H, s, H_D), 7.79 [2 H, dd, $J(H_BH_C)$ = 8.2, $J(H_BH_A)$ =5.2, H_B], 7.13 (2 H, m, Ph), 6.97 (4 H, m, Ph), 6.76 (4 H, m, Ph), 4.99 (5 H, s, C_5H_5), 1.87 (3 H, s, Me)
8	9.92 [2 H, dd, $J(H_AH_B)$ = 5.2, $J(H_AH_C)$ = 1.2, H_A], 8.48 [2 H, dd, $J(H_CH_B)$ = 8.1, $J(H_CH_A)$ = 1.2, H_C], 7.99 (2 H, s, H_D), 7.73 [2 H, dd, $J(H_BH_C)$ = 8.1, $J(H_BH_A)$ = 5.2, H_B], 7.31 (3 H, m, Ph), 7.19 (6 H, m, Ph), 6.98 (6 H, m, Ph), 5.13 (5 H, s, C_5H_5)
9	9.78 [2 H, dd, $J(H_AH_B)$ = 5.2, $J(H_AH_C)$ = 1.1, H_A], 8.81 [2 H, dd, $J(H_CH_B)$ = 8.2, $J(H_CH_A)$ = 1.1, H_C], 8.26 (2 H, s, H_D), 7.79 [2 H, dd, $J(H_BH_C)$ = 8.2, $J(H_BH_A)$ = 5.2, H_B], 7.03 (1 H, t, J = 7.4, CH), 6.98 (2 H, d, J = 7.4, CH), 5.28 (5 H, s, C_5H_5), 1.89 (6 H, s, Me)
10	9.92 [1 H, dd, $J(H_AH_B)$ = 5.3, $J(H_AH_C)$ = 1.3, H_A], 9.89 [1 H, dd, $J(H_{A'}H_{B'})$ = 5.2, $J(H_{A'}H_{C'})$ = 1.2, $H_{A'}$], 9.23 (1 H, s, $H_{D'}$), 9.20 [1 H, dd, $J(H_{C'}H_{B'})$ =8.6, $J(H_{C'}H_{A'})$ = 1.2, $H_{C'}$], 9.02 [1 H, dd, $J(H_CH_B)$ = 8.2, $J(H_CH_A)$ = 1.3, H_C], 8.11 [1 H, dd, $J(H_{B'}H_{C'})$ = 8.6, $J(H_{B'}H_{A'})$ = 5.2, $H_{B'}$], 8.09 [1 H, dd, $J(H_BH_C)$ = 8.2, $J(H_BH_A)$ = 5.3, H_B], 5.08 (5 H, s, C_5H_5), 1.23 (9 H, s, Me)
11	9.26 [2 H, d, $J(H_AH_B)$ = 5.9, H_A], 7.98 (2 H, s, H_D), 7.38 (3 H, m, Ph), 7.30 (6 H, m, Ph), 7.15 [2 H, d, $J(H_BH_A)$ = 5.9, H_B], 7.11 (6 H, m, Ph), 4.81 (5 H, s, C_5H_5), 2.44 (6 H, s, Me)
12	9.59 [4 H, d, $J(H_AH_B)$ = 5.2, H_A], 8.73 [4 H, d, $J(H_CH_B)$ = 7.9, H_C], 8.25 (4 H, s, H_D), 7.90 [4 H, dd, $J(H_BH_C)$ = 7.9, $J(H_BH_A)$ = 5.2, H_B], 4.73 (10 H, s, C_5H_5), 1.91 (2 H, t, J = 7.7, CH_2), 0.92 (12 H, d, J = 45.5, Me)
13	9.38 [4 H, dd, $J(H_AH_B)$ = 5.4, $J(H_AH_C)$ = 1.0, H_A], 8.53 [4 H, dd, $J(H_CH_B)$ = 8.1, $J(H_CH_A)$ = 1.0, H_C], 8.01 (4 H, s, H_D), 7.76 [4 H, dd, $J(H_BH_C)$ = 8.1, $J(H_BH_A)$ = 5.4 H_B], 6.99 (4 H, m, Ph), 6.70 (8 H, m, Ph), 6.40 (8 H, m, Ph), 4.81 (10 H, s, C_5H_5), 3.21 (2 H, t, J = 7.7, CH_2)
14	9.70 [4 H, d, $J(H_AH_B)$ = 5.2, H_A], 8.71 [4 H, d, $J(H_CH_B)$ = 8.0, H_C], 8.23 (4 H, s, H_D), 7.88 [4 H, dd, $J(H_BH_C)$ = 8.0, $J(H_BH_A)$ = 5.2, H_B], 4.85 (10 H, s, C_5H_5), 1.51 (4 H, s, CH_2)
15	9.70 [4 H, d, $J(H_AH_B)$ = 5.2, H_A], 8.69 [4 H, d, $J(H_CH_B)$ = 7.9, H_C], 8.23 (4 H, s, H_D), 7.88 [4 H, dd, $J(H_BH_C)$ = 7.9, $J(H_BH_A)$ = 5.2, H_B], 4.82 (10 H, s, C_5H_5), 1.59 (4 H, m, CH_2), 1.09 (8 H, m, CH_2), 0.76 (12 H, m, Me)
16	9.26 [4 H, d, $J(H_AH_B)$ = 5.2, H_A], 8.41 [4 H, d, $J(H_CH_B)$ = 8.1, H_C], 7.91 (4 H, s, H_D), 7.61 [4 H, dd, $J(H_BH_C)$ = 8.1, $J(H_BH_A)$ = 5.2, H_B], 7.28 (4 H, m, Ph), 7.09 (8 H, m, Ph), 6.62 (8 H, m, Ph), 4.85 (10 H, s, C_5H_5), 1.70 (4 H, m, CH_2)
17	9.50 [2 H, dd, $J(H_AH_B)$ = 5.2, $J(H_AH_C)$ = 1.1, H_A], 9.32 [2 H, dd, $J(H_{A'}H_{B'})$ = 5.2, $J(H_{A'}H_{C'})$ = 1.1, $H_{A'}$], 8.41 (4 H, m, H_C, $H_{C'}$), 7.92 (2 H, s, H_D), 7.91 (2 H, s, $H_{D'}$), 7.65 [2 H, dd, $J(H_BH_C)$ = 8.0, $J(H_BH_A)$ = 5.28 H_B], 7.63 [2 H, dd, $J(H_{B'}H_{C'})$ = 8.0, $J(H_{B'}H_{A'})$ = 5.2, $H_{B'}$], 7.29 (2 H, m, Ph), 7.27 (2 H, m, Ph), 7.11 (4 H, m, Ph), 7.07 (4 H, m, Ph), 6.66 (4 H, m, Ph), 6.61 (4 H, m, Ph), 4.91 (5 H, s, C_5H_5), 4.89 (5 H, s, C_5H_5), 3.56 (1 H, m, CH_2), 1.91 (2 H, m, CH_2), 1.76 (1 H, m, CH_2)
18	9.65 [4 H, dd, $J(H_AH_B)$ = 5.2, $J(H_AH_C)$ = 1.1, H_A], 8.43 [4 H, dd, $J(H_CH_B)$ = 8.1, $J(H_CH_A)$ = 1.1, H_C], 7.89 (4 H, s, H_D), 7.72 [4 H, dd, $J(H_BH_C)$ = 8.1, $J(H_BH_A)$ = 5.2, H_B], 7.10 (4 H, m, Ph), 6.93 (8 H, m, Ph), 6.72 (8 H, m, Ph), 5.05 (10 H, s, C_5H_5), 2.40 (4 H, m, CH_2), 1.42 (2 H, m, CH_2), 1.31 (4 H, m, CH_2)
19	9.68 [4 H, dd, $J(H_AH_B)$ = 5.2, $J(H_AH_C)$ = 1.2, H_A], 8.71 [4 H, dd, $J(H_CH_B)$ = 8.2, $J(H_CH_A)$ = 1.2, H_C], 8.18 (4 H, s, H_D), 7.91 [4 H, dd, $J(H_BH_C)$ = 8.2, $J(H_BH_A)$ = 5.2, H_B], 5.01 (10 H, s, C_5H_5), 3.42 (4 H, t, J = 6.5, CH_2), 1.22 (4 H, m, CH_2), 0.80 (4 H, m, CH_2)
20	9.76 [2 H, d, $J(H_AH_B)$ = 5.5, H_A], 8.49 [2 H, d, $J(H_CH_B)$ = 8.2, H_C], 7.90 (2 H, s, H_D), 7.64 [2 H, dd, $J(H_BH_C)$ = 8.2, $J(H_BH_A)$ = 5.5, H_B], 5.10 (5 H, s, C_5H_5), 3.56 (2 H, q, J = 7.1, CH_2), 1.11 (3 H, t, J = 7.1, Me)
21	9.63 [2 H, dd, $J(H_AH_B)$ = 5.2, $J(H_AH_C)$ = 1.2, H_A], 8.43 [2 H, dd, $J(H_CH_B)$ = 8.1, $J(H_CH_A)$ = 1.2, H_C], 7.88 (2 H, s, H_D), 7.73 [2 H, dd, $J(H_BH_C)$ = 8.1, $J(H_BH_A)$ = 5.2, H_B], 7.30 (6 H, m, Ph), 7.25 (4 H, m, Ph), 7.02 (2 H, m, Ph), 6.80 (4 H, m, Ph), 6.76 (4 H, m, Ph), 5.14 (5 H, s, C_5H_5), 3.40 (2 H, m, CH_2)
22	9.77 [2 H, dd, $J(H_AH_B)$ = 5.2, $J(H_AH_C)$ = 1.1, H_A], 8.68 [2 H, dd, $J(H_CH_B)$ = 8.1, $J(H_CH_A)$ = 1.1, H_C], 8.20 (2 H, s, H_D), 7.89 [2 H, dd, $J(H_BH_C)$ = 8.1, $J(H_BH_A)$ = 5.2, H_B], 4.90 (5 H, s, C_5H_5), 1.41 (2 H, m, CH_2), 1.23 (2 H, m, CH_2)
23	9.64 [2 H, dd, $J(H_AH_B)$ = 5.3, $J(H_AH_C)$ = 1.1, H_A], 8.41 [2 H, dd, $J(H_CH_B)$ = 8.5, $J(H_CH_A)$ = 1.1, H_C], 7.87 (2 H, s, H_D), 7.71 [2 H, dd, $J(H_BH_C)$ = 8.5, $J(H_BH_A)$ = 5.3, H_B], 7.38 (2 H, m, Ph), 7.34 (4 H, m, Ph), 7.30 (4 H, m, Ph), 7.11 (2 H, m, Ph), 6.89 (4 H, m, Ph), 6.70 (4 H, m, Ph), 5.03 (5 H, s, C_5H_5), 2.58 (2 H, m, CH_2), 1.57 (2 H, m, CH_2), 1.51 (2 H, m, CH_2), 1.40 (4 H, m, CH_2)
24[b]	9.41 [2 H, d, $J(H_AH_B)$ = 5.2, H_A], 9.07 [2 H, d, $J(H_{A'}H_{B'})$ = 5.5, $H_{A'}$], 8.52 [2 H, d, $J(H_CH_B)$ = 8.1, H_C], 8.18 [2 H, d, $J(H_{D'}H_{C'})$ = 8.1, $H_{D'}$], 8.01 (2 H, s, H_D), 7.96 (2 H, m, $H_{C'}$), 7.76 [2 H, dd, $J(H_BH_C)$ = 8.1, $J(H_BH_A)$ = 5.2, H_B], 7.39 (2 H, m, $H_{B'}$), 7.16 (2 H, m, Ph), 7.00 (2 H, m, Ph), 6.89 (4 H, m, Ph), 6.74 (4 H, m, Ph), 6.59 (4 H, m, Ph), 6.47 (4 H, m, Ph), 4.84 (5 H, s, C_5H_5), 4.71 (5 H, s, C_5H_5), 3.22 (2 H, t, J = 5.7, CH_2)
25[b]	9.64 [2 H, dd, $J(H_AH_B)$ = 5.2, $J(H_AH_C)$ = 0.8, H_A], 9.31 [2 H, d, $J(H_{A'}H_{B'})$ = 5.5, $H_{A'}$], 8.42 [2 H, dd, $J(H_CH_B)$ = 8.2, $J(H_CH_A)$ = 0.8, H_C], 8.03 [2 H, d, $J(H_{D'}H_{C'})$ = 8.1, $H_{D'}$], 7.88 (2 H, s, H_D), 7.84 (2 H, m, $H_{C'}$), 7.71 [2 H, dd, $J(H_BH_C)$ = 8.2, $J(H_BH_A)$ = 5.2, H_B], 7.32 (4 H, br m, $H_{B'}$, Ph), 7.15 (4 H, m, Ph), 7.09 (2 H, m, Ph), 6.93 (8 H, br m, Ph), 6.71 (4 H, m, Ph), 5.04 (5 H, s, C_5H_5), 4.94 (5 H, s, C_5H_5), 2.39 (2 H, m, CH_2), 2.31 (2 H, m, CH_2), 1.42 (2 H, m, CH_2), 1.28 (4 H, m, CH_2)
26	9.33 [1 H, d, $J(H_AH_B)$ = 5.1, H_A], 8.90 [1 H, d, $J(H_{A'}H_{B'})$ = 5.4, $H_{A'}$], 8.26 [1 H, d, $J(H_{C'}H_{B'})$ = 8.1, $H_{C'}$], 8.02 [1 H, d, $J(H_CH_B)$ = 8.0, H_C], 7.69 [1 H, dd, $J(H_{B'}H_{C'})$ = 8.1, $J(H_{B'}H_{A'})$ = 5.4, $H_{B'}$], 7.61 (1 H, s, $H_{D'}$), 7.59 (1 H, s, H_D), 7.50 (1 H, m, Ph), 7.38 (1 H, m, Ph), 7.36 [1 H, dd, $J(H_BH_C)$ = 8.0, $J(H_BH_A)$ = 5.1, H_B], 7.32 (3 H, m, Ph), 7.18 (6 H, m, Ph), 7.07 (6 H, m, Ph), 7.02 (2 H, m, Ph), 6.95 (3 H, m, Ph), 6.74 (3 H, m, Ph), 6.58 (3 H, m, Ph), 6.52 (1 H, m, Ph), 6.07 (3 H, m, Ph), 4.98 (3 H, m, Ph), 4.86 (5 H, s, C_5H_5), 3.81 (5 H, s, C_5H_5), 2.86 (2 H, m, CH_2)
27	9.46 [2 H, d, $J(H_AH_B)$ = 5.2, H_A], 8.40 [2 H, d, $J(H_CH_B)$ = 8.1, H_C], 8.01 (2 H, s, H_D), 7.68 [2 H, dd, $J(H_BH_C)$ = 8.1, $J(H_BH_A)$ = 5.2, H_B], 7.50 (4 H, m, Ph), 7.36 (4 H, m, Ph), 7.26 (2 H, m, Ph), 7.17 (1 H, m, Ph), 6.90 (1 H, m, Ph), 6.81 (2 H, m, Ph), 6.61 (2 H, m, Ph), 6.58 (2 H, m, Ph), 6.30 (2 H, m, Ph), 5.54 (1 H, m, CH_2), 5.33 (5 H, s, C_5H_5), 5.05 (5 H, s, C_5H_5), 4.04 (2 H, t, J = 5.7, CH_2), 3.29 (1 H, m, CH_2)

[a] Positions recorded in ppm downfield of Me_4Si for acetone-d_6 solutions at 303 K; coupling constants in hertz; spectral frequency 500.13 MHz. [b] The labels $H_{A'}$–$H_{D'}$ refer to protons on the 2,2′-bipyridine ligand.

Table III. $^{13}C\{^1H\}$ NMR Data for the New Complexes[a]

complex	
1	199.3 (CO), 164.9 (C_{ipso}, Ph),[b] 158.8 (C_A), 148.7 (C_{bridge}), 138.9 (C_C), 137.0 (Ph), 131.9 (C_{bridge}), 128.4 (C_D), 126.4 (C_B), 126.0, 122.2 (Ph), 84.0 (C_5H_5)
2	157.1 (C_A), 148.2 (C_{bridge}), 135.8 (C_C), 133.4, 132.0 (Ph), 131.4 (C_{bridge}), 130.7, 128.9 (Ph), 128.1 (C_D), 125.2 (C_B), 78.9 (C_5H_5)
3	157.3 (C_A), 147.6 (C_{bridge}), 135.9 (C_C), 132.1 (Ph), 13.5 (C_{bridge}), 130.5, 130.1, 129.1 (Ph), 128.0 (C_D), 125.6 (C_B), 78.1 (C_5H_5)
4	157.2 (C_A), 147.9 (C_{bridge}), 135.7 (C_C), 133.9 (C_{bridge}), 132.3 (Ph), 131.5 (CH_2), 131.2 (CH), 130.4 128.8 (Ph), 128.0 (C_D), 125.4 (C_B), 78.5 (C_5H_5)
5	157.5 (C_A), 148.2 (C_{bridge}), 136.0 (C_C), 135.4 (Ph), 131.5 (C_{bridge}), 130.8, 130.3, 128.6 (Ph), 127.9 (C_D), 125.6 (C_B), 79.5 (C_5H_5), 63.6 (CH_2), 16.7 (Me)
6	157.7 (C_A), 149.3 (C_{bridge}), 136.4 (C_C), 131.6 (C_{bridge}), 128.0 (C_D), 125.3 (C_B), 78.6 (C_5H_5), 69.6 (CH), 24.1 (Me)
7	157.2 (C_A), 147.7 (C_{bridge}), 135.6 (C_C), 133.9, 131.5 (Ph), 131.4 (C_{bridge}), 130.1, 129.2 (Ph), 128.0 (C_D), 125.5 (C_B), 74.6 (C_5H_5), 11.8 (Me)
8	157.7 (C_A), 147.8 (C_{bridge}), 136.0 (C_C), 135.5 (Ph), 131.6 (C_{bridge}), 130.8, 130.3, 130.0 (Ph), 128.1 (C_D), 124.4 (C_B), 73.9 (C_5H_5)
9[c]	158.2 (C_A), 148.4 (C_{bridge}), 137.5 (C_C), 134.7 (CMe), 131.7 (C_{bridge}), 128.6, 128.5 (CH), 128.3 (C_D), 126.1 (C_B), 16.3 (Me)
10	160.6, 158.9 (C_A, $C_{A'}$), 149.6, 148.4 (C_{bridge}), 145.5 ($C_{D'}$), 139.1, 133.8 (C_C, $C_{C'}$), 128.6 (C_{bridge}), 127.6 (C_D), 126.9, 126.8 (C_B, $C_{B'}$), 124.4 (C_{bridge}), 78.8 (C_5H_5), 58.5 (CMe_3), 30.9 (Me)
11	156.4 (C_{bridge}), 156.3 (C_A), 149.3 (C_C), 133.8, 132.9, 130.8, 129.2 (Ph), 126.9 (C_D), 124.8 (C_B), 78.8 (C_5H_5), 20.8 (Me)
12	157.3 (C_A), 148.0 (C_{bridge}), 136.2 (C_C), 131.6 (C_{bridge}), 128.4 (C_B), 125.9 (C_D), 77.6 (C_5H_5), 30.8 (t, J 7, CH_2), 15.5 (d, J 15, Me), 15.4 (d, $J = 15$, Me)
13	157.0 (C_A), 147.8 (C_{bridge}), 136.0 (C_C), 132.4 (Ph), 131.4 (C_{bridge}), 130.5, 128.4 (Ph), 128.2 (C_D), 125.7 (C_B), 78.5 (C_5H_5), 30.5 (CH_2)
14	157.4 (C_A), 148.1 (C_{bridge}), 136.0 (C_C), 131.6 (C_{bridge}), 128.4 (C_B), 125.7 (C_D), 77.3 (C_5H_5), 26.3 (t, $J = 7$, CH_2), 12.8 (d, $J = 13$, Me), 12.6 (d, $J = 13$, Me)
15	157.7 (C_A), 148.3 (C_{bridge}), 139.9 (C_C), 131.7 (C_{bridge}), 128.4 (C_D), 125.8 (C_B), 77.2 (C_5H_5), 18.3 (CH_2), 17.7 (CH_2), 8.0 (Me)
16	156.9 (C_A), 147.6 (C_{bridge}), 135.8 (C_C), 132.2 (Ph), 131.2 (C_{bridge}), 130.8, 129.2, 129.1 (Ph), 128.0 (C_D), 125.6 (C_B), 77.9 (C_5H_5), 18.8 (CH_2)
17	157.1, 156.9 (C_A, $C_{A'}$), 148.0, 147.9 (C_{bridge}), 136.0, 135.9 (C_C, $C_{C'}$), 135.7, 133.7, 132.3, 132.1 (Ph), 131.6 (C_{bridge}), 131.3, 130.8 (Ph), 130.2 (C_{bridge}), 129.7, 129.5, 129.2, 128.8 (Ph), 128.1 (C_D, $C_{D'}$), 125.6 (C_B, $C_{B'}$), 78.0, 74.7 (C_5H_5
18	157.0 (C_A), 147.9 (C_{bridge}), 135.6 (C_C), 132.2 (Ph), 131.8 (C_{bridge}), 131.4 130.2, 128.6 (Ph), 128.0 (C_D), 125.5 (C_B), 77.6 (C_5H_5), 30.8, 30.5, 24.9 (CH_2)
19	157.9 (C_A), 148.2 (C_{bridge}), 137.0 (C_C), 131.5 (C_{bridge}), 128.2 (C_D), 125.9 (C_B), 78.3 (C_5H_5), 44.7, 25.5 (CH_2)
20	156.4 (C_A), 149.2 (C_{bridge}), 135.6 (C_C), 132.2 (C_{bridge}), 128.1 (C_D), 125.4 (C_B), 79.6 (C_5H_5), 61.5 (CH_2), 19.5 (Me)
21	157.1 (C_A), 148.0 (C_{bridge}), 135.7 (C_C), 133.4, 132.4 (Ph), 131.4 (C_{bridge}), 130.3, 129.7, 129.3, 128.5 (Ph), 128.0 (C_D), 125.5 (C_B), 78.0 (C_5H_5), 31.5 (CH_2)
22	157.4 (C_A), 148.0 (C_{bridge}), 135.8 (C_C), 131.5 (C_{bridge}), 128.2 (C_B), 125.8 (C_D), 77.1 (C_5H_5), 27.3 (d, $J = 14$, CH_2), 25.3 (d, $J = 14$, CH_2), 13.4 (d, $J = 15$, Me), 13.0 (d, $J = 28$, Me)
23	156.9 (C_A), 147.8 (C_{bridge}), 135.3 (C_C), 133.4, 133.3, 132.1, 131.9, 131.6 (Ph), 131.4 (C_{bridge}), 130.1, 129.3, 129.2 (Ph), 127.9 (C_D), 125.3 (C_B), 77.6 (C_5H_5), 30.4, 30.2, 28.1, 26.2, 24.8 (CH_2)
24	157.0 (C_A, $C_{A'}$), 156.2, 147.8 (C_{bridge}), 137.3 ($C_{C'}$), 136.0 (C_C), 132.8, 132.4 (Ph), 131.4 (C_{bridge}), 130.5, 128.9, 128.6, 128.4 (Ph), 128.2 (C_D), 126.5 (C_B'), 125.8 (C_B), 124.2 (C_D'), 79.1 (C_5H_5), 78.6 (C_5H_5), 30.2 (CH_2)
25[b]	157.0 (C_A, $C_{A'}$), 156.2, 147.9 (C_{bridge}), 136.7 ($C_{C'}$), 135.5 (C_C), 132.6, 132.1, 131.7, 131.4 (Ph), 131.3 (C_{bridge}), 130.4, 130.2, 129.2, 128.6 (Ph), 127.9 (C_D), 126.1 ($C_{B'}$), 125.4 (C_B), 124.0 ($C_{D'}$), 78.2 (C_5H_5), 77.6 (C_5H_5), 32.8, 30.3, 24.8 (CH_2)
26	155.4, 154.8 (C_A, $C_{A'}$), 147.0, 146.7 (C_{bridge}), 139.1 (Ph), 138.7 138.4 (C_C, $C_{C'}$), 136.2, 135.9, 135.4, 134.6, 134.3, 134.0, 131.0, 130.2, 129.6, 129.4, 129.1, 128.8, 128.4, 128.3, 127.9, 127.7, 127.5, 127.1, 127.0, 126.4, 124.3 (Ph), 81.5 (C_5H_5), 76.9 (C_5H_5), 24.6 (CH_2)
27	157.1 (C_A), 147.8 (C_{bridge}), 136.0 (C_C), 134.4, 132.5, 132.0, 131.7 (Ph), 131.2 (C_{bridge}), 131.1, 130.2, 129.5, 128.4 (Ph), 128.0 (C_B), 125.6 (C_D), 85.1 (C_5H_5), 78.2 (C_5H_5), 46.0 (CH_2), 39.3 (CH_2)

[a] Positions recorded in ppm downfield of Me_4Si for acetone-d_6 solutions at 303 K; coupling constants in hertz; spectral frequency 125.76 MHz. [b] The labels $C_{A'}$–$C_{D'}$ refer to carbons of the 2,2′-bipyridine ligand.

vents. Due to restriction in the availability of suitable precursors of this type, each with differing reactivity patterns,[15,16] the above procedure does not provide generalized routes to the cations $[(\eta^5\text{-}C_5H_5)Ru(diamine)(L)]^+$.

We have recently reported[8] the synthesis of the neutral *parent* diamine complexes $[(\eta^5\text{-}C_5H_5)Ru(diamine)X]$ (diamine = 1,10-phenanthroline, 2,2′-bipyridine, and substituted derivatives thereof; X = halide) obtained by reacting the versatile and highly reactive cyclopentadienyl–ruthenium(II) complexes $[(\eta^5\text{-}C_5H_5)Ru(\eta^4\text{-}diene)X]$[7] directly with diamine in acetone solution. This substitution process is remarkable in that diene ligands (typically cycloocta-1,5-diene in our systems) on ruthenium are only infrequently displaced by nitrogen donor ligands. Under the mild experimental conditions employed[8] (acetone, 25 °C) the substitution process occurs via initial ruthenium–olefin bond cleavage as the rate-determining step[19] (and not via the perhaps expected labilization of the halo group) and thus proceeds directly to the neutral substitution products without the intervention of cationic intermediates or the formation of cationic products.[8,19] As with $[(\eta^5\text{-}C_5H_5)Ru(\eta^4\text{-}diene)X]$,[7] however, we have found that under suitable experimental conditions, controlled labilization of the halo ligand in $[(\eta^5\text{-}C_5H_5)Ru(diamine)X]$ can readily be achieved, even under very mild conditions. Aspects of this reactivity we illustrate below in terms of (i) the generalized synthesis of cationic diamine complexes of the type $[(\eta^5\text{-}C_5H_5)Ru(diamine)(L)]PF_6$ and $[\{(\eta^5\text{-}C_5H_5)Ru(diamine)\}_2(\mu\text{-}L_2)](PF_6)_2$ (in which the nature of the diamine and of the monodentate and the bidentate ligands is varied), (ii) the isolation of the reactive intermediates $[(\eta^5\text{-}C_5H_5)Ru(diamine)(EtOH)]^+$ and $[(\eta^5\text{-}C_5H_5)Ru(diamine)(\eta^1\text{-}L_2)]^+$ in these processes, examples of highly reactive receptor and pendant functionality systems, and (iii) the systematic synthesis of novel bridged diruthenium cations containing cyclopentadienyl and diamine ligands and unsupported single bridging diphosphine ligands.

The Generalized Synthesis of $[(\eta^5\text{-}C_5H_5)Ru(diamine)(L)]^+$ and $[\{(\eta^5\text{-}C_5H_5)Ru(diamine)\}_2(\mu\text{-}L_2)]^{2+}$ Cations. Treatment of $[(\eta^5\text{-}C_5H_5)Ru(1,10\text{-}phen)Cl]$ (phen = phenanthroline) with excess carbon monoxide or with an equimolar amount of a monodentate donor ligand in

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[19] Albers, M. O.; De Waal, D. J. A.; Robinson, D. J.; Singleton, E., unpublished results.

Table IV. $^{31}P\{^1H\}$ NMR Data for the New Complexes[a]

complex	
2	53.39 (s)
3	26.33 (s)
4	45.15 (s)
5	145.08 (s)
6	142.26 (s)
11	52.79 (s)
12	17.49 (s)
13	49.39 (s)
14	15.43 (s)
15	31.52 (s)
16	48.98 (s)
17	49.65 (s)
18	44.90 (s)
21	44.58 (1 P, d, J = 74), −25.08 (1 P, d, J = 74)
22	14.60 (1 P, d, J = 28), −2.29 (1 P, d, J = 28)
23	45.46 (1 P, s), −15.32 (1 P, s)
24	49.70 (1 P, d, J 35), 48.85 (1 P, d, J = 35)
25	45.34 (1 P, s), 44.97 (1 P, s)
26	47.24 (1 P, d, J = 43), 42.84 (1 P, d, J = 43), 41.09 (1 P, t, J = 43)
27	52.47 (1 P, d, J = 36), 50.92 (1 P, m), 5.49 (2 P, d, J = 34)

[a] Positions recorded in ppm relative to H_3PO_4 for acetone-d_6 solutions at 303 K; coupling constants in hertz; spectral frequency of 121.50 MHz.

Table V. Visible Spectral Data for the New Complexes[a]

complex	λ_{max},[b] nm	$10^3\epsilon$
1[c]	(366, 403)	
2	403 (460)	6.9
3	395 (458)	6.3
4	403 (468)	5.6
5	388 (455)	6.2
6	384 (455)	6.4
7	413 (464)	6.5
8	407 (465)	6.4
9	379 (440)	6.6
10	415	6.2
11	415	3.9
12	411 (480)	12.2
13	401 (462)	7.2
14	410 (482)	8.1
15	418 (478)	12.7
16	404 (468)	10.0
17	402 (460)	11.4
18	408 (466)	12.6
19	386 (455)	12.8
20	375	5.6
21	404	6.7
22	415 (473)	6.0
23	409	7.0
24	401	10.0
25	413	10.0
26	402	10.3
27	387	8.0

[a] Visible spectra recorded in CH_2Cl_2 at 298 K. [b] Approximate shoulder positions given in parentheses. [c] Only shoulders to an intense absorption in the UV were observed.

boiling ethanol solution rapidly gives the cations $[(\eta^5\text{-}C_5H_5)Ru(1,10\text{-phen})(L)]^+$ [**1**–**9**; L = CO, PPh_3, PPh_2H, $P(CH{=}CH_2)Ph_2$, $P(OEt)Ph_2$, $P(O\text{-}i\text{-}Pr)_3$, $AsMePh_2$, $SbPh_3$, $2,6\text{-}Me_2C_6H_3NC$] isolated in high yield in the presence of bulky anions such as tetraphenylborate (for **1**) and hexafluorophosphate (for **2**–**9**). The cations $[(\eta^5\text{-}C_5H_5)Ru(5\text{-}NO_2\text{-}1,10\text{-phen})(CN\text{-}t\text{-}Bu)]^+$ (**10**) and $[(\eta^5\text{-}C_5H_5)Ru(4,4'\text{-}Me_2\text{-}2,2'\text{-bpy})(PPh_3)]^+$ (**11**; bpy = bipyridine) have been obtained by similar procedures using the appropriate diamine precursors[8] and have been isolated as the hexafluorophosphate salts.

Treatment of $[(\eta^5\text{-}C_5H_5)Ru(1,10\text{-phen})Cl]$ with a half-molar equivalent of bidentate ligands L_2 [bis(dimethylphosphino)methane, dmpm; bis(diphenylphosphino)methane, dppm; 1,2-bis(dimethylphosphino)ethane, dmpe; 1,2-bis(diethylphosphino)ethane, depe; 1,2-bis(diphenylphosphino)ethane, dppe; 1-(diphenylphosphino)-2-(diphenylarsino)ethane, dppae; 1,5-bis(diphenylphosphino)pentane, dppp; 1,6-diisocyanohexane] yields the corresponding bimetallic cations $[\{(\eta^5\text{-}C_5H_5)Ru(1,10\text{-phen})\}_2(\mu\text{-}L_2)]^{2+}$ isolated in all cases in high yield as the hexafluorophosphate salts (**12**–**19**, respectively).

Compounds **1**–**19** (Table I) are all crystalline solids which range in color from yellow (e.g., **1**) to red-purple (**10**). They are indefinitely stable to air both in the solid state and in solution and are soluble in a wide range of common organic solvents, most particularly acetone and dichloromethane. **1**–**19** have been completely characterized by a combination of elemental analysis (Table I) and spectroscopic techniques (where applicable IR and ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopy) (Tables II–IV). The complete assignment of the ^1H NMR spectra of **1**–**19** (Table II) is simplified by comparisons with previously reported[8] data, by comparisons which may be made within a series of related compounds, and by the use of characteristic coupling patterns and coupling constants.[8] The spectra of **1**–**12**, **14**, **15**, and **19** are essentially predictable and will not be considered further. However, the ^1H NMR spectra of **13** and **16**–**18** while not displaying any remarkable features relating to assignment or multiplicity show a striking high-field chemical shift of certain of the μ-diphosphine phenyl protons. This ring shielding effect is probably a consequence of steric congestion within the coordination sphere of the metal atoms and the subsequent close proximity of some of the phenyl protons to the aromatic amine ligands. Indeed it is interesting that this effect is most noticeable for **13** involving the dppm ligand in what is expected to be one of the most congested systems (see below).

The $^{13}C\{^1H\}$ NMR spectra for **1**–**19** (Table III) have also been assigned, making use of previous studies[8] and comparisons within the series and when necessary (e.g., **10**) using $^1H/^{13}C$ heteronuclear shift correlation spectra. The spectra bear no remarkable features and will not be considered further.

The $^{31}P\{^1H\}$ NMR spectra of **2**–**6** and **11**–**18** (Table IV) all display the expected singlet resonances in the ranges characteristic of these ligands. The visible spectra of **2**–**19** comprise characteristic charge-transfer bands in the 379–415 nm range (Table V), typically shifted 80–90 nm to shorter wavelength than the range observed[8] for the neutral parent complexes $[(\eta^5\text{-}C_5H_5)Ru(\text{diamine})Cl]$. Complex **1** displays no absorption bands in the visible region of the spectrum but shoulders to what is clearly an intense peak in the near UV region. Typically high extinction coefficients in the range 3.9×10^3 to 12.8×10^3 are observed for the charge-transfer bands (Table V).

Perhaps the two most unusual features of the reactions leading to **1**–**19** detailed above relate (i) to the ease of formation of the cations, apparently irrespective of the nature of the entering ligand, and (ii) to the facile formation of the bridged dicationic systems. The well-established electronic properties of polyaromatic diamine ligands of the type used in this study (i.e., good electron-donating properties while the π-acceptor effects are not pronounced) would be expected to contribute to a buildup of electron density in the parent amine complexes $[(\eta^5\text{-}C_5H_5)Ru(\text{diamine})Cl]$, thereby favoring salt formation. This coupled together with the relatively modest steric

Table VI. Fractional Coordinates (×10⁴, ×10⁵ for Ru) and Equivalent Isotropic Temperature Factors (Å² × 10³; ×10⁴ for Ru) for 13

	x/*a*	*y*/*b*	*z*/*c*	*U*(eq)
Ru(1)	43771 (5)	10866 (4)	17814 (3)	359 (3)
Ru(2)	21283 (5)	42526 (4)	30118 (3)	369 (3)
P(1)	2252 (2)	1484 (1)	2043 (1)	33 (1)
P(2)	1587 (2)	2761 (1)	3157 (1)	33 (1)
C(1)	2163 (7)	2543 (5)	2276 (4)	41 (3)
C(111)	1340 (6)	1799 (5)	1218 (4)	38 (3)
C(112)	1231 (7)	2691 (5)	719 (4)	51 (4)
C(113)	588 (9)	2869 (7)	80 (5)	65 (5)
C(114)	99 (9)	2156 (8)	-50 (5)	65 (6)
C(115)	217 (8)	1266 (7)	432 (5)	58 (5)
C(116)	843 (7)	1071 (5)	1072 (4)	44 (4)
C(121)	1201 (7)	569 (4)	2747 (4)	37 (3)
C(122)	-145 (7)	628 (5)	2821 (4)	45 (4)
C(123)	-911 (8)	-87 (6)	3323 (5)	54 (5)
C(124)	-362 (10)	-898 (6)	3773 (5)	59 (5)
C(125)	953 (10)	-970 (5)	3704 (5)	58 (5)
C(126)	1734 (8)	-240 (5)	3201 (4)	46 (4)
N(31)	3783 (5)	46 (4)	1447 (3)	38 (3)
N(32)	4269 (5)	1794 (4)	614 (3)	39 (3)
C(31)	3634 (6)	330 (5)	687 (4)	38 (4)
C(32)	3896 (6)	1272 (5)	247 (4)	40 (4)
C(33)	4519 (7)	2687 (5)	216 (4)	52 (4)
C(34)	4416 (8)	3083 (7)	-573 (5)	62 (5)
C(35)	4054 (8)	2559 (7)	-941 (5)	61 (5)
C(36)	3777 (7)	1628 (6)	-536 (4)	47 (4)
C(37)	3384 (8)	1008 (8)	-858 (5)	57 (6)
C(38)	3126 (8)	111 (8)	-437 (5)	56 (6)
C(39)	3249 (7)	-273 (6)	364 (5)	47 (4)
C(310)	3032 (8)	-1183 (6)	816 (5)	54 (5)
C(311)	3221 (8)	-1474 (6)	1573 (5)	56 (5)
C(312)	3580 (7)	-835 (5)	1862 (4)	46 (4)
C(51)	6254 (8)	519 (8)	2161 (6)	55 (6)
C(52)	6394 (8)	1466 (8)	1764 (6)	61 (6)
C(53)	5556 (9)	1918 (7)	2133 (7)	64 (6)
C(54)	4898 (8)	1228 (8)	2793 (5)	54 (6)
C(55)	5312 (9)	354 (7)	2798 (5)	58 (5)
C(211)	2197 (6)	1826 (4)	3948 (4)	35 (3)
C(212)	1646 (7)	947 (5)	4263 (4)	42 (4)
C(213)	2197 (8)	251 (5)	4830 (4)	54 (4)
C(214)	3292 (8)	432 (6)	5087 (5)	54 (5)
C(215)	3810 (7)	1298 (6)	4802 (4)	49 (4)
C(216)	3276 (7)	2004 (5)	4240 (4)	46 (4)
C(221)	-155 (6)	2551 (4)	3335 (4)	34 (3)
C(222)	-811 (6)	2290 (4)	4071 (4)	41 (3)
C(223)	-2153 (7)	2276 (5)	4199 (5)	53 (4)
C(224)	-2829 (8)	2521 (6)	3579 (6)	60 (5)
C(225)	-2199 (8)	2798 (6)	2860 (6)	59 (5)
C(226)	-871 (7)	2820 (5)	2718 (4)	45 (4)
N(41)	1100 (5)	4017 (4)	4096 (3)	37 (3)
N(42)	263 (5)	4682 (4)	2769 (3)	40 (3)
C(41)	-178 (6)	4242 (4)	4108 (4)	37 (3)
C(42)	-620 (7)	4603 (4)	3382 (4)	40 (3)
C(43)	-166 (9)	5021 (5)	2075 (5)	55 (4)
C(44)	-1435 (10)	5284 (6)	2002 (6)	64 (6)
C(45)	-2326 (9)	5212 (6)	2619 (6)	65 (5)
C(46)	-1927 (8)	4862 (5)	3344 (5)	51 (4)
C(47)	-2755 (8)	4723 (6)	4040 (6)	60 (5)
C(48)	-2335 (8)	4367 (6)	4716 (6)	62 (5)
C(49)	-1027 (7)	4124 (5)	4774 (5)	48 (4)
C(410)	-520 (9)	3757 (6)	5471 (5)	60 (5)
C(411)	761 (9)	3552 (6)	5456 (5)	58 (5)
C(412)	1553 (8)	3690 (5)	4774 (4)	47 (4)
C(61)	3344 (10)	5445 (8)	2815 (8)	69 (7)
C(62)	4002 (9)	4646 (9)	3164 (7)	71 (7)
C(63)	4179 (8)	4154 (7)	2666 (6)	63 (5)
C(64)	3642 (8)	4661 (6)	2021 (5)	58 (5)
C(65)	3136 (9)	5449 (6)	2120 (6)	63 (5)
P(3)	2594 (3)	5596 (2)	-292 (2)	71 (1)
F(31A)	1386 (18)	5103 (13)	302 (11)	137 (6)[a]
F(32A)	2754 (16)	4738 (10)	-527 (9)	101 (4)[a]
F(33A)	3535 (17)	5930 (11)	-1089 (10)	127 (6)[a]
F(34A)	2562 (15)	6680 (11)	-358 (10)	130 (5)[a]
F(35A)	1423 (13)	5881 (10)	-803 (7)	101 (4)[a]
F(36A)	3775 (13)	5453 (10)	137 (8)	107 (4)[a]
F(31B)	1543 (16)	5457 (12)	431 (9)	118 (5)[a]
F(32B)	2177 (27)	4745 (20)	-429 (17)	203 (13)[a]
F(33B)	3951 (20)	5977 (13)	-800 (12)	150 (7)[a]
F(34B)	2719 (16)	6230 (12)	159 (11)	136 (5)[a]
F(35B)	1951 (17)	6373 (12)	-887 (10)	132 (5)[a]
F(36B)	3245 (16)	4715 (12)	332 (9)	138 (5)[a]
P(4)	4604 (3)	2690 (2)	6325 (2)	72 (2)
F(41A)	4280 (11)	1878 (8)	7162 (7)	89 (3)[a]
F(42A)	5555 (26)	3215 (19)	6488 (15)	198 (9)[a]
F(43A)	4585 (18)	3352 (13)	5479 (11)	146 (6)[a]
F(44A)	3395 (14)	2148 (10)	6170 (8)	112 (4)[a]
F(45A)	3430 (15)	3249 (11)	6628 (9)	127 (5)[a]
F(46A)	5542 (13)	1999 (9)	6126 (7)	99 (4)[a]
F(41B)	4555 (18)	2584 (14)	7171 (11)	158 (6)[a]
F(42B)	6167 (19)	2643 (14)	6413 (11)	157 (6)[a]
F(43B)	5015 (20)	2855 (15)	5414 (12)	165 (7)[a]
F(44B)	3240 (18)	3012 (13)	6233 (11)	146 (6)[a]
F(45B)	4338 (28)	1690 (19)	6543 (17)	228 (10)[a]
F(46B)	5059 (13)	3775 (10)	6004 (8)	110 (4)[a]
Cl(1)	319 (3)	7008 (2)	2425 (2)	95 (2)
Cl(2)	-572 (4)	8849 (2)	1754 (3)	127 (3)
C(7)	-878 (20)	7800 (11)	2259 (10)	152 (14)
Cp(1)	5683 (8)	1097 (8)	2330 (6)	0 (1)[a]
Cp(2)	3661 (9)	4871 (7)	2557 (6)	0 (1)[a]

[a] Isotropic temperature factor.

requirements of the diamine ligands (see below), could provide a rationalization for the facile formation of cations of the type $[(\eta^5\text{-}C_5H_5)Ru(diamine)(L)]^+$. The observations concerning the formation of the ligand-bridged diruthenium complexes are noteworthy in that such facile single, diphosphine bridge formation in the absence of other bridging ligands or a metal–metal bond is an exceedingly rare occurrence.[2] In order to evaluate the factors that favor bridge formation in these systems and not in others,[10] and in so doing to evaluate the possibilities for the synthesis of unsymmetrical diruthenium and heterobimetallic complexes, the X-ray crystal structure of 13 has been determined.

The X-ray Structure of $[\{(\eta^5\text{-}C_5H_5)Ru(1,10\text{-phen})\}_2(\mu\text{-dppm})](PF_6)_2 \cdot CH_2Cl_2$ (13). A perspective view of the cation of 13 is given in Figure 1. The unit cell contents are shown in Figure 2. Selected interatomic distances and bond angles are listed in Table VII. The most salient features of the cation of 13 are (i) the very long Ru···Ru internuclear distance of 6.445 (1) Å, (ii) the relatively large P–C–P angle subtended by the bridging dppm ligand [133.1 (3)° compared to the P–C–P range of 114.4 (4)–118.7 (6)° for monodentate dppm ligands[6b,20]], and (iii) the ap-

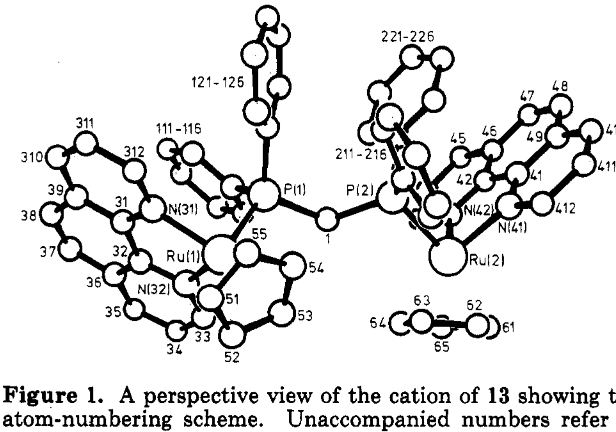

Figure 1. A perspective view of the cation of 13 showing the atom-numbering scheme. Unaccompanied numbers refer to carbon atoms.

proximate cis conformation adopted with respect to the Ru···Ru (or P···P) vector with a Ru–P···P–Ru torsion angle of 65.1 (2)°.

These features reflect an accommodation within the cation of the steric requirements of the two ruthenium atoms and their associated ligands, as well as reduced phenyl–phenyl steric interactions between rings on opposite phosphorus atoms [leaving shortest phenyl···phenyl distances of C(121)···C(212) = 3.242 (10) and C(121)···H(212) = 2.70 (1) Å] and minimized C_5H_5···C_5H_5 contacts [the shortest contact is H(53)···H(63) = 2.60 (1) Å]. It is thus apparent that it is the relatively small volume requirements of the cyclopentadienyl but most particularly of the 1,10-phenanthroline ligands which project out in sterically constrained planes from the ruthenium atom, which are largely instrumental in accommodating the dppm phosphorus atoms and their associated phenyl substituents in the coordination sphere of the ruthenium atoms. This probably accounts for the previous lack of success in preparing related complexes[10] with a single bridging dppm ligand and, further, in a more general sense, represents the first occasion on which the importance of steric constraints to single diphosphine bridge formation have been explicitly explored. The ring shielding effects are thus readily rationalized in terms of the steric congestion within the core of **13** which by necessity places one of the phenyl substituents on each phosphorus atom in a plane approximately parallel with [dihedral angle = 19.7 (6) or 12.8 (7)°], and ca. 3.4 Å above, the plane of the delocalized 1,10-phenanthroline ligand system. This is shown in more detail in Figure 3. More generally, the consistent appearance of similar effects for phenyl substituents in several other diphosphine-bridged complexes (**16–18** and **24–27**) is diagnostic of steric congestion in these systems, emphasizing the importance of steric factors in the formation and stability of the complexes described in this study and, we believe, in this class of diphosphine-bridged complexes in general.

The Reactive Intermediates $[(\eta^5\text{-}C_5H_5)Ru(diamine)(EtOH)]^+$ and $[(\eta^5\text{-}C_5H_5)Ru(diamine)(\eta^1\text{-}L_2)]^+$. $[(\eta^5\text{-}C_5H_5)Ru(1,10\text{-phen})Cl]$ dissolves in warm ethanol to give an orange solution which on treatment with NH_4PF_6 in ethanol, followed by cooling, deposits orange crystals of $[(\eta^5\text{-}C_5H_5)Ru(1,10\text{-phen})(EtOH)]PF_6$ (**20**). Visible spectroscopy confirms that the formation of the cation $[(\eta^5\text{-}C_5H_5)Ru(1,10\text{-phen})(EtOH)]^+$ from $[(\eta^5\text{-}C_5H_5)Ru(1,10\text{-phen})Cl]$ is quantitative in hot ethanol,[19] and the relatively low isolated yield of **20** (48%) is simply a reflection of the solubility of the salt in ethanol. **20** has been characterized by elemental analysis (Table I) and by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy (Tables II and III). Characteristic visible absorption bands are listed in Table V.

While it is not clear yet whether the cationic products **1–19** are not, at least in part, formed by the direct attack of nucleophile on the neutral diamine complexes $[(\eta^5\text{-}C_5H_5)Ru(diamine)Cl]$,[21] it is certain that preformed $[(\eta^5\text{-}C_5H_5)Ru(diamine)(EtOH)]Cl$ (obtained simply by reacting the neutral precursor into warm ethanol) reacts quantitatively and very rapidly with the ligands used in this study (identical mole ratios as described in (a)–(d) of the Experimental Section) to give the same products **1–19**.

We have found that the formation of solvolyzed cations of the type $[(\eta^5\text{-}C_5H_5)Ru(diamine)(solvent)]^+$ is general for a range of different solvents,[22] all of the diamine ligands we have so far utilized in our studies,[8] and a diversity of cyclopentadienyl ligands.[22] These studies will be discussed in more detail elsewhere, but it is sufficient to point out here that the cations $[(\eta^5\text{-}C_5H_5)Ru(diamine)(EtOH)]^+$ are exceptionally labile toward ligand substitution, not only by the ligands described in this study but also by a wide diversity of other systems.[9] Thus, in their reactivity patterns the cations mirror the versatile and reactive manganese(I) complex $[(\eta^5\text{-}C_5H_5)Mn(CO)_2(THF)]$ (THF = tetrahydrofuran) which has found extensive application in organometallic chemistry[23] including in the synthesis of bimetallic complexes.[24] Surprisingly though, $[(\eta^5\text{-}C_5H_5)Ru(diamine)(EtOH)]^+$ is remarkably different from $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2(MeOH)]^+$ which exists in equilibrium with $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2Cl]$ in methanol[25] and which to date has shown only limited formal synthetic potential.[25] Examination of the $\{(\eta^5\text{-}C_5H_5)Ru(1,10\text{-phen})\}$ portion of the structure of **13** (Figure 1) suggests that the differences in the reactivity of the $[(\eta^5\text{-}C_5H_5)Ru(diamine)(EtOH)]^+$ cations when compared to $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2(MeOH)]^+$ are largely steric in origin.

Treatment of $[(\eta^5\text{-}C_5H_5)Ru(1,10\text{-phen})Cl]$ with diphosphine (mole ratio 1:1) in ethanol at 0 °C gives the cations $[(\eta^5\text{-}C_5H_5)Ru(1,10\text{-phen})(\eta^1\text{-}L_2)]PF_6$ (e.g. **21**, L_2 = dppm; **22**, L_2 = dmpe; **23**, L_2 = dppp) which have been characterized by a combination of elemental analysis (Table I) and NMR spectroscopy (Tables II–IV). However, when the reactions of $[(\eta^5\text{-}C_5H_5)Ru(1,10\text{-phen})Cl]$ are carried out in boiling ethanol with excess diphosphine ligand to complex mole ratios, product mixtures are obtained. In all cases the major component is the diphosphine-bridged species $[\{(\eta^5\text{-}C_5H_5)Ru(1,10\text{-phen})\}(\mu\text{-}L_2)]^{2+}$. The minor component of the mixture, identified by $^{31}P\{^1H\}$ NMR, is $[(\eta^5\text{-}C_5H_5)Ru(1,10\text{-phen})(\eta^1\text{-}L_2)]^+$.

The controlled and facile formation of η^1-diphosphine complexes from $[(\eta^5\text{-}C_5H_5)Ru(diamine)Cl]$ complexes is noteworthy in view of the generality of the process and also in terms of the fact that under dilute conditions and at 0 °C, only the single product is found with no contamination by the thermodynamically favored bridged species. These systems thus represent the largest class of η^1-diphosphine complexes known to date.[1,2,6] Most other systems reported thus far represent ad hoc syntheses[1,2,6] which have not been generalized, and the required pendant functionality system is very often contaminated with varying quantities of the thermodynamically preferred products of the reaction, e.g., ligand-bridged or -chelated products.[2]

In support of the intermediacy of the pendant functionality complexes $[(\eta^5\text{-}C_5H_5)Ru(1,10\text{-phen})(\eta^1\text{-}L_2)]^+$ in the formation of the diphosphine-bridged cations, treatment of either $[(\eta^5\text{-}C_5H_5)Ru(1,10\text{-phen})Cl]$ or $[(\eta^5\text{-}C_5H_5)Ru(1,10\text{-phen})(EtOH)]Cl$ with a single molar equivalent of

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Table VII. Selected Bond Lengths (Å) and Angles (deg) for 13

Bond Distances

Ru(1)–P(1)	2.316 (2)	Ru(1)–N(31)	2.093 (7)	C(36)–C(37)	1.42 (2)	C(37)–C(38)	1.345 (14)
Ru(1)–N(32)	2.096 (5)	Ru(1)–C(51)	2.221 (9)	C(38)–C(39)	1.436 (12)	C(39)–C(310)	1.368 (11)
Ru(1)–C(52)	2.201 (9)	Ru(1)–C(53)	2.156 (13)	C(310)–C(311)	1.378 (14)	C(311)–C(312)	1.390 (14)
Ru(1)–C(54)	2.157 (12)	Ru(1)–C(55)	2.190 (9)	C(51)–C(52)	1.39 (2)	C(51)–C(55)	1.396 (13)
Ru(2)–P(2)	2.324 (2)	Ru(2)–N(41)	2.090 (5)	C(52)–C(53)	1.38 (2)	C(53)–C(54)	1.419 (13)
Ru(2)–N(42)	2.093 (6)	Ru(2)–C(61)	2.178 (12)	C(54)–C(55)	1.41 (2)	C(211)–C(212)	1.387 (9)
Ru(2)–C(62)	2.161 (12)	Ru(2)–C(63)	2.165 (8)	C(211)–C(216)	1.403 (11)	C(212)–C(213)	1.390 (10)
Ru(2)–C(64)	2.188 (8)	Ru(2)–C(65)	2.182 (8)	C(213)–C(214)	1.382 (14)	C(214)–C(215)	1.359 (13)
P(1)–C(1)	1.860 (8)	P(1)–C(111)	1.847 (7)	C(215)–C(216)	1.384 (10)	C(221)–C(222)	1.385 (9)
P(1)–C(121)	1.822 (6)	P(2)–C(1)	1.843 (8)	C(221)–C(226)	1.402 (11)	C(222)–C(223)	1.387 (10)
P(2)–C(211)	1.834 (6)	P(2)–C(221)	1.821 (6)	C(223)–C(224)	1.381 (14)	C(224)–C(225)	1.347 (14)
C(111)–C(112)	1.374 (9)	C(111)–C(116)	1.400 (12)	C(225)–C(226)	1.374 (11)	N(41)–C(41)	1.365 (8)
C(112)–C(113)	1.403 (13)	C(113)–C(114)	1.36 (2)	N(41)–C(412)	1.344 (10)	N(42)–C(42)	1.347 (9)
C(114)–C(115)	1.363 (13)	C(115)–C(116)	1.389 (12)	N(42)–C(43)	1.359 (10)	C(41)–C(42)	1.421 (10)
C(121)–C(122)	1.395 (10)	C(121)–C(126)	1.386 (9)	C(41)–C(49)	1.393 (10)	C(42)–C(46)	1.412 (10)
C(122)–C(123)	1.362 (10)	C(123)–C(124)	1.394 (11)	C(43)–C(44)	1.381 (14)	C(44)–C(45)	1.36 (2)
C(124)–C(125)	1.364 (14)	C(125)–C(126)	1.385 (10)	C(45)–C(46)	1.398 (14)	C(46)–C(47)	1.420 (14)
N(31)–C(31)	1.374 (9)	N(31)–C(312)	1.316 (8)	C(47)–C(48)	1.33 (2)	C(48)–C(49)	1.411 (11)
N(32)–C(32)	1.350 (11)	N(32)–C(33)	1.331 (9)	C(49)–C(410)	1.404 (12)	C(410)–C(411)	1.361 (13)
C(31)–C(32)	1.410 (10)	C(31)–C(39)	1.398 (14)	C(411)–C(412)	1.382 (11)	C(61)–C(62)	1.38 (2)
C(32)–C(36)	1.403 (10)	C(33)–C(34)	1.411 (12)	C(61)–C(65)	1.37 (2)	C(62)–C(63)	1.41 (2)
C(34)–C(35)	1.35 (2)	C(35)–C(36)	1.388 (13)	C(63)–C(64)	1.371 (13)	C(64)–C(65)	1.39 (2)

Bond Angles

P(1)–Ru(1)–N(31)	91.3 (2)	P(1)–Ru(1)–N(32)	88.6 (2)	N(31)–C(31)–C(39)	122.4 (6)	C(32)–C(31)–C(39)	121.7 (7)
N(31)–Ru(1)–N(32)	77.5 (2)	P(1)–Ru(1)–C(51)	151.1 (3)	N(32)–C(32)–C(31)	116.9 (6)	N(32)–C(32)–C(36)	122.8 (7)
N(31)–Ru(1)–C(51)	99.9 (4)	N(32)–Ru(1)–C(51)	119.8 (3)	C(31)–C(32)–C(36)	120.3 (8)	N(32)–C(33)–C(34)	121.2 (9)
P(1)–Ru(1)–C(52)	142.8 (4)	N(31)–Ru(1)–C(52)	125.9 (4)	C(33)–C(34)–C(35)	120.3 (8)	C(34)–C(35)–C(36)	119.4 (8)
N(32)–Ru(1)–C(52)	97.3 (3)	C(51)–Ru(1)–C(52)	36.6 (4)	C(32)–C(36)–C(35)	117.8 (9)	C(32)–C(36)–C(37)	117.6 (7)
P(1)–Ru(1)–C(53)	106.4 (3)	N(31)–Ru(1)–C(53)	161.7 (3)	C(35)–C(36)–C(37)	124.6 (8)	C(36)–C(37)–C(38)	122.1 (9)
N(32)–Ru(1)–C(53)	107.1 (3)	C(51)–Ru(1)–C(53)	62.2 (4)	C(37)–C(38)–C(39)	121.4 (11)	C(31)–C(39)–C(38)	116.9 (8)
C(52)–Ru(1)–C(53)	36.9 (4)	P(1)–Ru(1)–C(54)	92.3 (2)	C(31)–C(39)–C(310)	119.0 (8)	C(38)–C(39)–C(310)	124.0 (18)
N(31)–Ru(1)–C(54)	138.5 (3)	N(32)–Ru(1)–C(54)	143.8 (3)	C(39)–C(310)–C(311)	118.6 (10)	C(310)–C(311)–C(312)	119.5 (7)
C(51)–Ru(1)–C(54)	61.8 (4)	C(52)–Ru(1)–C(54)	62.0 (4)	N(31)–C(312)–C(311)	123.6 (8)	Ru(1)–C(51)–C(52)	70.9 (5)
C(53)–Ru(1)–C(54)	38.4 (4)	P(1)–Ru(1)–C(55)	114.4 (2)	Ru(1)–C(51)–C(55)	70.4 (5)	C(52)–C(51)–C(55)	108.9 (10)
N(31)–Ru(1)–C(55)	104.7 (3)	N(32)–Ru(1)–C(55)	156.6 (3)	Ru(1)–C(52)–C(51)	72.5 (6)	Ru(1)–C(52)–C(53)	69.8 (6)
C(51)–Ru(1)–C(55)	36.9 (3)	C(52)–Ru(1)–C(55)	62.1 (3)	C(51)–C(52)–C(53)	109.5 (8)	Ru(1)–C(53)–C(52)	73.4 (7)
C(53)–Ru(1)–C(55)	63.9 (4)	C(54)–Ru(1)–C(55)	37.9 (4)	Ru(1)–C(53)–C(54)	70.8 (7)	C(52)–C(53)–C(54)	106.6 (9)
P(2)–Ru(2)–N(41)	88.7 (2)	P(2)–Ru(2)–N(42)	90.0 (2)	Ru(1)–C(54)–C(53)	70.8 (7)	Ru(1)–C(54)–C(55)	72.3 (7)
N(41)–Ru(2)–N(42)	77.2 (2)	P(2)–Ru(2)–C(61)	158.7 (3)	C(53)–C(54)–C(55)	108.7 (9)	Ru(1)–C(55)–C(51)	72.7 (5)
N(41)–Ru(2)–C(61)	102.8 (4)	N(42)–Ru(2)–C(61)	109.9 (3)	Ru(1)–C(55)–C(54)	69.8 (5)	C(51)–C(55)–C(54)	106.3 (8)
P(2)–Ru(2)–C(62)	123.6 (4)	N(41)–Ru(2)–C(62)	100.5 (4)	P(2)–C(211)–C(212)	122.7 (6)	P(2)–C(211)–C(216)	118.5 (5)
N(42)–Ru(2)–C(62)	146.4 (4)	C(61)–Ru(2)–C(62)	37.2 (4)	C(212)–C(211)–C(216)	118.7 (6)	C(211)–C(212)–C(213)	120.2 (7)
P(2)–Ru(2)–C(63)	96.1 (3)	N(41)–Ru(2)–C(63)	130.2 (3)	C(212)–C(213)–C(214)	120.2 (7)	C(213)–C(214)–C(215)	120.0 (7)
N(42)–Ru(2)–C(63)	151.9 (3)	C(61)–Ru(2)–C(63)	62.8 (4)	C(214)–C(215)–C(216)	120.9 (8)	C(211)–C(216)–C(215)	119.9 (7)
C(62)–Ru(2)–C(63)	38.1 (5)	P(2)–Ru(2)–C(64)	103.1 (3)	P(2)–C(221)–C(222)	120.3 (6)	P(2)–C(221)–C(226)	119.7 (5)
N(41)–Ru(2)–C(64)	162.5 (3)	N(42)–Ru(2)–C(64)	115.2 (3)	C(222)–C(221)–C(226)	118.8 (6)	C(221)–C(222)–C(223)	120.7 (7)
C(61)–Ru(2)–C(64)	62.1 (5)	C(62)–Ru(2)–C(64)	62.2 (4)	C(222)–C(223)–C(224)	119.0 (8)	C(223)–C(224)–C(225)	120.7 (8)
C(63)–Ru(2)–C(64)	36.7 (3)	P(2)–Ru(2)–C(65)	137.1 (3)	C(224)–C(225)–C(226)	121.5 (9)	C(221)–C(226)–C(225)	119.3 (7)
N(41)–Ru(2)–C(65)	134.1 (4)	N(42)–Ru(2)–C(65)	95.9 (3)	Ru(2)–N(41)–C(41)	115.5 (5)	Ru(2)–N(41)–C(412)	127.8 (5)
C(61)–Ru(2)–C(65)	36.5 (5)	C(62)–Ru(2)–C(65)	61.2 (4)	C(41)–N(41)–C(412)	116.7 (6)	Ru(2)–N(42)–C(42)	115.4 (5)
C(63)–Ru(2)–C(65)	61.5 (3)	C(64)–Ru(2)–C(65)	37.0 (4)	Ru(2)–N(42)–C(43)	128.1 (5)	C(42)–N(42)–C(43)	116.4 (6)
Ru(1)–P(1)–C(1)	111.4 (2)	Ru(1)–P(1)–C(111)	113.8 (2)	N(41)–C(41)–C(42)	115.3 (6)	N(41)–C(41)–C(49)	124.1 (7)
C(1)–P(1)–C(111)	103.0 (3)	Ru(1)–P(1)–C(121)	116.1 (2)	C(42)–C(41)–C(49)	120.6 (6)	N(42)–C(42)–C(41)	116.6 (6)
C(1)–P(1)–C(121)	111.3 (3)	C(111)–P(1)–C(121)	100.0 (3)	N(42)–C(42)–C(46)	124.6 (7)	C(41)–C(42)–C(46)	118.8 (7)
Ru(2)–P(2)–C(1)	110.7 (2)	Ru(2)–P(2)–C(211)	116.3 (3)	N(42)–C(43)–C(44)	121.7 (8)	C(43)–C(44)–C(45)	122.0 (10)
C(1)–P(2)–C(211)	106.9 (3)	Ru(2)–P(2)–C(221)	112.6 (2)	C(44)–C(45)–C(46)	118.2 (9)	C(42)–C(46)–C(45)	117.1 (8)
C(1)–P(2)–C(221)	105.7 (4)	C(211)–P(2)–C(221)	103.9 (3)	C(42)–C(46)–C(47)	118.4 (8)	C(45)–C(46)–C(47)	124.4 (8)
P(1)–C(1)–P(2)	133.1 (3)	P(1)–C(111)–C(112)	123.3 (6)	C(46)–C(47)–C(48)	122.1 (8)	C(47)–C(48)–C(49)	121.1 (9)
P(1)–C(111)–C(116)	116.8 (5)	C(112)–C(111)–C(116)	119.6 (7)	C(41)–C(49)–C(48)	119.0 (8)	C(41)–C(49)–C(410)	117.2 (7)
C(111)–C(112)–C(113)	119.9 (9)	C(112)–C(113)–C(114)	119.7 (8)	C(48)–C(49)–C(410)	123.8 (9)	C(49)–C(410)–C(411)	118.6 (8)
C(113)–C(114)–C(115)	121.2 (9)	C(114)–C(115)–C(116)	120.3 (10)	C(410)–C(411)–C(412)	121.3 (8)	N(41)–C(412)–C(411)	122.0 (7)
C(111)–C(116)–C(115)	119.3 (7)	P(1)–C(121)–C(122)	122.2 (5)	Ru(2)–C(61)–C(62)	70.7 (7)	Ru(2)–C(61)–C(65)	71.9 (7)
P(1)–C(121)–C(126)	119. (5)	C(122)–C(121)–C(126)	117.9 (6)	C(62)–C(61)–C(65)	107.2 (12)	Ru(2)–C(62)–C(61)	72.1 (7)
C(121)–C(122)–C(123)	121.0 (6)	C(122)–C(123)–C(124)	120.5 (8)	Ru(2)–C(62)–C(63)	71.1 (6)	C(61)–C(62)–C(63)	107.9 (11)
C(123)–C(124)–C(125)	119.2 (7)	C(124)–C(125)–C(126)	120.4 (7)	Ru(2)–C(63)–C(62)	70.8 (5)	Ru(2)–C(63)–C(64)	72.6 (5)
C(121)–C(126)–C(125)	121.0 (8)	Ru(1)–N(31)–C(31)	114.6 (4)	C(62)–C(63)–C(64)	107.5 (9)	Ru(2)–C(64)–C(63)	70.7 (5)
Ru(1)–N(31)–C(312)	128.5 (6)	C(31)–N(31)–C(312)	116.8 (7)	Ru(2)–C(65)–C(61)	71.6 (6)	Ru(2)–C(65)–C(64)	71.7 (5)
Ru(1)–N(32)–C(32)	115.0 (4)	Ru(1)–N(32)–C(33)	126.5 (6)	C(61)–C(65)–C(64)	109.9 (9)		
C(32)–N(32)–C(33)	118.5 (6)	N(31)–C(31)–C(32)	115.9 (8)				

$[(\eta^5\text{-}C_5H_5)Ru(1,10\text{-phen})(\eta^1\text{-dppm})]PF_6$ in boiling ethanol rapidly gives, after the addition of NH_4PF_6, the expected product $[\{(\eta^5\text{-}C_5H_5)Ru(1,10\text{-phen})\}_2(\mu\text{-dppm})](PF_6)_2$ in quantitative yield. Thus the formation of the ligand-bridged diruthenium cations is to be generally interpreted in terms of the interaction between solvolyzed ruthenium cations (as the receptor systems) and η^1-diphosphine complexes which provide the pendant functionality.

The Systematic Synthesis of Unsymmetrical Bridged Diruthenium Cations. The isolation of both

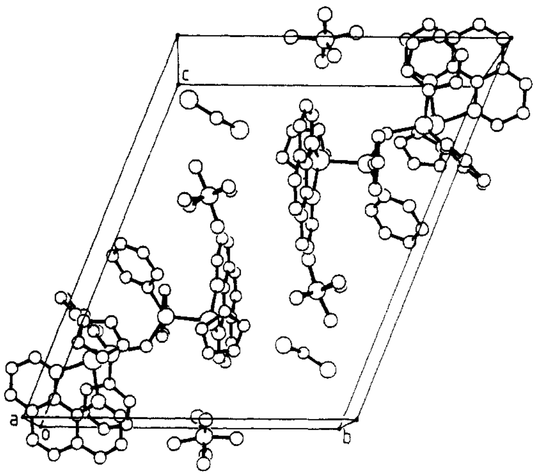

Figure 2. The unit cell of **13** viewed perpendicular to the *b*–*c* plane.

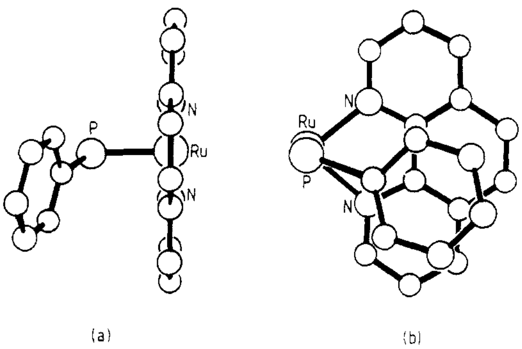

Figure 3. Views of part of the cation of **13** showing the relative dispositions of the phenanthroline (phen) ligand [N(31), N(32), C(31)–C(312)] and the phenyl group [C(111)–C(116)]: (a) viewed parallel with the plane of the phen ligand; (b) viewed perpendicular to the phen ligand. The relative dispositions of the phen ligand [N(41), N(42), C(41)–C(412)] and the phenyl group [C(221)–C(226)] are essentially similar.

reactive intermediates in the formation of the complexes $[\{(\eta^5\text{-}C_5H_5)Ru(1,10\text{-phen})\}_2(\mu\text{-}L_2)](PF_6)_2$ (**12**–**18**), and the fact that both of these can be obtained in high yield, has prompted us to explore the applicability of $[(\eta^5\text{-}C_5H_5)Ru(diamine)(EtOH)]^+$ and $[(\eta^5\text{-}C_5H_5)Ru(diamine)(\eta^1\text{-}L_2)]^+$ to the synthesis of first, unsymmetrical diruthenium cations containing diamine and cyclopentadienyl ligands and second, unsymmetrical diruthenium cations obtained by using the solvolyzed ruthenium cations as receptors for dppm functionality of a more general and sterically congested kind.

Treatment of $[(\eta^5\text{-}C_5H_5)Ru(2,2'\text{-bpy})Cl]$ in ethanol with a single molar equivalent of $[(\eta^5\text{-}C_5H_5)Ru(1,10\text{-phen})(\eta^1\text{-dppm})]PF_6$ or $[(\eta^5\text{-}C_5H_5)Ru(1,10\text{-phen})(\eta^1\text{-dppp})]PF_6$ in ethanol at 80 °C gives after cooling and the addition of NH_4PF_6, quantitative yields of the unsymmetrical, mixed diamine complexes $[\{(\eta^5\text{-}C_5H_5)Ru(1,10\text{-phen})\}\{(\eta^5\text{-}C_5H_5)Ru(2,2'\text{-bpy})\}(\mu\text{-}L_2)](PF_6)_2$ (**24**, L_2 = dppm; **25**, L_2 = dppp). Both **24** and **25** have been completely characterized by elemental analysis (Table I) and by NMR spectroscopy (Tables II–IV). In particular the $^{31}P\{^1H\}$ NMR spectra display the expected two resonances in the regions of the spectrum associated with similar coordinated phosphine ligands.

Similar treatment of $[(\eta^5\text{-}C_5H_5)Ru(1,10\text{-phen})(EtOH)]^+$ with the known complexes $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)(\eta^1\text{-dppm})Cl]$[10] and $[(\eta^5\text{-}C_5H_5)Ru(dppm)(\eta^1\text{-dppm})]PF_6$[10] gives within minutes in boiling ethanol and after the addition of NH_4PF_6, high yields of the salts $[\{(\eta^5\text{-}C_5H_5)Ru(PPh_3)Cl\}\{(\eta^5\text{-}C_5H_5)Ru(1,10\text{-phen})\}(\mu\text{-dppm})]PF_6$ (**26**) and $[\{(\eta^5\text{-}C_5H_5)Ru(dppm)\}\{(\eta^5\text{-}C_5H_5)Ru(1,10\text{-phen})\}(\mu\text{-dppm})](PF_6)_2$ (**27**), respectively. Both **26** and **27** are obtained as crystalline, orange solids, air-stable in the solid state as well as in solution for indefinite periods. Recrystallization is readily achieved from either dichloromethane– or acetone–ethanol mixtures.

Elemental analysis (Table I) as well as ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopy (Tables II–IV) are entirely consistent with the formulation of **26** and **27** as diruthenium complexes containing single dppm bridges. In common with **13** and **16**–**18**, the ^1H NMR spectra of **26** and **27** each show corresponding significant high-field chemical shifts of certain of the μ-dppm phenyl protons, suggesting that these complexes show similar steric congestion at the metal centers.

It is interesting to contrast here these results for the preparation of **26** and **27** with the observations reported by Bruce and co-workers[10] concerning the reactivity of the η^1-dppm system $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)(\eta^1\text{-dppm})Cl]$. These authors were thwarted in their attempts to obtain bimetallic systems (using as the dppm receptors the complexes $[Fe_2(CO)_9]$, $[\{RhCl(CO)_2\}_2]$, $[Ru_3(CO)_{12}]$, and $[PdCl_2(NCPh)_2]$) by the facile transfer of triphenylphosphine from $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)(\eta^1\text{-dppm})Cl]$ to the second metal atom, followed by chelated dppm formation giving as the cyclopentadienyl–ruthenium-containing product $[(\eta^5\text{-}C_5H_5)Ru(dppm)Cl]$. It is also interesting to note that a second reaction pathway reported[10] for $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)(\eta^1\text{-dppm})Cl]$, namely, rapid chloride expulsion in polar solvents giving $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)(dppm)]Cl$, also does not occur in our systems. These differences serve to testify to the effectiveness of the $[(\eta^5\text{-}C_5H_5)Ru(diamine)(EtOH)]^+$ cation as a receptor system for pendant functionality, especially when it is considered that three of the receptor systems investigated previously,[10] $[Fe_2(CO)_9]$ [source of the reactive 16-electron fragment $Fe(CO)_4$], $[\{RhCl(CO)_2\}_2]$, and $[PdCl_2(NCPh)_2]$, are traditionally successfully employed in the role of pendant functionality receptors.

With regard to $[(\eta^5\text{-}C_5H_5)Ru(dppm)(\eta^1\text{-dppm})]PF_6$,[10] we are unaware that any previous attempts have been made to synthesize bimetallic complexes utilizing this complex as a provider of pendant functionality. In this regard though, we would expect that steric factors may play an even more important role than in the corresponding reactions of $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)(\eta^1\text{-dppm})Cl]$ and that for any attempts to be successful, the steric requirements of the receptor systems should reasonably approximate those of the fragment utilized in this study, $\{(\eta^5\text{-}C_5H_5)Ru(1,10\text{-phen})\}$.

Conclusions

The lability of the chloro ligand in $[(\eta^5\text{-}C_5H_5)Ru(diamine)Cl]$ and of the ethanol ligand in $[(\eta^5\text{-}C_5H_5)Ru(diamine)(EtOH)]^+$, in conjunction with the modest steric demands of the cyclopentadienyl and diamine ligands within the coordination sphere of the ruthenium atom, underlies a remarkable pattern of reactivity which has been illustrated here in terms of novel, rational synthetic routes to symmetrical and unsymmetrical diruthenium complexes. Further implications of this pattern of reactivity will, however, be discussed elsewhere.

Registry No. **1**, 108970-20-3; **2**, 100412-74-6; **3**, 108970-22-5; **4**, 108970-24-7; **5**, 108970-26-9; **6**, 108970-28-1; **7**, 108970-30-5; **8**, 108970-32-7; **9**, 108970-34-9; **10**, 108970-36-1; **11**, 108970-38-3; **12**, 108970-40-7; **13**, 108970-42-9; **14**, 108970-44-1; **15**, 108970-46-3; **16**, 108970-48-5; **17**, 109011-10-1; **18**, 108970-50-9; **19**, 108970-52-1; **20**, 108970-54-3; **21**, 108970-56-5; **22**, 108970-58-7; **23**, 108970-60-1;

24, 108970-62-3; **25**, 108970-64-5; **26**, 108970-66-7; **27**, 108970-68-9; (η^5-C_5H_5)Ru(1,10-phen)Cl, 108970-69-0; (η^5-C_5H_5)Ru(5-NO_2-1,10-phen)Cl, 108970-70-3; (η^5-C_5H_5)Ru(4,4′-Me_2-2,2′-bpy)Cl, 108970-71-4; (η^5-C_5H_5)Ru(PPh_3)(η^1-dppm)Cl, 89298-92-0; [(η^5-C_5H_5)Ru(dppm)(η^1-dppm)]PF_6, 89298-97-5.

Supplementary Material Available: Tables of thermal parameters, hydrogen atom coordinates, and bond lengths, and angles (12 pages); a listing of observed and calculated structure factors (45 pages). Ordering information is given on any current masthead page.

Ring Opening of Three-Membered Heterocycles by Terminal Phosphinidene Complexes

Angela Marinetti and François Mathey*

Laboratoire de Chimie du Phosphore et des Métaux de Transition DCPH-Ecole Polytechnique, 91128 Palaiseau Cedex, France

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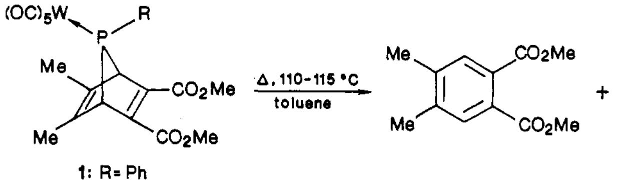
(Phenylphosphinidene)pentacarbonyltungsten as produced by thermal decomposition of the appropriate 7-phosphanorbornadiene complex reacts with phenyloxirane to give (2,4-diphenyl-1,3,2-dioxaphospholane)- and (1,2-diphenylphosphirane)pentacarbonyltungsten complexes. Their formation is explained by the insertion of the phosphinidene into the oxirane ring giving a transient 1,2-oxaphosphetane, which then undergoes a [2 + 2] cycloreversion. With 1-*tert*-butyl-2-phenylaziridine, the same insertion takes place but the isomeric 1,2-azaphosphetane complexes thus formed are thermally stable. With *trans*-2,3-diphenylthiirane, decomposition into stilbene and formation of phosphirane complexes take place in lieu of the expected insertion.

Two theoretical studies of [HP=Cr(CO)$_5$] are available at the moment.[1,2] Even though their results are somewhat different, both studies agree to predict that the phosphorus atom of this type of terminal phosphinidene complex will behave as a strong electrophilic center both in charge- and frontier-orbital-controlled reactions. A striking experimental confirmation of this electrophilicity has been provided inter alia by the recently discovered insertion of terminal phosphinidene complexes into the C–H bonds of ferrocene.[3]

On the other hand, classical three-membered heterocycles such as oxirane, thiiranes, and aziridines are well-known to open rings by reaction with electrophiles. This kind of considerations prompted us to study the reactions of terminal phosphinidene complexes with some representative examples of these heterocycles. We describe here the results of this study.

Results and Discussion

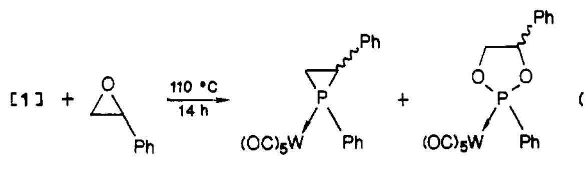
All our experiments have been carried out with the transient (phenylphosphinidene)- and (methylphosphinidene)pentacarbonyltungsten complexes [RP=W(CO)$_5$] which have been produced by thermal decomposition of the appropriate 7-phosphanorbornadiene complexes as described previously[4] (eq 1). We have first investigated the reaction of **1** with phenyloxirane (eq 2).



1: R = Ph
2: R = Me

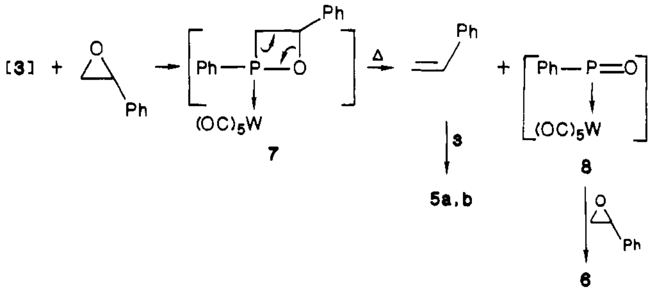
$\cdot$[RP=W(CO)$_5$] (1)

3: R = Ph
4: R = Me



5a,**b** **6** (2)

The main products of this reaction are the two already known isomeric phosphirane complexes **5a**,**b**,[5] formally resulting from the condensation of **3** with styrene[5] and mainly characterized by their typical ^{31}P NMR resonances at high fields[5] together with several isomers of **6**, the most abundant of which has been obtained in the pure state and fully analyzed. The formation of these two series of products can be rationalized by the mechanism outlined in eq 3. The initial ring insertion leading to **7** would be followed by a Wittig-like [2 + 2] cycloreversion giving styrene and the phenylphosphinidene oxide complex **8**. Even when the reaction is monitored by ^{31}P NMR, we have never been able to observe the appearance of **8** in the reaction mixture. Contrary to a bulky substituted aminophosphinidene oxide Cr(CO)$_5$ complex described by Niecke,[6] **8** is probably highly unstable and immediately cycloadds onto another molecule of phenyloxirane to give the dioxaphospholane complex **6**. Phosphirane complexes **5a**,**b** would be simultaneously formed through the already



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