Syntheses and Properties of Ruthenium(II) Complexes with *o*-Quinodiimine Ligands. Crystal and Molecular Structure of Ru(bpy)₂(C₆H₄(NH)₂)(PF₆)₂

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The syntheses of four complexes of Ru(II) with bipyridyl and *o*-quinodiimine ligands are described. These ligands are derived from the aromatic *o*-diamines 1,2-diaminobenzene, 1,2-diaminonaphthalene, and 9,10-diaminophenanthrene. Electrochemically, these complexes are reduced at less negative potentials than Ru(bpy)₃²⁺, whereas the oxidation to the +3 state is little affected by the replacement of bipyridyl by one *o*-quinodiimine ligand. The metal to ligand charge-transfer absorption bands in the visible spectra are strongly shifted to longer wavelengths. The crystal and molecular structure of Ru(bpy)₂(*o*-quinodiimine)(PF₆)₂ is reported: space group $P2_1/n$, $a = 15.957$ (5) Å, $b = 19.205$ (7) Å, $c = 9.522$ (4) Å, $\beta = 92.108$ (2)°, $Z = 4$, and $d = 1.832$ g cm⁻³. The bond lengths in the diimine ligand show clearly quinoid character.

Introduction

There has been considerable interest exhibited in the complex Ru(bpy)₃²⁺ in recent years because of its almost unique combination of spectral, photochemical, and reduction/oxidation properties.[1] The behavior of this complex is principally determined by the existence of relatively low-lying π^* orbitals of the bipyridyl ligands, which cause a stabilization of the +2 oxidation state by back-bonding, as compared to simple amine ligands which stabilize the +3 oxidation state of ruthenium. The π^* orbitals are, at the same time, responsible for the low-energy (22 400 cm⁻¹) MLCT absorption band and for the long-lived emissive ³CT state which lies 16 470 cm⁻¹ above the ground state. In an attempt to modify the properties of this complex, a series of ruthenium compounds containing ligands derived from bipyridyl[2] have been described recently. In this paper, the series of complexes was extended to species containing ligands which can be formulated as *o*-quinodiimines. They can be represented by the structures **1–3** (as a general abbreviation for **1–3**, qH₂ will be used).
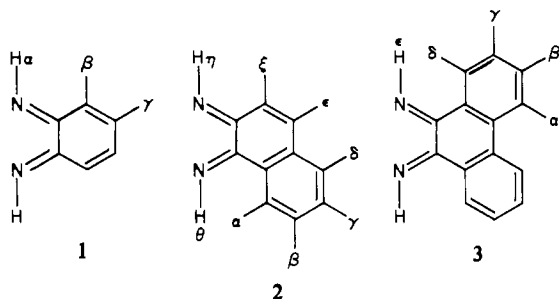
Experimental Part

Syntheses. Substances: 9,10-Phenanthroquinone, 1,2-diaminobenzene, 1,2-diaminonaphthalene, 2,2′-bipyridyl, and RuCl₃·3H₂O were purchased from Fluka AG Buchs and used without further purification. Ru(bpy)₂Cl₂·2H₂O,[3] Ru(bpy)Cl₃·H₂O,[4] and 9,10-diaminophenanthrene hydrochloride[5] were synthesized according to literature procedures.

Ruthenium Complexes. Ru(bpy)₂(1)(PF₆)₂. A 0.615-mmol sample of Ru(bpy)₂Cl₂·2H₂O and a stoichiometric amount of 1,2-diaminobenzene were dispersed into 8 mL of water and heated under argon

for 2 h at 100 °C. To the cold solution was added 50 mL of water and 1 mL of concentrated ammonia, and the resulting solution was vigorously stirred for 16 h in an open beaker. The hexafluorophosphate was then precipitated by adding approximately a 3-fold excess of NH₄PF₆ (10% hydrous solution). The precipitate was dissolved in acetone and chromatographed once on a Al₂O₃ column (ϕ 1 cm, 15 cm long): red-brown crystals with a golden reflection (230 mg, 46.2%); IR (KBr pellets) 3290 (m) (=N—H), 3080 (w) (aromatic H), 1600 (m) (aromatic), 1518 (m), 1461 (m), 1444 (s), 1421 (w), 1380 (w), 1313 (w), 1240 (w), 1220 (w), 1160 (w), 1123 (w), 1070 (w), 1048 (w), 830 (s, br) (PF₆⁻), 760 (s), 738 (m), 728 (m), 647 (w), 619 (m), 558 (s) (PF₆⁻), 438 (w), 342 (w) cm⁻¹; ¹H NMR (CD₃COCD₃, 25 °C) δ 8.78 (d, 4 H$_{\delta,bpy}$, $J = 8.1$ Hz), 8.23 (t, 4 H$_{\gamma,bpy}$, $J = 8.1$ Hz), 7.98 (d, 2 H$_{\alpha(outside),bpy}$, $J = 5.5$ Hz), 7.87 (d, 2 H$_{\alpha(inside),bpy}$, $J = 5.5$ Hz), 7.7 (t, 2 H$_{\beta(outside),bpy}$, $J = 6$ Hz), 7.62 (t, 2 H$_{\beta(inside),bpy}$, $J = 6$ Hz), 7.3 (d, 2 H$_{\gamma,1}$, $J = 6.6$ Hz), 7.13 (s, 2 H$_{\alpha,1}$), 705 (d, 2 H$_{\beta,1}$, $J = 6.6$ Hz). Anal. Calcd for C₂₆H₂₂F₁₂N₆P₂Ru: C, 38.58; H, 2.74; N, 10.38; Ru, 12.49. Found: C, 38.31; H, 2.71; N, 10.44; Ru, 12.21.

Ru(bpy)(1)₂(PF₆)₂. For 1 h, 1.25 mmol Ru(bpy) Cl₃·3H₂O and 3.75 mmol 1,2-diaminobenzene in 16 mL of water were refluxed under argon. During this time, three portions of 20 mg of zinc each were added. After the solution had reached room temperature, 1 mL of concentrated ammonia was added and the solution was stirred in a open breaker for 16 h. Ru(bpy)(1)₂(PF₆)₂ was crystallized in the same manner as Ru(bpy)₂(1)(PF₆)₂: violet crystals (300 mg, 32.2%); IR (KBr pellets) 3400 (m, br), 3280 (s) (=N—H), 3050 (m) (aromatic H), 1642 (m), 1598 (m) (aromatic), 1517 (s), 1445 (s), 1367 (s), 1309 (w), 1235 (w), 1212 (w), 1153 (m), 1123 (w), 1100 (w), 1067 (w), 1042 (w), 967 (w), 830 (s, br) (PF₆⁻), 760 (s), 735 (m), 722 (m), 642 (w), 615 (m), 595 (m), 553 (s) (PF₆⁻) cm⁻¹; ¹H NMR (CD₃CN, 25 °C) δ 8.45 (d, 2 H$_{\delta,bpy}$, $J = 7.8$ Hz), 8.16 (t, 2 H$_{\gamma,bpy}$, $J = 8.4$ Hz), 8.09 (d, 2 H$_{\alpha,bpy}$, $J = 5.1$ Hz), 7.62 (t, 2 H$_{\beta,bpy}$, $J = 6.6$ Hz), 7.06 (br s, 8 H$_{\beta+\gamma,1}$). Anal. Calcd for C₂₂H₂₀F₁₂N₆P₂Ru: C, 34.79; H, 2.65; N, 11.07; Ru, 13.13. Found: C, 34.89; H, 2.70; N, 11.05; Ru, 13.63.

Ru(bpy)₂(2)(PF₆)₂ was synthesized in an analogous way as Ru(bpy)₂(1)(PF₆)₂: red-brown crystals (153 mg, 46.3%); IR (KBr pellets) 3640 (m), 3400 (m), 3290 (m) (=N—H), 3090 (m), (aromatic H), 1608 (s) (aromatic), 1558 (w), 1470 (s), 1450 (s), 1432 (s), 1395 (m), 1345 (w), 1318 (m), 1288 (w), 1249 (w), 1222 (w), 1168 (w), 1150 (w), 1129 (w), 1115 (w), 1075 (w), 1055 (w), 1043 (w), 830 (s, br) (PF₆⁻), 766 (s), 735 (m), 695 (w), 675 (w), 665 (w), 650 (w), 612 (m) cm⁻¹; ¹H NMR (CD₃CN, 25 °C) δ 8.55 (d, 4 H$_{\delta,bpy}$, $J = 8.4$ Hz), 8.40 (t, 1 H$_{\gamma,2}$, $J = 3.6$ Hz), 8.17 (t, 4 H$_{\gamma,bpy}$, $J = 7.8$ Hz), 8.11 (t, 1 H$_{\beta,2}$, $J = 7.5$ Hz), 7.88 (d, 2 H$_{\epsilon+\zeta,2}$, $J = 5.7$ Hz), 7.78–7.4 (m, 6 H$_{\beta,bpy, and \alpha+\delta,2}$), 7.6 (d, 4 H$_{\alpha,bpy}$, $J = 8.1$ Hz), 7.42 (d, 1 H$_{\eta,2}$, $J = 9.3$ Hz), 7.1 (d, 1 H$_{\theta,2}$, $J = 9.6$ Hz). Anal. Calcd for C₃₀H₂₄F₁₂N₆P₂Ru: C, 41.92; H, 2.81; N, 9.78; Ru, 11.76. Found: C, 41.41; H, 2.77; N, 9.72; Ru, 11.71.

Ru(bpy)₂(3)(PF₆)₂: To 1.33 mmol of 9,10-diaminophenanthrene hydrochloride in 10 mL of water were added 2.3 mL of 0.1 M NaOH and then 0.38 mmol of Ru(bpy)₂Cl₂·2H₂O. After the reaction mixture refluxed for 2 h under argon, 1 mL of concentrated ammonia was added to the cold solution which was then stirred for 16 h in an open beaker. Ru(bpy)₂(3)(PF₆)₂ was crystallized in the same manner as

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Table I. Positional and Thermal Parameters of the Nonhydrogen Atoms and Their Standard Deviations[a]

atom[b]	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
				Cation					
Ru	0.4537 (1)	0.2800 (1)	0.0728 (1)	0.0243 (1)	0.0212 (1)	0.0263 (1)	−0.0014 (1)	0.0012 (1)	−0.0030 (1)
N(1)	0.3274 (5)	0.2904 (4)	0.0905 (8)	0.0321 (4)	0.0255 (5)	0.0358 (5)	−0.0018 (4)	0.0026 (4)	−0.0037 (4)
N(2)	0.4466 (5)	0.3296 (4)	0.2548 (8)	0.0279 (4)	0.0285 (5)	0.0348 (5)	−0.0024 (4)	−0.0002 (4)	−0.0008 (4)
N(3)	0.4376 (4)	0.1790 (4)	0.1478 (7)	0.0287 (4)	0.0281 (5)	0.0251 (4)	−0.0054 (4)	0.0093 (3)	−0.0011 (4)
N(4)	0.4590 (4)	0.2209 (4)	−0.1103 (8)	0.0240 (4)	0.0303 (4)	0.0375 (5)	−0.0059 (4)	0.0046 (3)	0.0030 (4)
N(5)	0.5842 (4)	0.2847 (4)	0.0781 (8)	0.0314 (4)	0.0286 (4)	0.0315 (4)	−0.0108 (4)	0.0045 (3)	0.0044 (4)
N(6)	0.4742 (5)	0.3711 (4)	−0.0335 (8)	0.0394 (5)	0.0251 (4)	0.0269 (4)	−0.0084 (4)	0.0042 (4)	−0.0040 (4)
C(1)	0.3028 (5)	0.3199 (5)	0.2043 (10)	0.0205 (5)	0.0267 (5)	0.0366 (6)	0.0116 (5)	0.0057 (4)	0.0000 (4)
C(2)	0.2181 (6)	0.3299 (6)	0.2434 (12)	0.0451 (7)	0.0455 (7)	0.0472 (7)	0.0182 (6)	−0.0010 (6)	0.0031 (5)
C(3)	0.2033 (7)	0.3643 (7)	0.3637 (13)	0.0487 (7)	0.0586 (8)	0.0564 (8)	0.0101 (7)	0.0091 (6)	0.0045 (6)
C(4)	0.2690 (8)	0.3917 (6)	0.4516 (12)	0.0605 (8)	0.0421 (7)	0.0582 (8)	0.0026 (6)	0.0224 (7)	0.0089 (6)
C(5)	0.3515 (7)	0.3825 (6)	0.4231 (11)	0.0641 (8)	0.0373 (7)	0.0412 (7)	−0.0073 (5)	0.0082 (6)	0.0010 (6)
C(6)	0.3693 (6)	0.3444 (5)	0.2964 (9)	0.0504 (7)	0.0195 (5)	0.0280 (5)	0.0019 (4)	0.0043 (5)	0.0020 (5)
C(7)	0.4198 (6)	0.1639 (5)	0.2812 (10)	0.0343 (6)	0.0403 (6)	0.0376 (6)	0.0053 (5)	0.0063 (5)	0.0050 (5)
C(8)	0.3946 (6)	0.0977 (5)	0.3200 (11)	0.0281 (5)	0.0433 (6)	0.0514 (7)	0.0136 (6)	0.0012 (5)	0.0032 (5)
C(9)	0.3854 (6)	0.0460 (5)	0.2179 (11)	0.0420 (6)	0.0368 (6)	0.0496 (7)	0.0130 (6)	0.0126 (5)	−0.0025 (5)
C(10)	0.4034 (6)	0.0615 (5)	0.0803 (11)	0.0343 (6)	0.0265 (6)	0.0587 (7)	−0.0014 (5)	0.0004 (5)	−0.0014 (5)
C(11)	0.4293 (5)	0.1284 (4)	0.0475 (10)	0.0259 (5)	0.0106 (5)	0.0514 (6)	−0.0087 (4)	−0.0060 (4)	−0.0111 (4)
C(12)	0.4498 (6)	0.1506 (5)	−0.0933 (9)	0.0305 (5)	0.0326 (5)	0.0292 (5)	−0.0102 (4)	0.0002 (4)	0.0006 (4)
C(13)	0.4648 (6)	0.1036 (5)	−0.2010 (10)	0.0299 (5)	0.0434 (6)	0.0409 (6)	−0.0105 (5)	−0.0038 (5)	−0.0017 (5)
C(14)	0.4899 (6)	0.1290 (6)	−0.3298 (11)	0.0298 (6)	0.0593 (7)	0.0454 (7)	−0.0081 (6)	0.0036 (5)	−0.0024 (5)
C(15)	0.4967 (6)	0.2005 (6)	−0.3472 (10)	0.0397 (6)	0.0446 (7)	0.0415 (6)	−0.0135 (5)	−0.0012 (5)	−0.0080 (5)
C(16)	0.4796 (6)	0.2453 (5)	−0.2364 (9)	0.0303 (5)	0.0387 (6)	0.0311 (6)	−0.0001 (5)	−0.0016 (4)	−0.0058 (4)
C(17)	0.6357 (6)	0.2397 (5)	0.1491 (10)	0.0305 (6)	0.0500 (7)	0.0351 (6)	−0.0071 (5)	−0.0058 (4)	0.0106 (5)
C(18)	0.7233 (7)	0.2519 (6)	0.1560 (12)	0.0462 (7)	0.0594 (8)	0.0538 (7)	−0.0035 (6)	0.0005 (6)	0.0065 (6)
C(19)	0.7546 (7)	0.3091 (7)	0.0910 (14)	0.0429 (7)	0.0812 (10)	0.0729 (9)	−0.0021 (8)	0.0068 (6)	−0.0111 (7)
C(20)	0.7017 (6)	0.3548 (6)	0.0194 (13)	0.0286 (6)	0.0601 (8)	0.0758 (8)	−0.0045 (7)	0.0082 (6)	−0.0041 (6)
C(21)	0.6176 (6)	0.3424 (5)	0.0143 (10)	0.0510 (6)	0.0351 (6)	0.0319 (6)	−0.0077 (5)	0.0102 (5)	−0.0093 (5)
C(22)	0.5566 (6)	0.3872 (5)	−0.0556 (10)	0.0393 (6)	0.0254 (5)	0.0377 (6)	−0.0003 (5)	0.0038 (5)	−0.0033 (5)
C(23)	0.5773 (7)	0.4433 (5)	−0.1407 (11)	0.0711 (8)	0.0252 (6)	0.0475 (7)	−0.0021 (5)	0.0093 (6)	−0.0121 (6)
C(24)	0.5113 (9)	0.4819 (6)	−0.2041 (12)	0.1007 (11)	0.0253 (6)	0.0529 (8)	0.0056 (6)	0.0129 (7)	−0.0013 (7)
C(25)	0.4277 (8)	0.4660 (5)	−0.1806 (12)	0.0768 (9)	0.0310 (6)	0.0521 (7)	−0.0027 (5)	0.0108 (6)	0.0015 (6)
C(26)	0.4105 (7)	0.4104 (5)	−0.0934 (11)	0.0558 (7)	0.0227 (6)	0.0548 (7)	0.0033 (5)	−0.0103 (6)	−0.0025 (5)
				Anions					
P(1)	0.6506 (2)	0.3656 (2)	0.5001 (3)	0.0490 (2)	0.0455 (2)	0.0487 (2)	−0.0059 (1)	−0.0081 (1)	0.0009 (1)
F(1)	0.1324 (8)	0.2131 (4)	0.9583 (9)	0.2460 (12)	0.0550 (5)	0.0912 (6)	0.0172 (5)	0.0451 (7)	0.0427 (7)
F(2)	0.1212 (5)	0.1155 (4)	0.8451 (7)	0.0891 (5)	0.0829 (6)	0.0666 (5)	−0.0199 (4)	−0.0085 (4)	−0.0083 (4)
F(3)	0.1670 (8)	0.0595 (4)	1.0428 (12)	0.2230 (12)	0.0572 (5)	0.1526 (9)	0.0371 (6)	−0.0002 (9)	0.0341 (7)
F(4)	0.1770 (7)	0.1563 (6)	0.1544 (8)	0.1815 (10)	0.1568 (9)	0.0554 (5)	0.0025 (6)	−0.0237 (6)	−0.0550 (8)
F(5)	0.0572 (5)	0.1291 (6)	1.0464 (10)	0.0661 (5)	0.2045 (11)	0.1085 (7)	0.0390 (7)	0.0214 (5)	0.0014 (6)
F(6)	0.2421 (5)	0.1479 (6)	0.9547 (10)	0.0520 (5)	0.2061 (11)	0.1083 (7)	0.0242 (7)	−0.0039 (5)	−0.0162 (6)
P(2)	0.6592 (2)	0.0564 (2)	0.3650 (3)	0.0495 (2)	0.0417 (2)	0.0389 (2)	0.0018 (1)	0.0050 (1)	−0.0096 (1)
F(7)	0.6920 (5)	−0.0156 (4)	0.3145 (10)	0.1068 (7)	0.0862 (6)	0.1324 (8)	−0.0331 (6)	−0.0209 (6)	0.0545 (5)
F(8)	0.7139 (5)	0.0470 (4)	0.5066 (7)	0.1120 (6)	0.0992 (6)	0.0574 (5)	0.0249 (4)	−0.0267 (4)	−0.0377 (5)
F(9)	0.5817 (5)	0.0179 (4)	0.4286 (8)	0.0724 (5)	0.0782 (5)	0.1009 (6)	0.0264 (5)	0.0176 (4)	−0.0165 (4)
F(10)	0.6197 (6)	0.1278 (4)	0.4141 (8)	0.1552 (8)	0.0480 (4)	0.0875 (6)	−0.0202 (4)	0.0261 (5)	−0.0031 (5)
F(11)	0.7331 (4)	0.0968 (5)	0.2983 (8)	0.0521 (4)	0.1627 (8)	0.0879 (6)	0.0450 (6)	−0.0036 (4)	−0.0458 (5)
F(12)	0.6064 (4)	0.0656 (4)	0.2212 (7)	0.0710 (4)	0.0676 (5)	0.0580 (4)	0.0003 (4)	−0.0117 (4)	−0.0050 (4)

[a] The temperature factors are of the form $T = \exp[-2\pi^2(U_{11}h^2a^{*2} + [-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + U_{12}hk2a^*b^* + U_{13}hl2a^*c^* + U_{23}kl2b^*c^*)] + 2U_{12}hka^*b^*)]$. [b] The numbering is that of Figure 2.

Table II. Positional Parameters Assigned to Selected H Atoms

	H atom	x	y	z
N(1)	HN(1)	0.2812	0.2808	0.0332
N(2)	HN(2)	0.4954	0.3545	0.3101
C(2)	HC(2)	0.1789	0.3151	0.2026
C(3)	HC(3)	0.1446	0.3618	0.4055
C(4)	HC(4)	0.2464	0.4123	0.5239
C(5)	HC(5)	0.4046	0.4032	0.4839

Ru(bpy)$_2$(1)(PF$_6$)$_2$: red-brown crystals (180 mg, 51.5%); IR (KBr pellets) 3630 (m), 3400 (m), 3295 (s) (=N—H), 3080 (m) (aromatic H), 1598 (s) (aromatic), 1493 (m), 1463 (s), 1442 (s), 1402 (s), 1315 (m), 1260 (w), 1240 (m), 1160 (m), 1120 (m), 1070 (w), 1046 (w), 1035 (w), 830 (s, br) (PF$_6^-$), 760 (s), 728 (s), 712 (w), 646 (w), 612 (m), 555 (s) (PF$_6^-$), 423 (m) cm^{-1}; ^{1}H NMR (CD$_3$CN, 25 °C) δ 8.53 (d, 4 H$_{\delta,bpy}$, J = 8.1 Hz), 8.42 (d, 4 H$_{\alpha,bpy}$, J = 7.8 Hz), 8.12 (t, 4 H$_{\gamma,bpy}$, J = 7.5 Hz), 7.93 (d, 2 H$_{\alpha,3}$, J = 5.1 Hz), 7.88–7.58 (m, 6 H$_{\beta,\gamma,\delta,3}$), 7.48 (t, 4 H$_{\beta,bpy}$, J = 8 Hz). Anal. Calcd for C$_{34}$H$_{26}$F$_{12}$N$_6$P$_2$Ru: C, 44.90; H, 2.88; N, 9.24; Ru, 11.11. Found: C, 44.48; H, 2.93; N, 8.93; Ru, 10.91.

Physical Measurements. Infrared spectra were obtained on a Perkin-Elmer 457 spectrophotometer. Proton NMR spectra (90 MHz) were recorded on a Varian EM-390 spectrometer. UV–visible spectra were obtained on a Perkin-Elmer 555 instrument. Electrochemical measurements were carried out by using a Polarecord E 506 Metrohm, a VA-Scanner E 612 Metrohm, and a X-Y recorder Hewlett-Packard 7044 A. Cyclic voltammograms were obtained by using a platinum working electrode, platinum counterelectrode, and a Ag/0.01 M AgNO$_3$ reference electrode. Solutions of the complexes (0.001 M) contained TBAP (0.1 M)[6] in CH$_3$CN.[7]

Crystal Data and Data Collection. Preliminary Weissenberg photographs indicated crystals of the monoclinic space group $P2_1/n$. Final unit cell parameters, obtained from accurate centring of 24 strong independent reflections, yielded $a = 15.957$ (5) Å, $b = 19.205$ (7) Å, $c = 9.592$ (4) Å, and $\beta = 92.108$ (2)°. The calculated density of 1.831 g cm^{-3} for four formula units per cell is in good agreement with the observed density of 1.832 g cm^{-3} determined by flotation

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Table III. Bond Distances and Selected Bond Angles in the Cation[a]

atoms	dist, Å	atoms	dist, Å
N(1)-Ru	2.038 (7)	N(4)-C(12)	1.369 (12)
N(2)-Ru	1.996 (8)	C(12)-C(13)	1.398 (13)
N(3)-Ru	2.087 (7)	C(13)-C(14)	1.400 (15)
N(4)-Ru	2.095 (8)	C(14)-C(15)	1.389 (15)
N(5)-Ru	2.084 (8)	C(15)-C(16)	1.401 (14)
N(6)-Ru	2.058 (8)	N(4)-C(16)	1.348 (12)
N(1)-C(1)	1.303 (12)	N(5)-C(17)	1.358 (12)
C(1)-C(2)	1.428 (14)	C(17)-C(18)	1.418 (14)
C(2)-C(3)	1.358 (17)	C(18)-C(19)	1.366 (18)
C(3)-C(4)	1.422 (17)	C(19)-C(20)	1.383 (17)
C(4)-C(5)	1.365 (17)	C(20)-C(21)	1.362 (14)
C(5)-C(6)	1.456 (14)	N(5)-C(21)	1.383 (12)
C(1)-C(6)	1.434 (13)	C(21)-C(22)	1.445 (13)
N(3)-C(7)	1.353 (12)	N(6)-C(23)	1.374 (12)
C(7)-C(8)	1.388 (14)	C(22)-C(23)	1.399 (14)
C(8)-C(9)	1.399 (15)	C(23)-C(24)	1.407 (17)
C(9)-C(10)	1.393 (15)	C(24)-C(25)	1.395 (19)
C(10)-C(11)	1.389 (13)	C(25)-C(26)	1.391 (15)
N(3)-C(11)	1.371 (11)	N(6)-C(26)	1.375 (13)
C(11)-C(12)	1.466 (13)		

atoms	angle, deg	atoms	angle, deg
N(1)-Ru-N(2)	78.0 (3)	C(1)-N(1)-Ru	116.2 (6)
N(1)-Ru-N(3)	85.9 (3)	C(6)-N(2)-Ru	116.3 (6)
N(1)-Ru-N(4)	101.2 (3)	N(1)-C(1)-C(2)	126.5 (9)
N(1)-Ru-N(6)	97.7 (3)	N(2)-C(6)-C(5)	124.4 (9)
N(2)-Ru-N(3)	97.5 (3)	C(7)-N(3)-Ru	123.9 (6)
N(2)-Ru-N(6)	92.4 (3)	C(11)-N(3)-Ru	115.3 (6)
N(3)-Ru-N(4)	78.2 (3)	C(12)-N(4)-Ru	115.2 (6)
N(3)-Ru-N(5)	99.6 (3)	C(16)-N(4)-Ru	125.7 (6)
N(4)-Ru-N(5)	88.4 (3)	C(21)-N(5)-Ru	115.1 (6)
N(4)-Ru-N(6)	91.9 (3)	C(22)-N(6)-Ru	123.0 (6)
N(5)-Ru-N(6)	78.3 (3)	C(17)-N(5)-Ru	124.8 (6)
		C(26)-N(6)-Ru	123.0 (6)

[a] N(3)-C(11)-C(12)-N(4) = 11.41°; N(5)-C(21)-C(22)-N(6) = 8.04°.

Figure 1. View of the cations down the *c* axis.

Figure 2. ORTEP drawing of the cation showing the atom numbering.

in chloroform/1,3-dibromopropane. Diffraction measurements were made on a Philips PW 1100 using the θ-2θ scan mode. The intensities of 3602 independent reflections were collected in the range $2 < \theta < 26°$ with a fine-focus molybdenum tube and a graphite monochromator to select Mo Kα (λ = 0.710 69 Å). No absorption correction was applied.

Solution and Refinement of the Structure

The positions of the ruthenium and two phosphorous atoms were determined from a three-dimensional sharpened Patterson map. Fourier maps and subsequent least-squares refinement located the remaining atoms. All positions of protons were determined, but only those of the quinodiimine ligand were considered and refined. According to the criterion $F_o > 2\sigma(F_o)$, 2869 reflections were used in the anisotropic refinement steps. All parameters converged and a final difference Fourier map showed no peak larger than 0.7 e/Å³; the R index is 0.0667 ($R = \sum||F_o| - |F_c||/\sum|F_o|$). Programs used were developed partly by G. M. Sheldrick (SHELX-76)[8] and partly by ourselves. Scattering factors for Ru²⁺ and neutral atoms (except those for hydrogen atoms) and terms for anomalous dispersion were those of Cromer et al.[9] Scattering factors for H atoms are from Stewart et al.[10] Atomic positional and thermal parameters for the nonhydrogen atoms are listed in Table I, positional parameters of relevant H atoms in Table II, while interatomic distances and selected bond angles are given in Table III. Figure 1 shows a sector from the unit cell (without anions), Figure 2 shows the ORTEP plot of the cation, and Figure 3 gives stereopair view of the cation.

Results and Discussion

Syntheses. The complex Ru(bpy)₂(qH₂)²⁺ can be prepared

in a one-step reaction from Ru(bpy)₂Cl₂ and the diamine qH₄, followed by air oxidation in basic solution.[11] Substitution of two Cl⁻ by qH₄ precedes the oxidation of qH₄ to qH₂. It was recently proved that metal ion catalysis of the air oxidation of H₂-1 to 2,3-diaminophenazine proceeds through the steps M(H₂-1)₃-M(1)₂(H-1) for M = Co, i.e., H₂-1 is coordinated in the reduced form and oxidized while coordinated.[12] The final step of the oxidation to 2,3-diaminophenazine apparently needs a relatively labile coordination sphere as provided by Co(II), whereas the substitution of inert Ru(II) does not give off the coordinated qH₂, and the reaction stops at this stage. Ru(bpy)(1)₂²⁺ and Ru(1)₃²⁺ require a two-step reaction. In the first step, a reduction of Ru(III) to Ru(II) is accomplished with a concomitant coordination of qH₄. The following oxidation with air leaves the oxidation state of Ru(II) unchanged but changes the ligand from the *o*-diamine to the *o*-quinodiimine state. The reaction sequence metal reduction–ligand oxidation is possible because the *oxidized* quinodiimine is a π *acceptor*, stabilizing the *low oxidation state* of ruthenium by back-bonding.

Molecular Structure of Ru(bpy)₂(1)²⁺. Figure 2 shows an ORTEP plot of the cation. The quinoid ligand **1** substitutes one

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(9) Cromer, D. T.; Mann, J. B. *Acta Crystallogr., Sect. A* **1968**, *A24*, 321. Cromer, D. T.; Libermann, D. *J. Chem. Phys.* **1970**, *53*, 1891.
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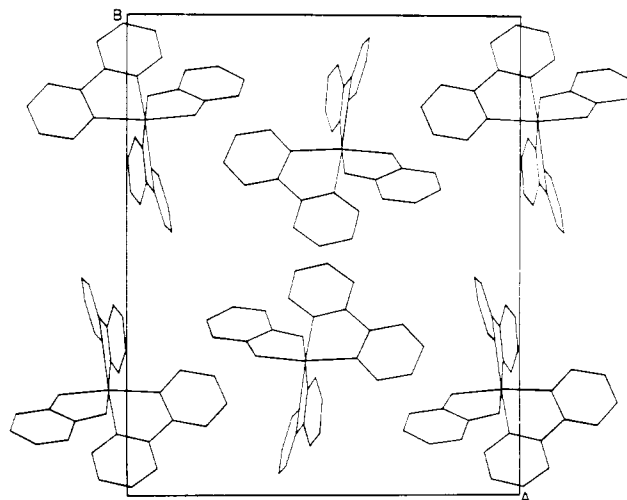
(11) Warren, L. F. *Inorg. Chem.* **1977**, *16*, 2814.
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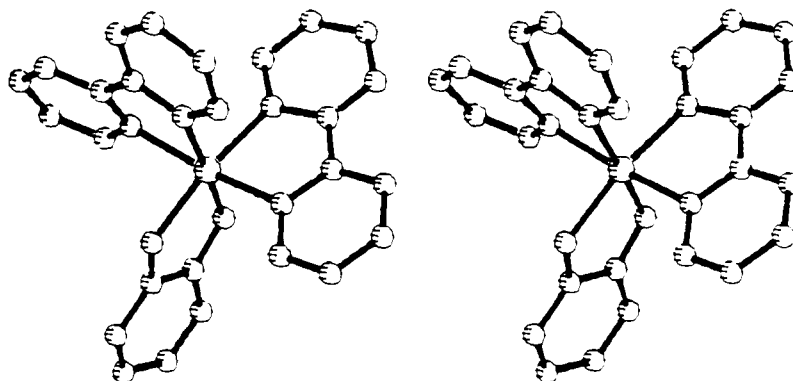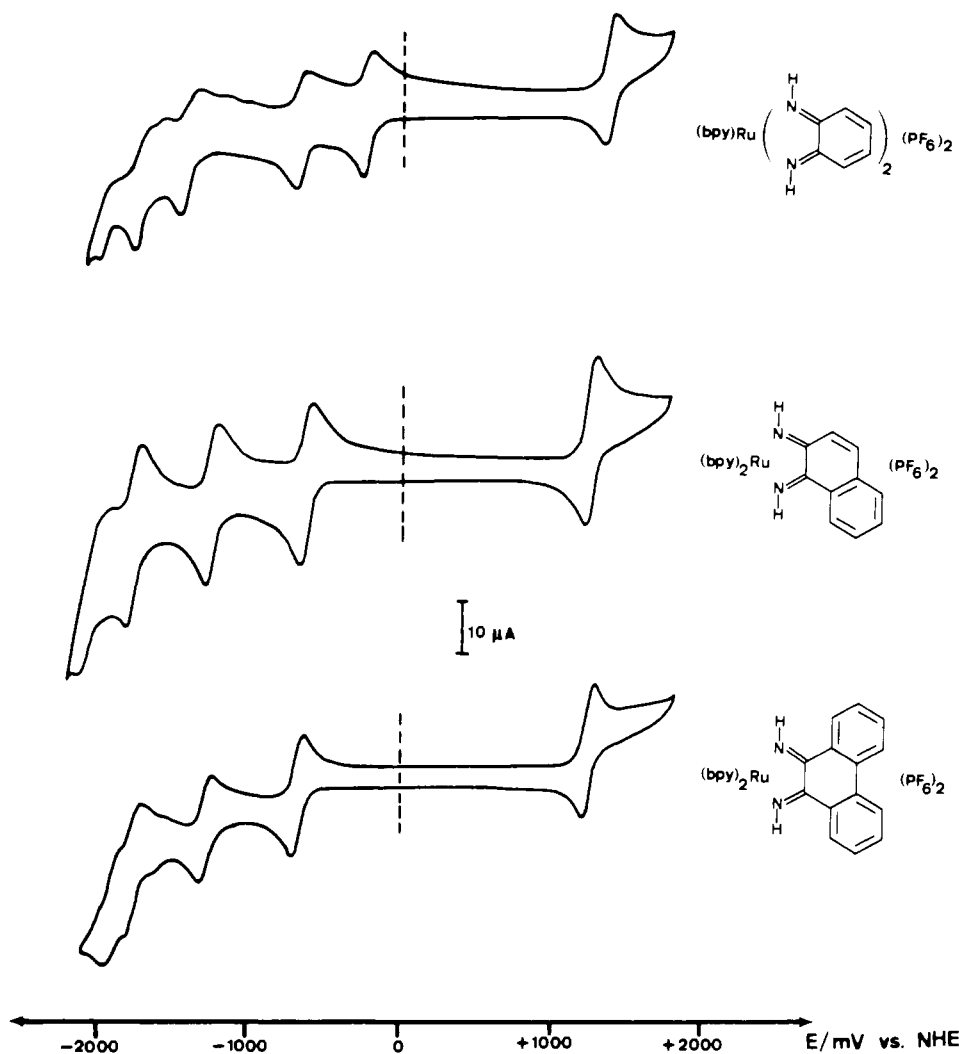**Figure 3.** Stereopair view of the cation.

Figure 4. Cyclic voltammograms of Ru(bpy)(1)$_2{}^{2+}$, Ru(bpy)$_2$(2)$^{2+}$, and Ru(bpy)$_2$(3)$^{2+}$ in acetonitrile: $C_{complex} = 1.10^{-3}$ M; $C_{TEAP} = 1.10^{-1}$ M; scan rate = 200 mV/s.

of the bipyridyl ligands of Ru(bpy)$_3{}^{2+}$,[13] preserving the original geometry to a large extent. The bite angles of the bidentate ligands remain at 78°, even for **1**. The latter shows clearly the quinoid nature of the ring, with localization of the double bonds (average distance 1.36 vs. 1.44 Å for the singly bonded atoms). The simultaneous presence of bipyridyl and **1** in the coordination sphere of Ru(II) gives an indication of the relative strength of the metal to ligand π-back-bonding. The average distance of 2.02 (1) Å for Ru–N (**1**) is significantly shorter

than that of 2.08 (1) Å for Ru–N(bpy). The amount of π-back-bonding to **1** is therefore more important than that for bipyridyl. The comparison of the Ru–N(bpy) (2.08 Å) distances in Ru(bpy)$_2$(1)$^{2+}$ and in Ru(bpy)$_3{}^{2+}$ (2.056 Å[13]) also indicates a slightly weaker π-back-bonding between Ru and the bipyridyl ligand in the complex with **1**, in which more negative charge is taken away from the metal by the quinodiimine ligand than by bipyridyl itself.

Electrochemistry. Three of the complexes can be reversibly oxidized to the +3 state (Figure 4). Ru(bpy)$_2$(1)$^{2+}$ shows highly irreversible behavior. Reduction is strongly favored in

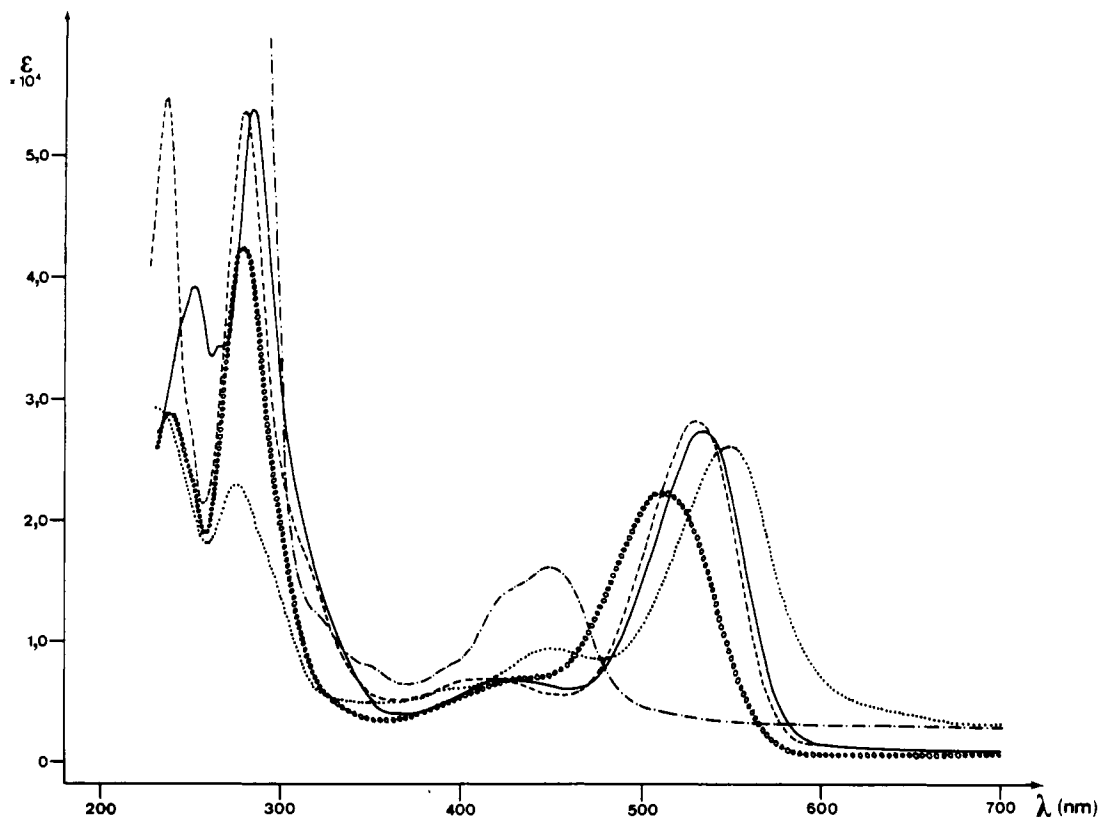(13) Rillema, D. P.; Jones, D. S. *J. Chem. Soc., Chem. Commun.* **1979**, 849.

Figure 5. Absorption spectra of $Ru(bpy)_3^{2+}$ (---), $Ru(bpy)_2(1)^{2+}$ (O), $Ru(bpy)(1)_2^{2+}$ (●), $Ru(bpy)_2(2)^{2+}$ (---), and $Ru(bpy)_2(3)^{2+}$ (—) in acetonitrile at room temperature.

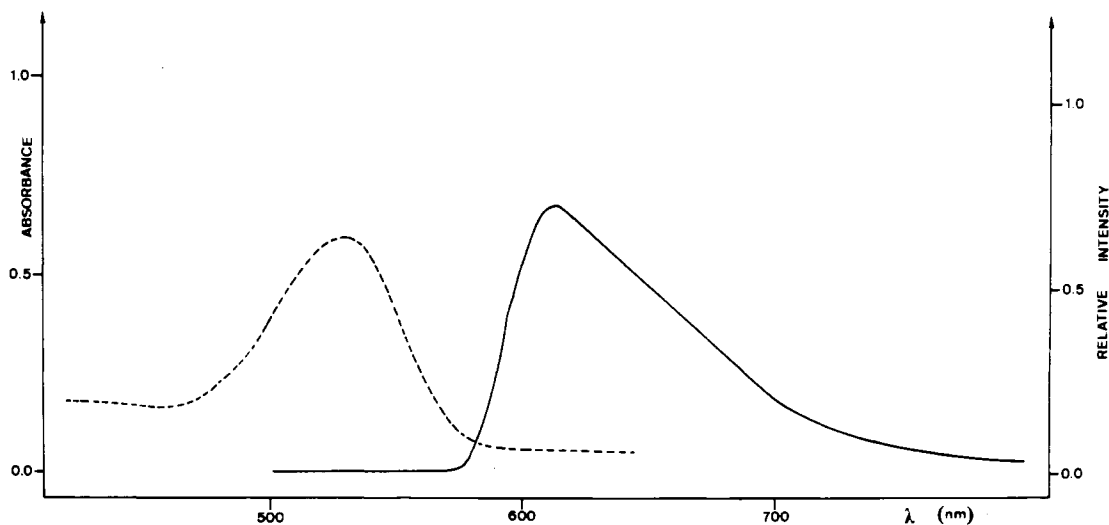**Figure 6.** Absorption (---) and luminescence spectra (—) of $Ru(bpy)_2(3)^{2+}$ in acetonitrile at room temperature (excitation wavelength 370 nm).

the complexes with the quinodiimine ligands as compared to $Ru(bpy)_3^{2+}$. The reversibility of the reduction depends on the sweep range of the cyclic voltammogram. Usually, the first or the first two reduction waves are fully reversible if the sweep is limited to these steps (Figure 4). If, however, the range is expanded, the back-oxidation is no longer reversible, indicating the formation of byproducts from the highly reduced forms of the complex. As in the case of $Ru(bpy)_3^{2+}$,[14] several reduction steps can be observed (Figure 4). Undoubtedly, the first step corresponds to a ligand-centered reduction in which the quniodiimine accepts an electron, yielding a coordinated semiquinodiimino ligand; this has also been observed in a cobalt complex.[12] Most probably, all of the observed reduction

steps are ligand centered.

Electronic Spectra. Parallel to the easier reduction of the +2 complexes with quinodiimine ligands in the ground state, is a longer wavelength MLCT transition observed in all these complexes. Figure 5 shows the absorption spectra of the complexes in the visible region. There is little doubt that the longest wavelength transition is to a π^* orbital of the quinodiimine ligand. A detailed interpretation of the absorption spectra is not yet feasible in view of the uncertainties still present in the definitive assignment of the bands of the $Ru(bpy)_3^{2+}$ despite its comparatively high molecular symmetry.[15] Only one of the complexes, namely, $Ru(bpy)_2(3)^{2+}$, luminesces at room temperature in liquid solution, as shown in Figure 6.

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Notes

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η⁵-(Triphenylphosphonium cyclopentadienylide)rhodium(I) and -rhodium(III) Complexes

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In connection with our current interest concerning the formation and chemical reactivity of new (η⁵-cyclopentadienyl)rhodium and -iridium organometallic complexes,[2] we have investigated the reactions of triphenylphosphonium cyclopentadienylide (1) with some rhodium(I) and rhodium(III) substrates. The interest for such a study arises from the fact that, in the ground state, 1 is considered to be the resonance hybrid of ylidic and ylenic structures with a predominant contribution of the former. Coordination to metals by the ylidic structure implies that the five-membered ylide ring is a 6π-electron donor, as the cyclopentadienyl ion. It is, therefore, of interest to compare the properties of some of the new complexes with that of analogous cyclopentadienylrhodium(I) and -rhodium(III) complexes.

Experimental Section

Triphenylphosphonium cyclopentadienylide (1)[3] and the complexes [Rh(CO)₂Cl]₂,[4] [Rh(1,5-C₈H₁₂)Cl]₂,[5] [Rh(C₇H₈)Cl]₂[6] and [Rh-(C₅Me₅)Cl₂]₂[7] were prepared by literature methods. Other reagents were commercial products and were used without purification. Infrared spectra were recorded on a Perkin-Elmer 457 spectrophotometer in KBr pellets. Proton NMR spectra were recorded by using a Perkin-Elmer R 24B spectrometer. ¹³C NMR spectra were recorded in 10-mm tubes at a probe temperature of 303 K on a Bruker WP-80 FT spectrometer working at 20.1 MHz and using ca. 10% (w/v) solutions containing tetramethylsilane (Me₄Si) as internal reference. The carbon spectra were recorded in the quadrature detection mode with use of a pulse angle of 20° and a pulse delay equal to the dwell time on 8192 (8 K) data points. Off-resonance decoupling experiments were carried out with the proton frequency offset approximately 500 Hz downfield from the center of the proton spectra region. Conductivity measurements were made with a WTW LBR conductivity meter.

Microanalyses were done by the laboratory of the Organic Chemistry Institute of Milan. All the reactions were carried out under an atmosphere of oxygen-free nitrogen. Analytical data, characteristic

IR bands, and ¹H and ¹³C NMR absorptions are reported in Tables I and II.

[Rh(Ph₃PC₅H₄)(CO)₂]PF₆ (2). To a stirred acetone solution of [Rh(CO)₂Cl]₂ (0.21 g) were added solid Ph₃PC₅H₄ (0.32 g) and Ag[PF₆] (0.25 g). The initial red solution changed to pale brown while AgCl precipitate was formed. After 40 min solid AgCl was separated by filtration, and the solvent was removed by evaporation. The solid was dissolved in 10 mL of CH₂Cl₂, and diethyl ether was added to precipitate the product as a yellow brown solid. The yield was 85%.

[Rh(Ph₃PC₅H₄)(1,5-C₈H₁₂)]PF₆ (3). Solid Ph₃PC₅H₄ (0.414 g) and Ag[PF₆] (0.32 g) were added to a stirred acetone solution of [Rh(1,5-C₈H₁₂)Cl]₂ (0.31 g). The reaction mixture was left with stirring, at room temperature, for ca. 2 h. The AgCl precipitate formed was separated by filtration and the resulting solution evaporated. The crude product was dissolved in 10 mL of CH₂Cl₂; with addition of diethyl ether a yellow brown solid was formed. This was collected, washed with diethyl ether, and dried. The yield was 82%.

[Rh(Ph₃PC₅H₄)(C₇H₈)]PF₆ (4). This compound was prepared in the same manner as 3, starting from [Rh(C₇H₈)Cl]₂. The yield was 80%.

[Rh(Ph₃PC₅H₄)(CO)PPh₃]PF₆ (5). To a dichloromethane solution of (2) (0.12 g) was added a slight excess of PPh₃ (0.052 g). The reaction was monitored by IR spectra and was allowed to proceed until the ν(CO) due to the starting complex had completely disappeared (ca. 2 days). With addition of petroleum ether a brown solid was formed; this was collected, washed with petroleum ether, and dried. The yield was 92%.

Tetraphenylborate Salts. Tetraphenylborate salts of complexes 2–5 were prepared by adding Na[BPh₄] dissolved in methanol to a solution of the hexafluorophosphate salts 2–5 in the same solvent. They closely resemble the corresponding PF₆⁻ salts except for lower solubility in organic solvents.

[(Ph₃PC₅H₄)(CO)Rh(μ-Ph₂PCH₂PPh₂)Rh(CO)(Ph₃PC₅H₄)]PF₆]₂ (6). To a dichloromethane solution of (2) (0.13 g) was added Ph₂PCH₂PPh₂ (0.042 g) and the mixture vigorously stirred at room temperature until the ν(CO) due to the starting material had completely disappeared (ca. 5 days). With addition of diethyl ether the product was obtained as a brown solid; this was collected, washed with diethyl ether, and dried. The yield was 82%.

{(Ph₃PC₅H₄)(CO)Rh[μ-Ph₂P(CH₂)₄PPh₂]Rh(CO)(Ph₃PC₅H₄)}-[PF₆]₂ (7). This compound was prepared by a method analogous to that given above. The product was recrystallized once from dichloromethane–diethyl ether, giving the pure compounds in 76% yield.

[Rh(C₅Me₅)(Ph₃PC₅H₄)][PF₆]₂ (8). To an acetone solution of [Rh(C₅Me₅)(acetone)₃][PF₆]₂, obtained from [Rh(C₅Me₅)Cl₂]₂ (0.45 g) and Ag[PF₆], was added Ph₃PC₅H₄ (0.36 g), and the mixture was stirred for 2 h. The initial yellow changed to brown. After filtration the solvent was evaporated off and the crude product dissolved in dichloromethane; with addition of diethyl ether the product was obtained as a yellow-brown solid. The yield was 78%.

Results and Discussion

Triphenylphosphonium cyclopentadienylide (1) is a poor nucleophile toward rhodium(I) substrates; this is shown by the lack of chloro bridge-splitting reactions with the binuclear complexes [Rh(CO)₂Cl]₂, [Rh(1,5-C₈H₁₂)Cl]₂, and [Rh(C₇-H₈)Cl]₂. The route followed for the preparation of (triphenylphosphinium cyclopentadienylide)rhodium(I) complexes involves the in situ formation of solvento species from the dimeric chloro-bridged complexes and the displacement of the

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