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Aryldiazenide Complexes. Synthesis and X-ray Structure of *trans*-Chlorobis(triphenylphosphine)((*p*-methoxyphenyl)diazenido)rhodium Tetrafluoroborate-Bis(dichloromethane), $[RhCl(PPh_3)_2(p\text{-}N_2C_6H_4OMe)][BF_4]\cdot 2CH_2Cl_2$

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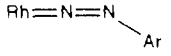
The complex $[RhCl(PPh_3)_2(p\text{-}N_2C_6H_4OMe)][BF_4]$ (**1**) and its bis(acetone) and bis(dichloromethane) solvates (**1**$\cdot 2Me_2CO$ and **1**$\cdot CH_2Cl_2$) have been synthesized from the reaction of $[RhCl(PPh_3)_2]_2$ with $[p\text{-}N_2C_6H_4OMe][BF_4]$ in acetone. The X-ray crystal structure of **1**$\cdot 2CH_2Cl_2$ has been determined. **1**$\cdot 2CH_2Cl_2$ crystallizes in the orthorhombic space group *Pnma* with $a = 22.573$ (3) Å, $b = 21.961$ (3) Å, $c = 9.522$ (2) Å, $V = 4720$ Å^3, $Z = 4$, and $D_{calcd} = 1.16$ g cm^{-3}. The structure was solved by using 2181 observed reflections in the range $4° < 2\theta < 50°$ and refined by least-squares methods to a final $R_F = 0.044$ ($R_{wF} = 0.052$). The cation $[RhCl(PPh_3)_2(p\text{-}N_2C_6H_4OMe)]^+$ is square-planar with a singly bent Rh-N_2Ar moiety (Ar = p-C_6H_4OMe), consistent with the formal view that it is a complex of Rh(I) and N_2Ar^+. Important dimensions are Rh-N(1) = 1.793 (8) Å, N(1)-N(2) = 1.157 (11) Å, Rh-N(1)-N(2) = 179.4 (7)°, and N(1)-N(2)-C(aryl) = 141.3 (9)°. Complex **1** reacts with hydrogen chloride to form first the new cationic aryldiazene complex (**4**) with δ(NH) at 10.64, formulated as $[RhCl_2(PPh_3)_2(p\text{-}NHNC_6H_4OMe)][BF_4]$, and subsequently the known neutral aryldiazene complex $RhCl_3(PPh_3)_2(p\text{-}NHNC_6H_4OMe)$ (**3**) with δ(NH) at 11.54. Complex **1** is transformed into the known neutral aryldiazenide complex $RhCl_2(PPh_3)_2(p\text{-}N_2C_6H_4OMe)$ (**2**) by LiCl, and the reaction is reversed with $AgBF_4$. Reaction of **1** with PPh_3 at low temperature forms an unstable green complex having ν(NN) at 1659 cm^{-1} that is also formed in the reaction of $RhCl(PPh_3)_3$ with $[p\text{-}N_2C_6H_4OMe][BF_4]$ and is tentatively identified as $[RhCl(PPh_3)_3(p\text{-}N_2C_6H_4OMe)][BF_4]$ as originally suggested by Baird and Wilkinson.

Introduction

Aryldiazenide (aryldiazo) complexes of rhodium were first reported some 20 years ago. Since that time, they have been the subject of much discussion as to their correct formulation, especially regarding the oxidation state of the metal and the geometry of the aryldiazenide ligand.[1-12] Those of the type $[L_nRhX(N_2Ar)]^+$ and $L_nRhX_2(N_2Ar)$ may, in principle, be formulated either as Rh^I complexes with the diazo ligand formally $[N_2Ar]^+$ or as Rh^{III} complexes with the diazo ligand formally $[N_2Ar]^-$. Ideally, these two possibilities may be distinguished by structural studies.[11] In the first case, the Rh-N-N skeleton is expected to be *linear* and the NNC angle less than 180°; i.e., the "singly bent" geometry (I) is adopted. The second case should result in a "doubly bent" arrangement (II) of the rhodium-diazenide moiety and a *nonlinear* Rh-N-N skeleton.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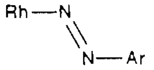
II

To date, the only rhodium complex in the literature for which the geometry of the aryldiazenide group has been established unequivocally by crystallography is the complex $[Rh(PPP)Cl(N_2Ph)][BF_4]$, where PPP is the terdentate phosphine $PhP\{(CH_2)_3PPh_2\}_2$. The Rh-N_2Ph group was found to adopt the doubly bent arrangement (II), and it is thus formally a complex of Rh(III) with $[N_2Ph]^-$. The terdentate PPP ligand is considered to make the rhodium(I) precursor Rh(PPP)Cl inert toward dissociation of a phosphine ligand site and, moreover, relatively basic. Thus, the doubly bent Rh-N_2Ph skeleton in $[Rh(PPP)Cl(N_2Ph)][BF_4]$ can be visualized to result from electrophilic oxidative addition of $[N_2Ph]^+$ to this Rh(I) complex.[3]

Until the present study, there had been no structural support for the alternative Rh^I-$(N_2Ar)^+$ formulation in rhodium aryldiazenide complexes, although its adoption in some of them has been suggested on the basis of IR spectroscopy,[3a,8] including a cation formulated as $[RhCl(PPh_3)_2(N_2Ph)]^+$, though no details of the synthesis or characterization of this compound have been published.

In this paper we describe the synthesis and some properties of the solvated and unsolvated complex $[RhCl(PPh_3)_2(p\text{-}N_2C_6H_4OMe)][BF_4]$. The crystal structure of the bis(dichloromethane) solvate has been determined. It unambiguously demonstrates that the aryldiazenide ligand is indeed singly bent and that the complex should be considered formally to be of the type Rh^I-$(N_2Ar)^+$. Consistent with this view, it is a typical square-planar complex, as expected for d^8 rhodium(I).

Experimental Section

General Procedures. All manipulations were carried out in Schlenk vessels under dry nitrogen. Solvents were dried by standard procedures and distilled under N_2 immediately before use. Infrared spectra were obtained on samples pressed in KBr or samples in solution in CaF_2 cells and were recorded by using a Perkin-Elmer Model 983G spectrometer. ^{1}H NMR spectra were obtained at 100 MHz on a Bruker SY-100 spectrometer or by M. M. Tracey on a Bruker WM-400 instrument at 400 MHz. Mass spectra were obtained by G. Owen on a Hewlett-Packard 5985 instrument equipped with a Phrasor Scientific Inc. fast atom bombardment source. Microanalyses were obtained by M. K. Yang of the SFU microanalytical service. $RhCl(PPh_3)_3$ and $[RhCl(PPh_3)_2]_2$ were synthesized according to the method of Osborn and Wilkinson[13] and were authenticated by IR spectroscopy and microanalyses.

Syntheses. A suspension of $[RhCl(PPh_3)_2]_2$[13] (62 mg, 0.047 mmol) in acetone (3 mL) was stirred for 35 min at room temperature with $[p\text{-}N_2C_6H_4OMe][BF_4]$ (20 mg, 0.090 mmol). The orange suspension quickly became green. The green suspension was removed, washed carefully with 1:1 acetone-hexane, and then dried under vacuum to yield fine green crystals of the bis(acetone)-solvated complex salt $[RhCl(PPh_3)_2(p\text{-}N_2C_6H_4OMe)][BF_4]\cdot 2Me_2CO$ (**1**$\cdot 2Me_2CO$; yield 75 mg, 0.085 mmol, 80%). Anal. Found: C, 58.30; H, 4.82; N, 2.92. Calcd for **1**$\cdot 2Me_2CO$: C, 58.80; H, 4.90; N, 2.80. ^{1}H NMR ($CDCl_3$): δ 2.17 (s, 12 H, Me_2CO), 3.87 (s, 3 H, OMe), 6.80 (AA'BB' q, 4 H, C_6H_4), 7.43 (m, 18 H, meta and para, PPh_3), 7.73 (m, 12 H, ortho, PPh_3). IR (KBr,

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cm^{-1}): 1984 (ν(NN)) [1935 (ν(^{15}NN))], 1709 (Me$_2$CO). The green crystals of **1**·2Me$_2$CO were stirred with diethyl ether. Following removal of the solvent there remained fine green-yellow crystals of the solvent-free complex [RhCl(PPh$_3$)$_2$(p-N$_2$C$_6$H$_4$OMe)][BF$_4$] (**1**). Anal. Found: C, 58.52; H, 4.14; N, 3.38. Calcd for **1**: C, 58.37; H, 4.19; N, 3.17. IR (KBr, cm^{-1}): 1931 (ν(NN)) [1894 (ν(^{15}NN))]. ^{1}H NMR (CDCl$_3$): δ 3.87 (3 H, OMe), 6.80 (AA'BB' q, 4 H, C$_6$H$_4$), 7.43 (m, 18 H, meta and para, PPh$_3$), 7.75 (m, 12 H, ortho, PPh$_3$). FABMS (based on ^{35}Cl): m/z 797 (M$^+$ of cation), 662 (M$^+$ – N$_2$C$_6$H$_4$OMe), 627 (M$^+$ – N$_2$C$_6$H$_4$OMe – Cl). Recrystallization of **1** from CH$_2$Cl$_2$–hexane at room temperature by slow diffusion provided well-formed blocklike single crystals of the bis(dichloromethane) solvate [RhCl(PPh$_3$)$_2$(p-N$_2$C$_6$H$_4$OMe)][BF$_4$]·2CH$_2$Cl$_2$ (**1**·2CH$_2$Cl$_2$). These crystals were very dark green (almost appearing black) in reflected light but appeared brown in transmission. The CH$_2$Cl$_2$ content was established by NMR. Anal. Found: C, 51.38; H, 4.01; N, 2.83. Calcd for **1**·2CH$_2$Cl$_2$: C, 51.23; H, 3.89; N, 2.66. ^{1}H NMR (CDCl$_3$): δ 3.88 (s, 3 H, OMe), 5.32 (s, 4 H, 2 CH$_2$Cl$_2$), 6.82 (AA'BB' q, 4 H, C$_6$H$_4$), 7.43 (m, 18 H, meta and para, PPh$_3$), 7.75 (m, 12 H, ortho, PPh$_3$). IR (KBr, cm^{-1}): 1982 ν(NN) [1928 (ν(^{15}NN))].

Reaction of [RhCl(PPh$_3$)$_2$(p-N$_2$C$_6$H$_4$OMe)][BF$_4$] with Hydrogen Chloride. (a) A green suspension of **1**·2Me$_2$CO (36 mg) was stirred in diethyl ether (4 mL) under an atmosphere of HCl(g) in a Schlenk tube for 1 h. The resulting yellow suspension was removed by centrifuging, washed twice with diethyl ether, and dried under vacuum. It was identified as RhCl$_3$(PPh$_3$)$_2$(p-NHNC$_6$H$_4$OMe) (**3**) by comparison with a sample synthesized by the published method.[2a] ^{1}H NMR (CDCl$_3$): δ 3.86 (s, 3 H, OMe), 6.57 (AA'BB' q, 4 H, C$_6$H$_4$), 7.18 (m), 7.96 (m, 30 H, PPh$_3$), 11.54 (br s, 1 H, NH). IR (KBr): ν(BF$_4$) absent; characteristic vibrations at 1603, 1508 cm^{-1}.

(b) A brown solution of **1**·2CH$_2$Cl$_2$ (20 mg) in CH$_2$Cl$_2$ (3 mL) was stirred under an atmosphere of HCl(g) for 30 min. A small amount of red precipitate was removed and pentane added to the orange solution to precipitate a yellow powder, which was washed with 1:1 CH$_2$Cl$_2$–pentane and dried under vacuum. This product could not be recrystallized without decomposition since it was unstable in solution in the absence of HCl (to produce compound **1** and some free [p-N$_2$C$_6$H$_4$OMe][BF$_4$]) or reacted further with HCl to give **3** (see below). The crude precipitate was not analytically pure and contained (by IR) some free [p-N$_2$C$_6$H$_4$OMe][BF$_4$] that could not easily be removed and was responsible for erroneously high nitrogen and low carbon analyses. It is identified as an aryldiazene complex from δ 10.64 (NH) and is formulated to be [RhCl$_2$(PPh$_3$)$_2$(p-NHNC$_6$H$_4$OMe)][BF$_4$] (**4**). Anal. Found: C, 52.84, 52.95; H, 4.20, 4.23; N, 4.75, 4.89. Calcd for [RhCl$_2$(PPh$_3$)$_2$(p-NHNC$_6$H$_4$OMe)][BF$_4$]: C, 56.03, H, 4.13; N, 3.04. ^{1}H NMR (CDCl$_3$): δ 3.97 (s, 3 H, OMe), 6.90 (AA'BB' q, 4 H, C$_6$H$_4$), 7.23, 7.74 (m, 30 H, PPh$_3$), 10.64 (br s (with ^{15}N$_\alpha$ doublet J_{NH} = 70 Hz), 1 H, NH). IR (KBr): characteristic bands at 1602, 1504 cm^{-1} and at 1058 cm^{-1} (ν(BF$_4$)).

Reaction of RhCl$_3$(PPh$_3$)$_2$(p-NHNC$_6$H$_4$OMe) (3) with AgBF$_4$. A yellow solution of **3** (43 mg) in CDCl$_3$ (14 mL) was degassed and added to solid AgBF$_4$ in a Schlenk tube and stirred for several hours. The reaction was followed by removing aliquots periodically for ^{1}H NMR. Resonances for **3** decreased with time as the buildup of resonances at δ 3.97 (OMe), 6.92, 6.88 (AA'BB' q, C$_6$H$_4$), and 10.65 (NH) typical of compound **4** occurred. Additional resonances of smaller intensity (for example δ 4.02 (OMe)) indicated the formation of other, unknown, products in the reaction. The appearance of resonances typical of compound **1** (δ 3.88 (OMe), 6.76, 6.82 (AA'BB' q, C$_6$H$_4$)) was observed in later stages of the reaction before all of **3** was consumed. These resonances increased upon addition of further AgBF$_4$ with decrease in resonances for **3** and **4**.

Reaction of RhCl(PPh$_3$)$_3$ with [p-N$_2$C$_6$H$_4$OMe][BF$_4$]. A deep brown solution/suspension of RhCl(PPh$_3$)$_3$ (14 mg) in CHCl$_3$ (0.3 mL) at 0 °C was treated with [p-N$_2$C$_6$H$_4$OMe][BF$_4$] (7 mg, 2 equiv) in CH$_3$OH (0.6 mL) and stirred for 48 min. The dark brown solution was evaporated at –10 °C to give a very dark solid residue, which contained no residual diazonium salt (by IR). The IR spectrum showed weak absorption in the 1900–2000-cm^{-1} region corresponding to compound **1** and strong absorptions at 1601 and 1502 cm^{-1} indicating compound **4**. The crude solid was dissolved in CH$_2$Cl$_2$ at 0 °C, and a yellow product was precipitated by addition of ethanol and evaporation. It was washed with ethanol, dried under vacuum, and identified as compound **4** by comparison of its IR and ^{1}H NMR spectra. ^{1}H NMR (CDCl$_3$): δ 3.97 (s, 3 H, OMe), 6.90 (AA'BB' q, 4 H, C$_6$H$_4$), 7.22, 7.70 (m, PPh$_3$), 10.64 (s, 1 H, NH). IR: 1601, 1503, 1058 (ν(BF$_4$)) cm^{-1}.

A similar reaction at –35 °C or below gave an immediate dark green solution, from which was isolated green crystalline compound **1** in good yield (identified by IR and ^{1}H NMR spectra). When the reagents were stirred for 4 h at –40 °C in a 1:1 ratio, a green solid was formed that had the following spectral characteristics. ^{1}H NMR (CDCl$_3$, –50 °C): δ 3.70 (s, 3 H, OMe), 6.65, 6.68 (inner peaks of AA'BB' q, 4 H, C$_6$H$_4$), 7.40 7.74 (m, 45 H, PPh$_3$). IR: 1659 (ν(NN)), 1058 (ν(BF$_4$)) cm^{-1}. These spectra are consistent with the formula [RhCl(PPh$_3$)$_3$(p-N$_2$C$_6$H$_4$OMe)][BF$_4$].

Reaction of 1·2Me$_2$CO with PPh$_3$. A brown solution/suspension of **1**·2Me$_2$CO (10 mg) in acetone (0.1 mL) was treated with PPh$_3$ (3 mg) in acetone (0.2 mL) at –50 °C. The mixture quickly became dark green and was stirred for 25 min; the solvent was then evaporated to give a dark green solid shown by the IR spectrum (KBr) to contain unreacted **1**·2Me$_2$CO (ν(NN) 1985 cm^{-1}) and a product with a characteristic absorption at 1658 cm^{-1} of equal intensity. The dark green solid was redissolved in acetone at –50 °C, a further 2 mg of PPh$_3$ added, and the mixture was stirred for 1 h. The IR spectrum of the dark green isolated product now exhibited a strong absorption at 1659 cm^{-1} (ν((NN)) and ν(BF$_4$) at 1058 cm^{-1} and indicated the absence of unreacted **1**. It decomposed to a brown product in acetone solution at room temperature with loss of the 1659-cm^{-1} band. It was not characterized further.

Reaction of 1·2CH$_2$Cl$_2$ with LiCl. An excess of LiCl (160 mg) suspended in acetone (1 mL) was added to **1**·2CH$_2$Cl$_2$ (20 mg) in acetone (1 mL) and the mixture stirred for 1 h. The insoluble material was separated from the pale yellow solution and washed with water to remove lithium salts then with ethanol and hexane. The resulting yellow complex was identified as RhCl$_2$(PPh$_3$)$_2$(p-N$_2$C$_6$H$_4$OMe) by a comparison of its IR spectrum with that of the same compound prepared from RhCl(PPh$_3$)$_3$ by the method of Robinson.[2a] IR (KBr): characteristic bands at 1612 and 1558 (ν(NN)) cm^{-1}.

Reaction of 1·2Me$_2$CO with CO. A brown solution of **1**·2Me$_2$CO (12 mg) in CH$_2$Cl$_2$ (2 mL) was stirred under an atmosphere of CO, and the reaction was followed by IR spectroscopy. The solution became orange in 10 min and showed ν(NN) at 2237 cm^{-1} ([p-N$_2$C$_6$H$_4$OMe]$^+$), ν(CO) at 2095, 2013, and 1980 cm^{-1}, and loss of the band at 1911 cm^{-1} (ν(NN) of **1**·2Me$_2$CO). After 1 h the 1980-cm^{-1} band was only weak and the 2095- and 2013-cm^{-1} bands were very strong; this spectrum was unchanged over a further 2 h. Nitrogen was now passed through the solution for 1 h, resulting in disappearance of the 2095- and 2013-cm^{-1} bands, and a new band at 1984 cm^{-1}. CO was now bubbled through the solution for 30 min, resulting in restoration of the bands at 2093 and 2013 cm^{-1} and a weak band at ca. 1980 cm^{-1}.

X-ray Structure Determination for 1·2CH$_2$Cl$_2$. A block-shaped crystal was selected from a sample recrystallized from CH$_2$Cl$_2$–hexane as described above and was mounted on a glass fiber. The crystal was cooled to 213 K by using a locally developed apparatus based on the commerical Enraf-Nonius system. Data were collected on an Enraf-Nonius CAD4-F diffractometer equipped with a graphite monochromator. The unit cell parameters and an orientation matrix were obtained from the accurate setting angles of 25 reflections in the range 27° < 2θ < 44°. Data were corrected for Lorentz and polarization effects, and for absorption by using an analytical method.[14] Two standard reflections were measured every 1 h and showed an overall variation of ±3.5%. These were used to scale the data. A total of 4278 unique reflections were measured, of which 2181 were considered to be observed ($I \geq 3\sigma(I)$) and were used in subsequent calculations. Pertinent crystallographic and experimental parameters are given in Table I.

A Patterson synthesis strongly suggested the space group to be *Pnma*, with the rhodium complex cation possessing exact mirror symmetry. A Fourier map based on the Rh atom position revealed the positions of all the expected non-hydrogen atoms except for one fluorine atom. The majority of hydrogen atoms were located from a difference map, but they were placed geometrically and periodically recalculated. The [BF$_4$]$^-$ anion appeared to be disordered about the mirror plane; F(3), F(4), B(1), and B(2) were assigned fixed occupancies based on difference map results. This model was refined by full-matrix least-squares methods, initially with isotropic and then with anisotropic thermal parameters. However, the thermal parameters for the [BF$_4$]$^-$ group became unreasonably large, and additional neighboring peaks in the difference Fourier map were interpreted to indicate further disorder of the [BF$_4$]$^-$ group in the form of a "windshield wiper" pivoting the remaining atoms of the [BF$_4$]$^-$ about the two fluorine atoms F(1) and F(2) located in the mirror plane. This is described in detail in the Results. The final residuals were R = 0.044 and R_w = 0.052, and the goodness of fit was 1.264. During the final cycles of refinement the weighting scheme employed was $w = 1/(\sigma^2(F) + 0.0008F^2)$. The reflections showed no systematic variation for $\langle w\Delta^2\rangle$ either as a function of F_o or $(\sin\theta)/\lambda$. The largest peak in the final difference map had a height of 0.052 (9) e Å^{-3} and was situated 1.56 Å from the Rh atom. Complex neutral atom scattering factors[15] were

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Table I. Crystallographic Data for $[RhCl(PPh_3)_2(p\text{-}N_2C_6H_4OMe)][BF_4]\cdot 2CH_2Cl_2$ ($\mathbf{1}\cdot 2CH_2Cl_2$)

formula	$C_{45}H_{41}BCl_5F_4N_2OP_2Rh$
fw	1054.7
cryst syst	orthorhombic
space group	*Pnma*
a/Å	22.573 (3)
b/Å	21.961 (3)
c/Å	9.522 (2)
V/Å^3	4720.2
Z	4
D_{calcd}/g cm^{-3}	1.160
cryst dimens/mm	0.07 × 0.42 × 0.32
temp/K	213
radiation	Mo Kα
μ(MoKα)/cm^{-1}	7.43
transmission factors	0.783–0.950
scan mode	ω–2θ
scan speed/deg min^{-1}	1.0–3.3
scan width (ω)/deg	0.80 + 0.35 tan θ
2θ scan range/deg	4–50
no. of unique rflns measd	4278
no. of rflns obsd ($I \geq 3\sigma(I)$)	2181
no. of variables	304
R_F	0.044
R_{wF}	0.052
goodness of fit	1.264

Table II. Final Positional and Equivalent Isotropic Thermal Parameters for $[RhCl(PPh_3)_2(p\text{-}N_2C_6H_4OMe)][BF_4]\cdot 2CH_2Cl_2$ ($\mathbf{1}\cdot 2CH_2Cl_2$)[a]

	x	y	z	B_{eq},[b] Å^2
Rh	0.01916 (3)	0.2500	0.10849 (8)	1.93
P	0.01783 (8)	0.14310 (7)	0.09186 (17)	2.01
Cl(1)	0.11046 (11)	0.2500	0.0011 (3)	2.93
N(1)	−0.0550 (3)	0.2500	0.1758 (7)	1.8
N(2)	−0.1031 (3)	0.2500	0.2181 (9)	2.5
O(1)	−0.3374 (3)	0.2500	0.0565 (8)	3.3
C(1)	−0.1622 (4)	0.2500	0.1715 (10)	2.2
C(2)	−0.2069 (4)	0.2500	0.2714 (9)	2.9
C(3)	−0.2653 (5)	0.2500	0.2286 (11)	3.2
C(4)	−0.2789 (4)	0.2500	0.0849 (9)	2.5
C(5)	−0.2334 (5)	0.2500	−0.0122 (11)	3.5
C(6)	−0.1756 (4)	0.2500	0.0289 (10)	3.2
C(8)	−0.3346 (5)	0.2500	−0.0867 (13)	4.8
C(11)	−0.0546 (3)	0.1121 (3)	0.1405 (6)	2.1
C(12)	−0.0716 (3)	0.1151 (3)	0.2809 (8)	3.1
C(13)	−0.1279 (4)	0.0979 (4)	0.3204 (9)	3.7
C(14)	−0.1673 (3)	0.0765 (4)	0.2201 (10)	4.2
C(15)	−0.1506 (3)	0.0733 (4)	0.0812 (9)	4.4
C(16)	−0.0946 (3)	0.0917 (3)	0.0403 (8)	3.4
C(21)	0.0295 (3)	0.1214 (3)	−0.0895 (6)	2.4
C(22)	−0.0004 (3)	0.1547 (3)	−0.1903 (7)	3.4
C(23)	0.0051 (4)	0.1412 (4)	−0.3317 (8)	4.4
C(24)	0.0417 (4)	0.0950 (4)	−0.3735 (7)	3.6
C(25)	0.0723 (3)	0.0628 (3)	−0.2752 (7)	3.4
C(26)	0.0664 (3)	0.0754 (3)	−0.1324 (7)	2.5
C(31)	0.0695 (3)	0.1001 (3)	0.1997 (6)	2.1
C(32)	0.1160 (3)	0.1296 (3)	0.2644 (7)	3.0
C(33)	0.1563 (3)	0.0972 (4)	0.3460 (7)	3.2
C(34)	0.1502 (3)	0.0359 (4)	0.3621 (7)	3.6
C(35)	0.1044 (3)	0.0059 (3)	0.2990 (8)	3.5
C(36)	0.0633 (3)	0.0377 (3)	0.2177 (7)	2.9
C(100)	0.2215 (4)	0.1298 (4)	0.8598 (9)	5.4
Cl(101)	0.22243 (11)	0.07994 (15)	1.00272 (25)	6.91
Cl(102)	0.23593 (15)	0.09193 (18)	0.7054 (3)	9.33
F(1)	0.3060 (3)	0.2500	0.8718 (8)	6.3
F(2)	0.3935 (3)	0.2500	0.7527 (7)	6.4
F(3)[c]	0.3975 (4)	0.2500	0.9834 (9)	7.0
F(4)[c]	0.3620 (6)	0.1704 (7)	0.8383 (23)	8.7
F(5)[c]	0.3746 (13)	0.3015 (13)	0.946 (3)	9.9 (8)
B(1)[c]	0.36430	0.2300	0.86646	5.2 (8)
B(2)[c]	0.36443	0.2500	0.87267	3.3 (10)

[a] Estimated standard deviations for the least significant digits are given in parentheses in this and the following table. [b] B_{eq} is the mean of the principal axes of the thermal ellipsoid. [c] Fixed occupancies were assigned as follows: F(3), 0.72; F(4), 0.36; F(5), 0.28; B(1), 0.36; B(2), 0.28 (note F(3) and B(2) have site symmetry *m*).

Table III. Selected Bond Distances (Å) and Interbond Angles (deg) for $[RhCl(PPh_3)_2(p\text{-}N_2C_6H_4OMe)][BF_4]\cdot 2CH_2Cl_2$ ($\mathbf{1}\cdot 2CH_2Cl_2$)

Rh–Cl(1)	2.301 (3)	C(16)–C(11)	1.388 (10)
Rh–P	2.353 (2)	C(21)–C(22)	1.382 (9)
Rh–N(1)	1.793 (8)	C(22)–C(23)	1.385 (10)
P–C(11)	1.831 (7)	C(23)–C(24)	1.366 (12)
P–C(21)	1.811 (6)	C(24)–C(25)	1.361 (11)
P–C(31)	1.818 (6)	C(25)–C(26)	1.394 (9)
N(1)–N(2)	1.157 (11)	C(26)–C(21)	1.371 (9)
N(2)–C(1)	1.406 (12)	C(31)–C(32)	1.381 (10)
C(1)–C(2)	1.388 (13)	C(32)–C(33)	1.393 (10)
C(2)–C(3)	1.379 (15)	C(33)–C(34)	1.361 (11)
C(3)–C(4)	1.403 (14)	C(34)–C(35)	1.396 (10)
C(4)–C(5)	1.381 (14)	C(35)–C(36)	1.386 (9)
C(5)–C(6)	1.362 (14)	Cl(101)–C(100)	1.746 (11)
C(6)–C(1)	1.392 (14)	Cl(102)–C(100)	1.720 (9)
C(4)–O	1.348 (12)	B(1)–F(1)	1.388 (7)
O–C(8)	1.417 (14)	B(1)–F(2)	1.341 (6)
C(11)–C(12)	1.392 (9)	B(1)–F(3)	1.412 (8)
C(12)–C(13)	1.379 (11)	B(1)–F(4)	1.337 (17)
C(13)–C(14)	1.387 (13)	B(2)–F(1)	1.312 (7)
C(14)–C(15)	1.377 (13)	B(2)–F(2)	1.317 (6)
C(15)–C(16)	1.383 (10)	B(2)–F(5)	1.350 (17)
Cl(1)–Rh–P	88.9 (1)	C(14)–C(15)–C(16)	120.3 (7)
Cl(1)–Rh–N(1)	174.6 (2)	C(15)–C(16)–C(11)	119.7 (6)
P–Rh–P	172.2 (1)	P–C(21)–C(22)	116.9 (5)
P–Rh–N(1)	90.7 (1)	P–C(21)–C(26)	124.5 (5)
Rh–P–C(11)	111.4 (2)	C(22)–C(21)–C(26)	118.6 (6)
Rh–P–C(21)	109.0 (2)	C(21)–C(22)–C(23)	121.2 (7)
Rh–P–C(31)	118.2 (2)	C(22)–C(23)–C(24)	119.8 (7)
C(11)–P–C(21)	105.8 (3)	C(23)–C(24)–C(25)	119.4 (7)
C(11)–P–C(31)	103.7 (3)	C(24)–C(25)–C(26)	121.3 (6)
C(21)–P–C(31)	108.3 (3)	C(25)–C(26)–C(21)	119.7 (6)
N(2)–N(1)–Rh	179.4 (7)	P–C(31)–C(32)	119.7 (5)
C(1)–N(2)–N(1)	141.3 (9)	P–C(31)–C(36)	121.3 (5)
N(2)–C(1)–C(2)	118.4 (9)	C(32)–C(31)–C(36)	119.0 (6)
N(2)–C(1)–C(6)	121.0 (9)	C(31)–C(32)–C(33)	120.4 (6)
C(2)–C(1)–C(6)	120.7 (9)	C(32)–C(33)–C(34)	120.1 (7)
C(1)–C(2)–C(3)	119.5 (8)	C(33)–C(34)–C(35)	120.3 (7)
C(2)–C(3)–C(4)	119.8 (9)	C(34)–C(35)–C(36)	120.4 (7)
C(3)–C(4)–C(5)	119.5 (9)	C(35)–C(36)–C(31)	119.8 (6)
C(4)–C(5)–C(6)	121.3 (9)	Cl(101)–C(100)–Cl(102)	112.2 (5)
C(5)–C(6)–C(1)	119.3 (9)	F(1)–B(1)–F(2)	113.1 (4)
C(3)–C(4)–O	114.2 (8)	F(1)–B(1)–F(3)	112.0 (5)
C(5)–C(4)–O	126.4 (9)	F(1)–B(1)–F(4)	106.3 (6)
C(4)–O–C(8)	117.5 (8)	F(2)–B(1)–F(3)	105.9 (4)
P–C(11)–C(12)	118.1 (5)	F(2)–B(1)–F(4)	100.2 (9)
P–C(11)–C(16)	121.8 (5)	F(3)–B(1)–F(4)	118.9 (9)
C(12)–C(11)–C(16)	119.8 (6)	F(1)–B(2)–F(2)	119.5 (5)
C(11)–C(12)–C(13)	120.2 (7)	F(1)–B(2)–F(5)	100.0 (13)
C(12)–C(13)–C(14)	119.7 (7)	F(2)–B(2)–F(5)	111.5 (12)
C(13)–C(14)–C(15)	120.3 (7)	F(5)–B(2)–F(5)′	113.7 (19)

employed. The NRCVAX programs[16] were run on an in-house MICRO-VAX II computer. Final positional parameters are given in Table II. Selected bond distances and interbond angles are listed in Table III. Tables of anisotropic thermal parameters, hydrogen atom coordinates, and calculated and observed structure factors are available as supplementary material.

Results

(a) Synthesis and Characterization. The binuclear rhodium complex $[RhCl(PPh_3)_2]_2$ reacted rapidly with an equimolar quantity of *p*-methoxybenzenediazonium tetrafluoroborate at room temperature in acetone to produce a green crystalline suspension and a brown solution from which no further solid material could be obtained upon addition of hexane. The green crystalline product was identified on the basis of elemental analysis and IR and NMR spectroscopy as the bis(acetone)-solvated complex salt $[RhCl(PPh_3)_2(p\text{-}N_2C_6H_4OMe)][BF_4]\cdot 2Me_2CO$ ($\mathbf{1}\cdot 2Me_2CO$). In addition to the expected absorptions for $[BF_4]^-$ and coordinated PPh_3, the IR spectrum in KBr showed a strong, sharp absorption at 1709 cm^{-1} for ν(CO) of coordinated acetone, a band at 356 cm^{-1} tentatively assigned to ν(RhCl), and, most importantly, a band at 1984 cm^{-1} assigned to ν(NN). When the complex was synthesized by using the terminally ^{15}N-labeled diazonium salt $[p\text{-}^{15}NNC_6H_4OMe][BF_4]$ (96% enriched), this band was absent, and

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[16] Larson, A. C.; Lee, F. L.; Le Page, Y.; Gabe, E. J. *The N.R.C. VAX Crystal System*; Chemistry Division, NRC: Ottawa, Ontario, Canada.

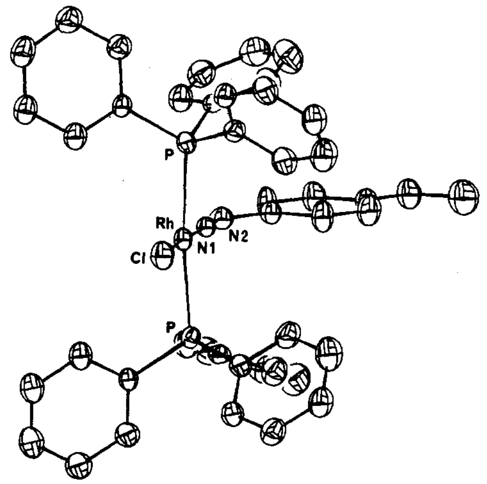

Figure 1. Perspective view of the cation $[RhCl(PPh_3)_2(p\text{-}N_2C_6H_4OMe)]^+$ in $1{\cdot}2CH_2Cl_2$.

a new band at 1935 cm^{-1} was assigned to $\nu(^{15}NN)$.[17] The integrated ^1H NMR spectrum established the presence of two molecules of acetone of solvation.

When the crystals were washed with diethyl ether, the elemental analysis and the IR and NMR spectra of the fine yellow-green crystals that resulted showed that loss of the acetone had occurred to give solvent-free **1**. In addition, the position of $\nu(NN)$ had shifted significantly to lower wavenumber, appearing now at 1931 cm^{-1} ($\nu(^{15}NN)$ 1894 cm^{-1}). The unsolvated product was further examined by fast atom bombardment mass spectroscopy. The highest mass values observed were for a group of peaks at m/z 797, 798, and 799. These masses and their relative intensities were in agreement with those calculated for the isotopic composition of the cation $[RhCl(PPh_3)_2(p\text{-}N_2C_6H_4OMe)]^+$, for which the calculated relative intensities of the masses with m/z 797, 798, and 799 are 100:50:45, respectively. Patterns at lower mass values corresponded first to loss of the aryldiazenide radical $p\text{-}N_2C_6H_4OMe$ and then to loss of Cl.

Recrystallization of **1** by diffusion of hexane into its brown solution in CH_2Cl_2 at room temperature gave excellent single crystals, which were analyzed as the bis(dichloromethane) solvate $1{\cdot}2CH_2Cl_2$. The degree of solvation was determined from the integrated ^1H NMR spectrum. In the IR spectrum $\nu(NN)$ had moved again to higher wavenumber than for **1**, to 1982 cm^{-1}, near that of $1{\cdot}2Me_2CO$.

(b) X-ray Crystal Structure. The structure of $1{\cdot}2CH_2Cl_2$ was determined by X-ray diffraction. The structure consists of discrete cation–anion pairs and solvent molecules, in agreement with the analytical and spectroscopic data. The cation is the square-planar, four-coordinate rhodium complex $[RhCl(PPh_3)_2(p\text{-}N_2C_6H_4OMe)]^+$. The trans PPh_3 groups are related by a crystallographic mirror plane in which the rhodium and chlorine atoms and the (p-methoxyphenyl)diazenide group are located (Figure 1).

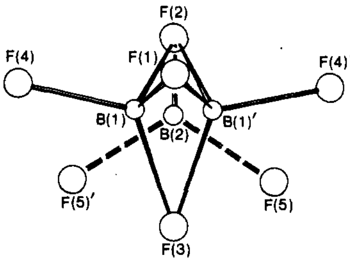

Figure 2. The disordered $[BF_4]^-$ anion in $1{\cdot}2CH_2Cl_2$. Two BF_4^- sites related by a mirror plane are B(1), F(1), F(2), F(3), F(4) and B(1)', F(1), F(2), F(3), F(4)'. The third site is B(2), F(1), F(2), F(5), F(5)'.

The rhodium–(p-methoxyphenyl)diazenide system clearly adopts the singly bent geometry (I), since the Rh–N–N skeleton is linear (Rh–N–N = 179.4 (7)°) and the N–N–C(phenyl) angle is 141.3 (9)°. The N–N–C(phenyl) angle is, in fact, the largest that has so far been observed in an aryldiazenide complex. The aryldiazenide complex that displays the next largest N–N–C(phenyl) angle is the ruthenium(II) complex $Ru(p\text{-}N_2C_6H_4Me)Cl_3(PPh_3)_2$,[18] where an angle of 137.1 (5)° was found.[18a] The dimensions of the M–N–N skeletons of these rhodium(I) and ruthenium(II) complexes are remarkably similar (Rh–N = 1.793 (8) Å, Ru–N = 1.784 (5) Å; N–N = 1.157 (11) Å (Rh), 1.158 (6) Å (Ru)) and are indicative of significant multiple bonding between the metal and the aryldiazenide ligand in both cases.

It is difficult to compare in a meaningful way the Rh–Cl and Rh–P dimensions with those of other rhodium complexes because values for another comparable square-planar, positively charged rhodium(I) chloro phosphine complex could not be located in the literature. It does seem, however, that the Rh–Cl bond length of 2.301 (3) Å is among the shortest observed for any rhodium complex. For comparison, the Rh–Cl bond lengths in the following neutral square-planar complexes are as follows: *trans*-$RhCl(CO)(PPh_3)_2$, 2.405 Å;[19] $RhCl(PPh_3)_3$, 2.376 and 2.404 Å;[20] $RhCl(N_2)(P\text{-}i\text{-}Pr_3)_2$, 2.356 Å.[21] Although allowance must be made for the cationic nature of the complex, it is possible that the Rh–Cl bond, by being trans to the aryldiazenide ligand, experiences some degree of shortening. Such an effect was observed for Cl trans to the nitrosyl ligand in $RuCl_3(NO)(PPh_3)_2$, but a much smaller (and barely significant) degree of shortening was detected for the corresponding Ru–Cl bond in $RuCl_3(p\text{-}N_2C_6H_4CH_3)(PPh_3)_2{\cdot}CH_2Cl_2$.[18a] The rhodium–phosphorus bonds (2.353 (2) Å) are somewhat longer than the comparable bonds in *trans*-$RhCl(CO)(PPh_3)_2$ (2.304 Å),[19] $RhCl(PPh_3)_3$ (2.304–2.338 Å),[20] and $RhCl(N_2)(P\text{-}i\text{-}Pr_3)_2$ (2.348 Å).[21]

The disordered single $[BF_4]^-$ anion was satisfactorily interpreted in terms of the model illustrated in Figure 2. It consists of partial occupancy of the five fluoride sites F(1)–F(5) and two boron sites B(1) and B(2). The crystallographic mirror plane contains F(1), F(2), F(3), and B(2) and generates the following mirror-related sites: B(1), B(1)'; F(4), F(4)'; F(5), F(5)'. One $[BF_4]^-$ site is described by B(2), F(1), F(2), F(5), and F(5)'. The second site consists of B(1), F(1), F(2), F(3), and F(4) and has the mirror-related image B(1)', F(1), F(2), F(3), and F(4)'. The model suggests that the $[BF_4]^-$ group executes a pivoting motion by using F(1) and F(2) as a fixed base. This causes the boron to move through the sites B(1), B(2), and B(1)' sequentially and produces the fluoride site movements F(4) → F(5) → F(3) and F(3) → F(5) → F(4)'. Note that the F(3) site is a common extremity for this motion.

(c) Properties. The rhodium complex **1** and its solvates are quite soluble in dichloromethane and chloroform to give brown

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[17] The isotopic shift of $\nu(NN)$ observed here is larger than predicted for pure $\nu(NN)$ vibrations, and there may be coupling with other vibrational modes. $[RhCl(N_2Ph)(PPh_3)_2]^+$ has been reported in different articles to have $\nu(NN)$ at 1899 cm^{-1} [3a] or "multiple bands near 1900, 1930, and 1980 cm^{-1}".[8] We have found that the broad $\nu(NN)$ band shape and maximum for **1** and its solvates are significantly affected by prolonged grinding in KBr or KCl, though the NMR spectrum of the recovered material is largely unaltered. As an example, a shoulder on the low-wavenumber side of the 1984-cm^{-1} absorption of $1{\cdot}2Me_2CO$ at ca. 1940 cm^{-1} grows in intensity and results in a band maximum at ca. 1911 cm^{-1} on grinding in KBr in a N_2-filled drybox for 25 min. We tentatively attribute this to perturbation of $\nu(NN)$ for the cation in contact with bromide anion sites compared with the case for contact with $[BF_4]^-$ sites. The development of a band at 1613 cm^{-1} also may indicate partial incorporation of halide X^- to form the neutral aryldiazenide complex $RhClX(PPh_3)_2(p\text{-}N_2C_6H_4OMe)$ (cf. reaction with LiCl in the text).

[18] Two independent determinations of the structure of solvated $Ru(p\text{-}N_2C_6H_4Me)Cl_3(PPh_3)_2$ have been reported. (a) CH_2Cl_2 solvate: Ibers, J. A.; Haymore, B. L. *Inorg.* Chem. **1975**, *14*, 1369. (b) Acetone solvate: McArdle, J. V.; Schultz, A. J.; Corden, B. J.; Eisenberg, R. *Inorg. Chem.* **1973**, *12*, 1676.

[19] Del Pra, A.; Zanotti, G.; Segala, P. *Cryst. Struct. Commun.* **1979**, *8*, 959.

[20] Bennett, M. J.; Donaldson, P. B. *Inorg. Chem.* **1977**, *16*, 655.

[21] Thorn, D. L.; Tulip, T. H.; Ibers, J. A. *J. Chem. Soc., Dalton Trans.* **1979**, 2022.

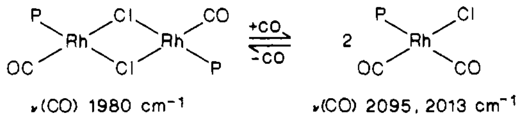
solutions but are less soluble in acetone and are insoluble in water and alcohols.

When a suspension of **1** in acetone was stirred with LiCl in ethanol, a brown product formed, which was shown to be $RhCl_2(p\text{-}N_2C_6H_4OMe)(PPh_3)_2$ (**2**) by a comparison of its IR spectrum and properties with those of the material synthesized according to the method of Robinson.[2a] In particular, we observed this product to have $\nu(NN)$ at 1612 cm^{-1} and $\nu(RhCl)$ at 342 cm^{-1} (KBr disk) and to undergo reversible formation of the aryldiazene complex $RhCl_3(p\text{-}NHNC_6H_4OMe)(PPh_3)_2$ (**3**) with HCl.

The reaction of **1** with HCl was found to be complex and resulted in different products or mixtures of products depending on the conditions. None of these appeared by ^1H NMR to contain hydride ligands, indicating that products of oxidative addition of HCl to the rhodium(I) center either were not occurring or were, at best, intermediates. Reaction of a suspension of **1** in diethyl ether with gaseous hydrogen chloride gave the known yellow neutral aryldiazene complex $RhCl_3(p\text{-}NHNC_6H_4OMe)(PPh_3)_2$ (**3**), which was confirmed by its separate synthesis from **2** and HCl.[2a] When, instead, a solution of **1** in CH_2Cl_2 was stirred under an atmosphere of HCl(g) (not bubbled through the solution), a quite different yellow complex was obtained, which appears to be the new *cationic* aryldiazene complex $[RhCl_2(p\text{-}NHNC_6H_4OMe)(PPh_3)_2][BF_4]$ (**4**). When hydrogen chloride was bubbled through a CH_2Cl_2 solution of **1**, this resulted in a mixture of **4** with some of the neutral aryldiazene complex **3**. Conversely, when CH_2Cl_2 solutions of **1** and HCl were mixed in 1:1 molar ratio, only a small conversion of **1** to **4** occurred. The ^1H NMR resonances of **3** and **4** in $CDCl_3$ are quite different: the neutral complex **3** has $\delta(NH) = 11.54$ and $\delta(OMe) = 3.86$ and $\delta(C_6H_4)$ is an AA′BB′ quartet with the two inner peaks at δ 6.52 and 6.62 ($J = 8$ Hz), whereas for **4** the resonances are $\delta(NH) = 10.64$ and $\delta(OMe) = 3.97$ and $\delta(C_6H_4)$ has the inner peaks of an AA′BB′ quartet at δ 6.93 and 6.86 ($J = 8$ Hz). The N_α–H assignment was confirmed by repeating the ^1H NMR with **4**-$^{15}N_\alpha$ and observing $\delta(NH)$ as a sharp doublet with $J(^{15}NH) = 70$ Hz.

The resonances attributed to the cationic aryldiazene complex **4** were, as anticipated, produced also by treatment of a $CDCl_3$ solution of the neutral aryldiazene complex **3** with $AgBF_4$ in an NMR experiment. However, before all of **3** was consumed, resonances indicative of the formation of **1** became observed (e.g. δ 3.88 (OMe), an AA′BB′ quartet at δ 6.79 (C_6H_4), and corresponding PPh_3 resonances). Compounds **1** and **4** were also shown to be formed in the reaction of $RhCl(PPh_3)_3$ with 2 equiv of $[p\text{-}N_2C_6H_4OMe][BF_4]$ in $CHCl_3$–MeOH. At −35 °C or below a dark green solution was produced, which yielded compound **1**, whereas at room temperature a brown solution was formed, from which compound **4** was isolated. A quite different reaction was observed when $RhCl(PPh_3)_3$ and $[p\text{-}N_2C_6H_4OMe][BF_4]$ were mixed in a 1:1 ratio in $CHCl_3$–MeOH at −55 °C. A dark green solution was again formed, but a dark green solid precipitated with a characteristic absorption at 1659 cm^{-1} (KBr) (as well as weaker bands at 1978 and 1918 cm^{-1} corresponding to **1**) and a ^1H NMR spectrum with $\delta(OMe)$ at 3.70, $\delta(C_6H_4)$ at 6.65 and 6.68 (inner peaks of AA′BB′ quartet), and a PPh_3 multiplet integrated for 3 PPh_3. A dark green product with an identical IR band at 1659 cm^{-1} and ^1H NMR spectrum was produced in the reaction of **1**·$2Me_2CO$ with PPh_3 in acetone at −50 °C. It seems likely that these materials are identical, and a plausible explanation is the formation of the tris(triphenylphosphine) aryldiazenide complex $[RhCl(PPh_3)_3(p\text{-}N_2C_6H_4OMe)][BF_4]$ (see Discussion).

The acetone-solvated complex **1**·$2Me_2CO$, dissolved in CH_2Cl_2, reacted quickly with 1 atm of CO. An IR spectrum taken immediately showed the production of some free diazonium ion and a band at 1980 cm^{-1} in addition to the $\nu(NN)$ band of **1** at 1911 cm^{-1}. The brown solution turned orange within 10 min, and the IR spectrum now showed $\nu(CO)$ absorptions at 2095, 2013, and 1980 cm^{-1} with similar relative intensities. During the next 1 h the intensity of the 1980-cm^{-1} band decreased, that of the other two absorptions increased, and the solution became orange-red. This could be reversed by bubbling N_2 through the solution and could be reestablished with CO. The aryldiazenide group is initially rapidly displaced (as the diazonium ion) by CO to give $RhCl(CO)(PPh_3)_2$ ($\nu(CO)$ 1980 cm^{-1}). This loses one PPh_3 group (which is probably scavenged by reaction with the diazonium ion[22,23]) to give $[RhCl(CO)(PPh_3)]_2$ ($\nu(CO)$ 1980 cm^{-1}). This dimer is known to undergo the CO equilibrium shown in eq 1.[24,25]



(1)

Exactly similar behavior was observed by reacting $RhCl(PPh_3)_3$ in CH_2Cl_2 with CO to form $RhCl(CO)(PPh_3)_2$ ($\nu(CO)$ 1979 cm^{-1}),[26] followed by addition of $[p\text{-}N_2C_6H_4OMe][BF_4]$.

Discussion

The literature on the reactions of arenediazonium ions with chlororhodium(I) triphenylphosphine complexes under various conditions is replete with incompletely (and at times, incorrectly) characterized products and speculative formulations. The reaction of $RhCl(PPh_3)_3$ with $[p\text{-}FC_6H_4N_2][BF_4]$ in $CHCl_3$ was first reported by Baird and Wilkinson as early as 1967.[1] An unstable green solution having a strong IR band at 1650 cm^{-1} was reported, and this was suggested to possibly contain the tris(phosphine) complex $[RhCl(PPh_3)_3(p\text{-}N_2C_6H_4F)][BF_4]$, but no evidence in support of this formulation was presented, and no solid was isolated. The solution was reported to turn dark brown within a few minutes with disappearance of the band at 1650 cm^{-1}. The only other reference to a tris(monodentate phosphine) complex of similar formulation, namely $[RhCl(PMePh_2)_3(N_2Ph)][PF_6]$, is in the assignment of a band at 1653 cm^{-1} in the IR spectrum to $\nu(NN)$, but no details of the synthesis, characterization, and composition were provided.[3a] The reaction of $RhCl(PPh_3)_3$ with diazonium salts was subsequently studied by several groups. Eisenberg and Toniolo observed,[4a] and later Toniolo[4b] claimed to have isolated, a green complex by reacting together concentrated solutions of $RhCl(PPh_3)_3$ in $CHCl_3$ and arenediazonium tetrafluoroborates $[p\text{-}XC_6H_4N_2][BF_4]$ (X = H, F) in methanol under H_2 or N_2. The compound was said to be isolated at −78 °C as green microcrystals from the reaction of the diazonium tetrafluoroborates with a concentrated solution (presumed to contain $RhH_2Cl(PPh_3)_2$) prepared by shaking $RhCl(PPh_3)_3$ in $CHCl_3$ under H_2 (1–3 atm) or from similar reactions in benzene–methanol.[4b] These green products were reported to have IR spectra with no bands in the $\nu(NH)$ region and no bands assignable to $[BF_4]^-$ but to have several bands in the 1600-cm^{-1} region that the authors believed possibly to be $\nu(NN)$. This was not supported by any isotopic substitution experiment. A band at 341–343 cm^{-1} was assigned to RhCl. A strong band at 1965 cm^{-1} was reported to be absent both when $CDCl_3$–MeOD was used and when benzene replaced $CHCl_3$ even under H_2. On this basis, assignment of the 1965-cm^{-1} band as $\nu(RhH)$ was rejected and it was attributed to "$CHCl_3$ of solvation". These green compounds were formulated as benzene or chloroform solvates of "$RhCl_2(PPh_3)_2(N_2C_6H_4X)$" with 0.5 C_6H_6 or 0.5 $CHCl_3$ on the basis of analytical data. The situation is further confused by an evidently incorrect report by Baird and Wilkinson[1] claiming that a compound of similar formulation, "$RhCl_2(PPh_3)_2(p\text{-}N_2C_6H_4F)\cdot 0.5CHCl_3$", was obtained from the reaction of $[p\text{-}FC_6H_4N_2][BF_4]$ with $RhHCl_2(PPh_3)_2$ (formed in situ by passing anhydrous HCl through $RhCl(PPh_3)_3$ in $CHCl_3$). This orange-yellow crystalline

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(22) Carroll, J. A.; Fisher, D. R.; Rayner-Canham, G. W.; Sutton, D. *Can. J. Chem.* **1974**, *52*, 1914.

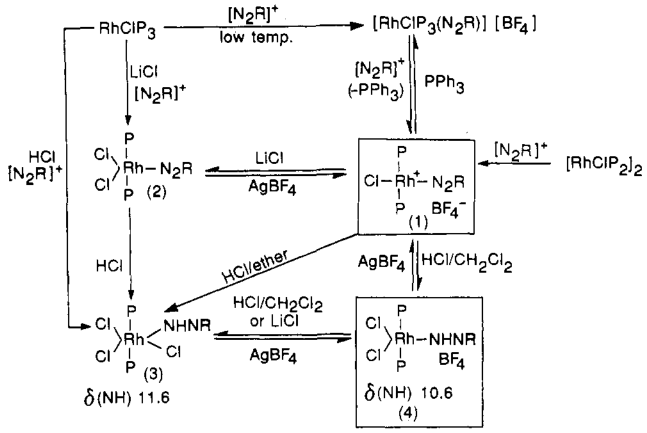
(23) In a separate experiment, *trans*-$RhCl(CO)(PPh_3)_2$ was shown to react with CO in the presence of diazonium ion to produce a solution with identical $\nu(CO)$ absorptions and reversible changes. In the absence of the diazonium ion the single $\nu(CO)$ absorption of $RhCl(CO)(PPh_3)_2$ at 1980 cm^{-1} was unchanged by added CO.

(24) Literature $\nu(CO)$ values for *cis*-$RhCl(CO)_2(PPh_3)$ are 2090 and 2018 cm^{-1} in CH_2Cl_2 or benzene.[25]

(25) Steele, F.; Stephenson, T. A. *Inorg. Nucl. Chem. Lett.* **1971**, *7*, 877.

(26) (a) Vallarino, L. M. *J. Chem. Soc.* **1957**, 2287. (b) Uguagliati, P.; Deganello, G.; Busetto, L.; Belluco, U. *Inorg. Chem.* **1969**, *8*, 1625.

Scheme I. Reactions of **1** (P = PPh_3, R = p-$MeOC_6H_4$)



material has been reformulated subsequently by Robinson[2] after a detailed spectroscopic study (vide infra) as the aryldiazene complex $RhCl_3(PPh_3)_2(p\text{-}NHNC_6H_4F)$. Unfortunately, a Raman study of this and similar materials was carried out in the meantime by one of us and in this study the Baird and Wilkinson formulation was inadvertently assumed to be correct.[12] The frequencies attributed in that study to $\nu(NN)$ of $RhCl_2(PPh_3)_2(N_2Ar)$ complexes are to be reinterpreted as the $\nu(NN)$ frequencies of $RhCl_3(PPh_3)_2(NHNAr)$ complexes (of which complex **3** in the present study is one member). Robinson further showed that authentic $RhCl_2(PPh_3)_2(N_2Ar)$ complexes may be obtained as *brown* or *red-brown* solids (not green) from reactions of $RhCl(PPh_3)_3$ with diazonium tetrafluoroborates in the presence of added LiCl or by treatment of the aryldiazene complexes with base (eq 2).

$$RhCl_3(PPh_3)_2(NHNAr) \underset{+HCl}{\overset{-HCl}{\rightleftharpoons}} RhCl_2(PPh_3)_2(N_2Ar) \quad (2)$$

In more than one paper, Ibers and Haymore make reference to a compound of formula $[RhCl(PPh_3)_2(N_2Ph)][PF_6]$,[3a,8] but no details of the synthesis and characterization of this compound, apart from the IR $\nu(NN)$ values,[3a,8,17] appear to have been published. However, the closely related iridium complex $[IrCl(PPh_3)_2(N_2Ph)][PF_6]$ is a deep green material synthesized from the reaction of $IrCl(CO)(PPh_3)_2$ with an aroyl azide followed by addition of benzenediazonium hexafluorophosphate.[27]

From the foregoing, it will be recognized that the chemistry of the products formed between $RhCl(PPh_3)_3$ and arenediazonium ions under various experimental conditions is neither straightforward nor well-understood. Our new results shown in Scheme I shed some light on this problem, but we cannot claim to have resolved it entirely.

First, by changing from $RhCl(PPh_3)_3$ to the binuclear chloride-bridged compound $[RhCl(PPh_3)_2]_2$ as the starting material, we have been able to isolate a green acetone-solvated or a green-yellow nonsolvated crystalline product from the reaction with p-methoxybenzenediazonium tetrafluoroborate and have completely characterized it as the salt $[RhCl(PPh_3)_2(p\text{-}N_2C_6H_4OMe)][BF_4]$ (**1**). This compound could be recrystallized readily from CH_2Cl_2–hexane to give blocklike crystals of the bis(dichloromethane) solvate **1**·$2CH_2Cl_2$, which provided X-ray structure confirmation. The solvated or unsolvated complex **1** has a strong $\nu(NN)$ absorption band in the 1900–2000-cm^{-1} region, and this agrees essentially with the assignment[3a,8,27a] of $\nu(NN)$ in the compound $[RhCl(PPh_3)_2(N_2Ph)][PF_6]$ just mentioned. We have found that the exact position of $\nu(NN)$ in **1** is extremely dependent on the presence or absence of a solvating molecule, on the identity of this molecule, and on the method of sample preparation for the IR determination. In particular, the band profile and maximum change on prolonged grinding in KBr or KCl.[17] For these reasons a comparison of IR data from different laboratories must be treated with caution, but it does seem reasonable that the band reported by Toniolo[4b] at 1965 cm^{-1} and the color of the green product may indeed indicate the formation of the analogous cation $[RhCl(PPh_3)_2(N_2Ar)]^+$ (though it now seems that the product must be a mixture). Certainly, Toniolo's formulation of the green material as the neutral complex $RhCl_2(PPh_3)_2(N_2Ar)$ (**2**) is inconsistent with the color and properties of this type of complex as determined in detailed work by Robinson[2] and confirmed here. We find, as one might anticipate, that complex **1** is converted to **2** by treatment with LiCl and that **2** can be reconverted to **1** by reaction with $AgBF_4$ (eq 3).

$$\underset{\mathbf{1}}{[RhCl(PPh_3)_2(p\text{-}N_2C_6H_4OMe)][BF_4]} \underset{AgBF_4}{\overset{LiCl}{\rightleftharpoons}} \underset{\mathbf{2}}{RhCl_2(PPh_3)_2(p\text{-}N_2C_6H_4OMe)} \quad (3)$$

Second, we wished to investigate the possibility that the green, unstable compounds with IR absorption attributed to $\nu(NN)$ in the ca. 1650-cm^{-1} region observed by Toniolo[4b] and by Baird and Wilkinson[1] might, in fact, be the tris(triphenylphosphine) complexes $[RhCl(PPh_3)_3(N_2Ar)][BF_4]$ as suggested by the latter. In agreement with this formulation we found that complex **1**·$2Me_2CO$ in acetone reacted with 1 mol of PPh_3 at −50 °C to give a green solution and, following removal of the solvent, a new green solid with a strong band at 1659 cm^{-1} attributable to $\nu(NN)$. Furthermore, upon repeating the $RhCl(PPh_3)_3$ reaction with $[p\text{-}N_2C_6H_4OMe][BF_4]$ at low temperature in a 1:1 ratio in $CHCl_3$–MeOH, we observed a similar green solution just as reported by the previous workers[1,4] from which precipitated a green material that was obviously a mixture of **1** (minor product; weak bands at 1978 and 1918 cm^{-1}) and the same compound as above (major product; band at 1659 cm^{-1}). The integrated ^1H NMR spectrum supports the formulation of the latter as $[RhCl(PPh_3)_3(p\text{-}N_2C_6H_4OMe)][BF_4]$ as suggested by Baird and Wilkinson. The shift of $\nu(NN)$ from the 1900-cm^{-1} region in the four-coordinate cation **1** to the 1600-cm^{-1} region in this five-coordinate cation upon addition of PPh_3 is not unexpected,[28] and the green complex would be anticipated possibly to have a partly[28] or a fully doubly bent N_2Ar ligand.[29]

Third, noticing the above evidence that complex **1** is implicated to be at least a partial product of the reaction[4b] of $RhCl(PPh_3)_3$ with $[p\text{-}N_2C_6H_4OMe][BF_4]$, we sought to find reaction conditions that enhanced its formation. Essentially, in the formation of **1**, $RhCl(PPh_3)_3$ has to "lose" a PPh_3 group (a common mode of reaction[30]), as it does indeed when it reacts[2] with diazonium salts in the presence of LiCl to form $RhCl_2(PPh_3)_2(N_2Ar)$. We therefore repeated the direct reaction of $RhCl(PPh_3)_3$ with $[p\text{-}N_2C_6H_4OMe][BF_4]$ in $CHCl_3$–MeOH in a 1:2 ratio following a previous strategy.[31] At −35 °C or below a dark green solution formed from which **1** could be isolated. However, at room temperature a brown solution formed that contained only a small amount of **1**. The major product now was the new yellow *aryldiazene* complex $[RhCl_2(PPh_3)_2(NHNC_6H_4OMe)][BF_4]$ (**4**) with $\delta(NH)$ at 10.64. In effect, the reaction then seems to proceed with the abstraction of HCl from the solvent (eq 4) under these conditions.[32]

$$RhCl(PPh_3)_3 \xrightarrow[{[p\text{-}N_2C_6H_4OMe][BF_4]}]{CHCl_3\text{-}MeOH} \underset{\mathbf{4}}{[RhCl_2(PPh_3)_2(p\text{-}NHNC_6H_4OMe)][BF_4]} \quad (4)$$

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[27] (a) Haymore, B. L.; Ibers, J. A. *J. Am. Chem. Soc.* **1973**, *95*, 3052. $[RhCl(N_2Ph)(PPh_3)_2][PF_6]$ was prepared as an analytically pure green/brown solid from $RhCl(C_2H_4)(PPh_3)_2$ and has $\nu(NN)$ = 1899, 1930 cm^{-1} in CH_2Cl_2 (cf. ref 3a and 8). It is isomorphous (*Pnma*, *Z* = 4) with the p-methoxy derivative **1** and the analogous Ir complex. Some structural data for the Ir complex are available.[27b] $[RhCl(N_2Ph)(PMePh_2)_3][PF_6]$ is a stable red complex, which is isomorphous with the known Ir analogue (Haymore, B. L., personal communication). (b) Schramm, K. D.; Ibers, J. A. *Inorg. Chem.* **1980**, *19*, 1231.

[28] Cowie, M.; Haymore, B. L.; Ibers, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 7608.

[29] The complex $[RhCl(PPP)(N_2Ph)]^+$ with a doubly bent N_2Ph group has $\nu(NN)$ at 1627 and 1561 cm^{-1} (ref 3a).

[30] Jardine, F. H. *Prog. Inorg. Chem.* **1981**, *28*, 63.

[31] Carroll, J. A.; Cobbledick, R. E.; Einstein, F. W. B.; Farrell, N.; Sutton, D.; Vogel, P. L. *Inorg. Chem.* **1977**, *16*, 2462.

Finally, it was necessary to establish the relationship of this new aryldiazene complex **4** with respect to the diazenide **1** and the aryldiazene complex **3**. We observed separately that, provided the supply of HCl is restricted (e.g., by stirring under an atmosphere of HCl rather than bubbling), then compound **4** is indeed obtained from **1** by HCl addition.

Not only is complex **4** formed in the two above ways but it is also produced by the careful removal of one chloride from the neutral aryldiazene complex **3** by reaction with $AgBF_4$ (eq 5).

$$\underset{\mathbf{3}}{[RhCl_3(PPh_3)_2(p\text{-}NHNC_6H_4OMe)]} \xrightarrow[CH_2Cl_2]{AgBF_4} \underset{\mathbf{4}}{[RhCl_2(PPh_3)_2(p\text{-}NHNC_6H_4OMe)][BF_4]} \quad (5)$$

The reaction is reversed with HCl, and therefore application of an excess of HCl to compound **1** drives the reaction beyond the intermediate **4** to give **3**. It is therefore understandable that neither **1** nor **4** has been previously recognized in reactions of $RhCl(PPh_3)_3$ with arenediazonium salts in $CHCl_3$, especially in the presence of additional HCl.[1]

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Registry No. **1**, 112793-51-8; **1**·$2CH_2Cl_2$, 112793-52-9; **2**, 36581-28-9; **3**, 112837-81-7; **4**, 112817-43-3; $[RhCl(PPh_3)_2]_2$, 14653-50-0; $RhCl(PPh_3)_3$, 14694-95-2; $[RhCl(PPh_3)_3(p\text{-}N_2C_6H_4OMe)][BF_4]$, 112793-54-1.

Supplementary Material Available: Tables of anisotropic thermal parameters and hydrogen atom coordinates (3 pages); a table of observed and calculated structure amplitudes (30 pages). Ordering information is given on any current masthead page.

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(32) (a) Robinson et al. reported that $RhCl_2(PPh_3)_2(N_2Ar)$ complexes (e.g., complex **2**) abstract the elements of HCl from $CHCl_3$ to give the aryldiazene complexes $RhCl_3(PPh_3)_2(NHNAr)$ (e.g., complex **3**).[2a] The aryldiazene complex **4** is conveniently synthesized for comparison by addition of HBF_4 to $RhCl_2(PPh_3)_2(p\text{-}N_2C_6H_4OMe)$ (**2**). (b) With acetone as the solvent, HCl abstraction is circumvented; further **1**·$2Me_2CO$ has quite low solubility in acetone and is precipitated from this reaction (1:1 or 1:2 stoichiometry) in reasonable yield.

Contribution from the Department of Chemistry and Laboratory for Molecular Structure and Bonding, Texas A&M University, College Station, Texas 77843, and Departamento de Química Inorgánica, Universitat de Valencia, 46100 Burjassot, Valencia, Spain

Ortho-Metalation Reactions in Binuclear Dirhodium Compounds. Synthesis and Molecular Structure of an Unsymmetrical Rh_2^{4+} Compound with Two Different Ortho-Metalated Phosphines

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The complex $Rh_2(O_2CCH_3)_4 \cdot 2PCCl$ [$PCCl = P(o\text{-}ClC_6H_4)Ph_2$] undergoes ortho metalation in refluxing chloroform to give a new dirhodium compound $Rh_2(O_2CCH_3)_3[(C_6H_4)P(o\text{-}ClC_6H_4)(C_6H_5)] \cdot PCCl$; when this compound is stirred with PPh_3 (1:2 molar ratio) in CH_2Cl_2 at room temperature, it yields a new product $Rh_2(O_2CCH_3)_2[(C_6H_4)P(o\text{-}ClC_6H_4)(C_6H_5)][(C_6H_4)P(C_6H_5)_2] \cdot P(C_6H_5)_3$, which has been characterized by X-ray crystallography. This first example of a Rh_2^{4+} unit with two different ortho-metalated phosphines bridging the two rhodium atoms also presents a nonsymmetrical coordination and might be formally described as a Rh(I)–Rh(III) dimer. It crystallizes in space group $P2_1/n$ with unit cell dimensions of a = 13.905 (3) Å, b = 19.825 (1) Å, c = 21.742 (3) Å, β = 102.77 (5)°, V = 5845 (3) Å^3, and Z = 4. Some important distances (Å) are as follows: Rh–Rh, 2.558 (1); Rh(1)–P, 2.222 (2), 2.215 (2); Rh(1)–O, 2.124 (5), 2.074 (6); Rh(2)–C, 2.041 (7), 2.044 (8); Rh(2)–O, 2.186 (5), 2.177 (6); Rh(2)–P(of $P(C_6H_5)_3$), 2.370 (2).

Introduction

Following the isolation of the doubly metalated compound $Rh_2(O_2CCH_3)_2[(C_6H_4)P(C_6H_5)_2]_2 \cdot 2HO_2CCH_3$ by thermal reaction of $Rh_2(O_2CCH_3)_4 \cdot 2PPh_3$ in refluxing acetic acid, we have acquired further knowledge about the mechanism of this type of ortho-metalation reaction.[1,2] By heating the adduct $Rh_2(O_2CCH_3)_4 \cdot 2P(C_6F_4Br)(C_6H_5)_2$ in different reaction conditions (Scheme I), we have isolated three intermediate reaction products (I–III), in addition to the doubly metalated compound $Rh_2(O_2CCH_3)_2[P(C_6H_4)(C_6H_5)(C_6F_4Br)]_2$ (IV), analogous to the one previously reported.[2,3]

From all these data we proposed that the important step in the metalation reaction is the I → III conversion, where a proton-transfer process from one phenyl group of the phosphine to one acetate takes place. Compound IV, as well as the homologous one with triphenylphosphine, contains a dirhodium unit with two ortho-metallated phosphines acting as bridging ligands. In each case the molecules have a head-to-tail relationship of the two ortho-metalated ligands and lie on a crystallographic 2-fold axis perpendicular to the metal–metal bond.

Experimental Section

Synthesis of Compounds 1–6. $Rh_2(O_2CCH_3)_4 \cdot 2CH_3OH$[4] and PCCl[5] were prepared according to literature procedures. Commercially available $P(C_6H_5)_3$ (Aldrich) was recrystallized from hot ethanol prior to use.

Compound 1. An orange suspension of $Rh_2(O_2CCH_3)_4 \cdot 2PCCl$ in 100 mL of $CHCl_3$ was refluxed under an atmosphere of nitrogen for 80 min to yield a brown-red solution. The solution was concentrated under reduced pressure to one-third of its initial volume, and hexane was added to precipitate a brown-red solid (240 mg). Yield: 85%. Anal. Calcd for $Rh_2C_{42}H_{36}Cl_2P_2O_6$: C, 51.71, H, 3.64. Found: C, 51.27; H, 3.73. ^{31}P NMR: $\delta_1 = 23.2$ ($^1J_{Rh-P} = 168$ Hz), $\delta_2 = 9.8$ ($^1J_{Rh-P} = 111$ Hz). ^1H

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[‡] Universitat de Valencia.

(1) Chakravarty, A. R.; Cotton, F. A.; Tocher, D. A.; Tocher, J. H.; *Organometallics* **1985**, *4*, 8. Chakravarty, A. R.; Cotton, F. A.; Tocher, D. A. *J. Chem. Soc., Chem. Commun.* **1984**, 501.

(2) Barcelo, F.; Cotton, F. A.; Lahuerta, P.; Llusar, R.; Sanau, M.; Schwotzer, W.; Ubeda, M. A. *Organometallics* **1986**, *5*, 808.

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