filtration produced a pale yellow solution. This solution was concentrated by rotary evaporation and placed on a silica gel TLC plate. Development with methylene chloride in *n*-hexane (1:3) gave an orange band (R_f 0.47), which produced 3 mg of $(\eta^7\text{-}C_7H_7)Cr[(C_2H_5)_2C_2B_4H_4]$ (**3**) as an air-stable yellow-green solid.

X-ray Structure Determinations on $(\eta^8\text{-}C_8H_8)Ti[(C_2H_5)_2C_2B_4H_4]$ (1), $(\eta^8\text{-}C_8H_8)V[(C_2H_5)_2C_2B_4H_4]$ (2), and $(\eta^7\text{-}C_7H_7)Cr[(C_2H_5)_2C_2B_4H_4]$ (3). Single crystals of **1**, **2**, **3** were grown by slow evaporation in air of dichloromethane, benzene, and acetone solutions, respectively. In each case, selected crystals were mounted on glass fibers, examined by precession photography, and found acceptable.

Relevant parameters for the data collection and structure determination are given in Table III. The procedures followed in data collection and processing have been described elsewhere.[25] Space groups were chosen on the basis of chemical and spectroscopic information taken together with systematic absences.

The intensities of three standard reflections, monitored at regular intervals, showed no greater fluctuations during the data collection than those expected from Poisson statistics. The raw intensity data were corrected for Lorentz-polarization effects and then for absorption. Only those reflections for which $F_o^2 > 3\sigma(F_o^2)$, where $\sigma(F_o^2)$ was estimated from counting statistics ($p = 0.03$),[26] were used in the final refinement of the structural parameters, after averaging for equivalent reflections.

Solution and Refinement of the Structures. Full-matrix least-squares refinement was based on *F*, and the function minimized was $w(|F_o| - |F_o|)^2$. The weights *w* were taken as $[2F_o/\sigma(F_o^2)]^2$, where $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes. The atomic scattering factors for non-hydrogen atoms were taken from Cromer and Waber[27] and those for hydrogen from Stewart et al.[28] The effects of anomalous dispersion for all non-hydrogen atoms were included in *F*, using the values of Cromer and Ibers[29] for $\Delta f'$ and $\Delta f''$.

In each structure, the metal atom was located from a three-dimensional Patterson difference map calculated from all intensity data. Subsequent Fourier difference maps revealed the positions of all other non-hydrogen atoms. After introducing anisotropic thermal parameters for all cage non-hydrogen atoms, additional Fourier syntheses located most of the hydrogen atoms. Several of the ethyl hydrogens were inserted into calculated positions and included in subsequent refinement. All hydrogen positions were held fixed in the final least-squares cycles. In the structure of **3**, the ring carbon atoms exhibited slight librational disorder and were refined isotropically; otherwise the refinement of the data was handled as for the structures of **1** and **2**.

In each case, the model converged to the final *R* and R_w values given in Table III, where $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$. Tables of observed and calculated structure factors and thermal parameters are available (see paragraph at end of paper on supplementary material). The computing system and programs are described elsewhere.[30]

Acknowledgment. This work was supported by the National Science Foundation, Grant No. CHE 81-19936. We are grateful to Dr. Greg Brewer for the magnetic and ESR measurements on compound **2**.

Registry No. **1**, 88946-15-0; **1A**, 88946-17-2; **1B**, 88968-33-6; **2**, 84987-58-6; **3**, 88946-16-1.

Supplementary Material Available: Tables of calculated and observed structure factors, thermal parameters, and mean planes (29 pages). Ordering information is given on any current masthead page.

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η^4-Bonding in (Arene)ruthenium Complexes of Octamethylnaphthalene

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Received November 14, 1983

The reaction of $[RuCl_2(arene)]_2$ (arene = *p*-cymene, benzene, mesitylene, prehnitene, hexamethylbenzene, 1,3,5-triethylbenzene, and 1,3,5-triisopropylbenzene) with octamethylnaphthalene (OMN) under three sets of conditions leads to the bis(arene) complexes $[Ru(OMN)(arene)]^{2+}$. These 18-electron cations containing two η^6-rings can be easily reduced with sodium amalgam to complexes with the formula Ru(OMN)(arene). The neutral complexes contain a η^6-arene and a η^4-OMN ring as shown by a single-crystal X-ray crystallographic analysis of $Ru(OMN)(C_6Me_6)$ [$P2_1/n$ space group, $Z = 8$, $a = 19.768$ (6) Å, $b = 14.524$ (3) Å, $c = 19.676$ (6) Å, $\beta = 117.13$ (2)°]. Protonation of the complexed OMN ring in $Ru(OMN)(C_6H_6)$ yields an isolable cyclohexadienyl species, $[Ru(C_{10}Me_8H)(C_6H_6)]^+$, while reaction of $Ru(OMN)(C_6H_6)$ with $Cr(CO)_3(CH_3CN)_3$ produces the binuclear compound $(C_6H_6)Ru(\mu\text{-}OMN)Cr(CO)_3$. The reactivity of the neutral complexes with hydrogen is discussed.

Introduction

Structurally characterized examples of the η^4-bonding of aromatic rings to transition metals remain rare.[2] The reduction of hapticity is often invoked as a route to arene substitution and other reactions, the most interesting of which is the homogeneous hydrogenation of arenes.[2-4] One of the premier examples of η^4-bonding occurs in $Ru(C_6Me_6)_2$, I, that was reported[5] by Fischer and Elschen-

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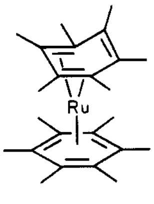
broich in 1970 and structurally characterized by Huttner and Lange.[6] Recently, Muetterties and co-workers have reported that this complex can catalyze arene hydrogenations under mild conditions.[7,8]



I

We recently reported[9] the synthesis and characterization of the M(CO)$_3$ (M = Cr, Mo, and W) complexes of octamethylnaphthalene (OMN). The interest in OMN stems from the distortions caused by the steric interactions of the *peri*-methyl groups. The twisted ring system does bind to the metal tricarbonyl fragment as a hexahapto ligand. In this study we have turned our attention to the (arene)ruthenium complexes of OMN. In particular we sought to prepare the zerovalent complexes to determine the effect the molecular distortions of OMN would have on the η^4-bonding mode.

Experimental Section

General Information. Literature procedures were used to prepare octamethylnaphthalene,[10] [RuCl$_2$(arene)]$_2$ (arene = benzene,[11] *p*-cymene,[11] or hexamethylbenzene[12]), 1,3,5-triethylbenzene,[13] and [Ru(C$_6$Me$_6$)(C$_{10}$H$_8$)](PF$_6$)$_2$.[14] Anhydrous aluminum trichloride was sublimed prior to use and stored in a glovebox. The solid arenes were recrystallized from hexane or benzene, and the liquid arenes were distilled over calcium hydride. All reactions were carried out under an atmosphere of nitrogen by using normal Schlenk-line techniques unless otherwise noted. Elemental analyses were obtained from Galbraith Laboratories. NMR spectra were obtained with a Varian HFT-80 or a Nicolet NTCFT-1180 300-MHz spectrometer. Mass spectra were obtained with an AEI-MS30 instrument with a source temperature of 200 °C, an accelerating voltage of 4 kV, an electron energy of 70 eV, and a solid probe temperature of 100 °C.

[RuCl$_2$(1,2,3,4-Me$_4$C$_6$H$_2$)]$_2$. [RuCl$_2$(1-Me-4-(CHMe$_2$)C$_6$H$_4$)]$_2$ (362 mg, 0.59 mmol) was stirred in excess (~25 mL) refluxing 1,2,3,4-tetramethylbenzene (prehnitene) under nitrogen for 24 h. Initially, the *p*-cymene complex dissolved in the hot hydrocarbon solvent, but by completion of the exchange, solid [RuCl$_2$(1,2,3,4-Me$_4$C$_6$H$_2$)]$_2$ precipitated from the solution. The solution was cooled, and the red-orange solid was collected on a frit and washed with hexane to yield 339 mg (94%) of product. Proton NMR (CDCl$_3$) δ 5.27 (s, 2 H), 2.09 (s, 6 H), 2.01 (s, 6 H).

[RuCl$_2$(1,3,5-Me$_3$C$_6$H$_3$)]$_2$. [RuCl$_2$(1-Me-4-(CHMe$_2$)C$_6$H$_4$)]$_2$ (437 mg, 0.71 mmol) was stirred as above in refluxing mesitylene (~25 mL) for 24 h. After workup, 383 mg (92%) of light brown [RuCl$_2$(1,3,5-Me$_3$C$_6$H$_3$)]$_2$ was obtained. The material was identical with the product previously prepared by a different route.[11]

[RuCl$_2$(1,3,5-Et$_3$C$_6$H$_3$)]$_2$. [RuCl$_2$(1-Me-4-(CHMe$_2$)C$_6$H$_4$)]$_2$ (221 mg, 0.36 mmol) was stirred in refluxing 1,3,5-triethylbenzene (~25 mL) for 3 h under a nitrogen atmosphere. The solution was cooled to room temperature and [RuCl$_2$(1,3,5-Et$_3$C$_6$H$_3$)]$_2$ crystallized from the solution. The red crystals were collected on a frit and rinsed with hexane to obtain 203 mg (84%). Proton NMR (CDCl$_3$) δ 4.99 (s, 3 H), 2.55 (q, J = 7.5 Hz, 6 H), 1.22 (t, J = 7.5 Hz, 9 H).

[RuCl$_2$(1,3,5-*i*-Pr$_3$C$_6$H$_3$)]$_2$. [RuCl$_2$(1-Me-4-(CHMe$_2$)C$_6$H$_4$)]$_2$ (503 mg, 0.82 mmol) was stirred vigorously under a nitrogen atmosphere in 60 mL of refluxing 1,3,5-triisopropylbenzene for 25 min. The solution became deep red as the *p*-cymene complex dissolved in the hot solution and then darkened to a violet color. The solution was cooled to room temperature and then placed in a freezer overnight to allow the product to precipitate from solution. The cold viscous solution was filtered on a frit to obtain a light orange solid, which was rinsed with hexane. The filtration flask was changed, and the orange solid was washed through the frit with CH$_2$Cl$_2$, leaving behind a small amount of insoluble black material. An equal volume of hexane was added to the CH$_2$Cl$_2$ filtrate, and the solution was warmed to reduce the volume resulting in the formation of red microcrystals. These were collected on a frit and rinsed with hexane to obtain 217 mg (35%). Proton NMR (CDCl$_3$) δ 5.13 (s, 3 H), 3.02 (J = 6.9 Hz, 3 H), 1.27 (d, J = 6.9 Hz, 18 H). Anal. Calcd for C$_{30}$H$_{48}$Cl$_4$Ru$_2$: C, 47.87; H, 6.43. Found: C, 48.37; H, 6.58.

[Ru(OMN)(1-Me-4-(CHMe$_2$)C$_6$H$_4$)](PF$_6$)$_2$. [RuCl$_2$(1-Me-4-(CHMe$_2$)C$_6$H$_4$)]$_2$ (300 mg, 0.49 mmol) and AlCl$_3$ (274 mg, 2.1 mmol) were stirred together in 10 mL of hot 1,2-dichloroethane under nitrogen until all of the AlCl$_3$ was dissolved, and then octamethylnaphthalene (590 mg, 2.45 mmol) was added under a slow nitrogen purge and the dark solution was refluxed under nitrogen with good stirring for 22 h. The solution was cooled in an ice bath, opened to air, and about 20 mL of water was added rapidly to the stirring solution. After vigorous stirring, the contents were transferred to a separatory funnel and the layers separated (an emulsion forms initially but slowly dissipates with gentle turbulence of the solution). The organic layer was washed with additional 15-mL portions of water, and the combined aqueous washings were filtered through a layer of diatomaceous earth. Addition of excess NH$_4$PF$_6$ to the bright yellow filtrate precipitated yellow [Ru(OMN)(1-Me-4-(CHMe$_2$)C$_6$H$_4$)](PF$_6$)$_2$ (543 mg, 72%), which was collected on a frit, washed with water and then diethyl ether, dried in air, and recrystallized from CH$_3$CN/EtOH to give orange crystals. Proton NMR (acetone-d_6) δ 6.66 (d of d, 4 H), 3.03 (s, 6 H), 2.77 (s, 6 H), 2.72 (s, 6 H), 2.56 (s, 6 H), 2.32 (s, 3 H), 1.02 (d, J = 6.8 Hz, 6 H). Anal. Calcd for C$_{28}$H$_{38}$F$_{12}$P$_2$Ru: C, 43.93; H, 5.00. Found: C, 44.11; H, 5.08.

[Ru(OMN)(C$_6$H$_6$)](PF$_6$)$_2$. [RuCl$_2$(C$_6$H$_6$)]$_2$ (1.0 g, 2.0 mmol), AlCl$_3$ (1.2 g, 9.0 mmol), and OMN (2.4 g, 10.0 mmol) were treated as above for 44 h to obtain bright yellow [Ru(OMN)(C$_6$H$_6$)](PF$_6$)$_2$ (2.3 g, 82%). Crystallization from CH$_3$CN/EtOH gave the CH$_3$CN solvate. Proton NMR (acetone-d_6) δ 6.71 (s, 6 H), 3.09 (s, 6 H), 2.81 (s, 6 H), 2.77 (s, 6 H), 2.52 (s, 6 H), 2.04 (s, 3 H). Anal. Calcd for C$_{26}$H$_{33}$F$_{12}$NP$_2$Ru: C, 41.61; H, 4.43. Found: C, 41.84; H, 4.41.

[Ru(OMN)(1,2,3,4-Me$_4$C$_6$H$_2$)](PF$_3$)$_2$. [RuCl$_2$(1,2,3,4-Me$_4$C$_6$H$_2$)]$_2$ (0.27 g, 0.44 mmol), AlCl$_3$ (0.71 g, 5.3 mmol), and OMN (1.82 g, 7.55 mmol) were treated as above for 24 h to give bright yellow [Ru(OMN)(1,2,3,4-Me$_4$C$_6$H$_2$)](PF$_6$)$_2$ (0.60 g, 89%). Crystallization from acetone/diethyl ether gave orange crystals. Proton NMR (acetone-d_6) δ 6.52 (s, 2 H), 2.98 (s, 6 H), 2.74 (s, 6 H), 2.59 (s, 12 H), 2.03 (s, 12 H). Anal. Calcd for C$_{28}$H$_{38}$F$_{12}$P$_2$Ru: C, 43.93; H, 5.00. Found: C, 44.06; H, 5.12.

[Ru(OMN)(1,3,5-Me$_3$C$_6$H$_3$)](PF$_6$)$_2$. [RuCl$_2$(1,3,5-Me$_3$C$_6$H$_3$)]$_2$ (0.3 g, 0.51 mmol), AlCl$_3$ (0.82 g, 6.15 mmol), and OMN (2.09 g, 8.71 mmol) were treated as above in 20 mL of 1,2-dichloroethane for 41 h to obtain 0.58 g (76%) of [Ru(OMN)(1,3,5-Me$_3$C$_6$H$_3$)][PF$_6$]$_2$. Recrystallization from acetone/diethyl ether gave bright orange crystals as the acetone solvate. ^{1}H NMR (acetone-d_6) δ 6.37 (s, 3 H), 2.99 (s, 6 H), 2.75 (s, 6 H), 2.68 (s, 6 H), 2.57 (s, 6 H), 2.18 (s, 9 H), 2.09 (s, 6 H, acetone). Anal. Calcd for C$_{30}$H$_{42}$F$_{12}$OP$_2$Ru: C, 44.50; H, 5.23. Found: C, 44.45; H, 5.23.

[Ru(OMN)(C$_6$Me$_6$)](BPh$_4$)$_2$. A. With AlCl$_3$. [RuCl$_2$(C$_6$Me$_6$)]$_2$ (439 mg, 0.66 mmol), AlCl$_3$ (1.20 g, 9.0 mmol unsublimed), and octamethylnaphthalene (1.70 g, 7.1 mmol) were heated together to the melting point (ca. 181 °C) under nitrogen with stirring for 10 min. After cooling of the mixture to room temperature, excess hexane was added to the solid residue with rapid stirring. Water was carefully added, and the contents were

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transferred to a separatory funnel. After separation of layers and additional washing of the organic layer with water, the combined aqueous washings were filtered through diatomaceous earth. Addition of NH_4PF_6 to the bright yellow filtrate precipitated crude $[Ru(OMN)(C_6Me_6)](PF_6)_2$, which was collected and washed with water and diethyl ether to obtain 834 mg (80%). This material would not readily crystallize as the PF_6^- salt, so methathesis to the tetraphenylborate salt was carried out by addition of excess $NaBPh_4$ to an acetonitrile solution of $[Ru(OMN)(C_6Me_6)](PF_6)_2$. Sparingly soluble $[Ru(OMN)(C_6Me_6)](BPh_4)_2$ precipitated from solution as a bright yellow solid. This solid was collected on a frit, rinsed with cold acetonitrile, and then recrystallized from hot acetonitrile as bright yellow prisms. Proton NMR (CD_3CN) δ 7.26 (br, BPh_4^-), 6.85 (d of d, BPh_4^-), 2.60 (s, 6 H), 2.50 (s, 6 H), 2.18 (s, 6 H), 2.11 (s, 6 H), 1.75 (s, 18 H). Anal. Calcd for $C_{78}H_{82}B_2Ru$: C, 82.02; H, 7.24. Found: C, 81.85; H, 7.19.

B. With $AgBF_4$. $[RuCl_2(C_6Me_6)]_2$ (502 mg, 0.75 mmol) and $AgBF_4$ (585 mg, 3.0 mmol) were stirred vigorously together in acetone for about 15 min and then filtered to remove the silver chloride precipitate. The red acetone solution was evaporated under vacuum and then octamethylnaphthalene (2.71 g, 11.3 mmol) was added to the residue. Trifluoroacetic acid (5 mL) was added to the mixture and refluxed with magnetic stirring for 20 min. The solution was evaporated under vacuum to a solid residue, to which excess water was added, and the residue was thoroughly extracted and filtered. Excess $NaBPh_4$ was added to the yellow-orange aqueous filtrate with magnetic stirring, and after a few minutes the thick solution was filtered, collecting the resultant crude $[Ru(OMN)(C_6Me_6)](BPh_4)_2$ as a bright yellow precipitate. The precipitate was rinsed with water and Et_2O to obtain 1.308 g as a first crop and 0.170 g as a second crop (total yield 86%). This material was then recrystallized from hot CH_3CN to give bright yellow crystals.

The solid OMN residue collected above from the aqueous extraction was dissolved in CH_2Cl_2, filtered, dried over $MgSO_4$, filtered, and evaporated. The residue was triturated with methanol and collected on a frit to recover 1.620 g OMN.

$[Ru(OMN)(1,3,5\text{-}Et_3C_6H_3)](BPh_4)_2$. $[RuCl_2(1,3,5\text{-}Et_3C_6H_3)]_2$ (171 mg, 0.26 mmol) and $AgPF_6$ (259 mg, 1.0 mmol) were stirred vigorously together in acetone for 15 min. After removal of the silver chloride precipitate by filtration and evaporation of the acetone solution, 1.23 g (5.1 mmol) of octamethylnaphthalene was added, and the mixture was refluxed in CF_3COOH for 10 min. The acid was removed under vacuum and the solid residue was triturated with Et_2O and CH_2Cl_2 (benzene could also be used). Water was added to the reaction flask with shaking and the yellow solution was filtered. The Et_2O/CH_2Cl_2 solution was also washed with three portions of water, and the bright yellow aqueous washings were filtered and combined with the previous filtrate. Addition of NH_4PF_6 precipitated a bright yellow solid, which was collected on a frit and rinsed with Et_2O to yield 194 mg (48%) of $[Ru(OMN)(1,3,5\text{-}Et_3C_6H_3)](PF_6)_2$. Since crystallization was difficult as the PF_6^- salt, methathesis to the tetraphenylborate salt was carried out by dropwise addition of an ethanol solution of $NaBPh_4$ to a concentrated acetone solution of the ruthenium cation. Cooling of this solution in a freezer for 1–2 days resulted in the formation of orange crystals of $[Ru(OMN)(1,3,5\text{-}Et_3C_6H_3)](BPh_4)_2$ as the acetone solvate. Proton NMR (acetone-d_6) δ 7.34 (m, 8 H, BPh_4^-), 6.82 (d of d 12 H, BPh_4^-), 6.52 (s, 3 H), 3.1–2.2 (complex pattern, 30 H), 2.09 (6 H, acetone), 1.20 (t, J = 8 Hz, 9 H). Anal. Calcd for $C_{81}H_{88}B_2ORu$: C, 81.06; H, 7.39. Found: C, 81.54; H, 7.47.

$[Ru(OMN)(1,3,5\text{-}i\text{-}Pr_3C_6H_3)](PF_6)(BPh_4)$. $[RuCl_2(1,3,5\text{-}i\text{-}Pr_3C_6H_3)]_2$ (0.49 g, 0.65 mmol), $AgPF_6$ (1.32 g, 5.2 mmol), and OMN (1.66 g, 6.9 mmol) were treated as above to obtain bright yellow $[Ru(OMN)(1,3,5\text{-}i\text{-}Pr_3C_6H_3)](PF_6)_2$ (0.83 g, 76%). Partial methathesis to $[Ru(OMN)(1,3,5\text{-}i\text{-}Pr_3C_6H_3)](PF_6)(BPh_4)$ was carried out by addition of excess $NaBPh_4$ in ethanol to an acetonitrile solution of the PF_6^- salt and cooling in a freezer to give orange crystals. Proton NMR (acetone-d_6) δ 7.32 (m, 8 H, BPh_4^-), 6.86 (d of d, 12 H, BPh_4^-), 6.57 (s, 3 H), 2.75 (s, 6 H), 2.70 (s, 6 H), 2.59 (s, 15 H), 1.31 (d, J = 6 Hz, 18 H). Anal. Calcd for $C_{57}H_{68}BF_6PRu$: C, 67.78; H, 6.79. Found: C, 67.76; H, 6.70.

$Ru(OMN)(C_6Me_6)$. $[Ru(OMN)(C_6Me_6)](BPh_4)_2$ (0.32 g, 0.28 mmol) was dissolved in a few milliliters of acetonitrile and added dropwise to a flask containing 1% sodium amalgam (0.13 g, 5.53 mmol of Na in 13 g of Hg) with efficient magnetic stirring under a nitrogen atmosphere. The mixture was stirred at room temperature overnight, after which the solvent was removed under vacuum, leaving a green-yellow residue. This residue was extracted with hexane and filtered through a Schlenk frit to give a clear orange solution. Cooling the solution in a freezer gave 49.2 mg of orange crystalline $Ru(OMN)(C_6Me_6)$, which was collected on a frit in air, dried under vacuum, and then stored under nitrogen. In a similar way, an additional 16.0 mg of crystals was obtained from the mother liquor. The total yield was 65.2 mg (47%). Proton NMR (C_6D_6) δ 2.31 (s, 6 H), 2.00 (s, 12 H), 1.77 (s, 6 H), 1.72 (s, 18 H); MS [mass, relative intensity, ions formula (^{102}Ru)], 504, 78.7, P^+; 489, 63.6, $(P - CH_3)^+$; 252, 100.0, P^{2+}; 162, 10.7, $C_6Me_6^+$; 147, 17.5, $C_6Me_5^+$.

$Ru(OMN)(1\text{-}Me\text{-}4\text{-}(CHMe_2)C_6H_4)$. $[Ru(OMN)(1\text{-}Me\text{-}4\text{-}(CHMe)_2C_6H_4)](PF_6)_2$ (0.066 g, 0.086 mmol) was treated with sodium amalgam (0.026 g, 1.1 mmol of Na in 2.6 g of Hg) as above to obtain $Ru(OMN)(1\text{-}Me\text{-}4\text{-}(CHMe_2)C_6H_4)$ (0.030 g, 73%) as orange crystals from cold hexane. Proton NMR (C_6D_6) δ 4.51 (d, J = 6.0 Hz, 2 H), 4.07 (d, J = 6.0 Hz, 2 H), 2.30 (s, 6 H), 2.15 (s, 6 H), 2.06 (s, 6 H), 2.00 (s, 6 H), 1.74 (s, 3 H), 1.08 (d, J = 6.8 Hz, 6 H); MS, 476, 100.0, P^+; 461, 24.2, $(P - CH_3)^+$; 238, 53.6, P^{2+}; 134, 9.5, (cymene)$^+$; 119, 46.0 (cymene $- CH_3)^+$; 91, 16.7 (cymene $- C_3H_7)^+$. Anal. Calcd for $C_{28}H_{38}Ru$: C, 70.70; H, 8.05. Found: C, 70.86; H, 8.19.

$Ru(OMN)(1,3,5\text{-}Me_3C_6H_3)$. $[Ru(OMN)(1,3,5\text{-}Me_3C_6H_3)](PF_6)_2{\cdot}CH_3COCH_3$ (0.144 g, 0.178 mmol) was treated with sodium amalgam (0.053 g, 2.3 mmol of Na in 5.3 g of Hg) as above to obtain yellow $Ru(OMN)(1,3,5\text{-}Me_3C_6H_3)$ (0.059 g, 71%), which was purified by precipitation from cold hexane as a bright yellow powder. Proton NMR (C_6D_6) δ 4.27 (s, 3 H), 2.31 (s, 6 H), 2.12 (s, 6 H), 2.00 (s, 6 H), 1.90 (s, 6 H), 1.72 (s, 9 H); MS, 462, 100.0, P^+; 447, 72.0, $(P - CH_3)^+$; 240, 13.0, OMN^+; 231, 49.4, P^{2+}; 120, 22.1, $C_6H_3Me_3^+$; 105, 29.0, $C_6H_3Me_2^+$. Anal. Calcd for $C_{27}H_{36}Ru$: C, 70.25; H, 7.86. Found: C, 70.13; H, 8.02.

$Ru(OMN)(1,2,3,4\text{-}Me_4C_6H_2)$. $[Ru(OMN)(1,2,3,4\text{-}Me_4C_6H_2)](PF_6)_2$ (0.26 g, 0.34 mmol) was treated with sodium amalgam (0.16 g, 6.8 mmol of Na in 15.7 g of Hg) as above to obtain $Ru(OMN)(1,2,3,4\text{-}Me_4C_6H_2)$ as orange crystals from hexane (0.10 g, 59%). Proton NMR (C_6D_6) δ 4.76 (s, 2 H), 2.31 (s, 6 H), 2.03 (s, 6 H), 2.02 (s, 6 H), 1.89 (s, 6 H), 1.73 (s, 6 H), 1.49 (s, 6 H); MS, 476, 76.6, P^+; 461, 50.2, $(P - CH_3)^+$; 238, 65.0, P^{2+}; 134, 35.0, $C_6H_2Me_4^+$; 119, 72.8, $C_6H_2Me_3^+$. Anal. Calcd for $C_{28}H_{38}Ru$: C, 70.70; H, 8.05. Found: C, 71.06; H, 8.04.

$Ru(OMN)(C_6H_6)$. A suspension of $[Ru(OMN)(C_6H_6)](PF_6)_2{\cdot}CH_3CN$ (972 mg, 1.3 mmol) in 25 mL of dry benzene was stirred vigorously over 1% sodium amalgam (596 mg of Na, 25.9 mmol in 60 g of Hg) under nitrogen for 20 h. The solution was carefully decanted under nitrogen from the amalgam and filtered through a Schlenk frit. After rinsing of the reaction vessel with additional portions of benzene, the clear orange benzene solution was evaporated under vacuum to give orange microcrystalline $Ru(OMN)(C_6H_6)$ (347 mg, 64%). This material can be recrystallized from a larger volume of warm hexane, in which the complex is sparingly soluble. Proton NMR (C_6D_6) δ 4.52 (s, 6 H), 2.29 (s, 6 H), 2.18 (s, 6 H), 2.05 (s, 6 H), 2.01 (s, 6 H); MS, 420, 100.0, P^+; 405, 43.7, $(P - CH_3)^+$; 342, 11.9 $(RuOMN)^+$; 240, 15.6, OMN^+; 210, 40.7, P^{2+}; 78, 54.8, $C_6H_6^+$. Anal. Calcd for $C_{24}H_{30}Ru$: C, 68.70; H, 7.21. Found: C, 67.98; H, 7.37.

Attempted Reduction of $[Ru(C_6Me_6)(C_{10}H_8)](PF_6)_2$. The conditions used here were identical with those used for the OMN complexes above. $[Ru(C_6Me_3)(C_{10}H_8)](PF_6)_2$ (106 mg, 0.16 mmol) was treated with 1% sodium amalgam in acetonitrile at room temperature overnight. Evaporation of the solvent, extraction of the residue with hexane, and filtration under nitrogen gave a nearly colorless hexane filtrate. The off-white crystalline residue obtained upon evaporation of the solvent was found by NMR to be free naphthalene and hexamethylbenzene.

Protonation of $Ru(OMN)(C_6H_6)$: Preparation of $[Ru(C_{10}Me_8H)(C_6H_6)](PF_6)$. $Ru(OMN)(C_6H_6)$ was treated with neat trifluoroacetic acid in air. The solution immediately became deep red, and the acid was removed under vacuum, leaving a red oil, which was dissolved in hot water and filtered. Addition of NH_4PF_6 to the bright red aqueous filtrate gave orange $[Ru(C_{10}Me_8H)(C_6H_6)](PF_6)$ in essentially quantitative yield. The solid was collected, rinsed with water and then diethyl ether, and crystallized from acetonitrile/ethanol. ^{1}H NMR (CD_3CN) δ 5.32 (s, 6 H), 3.41 (q, J = 6.6 Hz, 1 H), 2.86 (s, 3 H), 2.54 (s, 3 H), 2.40 (s, 3 H), 2.21 (s, 3 H), 2.17 (s, 3 H), 2.04 (s, 6 H), 0.10 (d, J = 6.6 Hz, 3 H); ^{13}C NMR fully decoupled (CD_3CN) δ 89.8 (C_6H_6), 42.3 (protonated ring carbon), 24.6, 22.7, 21.8, 21.6, 17.8, 16.8, 2.3 (methyl region) (OMN ring carbons were not observed). Anal. Calcd for $C_{24}H_{31}F_6PRu$: C, 50.97; H, 5.53. Found: C, 50.66; H, 5.86.

$(C_6H_6)Ru(\mu$-OMN$)Cr(CO)_3$. Ru(OMN)(C_6H_6) (100 mg, 0.24 mmol) and $Cr(CO)_3(CH_3CN)_3$ (124 mg, 0.48 mmol) were refluxed together in 8 mL of hexane under nitrogen with efficient magnetic stirring for 44 h. The darkened solution was filtered through a Schlenk frit, leaving behind a dark green solid residue with traces of yellow material visible. This residue was washed with more hexane and then washed with dry benzene, collecting the benzene washings in a fresh Schlenk tube. The bright yellow benzene filtrate was evaporated under vacuum, leaving behind bright yellow product as a microcrystalline solid. Recrystallization from hexane/benzene afforded analytically pure material (20 mg, 15%). IR (hexane) ν_{CO} 1943 (s), 1871 (s), 1859 cm^{-1} (s); ^{1}H NMR (C_6D_6) δ 4.88 (s, 6 H), 2.05 (s, 12 H), 1.96 (s, 6 H), 1.74 (s, 6 H); MS, 556, 1.4, P$^+$; 528, 4.8, (P − CO)$^+$; 470, 14.7, (P − 3CO)$^+$; 420, 8.2, [Ru(OMN)(C_6H_6)]$^+$; 382, 9.4, ?; 292, 6.4, [Cr(OMN)]$^+$; 240, 80.6, OMN$^+$; 225, 44.2, (OMN − CH_3)$^+$; 78, 100.0, $C_6H_6^+$. Anal. Calcd for $C_{27}H_{30}CrO_3Ru$: C, 58.37; H, 5.44. Found: C, 58.79; H, 5.54.

Treatment of Ru(OMN)(1,2,3,4-$Me_4C_6H_2$) with Hydrogen Gas. Ru(OMN)(1,2,3,4-$Me_4C_6H_2$) (20 mg, 0.04 mmol) was placed into a Kontes reaction tube equipped with a magnetic stir bar, a gas inlet valve, and a septum for sampling the reaction contents. The system was repeatedly evacuated and flushed with nitrogen and then 5 mL of dry benzene was injected under nitrogen purge. After an additional evacuation and purging of the reaction tube, the system was pressurized with 3 atm of H_2 and allowed to stir at the desired temperature. Periodic analysis of the solution contents was carried out by withdrawal of small volumes and injection into a Packard Model 427 GC equipped with a Packard Alltech glass column (10% OV-101 on 80/100 Chromosorb W-HP), which afforded base line separation of standard solutions of benzene and cyclohexane.

After stirring of the complex overnight at room temperature under 3 atm of H_2, no cyclohexane was formed. The solution was then heated to 90 °C in an oil bath for up to 10 h under pure H_2, the solution remained homogeneous to visual inspection, and no cyclohexane formation was detected by GC analysis. At this point, the complex could be quantitatively recovered. If, however, some oxygen was allowed to enter the reaction vessel, slow decomposition of the ruthenium complex was observed at 90 °C, forming black insoluble material. In this case, periodic analysis of the solution by GC indicated steady cyclohexane formation. Similar results were obtained when, rather than oxygen, higher reaction temperatures (ca. 120 °C and higher) coupled with prolonged reaction times caused the ruthenium complex to begin to decompose thermally. As before, once decomposition is observed, cyclohexane formation commenced.

Treatment of Ru(OMN)(C_6H_6) with Hydrogen Gas. Ru(OMN)(C_6H_6) (ca. 10–20 mg) was placed into a Kontes reaction tube equipped with a magnetic stir bar and attached to a three-way stopcock, which was connected to a Schlenk line and a hydrogen tank. Deuterated benzene (ca. 5 mL) was injected into the tube, which was degassed under vacuum and flushed with nitrogen repeatedly. The tube was then placed under about 5 psi of hydrogen pressure and heated to 100 °C in an oil bath, with efficient stirring. The solution was then monitored periodically by withdrawing samples and observing the ^{1}H NMR spectrum of the ruthenium complex, for up to a period of 4 days. No change in the NMR spectrum was observed, with the exception that very slight exchange of coordinated benzene for C_6D_6 occurred after prolonged reaction times.

Table I

Crystal Parameters

cryst system: monoclinic
space group: $P2_1/n$
a = 19.768 (6) Å
b = 14.524 (3) Å
c = 19.676 (6) Å
β = 117.13 (2)°
V = 5027 (5) Å
Z = 8
calcd density = 1.33 g cm^{-3}
temp = 22 °C
abs coeff = 6.27 cm^{-1}
formula: $RuC_{30}H_{42}$

Measurement Intensity Data

diffractometer: Enraf-Nonius CAD4
radiation: Mo Kα (λ = 0.710 69 Å)
monochromator: graphite crystal
scan speed: variable from 1.05 to 20.0°/min
scan range: $0° \leqslant 2\theta \leqslant 52°$
reflctns measd: $+h$, $+k$, $\pm l$
check reflctns: {0100}, {0010}, {8$\bar{6}$0}; measd approximately every 300 reflcns
reflctns collected: 9836 unique reflctns; 6661 with $I > 2\sigma(I)$
P = 0.05
R = 0.042
R_w = 0.064
error in observation of unit weight = 1.87

Collection and Reduction of the X-ray Data. Orange crystals of Ru(OMN)(C_6Me_6) were obtained by slow cooling of a saturated hexane solution of the complex. A suitable, approximately equidimensional (~0.2 mm) crystal was mounted on a glass fiber and sealed in a Lindemann capillary under N_2. The crystal was found to be primitive monoclinic by the Enraf-Nonius CAD4-SDP peak search, centering, and indexing programs and by a Delauney reduction calculation.[15] Data collection was begun, and from the systematic absences ($0k0$, $k = 2n + 1$; $h0l$, $h + l = 2n + 1$) the unique space group $P2_1/n$ was unambiguously determined. A summary of the crystal and the intensity measurement data appears in Table I. Background counts were measured at both ends of the scan range with the use of an ω–2θ scan, equal at each side to one-fourth of the scan range of the peak. In this manner, the total duration of measuring background is equal to half of the time required for the peak scan. The three check reflections showed no decay throughout the entire data collection. The data were corrected for Lorentz, polarization, and background effects but not for absorption.[16]

Solution and Refinement of the Structure. With Z = 8 in the space group $P2_1/n$ two molecules appear in each asymmetric unit. Solving the structure using conventional heavy atom techniques, the positions of both Ru atoms were located by a Patterson synthesis. Subsequent least-squares and difference Fourier calculations quickly revealed the positions of all the carbon atoms. After convergence[17] the final difference Fourier revealed a few small peaks in the area surrounding some of the methyl groups that could be attributed to the hydrogen atoms. In the final calculations the hydrogen atoms were not included. No other significant features were present in this map. The final atom positions are listed in Table II. The values of the atomic scattering factors used in the calculations were taken from the usual tabulation, and the effects of anomalous dispersion were included.[18]

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(15) All calculations were carried out on PDP 8A and 11/34 computers using the Enraf-Nonius CAD 4-SDP programs. This crystallographic computing package is described in the following: Frenz, B. A. In "Computing in Crystallography"; Schenk, H., Olthof-Hazekamp, R., van Koningsveld, H., Bassi, G. C., Eds.; Delft University Press: Delft, Holland, 1978; pp 64–71. Also "CAD4 and SDP Users Manual"; Enraf-Nonius: Delft, Holland, 1978.

(16) The intensity data were processed as described in the following: "CAD 4 and SDP Users Manual"; Enraf-Nonius: Delft, Holland, 1978. The net intensity $I = (K/\mathrm{NPI})(C - 2B)$, where K = 20.1166× (attenuator factor); NPI = ratio of fastest possible scan rate to scan rate for the measurement, C = total count, and B = total background count. The standard deviation in the net intensity is given by $\sigma^2(I) = (K/\mathrm{NPI})^2[C + 4B + (pI)^2]$, where p is a factor used to downweight intense reflections. The observed structure factor amplitude F_o is given by $F_o = (I/\mathrm{Lp})^{1/2}$, where Lp = Lorentz and polarization factors. The $\sigma(I)$'s were converted to the estimated errors in the relative structure factors $\sigma(F_o)$ by $\sigma(F_o) = 1/2(\sigma(I)/I)F_o$.

(17) The function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w = 1/\sigma^2(F_o)$. The unweighted and weighted residuals are defined as $R = (\sum||F_o| - |F_c||)/\sum|F_o|$ and $R_w = [(\sum w(|F_o| - |F_c|))^2/(\sum w|F_o|)^2]^{1/2}$. The error in an observation of unit weight is $[\sum w(|F_o| - |F_c|)^2/(\mathrm{NO} - \mathrm{NV})]^{1/2}$, where NO and NV are the number of observations and variables, respectively.

(18) Cromer, D. T.; Weber, J. T. "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol IV, Table 2.2A. Cromer, D. T. *Ibid.* Table 2.3.1.

Table II. Positional Parameters

atom	x	y	z	atom	x	y	z
RUA	0.25112 (2)	0.00413 (3)	−0.13522 (2)	C30A	0.2561 (5)	0.0446 (6)	0.0416 (4)
RUB	0.19442 (2)	0.10500 (3)	0.32818 (2)	C1B	0.1050 (3)	0.2061 (4)	0.3055 (3)
C1A	0.2335 (3)	0.1518 (4)	−0.1483 (3)	C2B	0.0821 (3)	0.1156 (5)	0.3162 (3)
C2A	0.2957 (3)	0.1250 (4)	−0.1643 (3)	C3B	0.0840 (3)	0.0477 (4)	0.2644 (3)
C3A	0.2779 (3)	0.0579 (4)	−0.2216 (3)	C4B	0.1104 (3)	0.0832 (4)	0.2107 (3)
C4A	0.1982 (3)	0.0313 (4)	−0.2584 (3)	C5B	0.0541 (3)	0.1994 (4)	0.0967 (3)
C5A	0.0782 (3)	0.1236 (4)	−0.3477 (3)	C6B	0.0307 (3)	0.2887 (4)	0.0733 (3)
C6A	0.0238 (3)	0.1879 (5)	−0.3519 (3)	C7B	0.0195 (3)	0.3502 (4)	0.1211 (3)
C7A	0.0370 (3)	0.2430 (5)	−0.2894 (4)	C8B	0.0357 (3)	0.3232 (4)	0.1961 (3)
C8A	0.1052 (3)	0.2386 (5)	−0.2231 (3)	C9B	0.0729 (2)	0.2388 (3)	0.2247 (3)
C9A	0.1576 (3)	0.1680 (4)	−0.2157 (3)	C10B	0.0790 (2)	0.1754 (3)	0.1736 (3)
C10A	0.1417 (3)	0.1063 (4)	−0.2767 (2)	C11B	0.1235 (4)	0.2770 (5)	0.3684 (3)
C11A	0.2576 (5)	0.2078 (5)	−0.0733 (4)	C12B	0.0583 (3)	0.0914 (6)	0.3775 (3)
C12A	0.3755 (4)	0.1677 (5)	−0.1190 (4)	C13B	0.0602 (4)	−0.0523 (5)	0.2642 (4)
C13A	0.3353 (3)	0.0177 (6)	−0.2443 (3)	C14B	0.1290 (4)	0.0085 (5)	0.1668 (4)
C14A	0.1776 (4)	−0.0551 (5)	−0.3075 (3)	C15B	0.0469 (4)	0.1310 (6)	0.0345 (3)
C15A	0.0713 (5)	0.0793 (6)	−0.4205 (3)	C16B	0.0187 (4)	0.3203 (6)	−0.0065 (3)
C16A	−0.0517 (4)	0.1964 (7)	−0.4283 (5)	C17B	−0.0102 (4)	0.4476 (5)	0.0930 (4)
C17A	−0.0282 (5)	0.3110 (7)	−0.2969 (5)	C18B	0.0090 (3)	0.3867 (5)	0.2407 (4)
C18A	0.1204 (5)	0.3118 (6)	−0.1625 (5)	C19B	0.2842 (3)	0.1179 (5)	0.4522 (3)
C19A	0.3287 (3)	−0.0446 (4)	−0.0148 (3)	C20B	0.2722 (3)	0.0251 (5)	0.4307 (3)
C20A	0.3311 (3)	−0.1083 (4)	−0.0678 (3)	C21B	0.2842 (3)	−0.0070 (4)	0.3691 (4)
C21A	0.2623 (3)	−0.1506 (4)	−0.1210 (3)	C22B	0.3013 (3)	0.0564 (5)	0.3253 (3)
C22A	0.1914 (3)	−0.1234 (4)	−0.1253 (3)	C23B	0.3083 (3)	0.1518 (5)	0.3447 (3)
C23A	0.1887 (3)	−0.0557 (4)	−0.0753 (3)	C24B	0.3008 (3)	0.1806 (5)	0.4078 (4)
C24A	0.2588 (3)	−0.0178 (4)	−0.0189 (3)	C25B	0.2786 (5)	0.1454 (8)	0.5254 (4)
C25A	0.4023 (4)	−0.0035 (5)	0.0465 (4)	C26B	0.2502 (5)	−0.0432 (7)	0.4790 (5)
C26A	0.4067 (3)	−0.1388 (6)	−0.0630 (4)	C27B	0.2794 (5)	−0.1110 (6)	0.3523 (6)
C27A	0.2653 (4)	−0.2305 (5)	−0.1702 (4)	C28B	0.3177 (5)	0.0258 (8)	0.2596 (4)
C28A	0.1168 (3)	−0.1696 (5)	−0.1851 (4)	C29B	0.3302 (5)	0.2205 (7)	0.3002 (5)
C29A	0.1134 (3)	−0.0275 (6)	−0.0772 (4)	C30B	0.3149 (5)	0.2851 (6)	0.4307 (6)

Results

Preparation of [Ru(OMN)(arene)]$^{2+}$. The starting materials for the preparation of the dications are the chloro-bridged (arene)ruthenium dimers, $[RuCl_2(arene)]_2$, which can be readily prepared by using the arene exchange reactions developed by Bennett and co-workers.[12] The starting complex, $[RuCl_2(1\text{-}Me\text{-}4\text{-}(CHMe_2)C_6H_4)]_2$, is prepared by the dehydrogenation of the cyclohexadiene derivative, α-phallandrene, with $RuCl_3{\cdot}nH_2O$.[11] This dimer reacts with neat arene at high temperature to form the product in which the arene used as solvent is now complexed to the ruthenium. Reaction times vary depending on the boiling point of the arene; the higher the boiling point, the shorter the reaction time. Three new compounds of this type were prepared: $[RuCl_2(1,2,3,4\text{-}Me_4C_6H_2)]_2$, $[RuCl_2(1,3,5\text{-}Et_2C_6H_3)]$, and $[RuCl_2(1,3,5\text{-}i\text{-}Pr_3C_6H_3)]_2$. ^1H NMR data were consistent with this structure, but only the latter gave an acceptable elemental analysis. Although this exchange works well for benzene derivatives, we were never able to isolate the chloro-bridged product with naphthalene or OMN.

The addition of the OMN to the ruthenium was accomplished by three methods. They are closely related in that each uses a halide scavenger, either $AlCl_3$ or Ag^+. Bennett's method[14] of reacting $[RuCl_2(arene)]_2$ with $AgPF_6$ in acetone followed by the second arene (in our case, OMN) and trifluoroacetic acid was used for the complexes when the arene was hexamethylbenzene, 1,3,5-triethylbenzene, and 1,3,5-triisopropylbenzene. Aluminum trichloride dissolved in 1,2-dichloroethane with $[RuCl_2(arene)]_2$ followed by the addition of OMN was an alternative route to the bis(arene) complexes. Specifically, this was used to prepare [Ru(OMN)(arene)]$^{2+}$ when the arene was benzene, *p*-cymene, mesitylene, and prehnitene. The reaction mixture was stirred under nitrogen at reflux for 22–44 h. Water was added to the reaction mixture and then the mixture was separated and combined with excess NH_4PF_6. The resulting precipitate was recrystallized from acetonitrile to give orange crystals in yields that are comparable to Bennett's Ag^+ method. The complex $[Ru(OMN)(C_6Me_6)]^{2+}$ could also be prepared by dissolving $[RuCl_2(C_6Me_6)]_2$ in a molten mixture of OMN and $AlCl_3$. The yield by this procedure was also comparable to that of the Ag^+ method.

All of these complexes were readily chracterized by elemental analyses and ^1H NMR spectral data. In some cases the compounds crystallized with an acetone or acetonitrile of crystallization. Several of the dications did not easily crystallize as the PF_6^- salt but could be converted into the BPh_4^- salt by the addition of $NaBPh_4$ (dissolved in ethanol) to an acetone or acetonitrile solution of the cation. In one case, $[Ru(OMN)(1,3,5\text{-}i\text{-}PrC_6H_3)]^{2+}$, only one PF_6^- was metathesized and the mixed PF_6/BPh_4^- salt crystallized. The resonances for complexed OMN appear in a characteristic pattern of four between 2.50 and 3.09 ppm (in acetone-d_6). The arene hydrogens appear between 6.37 and 6.71 ppm.

Preparation of [Ru(OMN)(arene)]. The two-electron reduction of the dications to the neutral complexes proceeded smoothly with sodium amalgam. For the complexes in which the arene was *p*-cymene, mesitylene, prehnitene, and C_6Me_6, acetonitrile was used as the solvent for the reduction. In the case of the reduction of $[Ru(OMN)(C_6H_6)]^{2+}$, improved yields were obtained by using benzene as the solvent. Following the reduction, which was carried out at room temperature for 12–20 h, the solvent was removed and the entire residue was extracted with hexane. The product was obtained as orange crystals by reducing the volume of hexane and cooling the solution.

All of the zerovalent complexes are reasonably air-stable in the solid state and only slightly air-sensitive in solution. Each compound was characterized by elemental analysis, mass spectrometry, and ^1H NMR spectroscopy. All of the complexes exhibited an intense parent ion in the mass spectrometer followed by loss of CH_3 from the parent ion. Although these peaks exist as a mass envelope due to the seven naturally occurring isotopes of ruthenium, in all cases this envelope is complicated by fragments that differ by one or two mass units. In each compound a series of closely spaced fragments appears in the mass range of 300–342, the latter being $[Ru(OMN)]^+$. The ions due to $(arene)^+$ and $(OMN)^+$ are observed with the former always the dominant of the two and usually the third most prominent peak. By far the most interesting fragment is the $m/2e$ peak. It is always intense, and in $Ru(OMN)(C_6Me_6)$ it is the major peak in the spectrum. From a comparison of the five compounds studied there is clearly a trend of increasing intensity of the $m/2e$ peak as the number of alkyl groups is increased. The ^1H NMR spectra were similar to that of the dications except that all peaks were shifted upfield. The methyl resonances of OMN typically shifted 0.7 ppm toward Me_4Si, while the aromatic protons were shifted ~2.0 ppm.

Protonation of Coordinated OMN. When $Ru(OMN)(C_6H_6)$ is treated with neat CF_3COOH, the complex is immediately consumed and a deep red solution results. Evaporation of the acid leaves a red residue, which is extracted into hot water. Addition of NH_4PF_6 precipitates an orange solid that was recrystallized from acetonitrile and ethanol and characerized as the monocation $[Ru(C_{10}Me_8H)(C_6H_6)]^+$, using elemental analysis and ^1H and ^{13}C NMR spectroscopy. The aromatic protons of the coordinated benzene ring appear at 5.32 ppm, which is halfway between the chemical shift of the dication, $[Ru(OMN)(C_6H_6)]^{2+}$ (6.71 ppm), and the neutral analogue (4.52 ppm). The unique hydrogen resonance appears at 3.41 ppm as a quartet ($J = 6.6$ Hz). The methyl group that is coupled to this hydrogen is shifted upfield to 0.10 ppm. The ^{13}C NMR spectrum of the methyl also reflects this shielding effect. Seven resonances are grouped from 16.8 to 24.6 ppm (relative to Me_4Si), and the eighth methyl carbon appears at 2.3 ppm. No significant changes were observed when the spectrum was obtained at low temperature.

Formation of $(C_6H_6)Ru(\mu\text{-}OMN)Cr(CO)_3$. The binuclear complex containing a (benzene)ruthenium group on one ring and a chromium tricarbonyl moiety on the second ring was prepared by the reaction of $Ru(OMN)(C_6H_6)$ with $Cr(CO)_3(CH_3CN)_3$. The conditions involved refluxing hexane for 2 days, and the final recrystallized yield was 15%. The mass spectrum revealed a parent ion at 556 and fragments that appear as a combination of the separate molecules $Ru(OMN)(C_6H_6)$ and $Cr(OMN)(CO)_3$. The methyl resonances in the ^1H NMR spectrum are shifted upfield relative to $Ru(OMN)(C_6H_6)$, while the infrared absorbances of the $Cr(CO)_3$ are shifted ~20 cm^{-1} to lower energy relative to $Cr(OMN)(CO)_3$.[9]

Attempted Stoichiometric and Catalytic Arene Hydrogenations. Two of the Ru(OMN)(arene) complexes were investigated for their potential catalytic activity in the homogeneous hydrogenation of benzene to cyclohexane. Both $Ru(OMN)(1,2,3,4\text{-}Me_4C_6H_2)$ and $Ru(OMN)(C_6H_6)$ were placed under hydrogen pressure in benzene solvent, and the solution was examined periodically by gas chromatography in order to detect the presence of hydrogenated products. In the case of $Ru(OMN)(1,2,3,4\text{-}Me_4C_6H_2)$, an interesting observation was made. When the pressure tube is carefully evacuated and purged with pure hydrogen (ca. 3 atm), taking care to exclude oxygen from the system and the heated to 90 °C for a number of hours, the reaction solution remains clear yellow-orange, and no hydrogenated products are observed. When, however, some oxygen is present in the reaction atmosphere, or when extended periods (days) of higher reaction temperatures are used, some decomposition of the complex occurs as indicated by the presence of black precipitate. In these cases, cyclohexane is observed.

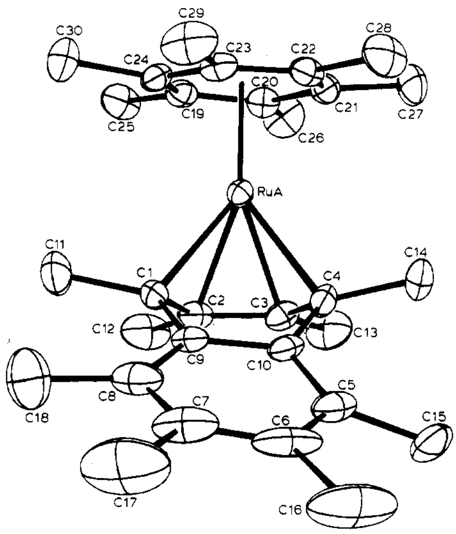


Figure 1. View of molecule A showing the atomic labeling scheme.

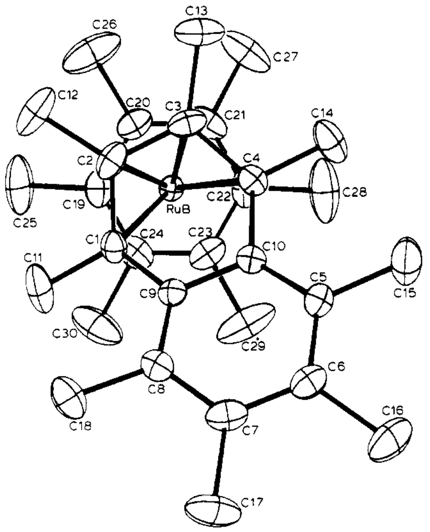


Figure 2. View of molecule B (with atom labels) illustrating the staggered conformation of the two rings.

$Ru(OMN)(C_6H_6)$ was also examined in C_6D_6 by ^1H NMR after exposure to hydrogen gas in an effort to observe possible hydrogenation of either the solvent or the coordinated benzene ligand. Neither of these two processes were observed in the NMR spectrum after exposure of the C_6D_6 solution to about 5 psig of hydrogen gas at 100 °C for a period of 4 days. The η^4-OMN complex remained unchanged, with the notable exception that some exchange of coordinated benzene with C_6D_6 was observed.

Description of the Structure. Tables III and IV list the bond distances and selected angles for $Ru(OMN)(C_6Me_6)$. Figures 1–3 show different views of the molecule. The coordination sphere about the Ru has an η^6-C_6Me_6 ring and an η^4-OMN ring. The C_6Me_6 ring shows only slight deviations from planarity, and the average Ru–C(ring) (both molecules) distance is 2.25 (2) Å. The methyls in the C_6Me_6 are pushed slightly out-of-plane toward the distal side of the ring with respect to the Ru. For A and B the average deviations are 0.079 and 0.056 Å, respectively. The Ru is located 1.750 Å above the C_6Me_6 plane in A and 1.759 Å in B. The average C–C distance within the C_6Me_6 ring is 1.42 (1) Å for molecule A and 1.40

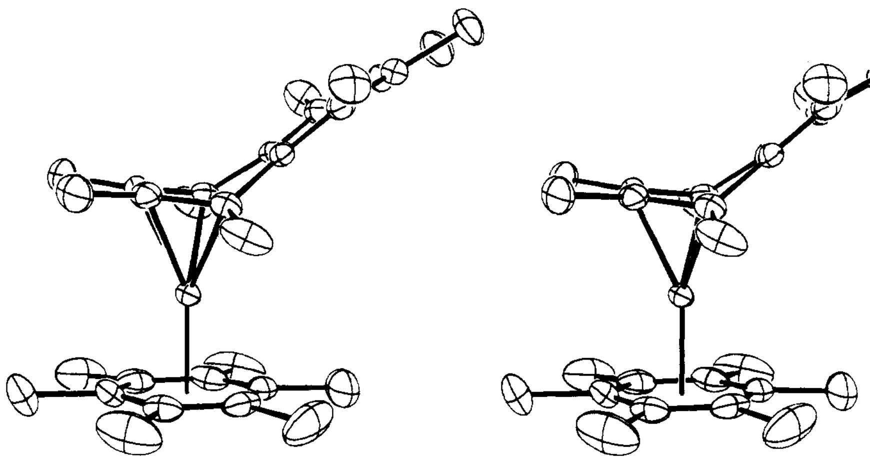


Figure 3. Stereoview of molecule B showing the distortions of the OMN.

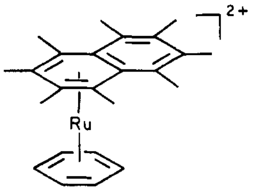
(2) Å for molecule B. The Ru–C bonds to the OMN ring follow the pattern having the Ru–C1/4 bonds longer (2.18 (2) Å for A, 2.18 (1) Å for B) and the Ru–C2/3 bonds shorter (2.150 (7) Å for A, 2.129 (4) Å for B). The closest distance between the Ru and the plane of C1–4 is 1.726 Å for A and 1.713 Å for B. The two planes comprised of C1–4 and C19–24 intersect with angles 8.3° for A and 6.4° for B.

The orientation of the C_6Me_6 and OMN rings is difficult to describe because of the lack of symmetry of the molecule. As a reasonable approximation we define the plane of symmetry as passing through the center of the C2–C3 bond and the C9–C10 bond and the Ru atom. When this is compared to the plane comprised of C20–Ru–C23, we find an angle of 14.3° for molecule A and 4.3° for molecule B.

Several points regarding the OMN ring are noteworthy. Of particular interest is the dihedral angle caused by the η^4-bonding to the Ru. The C1/2/3/4 plane makes a 41.5° (43.3 for B) angle with the C1/9/10/4 plane. In molecule A the C1–4 (diene) portion of the molecule exhibits the long–short–long pattern for the three C–C bond lengths. In B, however, the corresponding values are nearly equal. In both A and B the uncomplexed ring exhibits normal aromatic C–C bonds.

Discussion

Preparation of (Arene)ruthenium Complexes of Octamethylnaphthalene. The dications having the general formula $[Ru(OMN)(arene)]^{2+}$ can be synthesized by several methods. The Ag^+ method developed by Bennett and co-workers[14] is the most general and gives good yields, regardless of the arene. $AlCl_3$ can also be used in some examples, giving comparable yields, but it suffers from the major drawback that it degrades OMN. By electron counting the structure of each of the dications contains an η^6-arene ligand and η^6-OMN, II. In Fischer and Elschenbroich's study[5] of $[Ru(C_6Me_6)_2]^{2+}$, they found that a two-electron reduction occurred and caused one of the ligands to bind as an η^4-C_6Me_6, I. This reduction has recently been studied by using electrochemical techniques for complexes where one of the arenes is a $[2_n]$cyclophane.[19]



II

Table III. Bond Distances for Both Molecules of $Ru(OMN)(C_6Me_6)$

atoms	dist, Å	atoms	dist, Å
RuA-C1A	2.169 (4)	RuB-C1B	2.182 (4)
RuA-C2A	2.155 (4)	RuB-C2B	2.129 (4)
RuA-C3A	2.145 (4)	RuB-C3B	2.129 (4)
RuA-C4A	2.194 (4)	RuB-C4B	2.168 (4)
RuA-C9A	2.987 (4)	RuB-C9B	3.039 (4)
RuA-C10A	3.023 (4)	RuB-C10B	3.029 (4)
RuA-C19A	2.270 (4)	RuB-C19B	2.277 (4)
RuA-C20A	2.240 (4)	RuB-C20B	2.225 (5)
RuA-C21A	2.263 (4)	RuB-C21B	2.267 (4)
RuA-C22A	2.252 (4)	RuB-C22B	2.252 (4)
RuA-C23A	2.235 (4)	RuB-C23B	2.229 (4)
RuA-C24A	2.247 (4)	RuB-C24B	2.254 (5)
C1A-C2A	1.454 (6)	C1B-C2B	1.437 (6)
C1A-C9A	1.501 (6)	C1B-C9B	1.494 (5)
C2A-C3A	1.408 (6)	C2B-C3B	1.432 (7)
C3A-C4A	1.454 (6)	C3B-C4B	1.468 (6)
C4A-C10A	1.483 (6)	C4B-C10B	1.516 (5)
C10A-C9A	1.413 (6)	C10B-C9B	1.410 (5)
C10A-C5A	1.411 (6)	C10B-C5B	1.404 (5)
C5A-C6A	1.398 (8)	C5B-C6B	1.384 (6)
C6A-C7A	1.387 (9)	C6B-C7B	1.385 (7)
C7A-C8A	1.385 (8)	C7B-C8B	1.416 (6)
C8A-C9A	1.416 (6)	C8B-C9B	1.408 (5)
C19A-C20A	1.411 (6)	C19B-C20B	1.399 (7)
C20A-C21A	1.423 (6)	C20B-C21B	1.417 (8)
C21A-C22A	1.421 (6)	C21B-C22B	1.403 (8)
C22A-C23A	1.409 (6)	C22B-C23B	1.426 (8)
C23A-C24A	1.432 (6)	C23B-C24B	1.381 (7)
C24A-C19A	1.403 (6)	C24B-C19B	1.400 (7)
C1A-C11A	1.558 (6)	C1B-C11B	1.522 (6)
C2A-C12A	1.543 (6)	C2B-C12B	1.522 (6)
C3A-C13A	1.514 (6)	C3B-C13B	1.527 (6)
C4A-C14A	1.520 (6)	C4B-C14B	1.533 (6)
C5A-C15A	1.517 (8)	C5B-C15B	1.532 (7)
C6A-C16A	1.568 (7)	C6B-C16B	1.548 (6)
C7A-C17A	1.577 (8)	C7B-C17B	1.534 (6)
C8A-C18A	1.523 (9)	C8B-C18B	1.523 (6)
C19A-C25A	1.526 (6)	C19B-C25B	1.548 (7)
C20A-C26A	1.518 (6)	C20B-C26B	1.566 (8)
C21A-C27A	1.529 (6)	C21B-C27B	1.540 (7)
C22A-C28A	1.558 (6)	C22B-C28B	1.535 (8)
C23A-C29A	1.527 (6)	C23B-C29B	1.515 (8)
C24A-C30A	1.515 (6)	C24B-C30B	1.571 (8)

In this study we find two related characteristics of the OMN complexes that differentiate them from $Ru(C_6Me_6)_2$. The first is the ease with which the reduction takes place. Simply stirring an acetonitrile solution of the dication over

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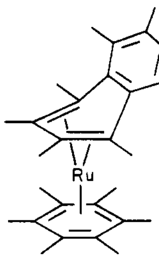
[19] Laganis, E. D.; Voegeli, R. H.; Swann, R. T.; Finke, R. G.; Hopf, H.; Boekelheide, V. *Organometallics* 1982, *1*, 1415.

Table IV. Selected Bond Angles

atoms	angle, deg	atoms	angle, deg
C1A-RuA-C21A	176.2 (2)	C1B-RuB-C21B	170.2 (2)
C1A-RuA-C4A	73.8 (2)	C1B-RuB-C4B	74.0 (2)
C3A-RuA-C20A	111.9 (2)	C3B-RuB-C20B	115.4 (2)
C19A-RuA-C20A	36.5 (2)	C19B-RuB-C20B	36.2 (2)
RuA-C1A-C11A	116.2 (3	RuB-C1B-C11B	114.7 (3)
RuA-C1A-C2A	69.9 (2)	RuB-C1B-C2B	68.6 (2)
RuA-C1A-C9A	107.6 (3)	RuB-C1B-C9B	110.1 (3)
C2A-C1A-C9A	117.1 (4)	C2B-C1B-C9B	115.9 (4)
C2A-C1A-C11A	114.9 (4)	C2B-C1B-C11B	118.3 (4)
C9A-C1A-C11A	120.3 (4)	C9B-C1B-C11B	118.6 (4)
RuA-C2A-C1A	70.9 (2)	RuB-C2B-C1B	72.5 (2)
RuA-C2A-C3A	70.5 (2)	RuB-C2B-C3B	70.3 (2)
RuA-C2A-C12A	127.4 (3)	RuB-C2B-C12B	125.4 (3)
C1A-C2A-C3A	115.5 (4)	C1B-C2B-C3B	114.4 (4)
C1A-C2A-C12A	120.7 (5)	C1B-C2B-C12B	124.1 (5)
C3A-C2A-C12A	123.8 (5)	C3B-C2B-C12B	121.5 (5)
C1A-C9A-C10A	113.3 (4)	C1B-C9B-C10B	114.7 (3)
C1A-C9A-C8A	126.5 (4)	C1B-C9B-C8B	126.3 (4)
C8A-C9A-C10A	120.1 (4)	C8B-C9B-C10B	118.9 (4)
C4A-C10A-C5A	127.0 (4)	C4B-C10B-C5B	127.1 (4)
C4A-C10A-C9A	114.2 (4)	C4B-C10B-C9B	112.5 (3)
C5A-C10A-C9A	118.8 (4)	C5B-C10B-C9B	120.3 (4)
C9A-C8A-C18A	123.4 (6)	C9B-C8B-C18B	123.5 (4)
C9A-C8A-C7A	118.9 (6)	C9B-C8B-C7B	119.1 (4)
C7A-C8A-C18A	117.8 (6)	C7B-C8B-C18B	117.4 (4)
C8A-C7A-C6A	121.1 (5)	C8B-C7B-C6B	120.0 (4)
C8A-C7A-C17A	121.3 (7)	C8B-C7B-C17B	119.9 (5)
C6A-C7A-C17A	117.6 (6)	C6B-C7B-C17B	120.2 (5)
C19A-C24A-C23A	121.1 (4)	C19B-C24B-C23B	121.0 (5)
C19A-C24A-C30A	120.6 (5)	C23B-C24B-C30B	118.2 (6)
C22A-C23A-C24A	118.6 (4)	C22B-C23B-C24B	119.8 (5)
C22A-C23A-C29A	121.1 (5)	C22B-C23B-C29B	120.3 (6)
C24A-C23A-C29A	120.2 (4)	C24B-C23B-C29B	119.7 (6)

a 1% sodium amalgam is effective for generating the ruthenium(0) product. The original synthesis of $Ru(C_6Me_6)_2$ makes use of sodium in liquid ammonia, and under our conditions $[Ru(C_6Me_6)_2]^{2+}$ is not reduced. The second difference is related in that it is a comparison of the ease of the reverse reaction. $Ru(C_6Me_6)_2$ is a very air-sensitive compound, while the OMN complexes can be handled easily in air as solids, and they decompose slowly in solution when exposed to the atmosphere. We know from the structure of $Ru(OMN)(C_6Me_6)$ that the OMN binds as the η^4-ligand, III. Apparently the difference in energy of the η^6- and η^4-bonding modes for OMN is much less than that for other arenes. The net result is that the η^4-OMN complexes are more readily synthesized and, once prepared, are more stable. Part of the cause of this difference can be attributed to the fact that when a metal binds to a naphthalene ring in an η^4 fashion the uncoordinated ring retains its aromaticity. This is not the only reason for the difference. We we able to prepare the dication $[Ru(C_6Me_6)(C_{10}H_8)]^{2+}$, but all attempts to reduce this to the zerovalent complex failed. The only products isolated were free naphthalene and C_6Me_6. The methyls of OMN must also add to the stability of the product. As discussed below, the η^4-bonding mode also reduces the steric repulsions between the *peri*-methyl groups. This certainly would serve to increase the driving force for promoting this bonding mode.



III

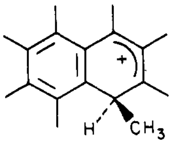
Structure of $Ru(OMN)(C_6Me_6)$. We begin this discussion of the structure with a comparison of the two molecules present in the asymmetric unit. We believe that the cause for most of the differences can be traced to one point; the different relative orientations of the C_6Me_6 and OMN rings in A and B. This examination is of value because it allows us to gauge the relative importance of the various interligand interactions in determining the ultimate structure. Molecule B most nearly approximates a species with a mirror plane present. With C20 and C23 of the C_6Me_6 lying on the mirror plane, the molecule has a staggered configuration of the C_6Me_6 and OMN rins. The comparison of the interplane angle between the mirror plane, which is defined by the center of the C2–C3 and C9–C10 bonds and the Ru, and the plane comprised of C20–Ru–C23 offers a reasonable method to quantitate the relative orientation. Ideally a staggered configuration would result in an angle of 0°, while the maximum value of 30° would indicate an eclipsed geometry.

The ring carbon atoms of the OMN and C_6Me_6 rings are all greater than 3.4 Å apart in both A and B. The close contacts that appear to be responsible for the observed effects are between the methyl groups on the two rings. In particular, the *peri*-methyl groups on the OMN ring (C11 and C14) are directed toward the C_6Me_6 (due to the interaction between the other *peri*-methyl groups C15 and C18, C11A/B–C18A/B = 2.89 (1)/2.965 (7) Å; C14A/B–C15A/B = 2.984 (9)/2.954 (8) Å). The distance between C11A and C30A is 3.284 (9) Å and represents the closest contact between the rings. In B this value is 3.406 (9) Å, while the C14B–C28B distance is shorter, 3.332 (9) Å. The contact between C14A and C28A is 3.556 (8) Å, but C14A also interacts with C27A (3.539 (8) Å). The other two methyls, C12 and C13, are greater than 3.9 Å from the nearest methyl on the C_6Me_6.

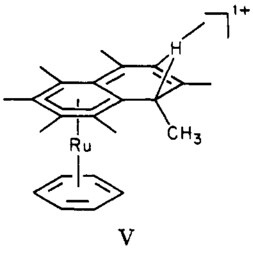
If the staggered configuration is preferred on steric grounds, there must be at least a slight electronic preference for the eclipsed configurations. The balance of these components leads to the conformations observed in Ru(OMN)(C_6Me_6). In the structure of Ru(C_6Me_6)$_2$, the two rings adopt a completely eclipsed conformation. Without the interaction of the *peri*-methyl groups on the uncoordinated ring to force the methyls toward the Ru side of the ring, the nonbonded interactions in Ru(C_6Me_6)$_2$ are smaller than those in Ru(OMN)(C_6Me_6). On the η^4-C_6Me_6 in Ru(C_6Me_6)$_2$ the methyls attached to the metal-coordinated carbons at the 1- and 4-positions are tilted toward the metal. However, the distances that they are out of the diene plane are 0.153 and 0.186 Å, which is substantially less than that observed for Ru(OMN)(C_6Me_6).

The only other structurally characterized complex that contains an η^4-naphthalene ring is TaCl(η^4-$C_{10}H_8$)(dmpe)$_2$ (dmpe = 1,2-bis(dimethylphosphino)ethane).[20] The dihedral angle between the complexed butadiene portion and the benzene portion of the ring is 43.0°. The C–C distances of the butadiene portion also show the long–short–long pattern found here.

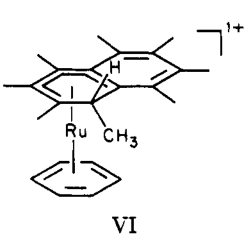
Reactivity of the Uncoordinated Ring. Dissolution of Ru(OMN)(C_6H_6) in neat CF_3COOH resulted in immediate addition of one proton. The site of protonation is not conclusively identified by spectroscopy. OMN itself has two unique carbons and studies have shown[21-23] that it forms the naphthalenium ion, IV. Complexation of OMN to the ruthenium increases the number of unique ring carbons to four as well as differentiating one side of the ring from the other. The net result is eight possible sites at which the proton can react. In complexed and uncomplexed OMN, both electronic and steric factors strongly favor the addition of the proton to the peri carbons. The ^{1}H and ^{13}C NMR data clearly show that the added proton appears in the normal allylic region, while the methyl group coupled to this proton is shifted upfield to 0.11 ppm. This is strong evidence that the proton is bound on the distal side of the OMN, which rules out prior formation of a metal hydride followed by migration of the hydrogen to the ring. These arguments leave two structures as candidates for this product, V and VI. Both structures have an 18-electron metal with a η^5-cyclohexadienyl ligand. The shift of the methyl to higher field would be attributed to the shielding effect of the metal as well as the naphthalene ring system. Although we favor structure VI because it allows one ring to remain cyclically conjugated, an X-ray crystallographic analysis would be required to unambiguously assign the structure.



IV

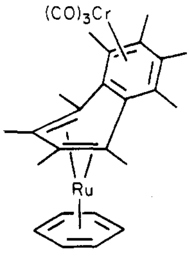


V



VI

The reaction of Ru(OMN)(C_6H_6) with Cr(CO)$_3$(CH_3CN)$_3$ illustrates the feasibility of putting a second metal on the OMN. The structure of the product, VII, is proposed to have the metals on the opposite sides of the OMN.



VII

Reactions with H_2. One of the most interesting properties of Ru(C_6Me_6)$_2$ is its ability to catalyze the homogeneous hydrogenation of benzene to cyclohexane.[7,8] Under conditions similar to those used for Ru(C_6Me_6)$_2$ we found no activity for catalytic benzene hydrogenation with Ru(OMN)(1,2,3,4-$Me_4C_6H_2$) and Ru(OMN)(C_6H_6). The benzene complex was of particular interest since the substrate is already complexed to the metal. When the benzene complex was dissolved in C_6D_6 and reacted with H_2 to determine if stoichiometric hydrogenation was possible, the only reaction observed by ^{1}H NMR was slow benzene exchange. Muetterties and co-workers have suggested that the reduction of the aromaticity by coordination of the benzene as a η^4-ligand is important in the catalysis.[2] Since these mixed arene complexes apparently all contain OMN as a *stable* η^4-ligand, it is not surprising that they do not catalyze the hydrogenation. This is entirely consistent with the ease of preparation as well as the general stability of these complexes relative to Ru(C_6Me_6)$_2$.

It is noteworthy that we did observe hydrogenation on several occasions. In each case, however, a small amount of solid material, presumably ruthenium metal, was visible in the reaction vessel. The solid formed as a result of thermal decomposition or decomposition induced by traces of oxygen.

Acknowledgment. We thank the Research Corp. and the National Science Foundation for supporting this research.

Registry No. [RuCl$_2$(1,2,3,4-$Me_4C_6H_2$)]$_2$, 88946-78-5; [RuCl$_2$(1,3,5-$Me_3C_6H_3$)]$_2$, 52462-31-4; [RuCl$_2$(1,3,5-$Et_3C_6H_3$)]$_2$, 88946-79-6; [RuCl$_2$(1,3,5-*i*-$Pr_3C_6H_3$)]$_2$, 88946-80-9; [Ru(OMN)(1-Me-4-($CHMe_2$)C_6H_4)](PF_6)$_2$, 88946-82-1; [Ru(OMN)(C_6H_6)](PF_6)$_2$, 88968-51-8; [Ru(OMN)(1,2,3,4-$Me_4C_6H_2$)](PF_6)$_2$, 88946-84-3; [Ru(OMN)(1,3,5-$Me_3C_6H_3$)](PF_6)$_2$, 88946-86-5; [Ru(OMN)(C_6Me_6)](BPh_4)$_2$, 88946-88-7; [Ru(OMN)(1,3,5-$Et_3C_6H_3$)](BPh_4)$_2$, 88946-90-1; [Ru(OMN)(1,3,5-*i*-$Pr_3C_6H_3$)](PF_6)(BPh_4), 88946-92-3; Ru(OMN)(C_6Me_6), 88946-93-4; Ru(OMN)(1-Me-4-($CHMe_2$)C_6H_4), 88946-94-5; Ru(OMN)(1,3,5-$Me_3C_6H_3$), 88946-95-6; Ru(OMN)(1,2,3,4-$Me_4C_6H_2$), 88946-96-7; Ru(OMN)(C_6H_6), 88946-97-8; [Ru($C_{10}Me_8H$)(C_6H_6)](PF_6), 88946-99-0; (C_6H_6)Ru(μ-OMN)Cr(CO)$_3$, 88947-00-6; [RuCl$_2$(1-Me-4-($CHMe_2$)C_6H_4)]$_2$, 52462-29-0.

Supplementary Material Available: A listing of the temperature factors, the least-squares planes, the complete distances and angles, and the observed and calculated structure factors is available (28 pages). Ordering information is given on any current masthead page.

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