Reactions of Ruthenium Triphenylphosphine Complexes with Diazadienes. Part 3.[1] Preparation, Characterization, *X*-Ray Crystal Structure, and Reactivity of a Formally Ruthenium(0) Tris(α-Di-imine) Complex †

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The reaction between [RuH$_2$(PPh$_3$)$_4$] or [RuH(C$_6$H$_4$PPh$_2$)(PPh$_3$)$_2$(C$_2$H$_4$)] and 3 equivalents of the α-di-imine p-MeOC$_6$H$_4$NCHCHNC$_6$H$_4$OMe-p (L) produces black crystalline [RuL$_3$]. This complex is diamagnetic below −10 °C and becomes paramagnetic at higher temperature. The *X*-ray crystal structure and u.v. spectra show that the three ligands are equivalent. The complex can be considered as containing 20-electron ruthenium(0). It is rapidly oxidized by molecular oxygen to [RuL$_3$]$^{2+}$. Crystals of [RuL$_3$]·C$_6$H$_5$CH$_3$ are triclinic, space group $P\bar{1}$, with a = 14.269(2), b = 24.999(2), c = 13.967(2) Å, α = 92.04(1), β = 95.01(1), γ = 104.33(1)°, and Z = 4. The structure was refined using 3 867 'observed' reflections to a final R value of 0.109.

In recent papers [1,2] we described the reaction between diazadiene ligands and some triphenylphosphine complexes of ruthenium. Although diazadienes are known to stabilize other metals [3-5] in their formal 'zero' oxidation state, we obtained in each case ruthenium(II) complexes.

The complex [Ru(bipy)$_3$]$^{2+}$ (bipy = 2,2′-bipyridyl) has been widely studied, particularly since the discovery of its capacity to produce hydrogen from water,[6] but the reduced species [Ru(bipy)$_3$]^0 has only been obtained as a brown material after electrochemical reduction and not further characterized,[7] or observed *in situ*.[8] Braterman and coworkers [8] have shown that the ligand and not the metal is reduced during the electrochemical reduction of [Ru(bipy)$_3$]$^{2+}$.

It was then of interest to study whether diazadiene would stabilize low-valent ruthenium species and whether the electronic structure of this ligand would be strongly modified. We report the preparation of a formally ruthenium(0) tris(diazadiene) complex [Ru(p-MeOC$_6$H$_4$NCHCHNC$_6$H$_4$OMe-p)$_3$], its characterization, crystal structure, and some chemical reactions. A preliminary account of this work has been published.[9]

Results and Discussion

Synthesis and Spectroscopic Properties.—During a study of the reaction of [RuH$_2$(PPh$_3$)$_4$] and the diazadiene p-MeOC$_6$H$_4$NCHCHNC$_6$H$_4$OMe-p (L) we noticed that when the reaction mixture was heated in the presence of an excess of diazadiene extra peaks appeared in the ^{1}H n.m.r. spectrum. After refluxing overnight, [RuH$_2$(PPh$_3$)$_4$] and 3 equivalents of diazadiene in toluene gave a low yield of black crystals analysing for RuL$_3$·C$_6$H$_5$CH$_3$ (see Table 1). The yield could be increased by carrying out the reaction at 80 °C in toluene and with [RuH(C$_6$H$_4$PPh$_2$)(PPh$_3$)$_2$(C$_2$H$_4$)] as the ruthenium starting material. After recrystallization from toluene–hexane (1 : 3), black crystals of RuL$_3$·C$_6$H$_5$CH$_3$ were obtained in *ca.* 70% yield.

Table 1. Microanalytical data (%) for ruthenium complexes with calculated values in parentheses

Compound	C	H	N
[Ru(p-MeOC$_6$H$_4$NCHCHNC$_6$H$_4$OMe-p)$_3$]·C$_6$H$_5$CH$_3$	65.3 (66.2)	5.6 (5.6)	7.9 (8.4)
[Ru(p-MeOC$_6$H$_4$NCHCHNC$_6$H$_4$OMe-p)$_3$]-[PF$_6$]$_2$	48.3 (48.2)	4.3 (4.0)	6.9 (7.0)
[Ru(p-MeOC$_6$H$_4$NCHCHNC$_6$H$_4$OMe-p)$_3$]-Cl$_2$·0.5CH$_2$Cl$_2$	56.7 (56.1)	5.1 (4.8)	8.2 (8.2)

The i.r. spectrum of this product is very similar to that of the free ligand, showing a small shift of the C=N bands from 1 610 to 1 590 cm^{-1}. The ^{1}H n.m.r. spectrum is very peculiar. Thus at −80 °C it consists of two singlets at δ 2.1 and 3.3 and a complex multiplet at δ 6.9 attributed respectively to the toluene methyl group, to the methoxy-protons of the ligand, and to the phenyl and imino (N=CH) protons. When the temperature is raised the methoxy-singlet moves slightly downfield, whereas the multiplet is split into three broad peaks, two moving upfield and one downfield. At 30 °C these three peaks are observed at δ −15.1, 0, and 10.2 and at 70 °C at δ −25, −3, and 11.4. This suggests a paramagnetic behaviour of the complex. We have not been able to assign these peaks to the different protons. The magnetic moment of this compound at < −10 °C is very small (*ca.* 0) and increases to 0.8 μ_B at 30 °C (taking into account approximate corrections for the diamagnetism of the ligand [10]).

All these data are in agreement with an equilibrium between a diamagnetic and a paramagnetic form of the compound. The photoelectron spectra and a Xα calculation, which should help in understanding the electronic structure of this compound, will be reported elsewhere.

As these magnetic properties could result from a change in the structure or in the mode of co-ordination of the ligand we undertook an *X*-ray diffraction study of the compound.

Crystal Structure.—The crystal structure consists of four RuL$_3$ units and solvent molecules (toluene). The asymmetric unit clearly contains two enantiomeric RuL$_3$ moieties, one of which is shown in the Figure. The geometry resembles that found [11] for [Ru(bipy)$_3$]$^{2+}$ whereas we are dealing with a neutral species. The six Ru–N(imine) bond lengths vary from 2.02 to 2.10 Å with an average of 2.06 Å (see Table 2). The diazadiene ligand is clearly σ-bound to the ruthenium by the nitrogen lone pair since the imino-carbon atoms are, with an average distance of 2.9 Å, too far away to allow the C=N

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† Tris[1,2-bis(p-methoxyphenylimino)ethane-*NN′*]ruthenium(0)–toluene (1/1).

Supplementary data available (No. SUP 23544, 25 pp.): thermal parameters, structure factors. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

Table 2. Interatomic distances (Å) with standard deviations in parentheses

Ru(1)–N(11)	2.04(2)	Ru(2)–N(21)	2.04(2)	C(124)–O(12)	1.42(4)	C(224)–O(22)	1.41(4)
Ru(1)–N(12)	2.08(2)	Ru(2)–N(22)	2.09(2)	O(12)–C(127)	1.44(5)	O(22)–C(227)	1.46(4)
Ru(1)–N(13)	2.02(2)	Ru(2)–N(23)	2.06(2)	C(131)–C(132)	1.36(4)	C(231)–C(232)	1.38(4)
Ru(1)–N(14)	2.04(3)	Ru(2)–N(24)	2.08(2)	C(132)–C(133)	1.42(4)	C(232)–C(233)	1.45(5)
Ru(1)–N(15)	2.07(2)	Ru(2)–N(25)	2.08(2)	C(133)–C(134)	1.40(5)	C(233)–C(234)	1.44(5)
Ru(1)–N(16)	2.10(3)	Ru(2)–N(26)	2.03(2)	C(134)–C(135)	1.39(4)	C(234)–C(235)	1.37(6)
N(11)–C(118)	1.28(3)	N(21)–C(218)	1 33(4)	C(135)–C(136)	1.38(4)	C(235)–C(236)	1.39(5)
N(12)–C(128)	1.34(4)	N(22)–C(228)	1.36(4)	C(134)–O(13)	1.39(3)	C(236)–C(231)	1.40(4)
N(13)–C(138)	1.35(5)	N(23)–C(238)	1.37(4)	O(13)–C(137)	1.42(4)	C(234)–O(23)	1.46(5)
N(14)–C(148)	1.35(5)	N(24)–C(248)	1.38(4)	C(136)–C(131)	1.45(5)	O(23)–C(237)	1.48(5)
N(15)–C(158)	1.38(3)	N(25)–C(258)	1.30(4)	C(141)–C(142)	1.46(5)	C(241)–C(242)	1.37(4)
N(16)–C(168)	1.38(4)	N(26)–C(268)	1.37(4)	C(142)–C(143)	1.39(4)	C(242)–C(243)	1.39(4)
C(118)–C(128)	1.39(5)	C(218)–C(228)	1.45(4)	C(143)–C(144)	1.38(5)	C(243)–C(244)	1.42(4)
C(138)–C(148)	1.37(4)	C(238)–C(248)	1.33(4)	C(144)–C(145)	1.39(6)	C(244)–C(245)	1.48(5)
C(158)–C(168)	1.38(4)	C(258)–C(268)	1.37(4)	C(145)–C(146)	1.44(4)	C(245)–C(246)	1.40(4)
N(11)–C(111)	1.43(4)	N(21)–C(211)	1.40(3)	C(146)–C(141)	1.38(5)	C(246)–C(241)	1.42(4)
N(12)–C(121)	1.45(4)	N(22)–C(221)	1.41(3)	C(144)–O(14)	1.43(4)	C(244)–O(24)	1.41(4)
N(13)–C(131)	1.43(3)	N(23)–C(231)	1.44(4)	O(14)–C(147)	1.45(4)	O(24)–C(247)	1.47(5)
N(14)–C(141)	1.45(4)	N(24)–C(241)	1.41(4)	C(151)–C(152)	1.42(4)	C(251)–C(252)	1.40(4)
N(15)–C(151)	1.37(4)	N(25)–C(251)	1.43(3)	C(152)–C(153)	1.39(5)	C(252)–C(253)	1.39(4)
N(16)–C(161)	1.39(4)	N(26)–C(261)	1.44(4)	C(153)–C(154)	1.44(5)	C(253)–C(254)	1.38(4)
C(111)–C(112)	1.40(4)	C(211)–C(212)	1.45(4)	C(154)–C(155)	1.39(5)	C(254)–C(255)	1.41(4)
C(112)–C(113)	1.40(5)	C(212)–C(213)	1.45(4)	C(155)–C(156)	1.42(5)	C(255)–C(256)	1.44(4)
C(113)–C(114)	1.39(5)	C(213)–C(214)	1.29(5)	C(156)–C(151)	1.43(4)	C(256)–C(251)	1.39(4)
C(114)–C(115)	1.37(4)	C(214)–C(215)	1.36(6)	C(154)–O(15)	1.44(5)	C(254)–O(25)	1.44(3)
C(115)–C(116)	1.38(5)	C(215)–C(216)	1.45(4)	O(15)–C(157)	1.42(5)	O(25)–C(257)	1.40(4)
C(111)–C(116)	1.47(5)	C(216)–C(211)	1.39(5)	C(161)–C(162)	1.36(5)	C(261)–C(262)	1.42(5)
C(114)–O(11)	1.38(4)	C(214)–O(21)	1.50(4)	C(162)–C(163)	1.43(5)	C(262)–C(263)	1.43(5)
O(11)–C(117)	1.54(8)	O(21)–C(217)	1.49(8)	C(163)–C(164)	1.39(6)	C(263)–C(264)	1.39(5)
O(11)–C(171)	1.38(7)	O(21)–C(271)	1.40(9)	C(164)–C(165)	1.41(6)	C(264)–C(265)	1.33(5)
C(121)–C(122)	1.37(5)	C(221)–C(222)	1.37(4)	C(165)–C(166)	1.43(5)	C(265)–C(266)	1.42(5)
C(122)–C(123)	1.40(5)	C(222)–C(223)	1.43(4)	C(166)–C(161)	1.38(5)	C(266)–C(261)	1.47(5)
C(123)–C(124)	1.35(4)	C(223)–C(224)	1.40(5)	C(164)–O(16)	1.45(5)	C(264)–O(26)	1.47(4)
C(124)–C(125)	1.42(5)	C(224)–C(225)	1.34(5)	O(16)–C(167)	1.55(12)	O(26)–C(267)	1.46(5)
C(125)–C(126)	1.37(5)	C(225)–C(226)	1.47(4)	O(16)–C(176)	1.56(60)		
C(126)–C(121)	1.47(3)	C(226)–C(221)	1.43(5)				

CT(11)–CT(12) 1.31(9) CT(11)–CT(13) 1.40(9) CT(12)–CT(13) 1.28(9) (CT represents a carbon atom of toluene)

Table 3. Selected bond angles (°) with estimated standard deviations in parentheses

N(12)–Ru(1)–N(11)	76.9(1.0)	N(22)–Ru(2)–N(21)	78.0(0.9)	C(138)–N(13)–Ru(1)	112.2(1.7)	C(238)–N(23)–Ru(2)	111.0(1.9)
N(13)–Ru(1)–N(11)	93.9(0.9)	N(23)–Ru(2)–N(21)	93.4(0.9)	C(138)–N(13)–C(131)	113.7(2.5)	C(238)–N(23)–C(231)	117.1(2.1)
N(13)–Ru(1)–N(12)	168.4(1.1)	N(23)–Ru(2)–N(22)	95.2(0.9)	C(132)–C(131)–N(13)	124.8(2.8)	C(232)–C(231)–N(23)	119.2(2.4)
N(14)–Ru(1)–N(11)	82.2(1.0)	N(24)–Ru(2)–N(21)	172.0(1.0)	C(136)–C(131)–N(13)	110.8(2.5)	C(236)–C(231)–N(23)	115.7(2.6)
N(14)–Ru(1)–N(12)	93.0(1.0)	N(24)–Ru(2)–N(22)	101.0(1.0)	C(136)–C(131)–C(132)	124.2(2.6)	C(236)–C(231)–C(232)	125.1(2.8)
N(14)–Ru(1)–N(13)	78.6(1.0)	N(24)–Ru(2)–N(23)	78.7(1.0)	C(128)–C(118)–N(11)	119.6(3.0)	C(228)–C(218)–N(21)	111.8(2.6)
N(15)–Ru(1)–N(11)	100.7(0.9)	N(25)–Ru(2)–N(21)	99.0(0.8)	C(148)–C(138)–N(13)	119.4(3.0)	C(248)–C(238)–N(23)	118.6(2.4)
N(15)–Ru(1)–N(12)	95.4(1.0)	N(25)–Ru(2)–N(22)	172.2(0.9)	C(141)–N(14)–Ru(1)	128.8(2.2)	C(241)–N(24)–Ru(2)	129.3(1.9)
N(15)–Ru(1)–N(13)	93.2(0.9)	N(25)–Ru(2)–N(23)	92.2(0.9)	C(148)–N(14)–Ru(1)	114.6(2.1)	C(248)–N(24)–Ru(2)	110.4(1.8)
N(15)–Ru(1)–N(14)	171.5(0.9)	N(25)–Ru(2)–N(24)	83.0(0.9)	C(148)–N(14)–C(141)	116.2(2.8)	C(248)–N(24)–C(241)	117.8(2.4)
N(16)–Ru(1)–N(11)	172.4(0.9)	N(26)–Ru(2)–N(21)	96.7(0.8)	C(142)–C(141)–N(14)	114.4(2.7)	C(242)–C(241)–N(24)	122.3(2.7)
N(16)–Ru(1)–N(12)	95.9(1.0)	N(26)–Ru(2)–N(22)	96.7(0.9)	C(146)–C(141)–N(14)	121.6(3.0)	C(246)–C(241)–N(24)	114.1(2.8)
N(16)–Ru(1)–N(13)	93.6(0.9)	N(26)–Ru(2)–N(23)	165.8(1.0)	C(146)–C(141)–C(142)	124.0(2.7)	C(246)–C(241)–C(242)	122.3(2.8)
N(16)–Ru(1)–N(14)	100.4(1.0)	N(26)–Ru(2)–N(24)	91.3(0.9)	N(14)–C(148)–C(138)	113.7(3.5)	N(24)–C(248)–C(238)	117.7(2.4)
N(16)–Ru(1)–N(15)	77.7(0.9)	N(26)–Ru(2)–N(25)	76.4(0.9)	C(151)–N(15)–Ru(1)	128.2(1.9)	C(251)–N(25)–Ru(2)	125.1(1.9)
C(111)–N(11)–Ru(1)	128.8(1.7)	C(211)–N(21)–Ru(2)	125.2(1.9)	C(158)–N(15)–Ru(1)	114.0(1.7)	C(258)–N(25)–Ru(2)	116.7(1.9)
C(118)–N(11)–Ru(1)	114.2(2.1)	C(218)–N(21)–Ru(2)	118.8(1.5)	C(158)–N(15)–C(151)	117.5(2.4)	C(258)–N(25)–C(251)	117.0(2.5)
C(118)–N(11)–C(111)	116.5(2.5)	C(218)–N(21)–C(211)	115.9(2.2)	C(152)–C(151)–N(15)	120.5(2.5)	C(252)–C(251)–N(25)	118.8(2.5)
C(112)–C(111)–N(11)	126.1(2.8)	C(212)–C(211)–N(21)	117.3(2.6)	C(156)–C(151)–N(15)	120.3(2.5)	C(256)–C(251)–N(25)	120.3(2.5)
C(116)–C(11)–N(11)	116.0(2.3)	C(216)–C(211)–N(21)	125.1(2.7)	C(156)–C(151)–C(152)	119.0(2.9)	C(256)–C(251)–C(252)	120.8(2.6)
C(116)–C(111)–C(112)	118.0(2.8)	C(216)–C(211)–C(212)	117.5(2.4)	C(168)–C(158)–N(15)	117.9(2.6)	C(268)–C(258)–N(25)	113.1(2.9)
C(121)–N(12)–Ru(1)	128.8(1.8)	C(221)–N(22)–Ru(2)	131.8(2.2)	C(161)–N(16)–Ru(1)	126.1(2.1)	C(261)–N(26)–Ru(2)	128.6(2.1)
C(128)–N(12)–Ru(1)	114.4(2.2)	C(228)–N(22)–Ru(2)	111.8(1.7)	C(168)–N(16)–Ru(1)	114.5(1.9)	C(268)–N(26)–Ru(2)	113.3(1.7)
C(128)–N(12)–C(121)	116.8(2.4)	C(228)–N(22)–C(221)	116.3(2.6)	C(168)–N(16)–C(161)	119.4(2.6)	C(268)–N(26)–C(261)	118.1(2.5)
C(122)–C(121)–N(12)	121.5(2.4)	C(222)–C(221)–N(22)	118.6(2.7)	C(162)–C(161)–N(16)	120.7(3.0)	C(262)–C(261)–N(26)	120.9(2.7)
C(126)–C(121)–N(12)	119.4(2.5)	C(226)–C(221)–N(22)	120.5(2.5)	C(166)–C(161)–N(16)	117.3(3.1)	C(266)–C(261)–N(26)	119.3(2.7)
C(126)–C(121)–C(122)	119.1(2.7)	C(226)–C(221)–C(222)	120.8(2.5)	C(166)–C(161)–C(162)	121.9(3.2)	C(266)–C(261)–C(262)	119.7(2.8)
N(12)–C(128)–C(118)	113.4(2.7)	N(22)–C(228)–C(218)	118.6(2.9)	N(16)–C(168)–C(158)	115.3(2.8)	N(26)–C(268)–C(258)	118.5(2.8)
C(131)–N(13)–Ru(1)	134.0(2.2)	C(231)–N(23)–Ru(2)	131.9(1.7)				

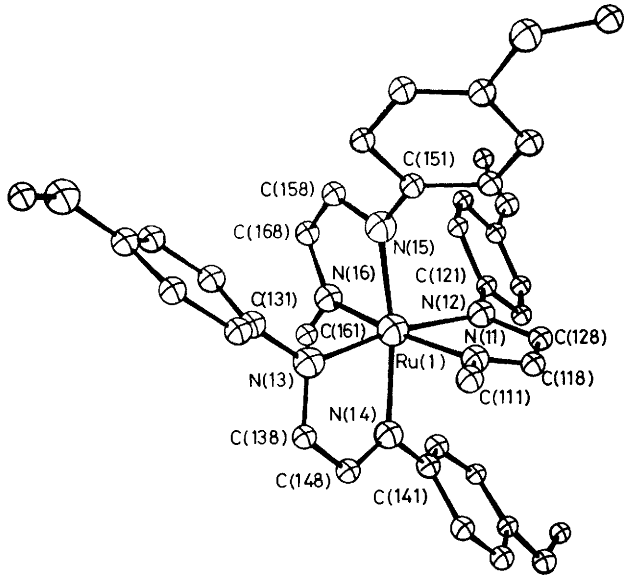

Figure. Structure of $[RuL_3]$; two *p*-methoxyphenyl groups are omitted for clarity

Table 4. U.v. spectra of diazadiene (L) complexes

Compound	λ/nm	ε/dm³ mol⁻¹ cm⁻¹
L	370	18 900
$[RuL_3]$	410	20 500
	550	6 000
$[RuL_3]^{2+}$	425	30 500
	550	8 500

double bond to be involved in ligand–metal bonding. The N–Ru–N(imine) angles for each bidentate ligand exhibit a range of 76.4—78.7° and can be considered as constant (see Table 3). The first carbon atoms of the aromatic rings, the nitrogen, and the imino-carbon atoms lie in the same plane with a maximum deviation of 0.1 Å.

Chemical Reactivity and U.v. Spectra.—We investigated the reactivity of $[RuL_3]$ with small molecules but did not observe any reaction with H_2, CO, NO, or C_2H_4. With oxidizing agents such as $CHCl_3$, I_2, HCl, or simply O_2 the complex is rapidly and quantitatively oxidized to the dication $[RuL_3]^{2+}$ isolated as its Cl^-, I^-, BPh_4^-, or PF_6^- salt. These salts are red air-stable products, shown to be 2 : 1 conductors in acetone (BPh_4^- and PF_6^-) or methanol (Cl^- and I^-).

The i.r. spectra of the salts only show the bands of the diazadiene. The ^1H n.m.r. spectra consist of four peaks at δ 8.55 (s, 1), 6.95 (d, 2), 6.5 (d, 2), and 3.85 (s, 3) attributed respectively to the imino (NCH), phenyl, and methoxy-protons. In the case of the BPh_4^- salt the two doublets near δ 6.7 are not seen, but the integration ratio for the phenyl and methoxy-protons is in agreement with the presence of two BPh_4^- anions per three diazadiene ligands. These data indicate clearly that $[RuL_3]^{2+}$ is isoelectronic and probably isostructural with $[Ru(bipy)_3]^{2+}$.

In order to see whether the diazadiene ligand could have been reduced during the formation of $[RuL_3]$ we examined the u.v. spectra of L, $[RuL_3]$, and $[RuL_3]^{2+}$ (see Table 4). The spectra of $[RuL_3]$ and $[RuL_3]^{2+}$ are very similar; this suggests (in agreement with the crystal structure) no important change in the ligand and thus a formal 20-electron ruthenium(0) structure for $[RuL_3]$. By comparison with the bipy system and particularly with $[Ru(bipy)_3]^{2+}$,[8] we attribute the band near 400 nm to the π→π* transition and the one near 550 nm to the metal-to-ligand one. The characteristic bands of $[RuL_3]^{2+}$ are shifted to low frequency and have smaller ε values than $[Ru(bipy)_3]^{2+}$. This could be one reason why any attempt to activate water according to Lehn and Sauvage's method[6] with $[RuL_3]^{2+}$ instead of $[Ru(bipy)_3]^{2+}$ was unsuccessful.

Experimental

Microanalyses were by Centre d'Analyse du C.N.R.S. or by Mlle. H. Magna of our laboratory. Infrared spectra were obtained using Perkin-Elmer PE 577 or PE 225 grating diffractometers, n.m.r. spectra using Perkin-Elmer R 12 (60 MHz) and Bruker WH 90 (90 MHz) spectrometers, the latter in the Fourier-transform mode. Conductivity measurements were performed on a Beckmann RC 18 A conductivity bridge.

All solvents were thoroughly degassed before use and all operations were carried out in a nitrogen or argon atmosphere using standard Schlenk-tube techniques. The diazadiene ligand was prepared according to published methods[1,2] by adding two equivalents of *p*-methoxyaniline to glyoxal (water solution) at 0 °C. The complexes $[RuH_2(PPh_3)_4]$[12] and $[RuH(C_6H_4PPh_2)(PPh_3)_2(C_2H_4)]$[13] were prepared according to published methods.

Preparations.—Tris[1,2-*bis*(p-*methoxyphenylimino*)*ethane*]-*ruthenium*(0)-*toluene*. The hydrido-orthometallated complex was prepared *in situ* by bubbling ethylene into a solution of $[RuH_2(PPh_3)_4]$ (1 g, 0.868 mmol) in toluene (50 cm³) for 15 min. The solution was then degassed under argon and 1,2-bis(*p*-methoxyphenylimino)ethane (0.7 g, 0.2612 mmol) added. The mixture was then heated overnight at 80 °C, whereupon it became dark brown. Its volume was then reduced to *ca.* 25 cm³, hexane was added, and the mixture filtered and allowed to crystallize at room temperature and then at −15 °C. Black crystals were formed, yield *ca.* 70%.

The reaction of $[RuH_2(PPh_3)_4]$ with diazadiene in the absence of ethylene, but with refluxing in toluene, gave a yield of *ca.* 25% of the same product.

Tris[1,2-*bis*(p-*methoxyphenylimino*)*ethane*]*ruthenium*(II) *salts*. To $[RuL_3]$ was added non-degassed methanol (30 cm³) containing an excess of the salt NaX (X = Cl, I, PF_6, or BPh_4). A red precipitate was formed immediately and was filtered off (X = BPh_4) or the red solution was evaporated to dryness and washed with water. Recrystallization from CH_2Cl_2–Et_2O (1 : 1) (X = Cl or BPh_4) or MeOH (X = I or PF_6) afforded red crystals of the ruthenium salts.

X-*Ray Crystallography.*—A small black cube was sealed under argon in a glass capillary tube and mounted on an Enraf-Nonius CAD-4 computer-controlled four-circle diffractometer. Unit-cell dimensions and the orientation matrix were obtained by a least-squares fit to the setting angles of 25 reflections.

Crystal data. $C_{55}H_{56}N_6O_6Ru$, $M = 998.09$, Triclinic, space group $P\bar{1}$, $a = 14.269(2)$, $b = 24.999(2)$, $c = 13.967(2)$ Å, $\alpha = 92.04(1)$, $\beta = 95.01(1)$, $\gamma = 104.33(1)$°, $U = 4\,799.5$ Å³, $Z = 4$, $D_c = 1.38$ g cm⁻³, $F(000) = 2\,079.98$, $\lambda(Mo\text{-}K_\alpha) = 0.7107$ Å, $\mu(Mo\text{-}K_\alpha) = 3.25$ cm⁻¹.

The intensities of 7 692 independent reflections with $2 < \theta < 19°$ were measured by an ω—2θ scan with a variable scan rate and a scan angle ω of (0.85 + 0.35 tan θ)°. Lorentz and polarization corrections were applied to all reflections, but only 3 867 reflections with $I > 3\sigma(I)$ were used for refinement and difference-Fourier calculations. No correction was made for absorption.

Table 5. Atomic co-ordinates

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
CT(21)	0.0496	0.5419	−0.0585
CT(22)	−0.0378	0.5435	−0.0233
CT(23)	−0.0902	0.5019	0.0128
CT(11)	0.4747	0.1133	0.4255
CT(12)	0.4068	0.1070	0.4943
CT(13)	0.5196	0.0755	0.5649
CT(31)	0.6299	0.0465	0.6144
Ru(1)	0.5556	0.3469	0.3386
N(11)	0.4495	0.3227	0.4277
C(111)	0.4310	0.3517	0.5119
C(112)	0.4971	0.3719	0.5926
C(113)	0.4700	0.3963	0.6732
C(114)	0.3750	0.4013	0.6733
C(115)	0.3103	0.3846	0.5950
C(116)	0.3331	0.3606	0.5124
O(11)	0.3602	0.4261	0.7595
C(117)	0.2576	0.4311	0.7565
C(171)	0.2744	0.4177	0.7943
C(118)	0.3848	0.2781	0.3974
N(12)	0.4843	0.2676	0.2830
C(121)	0.5132	0.2332	0.2128
C(122)	0.6058	0.2258	0.2190
C(123)	0.6360	0.1905	0.1538
C(124)	0.5682	0.1653	0.0820
C(125)	0.4706	0.1700	0.0682
C(126)	0.4429	0.2046	0.1319
O(12)	0.5840	0.1256	0.0155
C(127)	0.6801	0.1189	0.0193
C(128)	0.4016	0.2460	0.3217
N(13)	0.5983	0.4254	0.3965
C(131)	0.6794	0.4551	0.4602
C(132)	0.6746	0.4816	0.5457
C(133)	0.7623	0.5108	0.6004
C(134)	0.8532	0.5129	0.5656
C(135)	0.8527	0.4872	0.4764
C(136)	0.7703	0.4582	0.4194
O(13)	0.9385	0.5432	0.6160
C(137)	0.9427	0.5725	0.7065
C(138)	0.5322	0.4545	0.3746
N(14)	0.4550	0.3820	0.2701
C(141)	0.3763	0.3571	0.1962
C(142)	0.2813	0.3643	0.2140
C(143)	0.2068	0.3384	0.1446
C(144)	0.2208	0.3060	0.0658
C(145)	0.3116	0.3000	0.0481
C(146)	0.3932	0.3278	0.1158
O(14)	0.1389	0.2828	−0.0019
C(147)	0.1480	0.2440	−0.0781
C(148)	0.4538	0.4314	0.3080
N(15)	0.6691	0.3238	0.4139
C(151)	0.6729	0.3038	0.5030
C(152)	0.5997	0.2590	0.5276
C(153)	0.5984	0.2385	0.6196
C(154)	0.6790	0.2643	0.6866
C(155)	0.7519	0.3094	0.6680
C(156)	0.7469	0.3317	0.5753
O(15)	0.6832	0.2461	0.7834
C(157)	0.6200	0.1946	0.8011
C(158)	0.7533	0.3344	0.3699
N(16)	0.6610	0.3602	0.2406
C(161)	0.6492	0.3775	0.1469
C(162)	0.6205	0.4246	0.1308
C(163)	0.6150	0.4428	0.0340
C(164)	0.6436	0.4118	−0.0354
C(165)	0.6717	0.3625	−0.0234
C(166)	0.6725	0.3464	0.0744
O(16)	0.6429	0.4352	−0.1291
C(167)	0.6967	0.4078	−0.1957
C(176)	0.6347	0.4952	−0.1211
C(168)	0.7481	0.3517	0.2757
Ru(2)	0.0113	0.1683	0.4370
N(21)	−0.0282	0.0861	0.3949
C(211)	−0.1081	0.0601	0.3286
C(212)	−0.0867	0.0290	0.2466
C(213)	−0.1673	−0.0004	0.1786
C(214)	−0.2521	0.0053	0.1945
C(215)	−0.2818	0.0335	0.2659
C(216)	−0.2015	0.0634	0.3350
O(21)	−0.3371	−0.0244	0.1262
C(217)	−0.4359	−0.0162	0.1397
C(271)	−0.4117	−0.0545	0.1760
C(218)	0.0260	0.0544	0.4308
N(22)	0.1047	0.1370	0.5302
C(221)	0.1713	0.1618	0.6081
C(222)	0.2271	0.2147	0.6016
C(223)	0.3021	0.2409	0.6757
C(224)	0.3089	0.2089	0.7561
C(225)	0.2556	0.1582	0.7684
C(226)	0.1859	0.1323	0.6921
O(22)	0.3781	0.2341	0.8837
C(227)	0.4449	0.2892	0.8335
C(228)	0.1003	0.0836	0.5073
N(23)	0.1072	0.1876	0.3339
C(231)	0.1467	0.1533	0.2709
C(232)	0.1930	0.1161	0.3095
C(233)	0.2332	0.0823	0.2470
C(234)	0.2193	0.0940	0.1482
C(235)	0.1723	0.1315	0.1091
C(236)	0.1349	0.1625	0.1729
O(23)	0.2602	0.0619	0.0802
C(237)	0.3283	0.0313	0.1217
C(238)	0.1353	0.2442	0.3254
N(24)	0.0664	0.2528	0.4668
C(241)	0.0409	0.2877	0.5360
C(242)	0.0252	0.3381	0.5147
C(243)	0.0074	0.3743	0.5867
C(244)	0.0169	0.3574	0.6807
C(245)	0.0330	0.3045	0.7097
C(246)	0.0525	0.2720	0.6319
O(24)	−0.0039	0.3852	0.7645
C(247)	−0.0185	0.4398	0.7416
C(248)	0.1115	0.2769	0.3905
N(25)	−0.0971	0.1929	0.3536
C(251)	−0.0918	0.2081	0.2554
C(252)	−0.0984	0.2612	0.2329
C(253)	−0.0962	0.2797	0.1402
C(254)	−0.0920	0.2407	0.0692
C(235)	−0.0860	0.1860	0.0861
C(256)	−0.0862	0.1692	0.1845
O(25)	−0.0993	0.2478	−0.0325
C(257)	−0.0983	0.3013	−0.0619
C(258)	−0.1668	0.2058	0.3985
N(26)	−0.0949	0.1656	0.5276
C(261)	−0.1006	0.1434	0.6209
C(262)	−0.0807	0.0915	0.6376
C(263)	−0.0836	0.0720	0.7320
C(264)	−0.1082	0.1053	0.8029
C(265)	−0.1311	0.1532	0.7908
C(266)	−0.1267	0.1755	0.6999
O(26)	−0.1088	0.0869	0.8995
C(267)	−0.0504	0.0485	0.9328
C(268)	−0.1668	0.1896	0.4907

Structure solution and refinement. The structure was solved by standard Patterson and Fourier methods and refined by blocked full-matrix least-squares techniques (SHELX 76).[14] The Patterson function revealed the positions of the ruthenium and of the nitrogen atoms. Subsequent difference-Fourier maps showed the positions of all atoms except the hydrogen of the diazadiene ligands.

At the late stages of the refinement it became obvious that some methyl groups of the *p*-methoxy-groups were disordered. This was taken into account by setting up two different positions for the methyl groups with variable occupation factors X and $1 - X$.

As the integration of the n.m.r. spectrum indicated that one molecule of the solvent (toluene) cocrystallizes with one RuL_3 unit, the asymmetric unit must contain two toluene molecules. One toluene aromatic ring was detected; it is planar within experimental error. The centre of this ring coincides with a centre of symmetry. Nevertheless it was not possible to locate the methyl group of the toluene. It is probably six-fold disordered around its C_6 axis. Since the toluene is located on a centre of symmetry it contributes only half the electron density of toluene to the asymmetric unit.

Attempts to locate the other solvent molecule were unsuccessful. The last difference-Fourier map showed four peaks at 1.0—1.5 e $Å^{-3}$ accompanied by some peaks at <1 e $Å^{-3}$ in the vicinity of another centre of symmetry. This second toluene is probably located around this centre of symmetry in a many-fold disorder.

Besides this 'electron-dust' the difference-Fourier map is featureless; the remaining $\frac{1}{2}$ toluene is probably situated on a centre of symmetry like the first, but was not detected.

Only the core of the RuL_3 molecule, *e.g.* the ruthenium, nitrogen, and imino-carbon atoms, were refined anisotropically, the rest isotropically. The final R value $[=(\Sigma|F_o| - |F_c|)^2/\Sigma|F_o|^2]$ was 0.109. Atomic co-ordinates are given in Table 5.

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