*Organometallics* 1987, *6*, 1543–1552 1543

# Synthesis and Characterization of [Ru(1–3:5,6-$\eta$-cyclooctadienyl)($\eta^6$-cyclooctatriene)]$PF_6$ and Its Use as a Precursor into 1–3:5,6-$\eta$- and 1–5-$\eta$-Cyclooctadienyl Ruthenium(II) Complexes. The X-ray Crystal Structure Determinations of [Ru(1–3:5,6-$\eta$-cyclooctadienyl)($\eta^6$-cyclooctatriene)]$PF_6$ and [Ru(1–5-$\eta$-cyclooctadienyl)($PMe_2Ph)_3$]$PF_6$

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*Received June 3, 1986*

Treatment of the complex [RuH(cod)($NH_2NMe_2)_3$]$PF_6$ (**1**) (cod = cycloocta-1,5-diene) in methanol or acetone solutions with excess cyclooctatetraene gives the salt [Ru(1–3:5,6-$\eta$-cyclooctadienyl)($\eta^6$-1,3,5-cyclooctatriene)]$PF_6$ (**2**) in 30% yield. A mechanism involving intramolecular hydrogen transfer is proposed to explain the formation of the $\eta^6$-1,3,5-cyclooctatriene ligand. Variable-temperature NMR studies demonstrate that **2** is fluxional with two distinct species being observed at 303 and 190 K. The structure of **2** was assigned from the limiting slow-exchange $^{13}C$ (125.5 MHz) and $^1H$ (500.12 MHz) NMR at 190 K. The solution structure at low temperature can be readily related to the solid-state structure as determined by X-ray crystallography. Complex **2** reacts with isocyanides and CO to give [Ru(1–3:5,6-$\eta$-$C_8H_{11}$)$L_3$]$PF_6$ (**3**) (L = CO, CNR; R = *t*-Bu, 2,6-$Me_2C_6H_3$), whereas with more sterically demanding ligands, isomerization of the 1–3:5,6-$\eta$-$C_8H_{11}$ ligands occurs to give the 1–5-$\eta$-complexes [Ru(1-5-$\eta$-$C_8H_{11}$)$L_3$]$PF_6$ (**4**) (L = $P(OMe)_3$, $PMe_2Ph$, $AsMe_2Ph$, and $AsMePh_2$). **4** (L = $PMe_2Ph$, and $AsMePh_2$) may also be obtained by heating a solution of [RuH(cod)$L_3$]$PF_6$ (**5**) (L = $PMe_2Ph$ and $AsMePh_2$) in methanol or dioxane in the presence of excess cod that acts as a hydrogen acceptor. The crystal and molecular structures of **2** and **4** (L = $PMe_2Ph$) have been determined by X-ray diffraction techniques and refined to conventional *R* factors of 0.0673 and 0.0531, respectively. The activation energy for the isomerization of the $C_8H_{11}$ ligand from the 1–3:5,6-$\eta$- to the 1–5-$\eta$-form is provided, most likely, by the build-up of steric strain energy within the molecule. Projection diagrams reveal the larger cone angle of the 1–3:5,6-$\eta$-form. All the new compounds were isolated as analytically pure solids and were characterized by IR and $^1H$ and $^{13}C\{^1H\}$ NMR spectroscopy.

## Introduction

Previous studies have shown[1,2] that the interaction of dienes with ruthenium hydrides produced 1–5-$\eta$-dienyl complexes. In these reactions the excess diene acted as a hydrogen acceptor and the hydrogen transfer was assumed to be intramolecular, occurring between two hydrocarbon ligands derived from the diene molecule. Similar proposals were made to account for the formation of zerovalent polyolefin complexes and of related 1–5-$\eta$-dienyl species from zinc reductions of hydrated ruthenium trichloride in the presence of dienes.[3,4] Evidence for hydrogen transfer between coordinated olefin ligands has also been obtained in studies of complexes of zirconium,[5] rhodium,[6] iridium,[6] and molybdenum.[7] However, only in the study of the conversion of [Mo($\eta$-$C_7H_8)_2$] to [Mo($\eta$-$C_7H_7$)($\eta$-$C_7H_9$)] was the hydrogen migration shown[7] to be intramolecular from studies of the perdeuterio derivative. Since cationic complexes may show enhanced activity[8] in catalytic transformations of olefin substrates, we have chosen to study the reactivity of cationic complexes of the type [RuH(cod)$L_3$]$^+$ (L = phosphorus, arsenic, or nitrogen donor) as an extension of the earlier work[1-4] on neutral complexes of ruthenium. We have described previously, for example, the formation of $\eta^3$-enyl complexes of the type [Ru($\eta^3$-enyl)$L_3$]$PF_6$ (enyl = cyclooctadienyl,[9] butenyl, hexenyl, and heptenyl[10]). We now wish to report the synthesis and characterization of [Ru(1–3:5,6-$\eta$-$C_8H_{11}$)($\eta^6$-1,3,5-cyclooctatriene)]$PF_6$ and its conversion to a range of 1–3:5,6-$\eta$- and 1–5-$\eta$-cyclooctadienyl complexes. Our studies show two further examples of hydrogen-transfer processes. Both involve migration of hydrogen from a cycloocta-1,5-diene (cod) ligand coordinated at a cationic ruthenium(II) center leading to complexes containing the cyclooctadienyl moiety; in the one case the hydrogen acceptor is cyclooctatetraene and in the other case is cod. In addition the X-ray structural determinations of [Ru(1–3:5,6-$\eta$-$C_8H_{11}$)($\eta^6$-1,3,5-$C_8H_{10}$)]$PF_6$ and [Ru(1–5-$\eta$-$C_8H_{11}$)($PMe_2Ph)_3$]$PF_6$ show the conformation of the two dienyl forms of the $C_8H_{11}$ ring, viz., 1–3:5,6-$\eta$ and 1–5-$\eta$ and allow an assessment of the factors governing which form exists in a given molecule. Part of this work has been described in a preliminary communication.[11]

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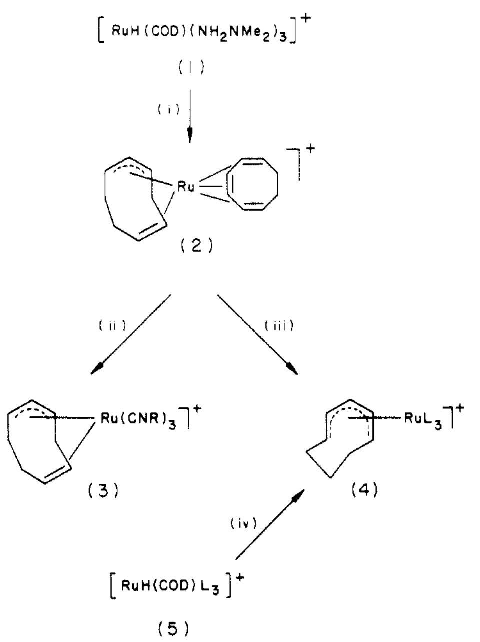
**Scheme I**



$^a$(i) cot, MeOH, 60 °C; (ii) RNC, acetone, 25 °C; (iii) PMe$_2$Ph, P(OMe)$_3$, AsMePh$_2$, MeOH, 60 °C; (iv) dioxane, cod, 100 °C.

## Results

The reactions studied are illustrated in Scheme I. The reaction of [RuH(cod)(NH$_2$NMe$_2$)$_3$]PF$_6$[12] (1) (cod = cycloocta-1,5-diene) with excess cyclooctatetraene (cot) in refluxing methanol rapidly (ca. 15 min) deposits a precipitate of the yellow air-stable compound [Ru(1–3:5,6-$\eta$-C$_8$H$_{11}$)($\eta^6$-1,3,5-C$_8$H$_{10}$)]PF$_6$ (2) in 30% yield. The low yield is a result of competing dimerization reactions of 1, giving products which do not react with cot.[13] Tkatchenko et al. have reported the preparation of 2 from reactions of [Ru(cod)($\eta^6$-cyclooctatriene)] with [Ph$_3$C]PF$_6$ or with allyloxyphosphonium salts.[14] We have confirmed that the former reaction does produce 2; however, Tkatchenko et al. characterized 2 by using NMR data recorded at 303 K and at lower field, whereas in our opinion, these data are insufficient as the compound is fluxional and can be unambiguously characterized in solution by using only low-temperature data (see NMR section).

The $\eta^6$-triene ligand of 2 is readily replaced by a range of neutral donor ligands to give compounds containing either 1–3:5,6-$\eta$- or 1–5-$\eta$-C$_8$H$_{11}$ ligands. Thus, treatment of 2 in acetone solution with 3 molar equiv of RNC at 25 °C rapidly produces [Ru(1–3:5,6-$\eta$-C$_8$H$_{11}$)(CNR)$_3$][PF$_6$] (R = *t*-Bu, 2,6-Me$_2$C$_6$H$_3$). Similarly, [Ru(1–3:5,6-$\eta$-C$_8$H$_{11}$)(CO)$_3$][PF$_6$][15] is obtained on passing a stream of carbon monoxide overnight through an acetone solution of 2.

**Table I. Color, Melting Points, and Analyses for the Complexes**

| compd | color | mp,$^a$ °C | anal.$^b$ C | H |
|---|---|---|---|---|
| [Ru(C$_8$H$_{10}$)(C$_8$H$_{11}$)]PF$_6$ | yellow | >180$^c$ | 41.80 (41.83) | 4.61 (4.61) |
| [Ru(C$_8$H$_{10}$)(C$_8$H$_{11}$)]BPh$_4$ | yellow | 205–207 | 75.90 (75.82) | 6.63 (6.52) |
| [Ru(C$_8$H$_{11}$){P(OMe)$_3$}$_3$]PF$_6$ | white | 163–164 | 28.10 (28.15) | 5.39 (5.28) |
| [Ru(C$_8$H$_{11}$)(PMe$_2$Ph)$_3$]PF$_6$ | yellow | 166–169 | 50.11 (50.07) | 5.76 (5.78) |
| [Ru(C$_8$H$_{11}$)(AsMePh$_2$)$_3$]PF$_6$ | yellow | 166–168 | 52.25 (52.00) | 4.93 (4.64) |
| [Ru(C$_8$H$_{11}$)(CN-*t*-Bu)$_3$]PF$_6$ | cream | 178–180 | 45.64 (45.84) | 6.57 (6.36) |
| [Ru(C$_8$H$_{11}$)(CNxylyl)$_3$]PF$_6$ | beige | 203–205 | 56.00 (56.30) | 5.09 (5.13) |

$^a$In air, melting points corrected. $^b$Calculated values are in parentheses. $^c$Decomposition without melting.

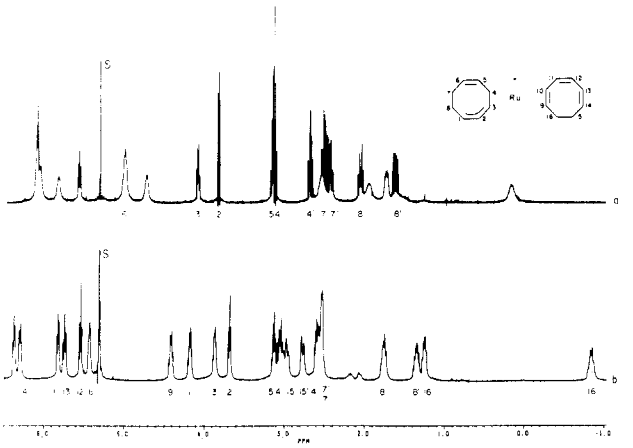


**Figure 1.** 500-MHz $^1$H NMR spectra of compound 2 in CD$_2$Cl$_2$ at (a) 303 K and (b) 193 K. Solvent resonance marked S.

In contrast to the reaction with isocyanides, 2 reacts with phosphorus or arsenic donor ligands to form complexes in which the C$_8$H$_{11}$ ligand is bonded to ruthenium as a 1–5-$\eta$-moiety. Thus, reaction of 2 in methanol under reflux with the appropriate amount of L yields the complexes [Ru(1–5-$\eta$-C$_8$H$_{11}$)L$_3$][PF$_6$] (4) [L = P(OMe)$_3$, PMe$_2$Ph, AsMe$_2$Ph, and AsMePh$_2$]. A recent communication claims[16] that compounds of the type 4 can be synthesized by protonation of [Ru($\eta^4$-C$_8$H$_{12}$)($\eta^6$-C$_8$H$_{10}$)] in the presence of tertiary phosphine ligands. Tkatchenko et al. have formulated[14] the product of the reaction of 2 with P(OMe)$_3$ as [Ru(1–3:5,6-$\eta$-C$_8$H$_{11}$){P(OMe)$_3$}$_3$]PF$_6$, a result which is difficult to reconcile with our own observations.

The $\eta^5$-salts 4 (L = PMe$_2$Ph and AsMePh$_2$) are also obtained by heating the hydrido diene complexes [RuH(cod)L$_3$]PF$_6$ (5) (L = PMe$_2$Ph and AsMePh$_2$) in dioxane at 100 °C in the presence of excess cycloocta-1,5-diene which is converted to a mixture of cyclooctene and 1,3-, 1,4-, and 1,5-cyclooctadiene. Under less severe reaction conditions (MeOH, 60 °C) 5 (L = PMe$_2$Ph) is converted into a mixture of 4 (40% yield) and the $\eta^3$-enyl [Ru($\eta^3$-C$_8$H$_{13}$)(PMe$_2$Ph)$_3$]PF$_6$ in the time taken to isomerize the added cod completely to cycloocta-1,3-diene. The detection (GC analysis) of cyclooctene in equimolar amounts with the product 4, together with the observation that neither the 1,3- nor the 1,4-isomer of cyclooctadiene is effective, establishes that the 1,5-isomer acts as the hydrogen acceptor in this reaction. This reaction is not general, however, and only the known[9] $\eta^3$-species [Ru($\eta^3$-C$_8$H$_{13}$)L$_3$]PF$_6$ [L = P(OMe)$_2$Ph and P(OMe)Ph$_2$] were obtained on reaction of the appropriate complexes 5 with excess cycloocta-1,5-diene in methanol or dioxane.

Compounds 2–4 are stable in air in the solid state. On the other hand, solutions of 2–4 [L = P(OMe)$_3$ or PMe$_2$Ph] decompose slowly in air while 4 (L = AsMePh$_2$) decom-

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**Table II. $^{13}C$ Chemical Shifts for $[Ru(1\text{-}3{:}5,6\text{-}\eta\text{-}C_8H_{11})L_3]^{+\,a}$**

| $L_3$ | $C_1$ | $C_2$ | $C_3$ | $C_4$ | $C_5$ | $C_6$ | $C_7$ | $C_8$ | ref | solv |
|---|---|---|---|---|---|---|---|---|---|---|
| $(CN\text{-}t\text{-}Bu)_3$ | 68.1 (158) | 99.5 (156) | 37.1 (169) | 20.7 (134) | 62.0 (163) | 104.9 (124) | 35.0 (124) | 27.0 (129) | this work | $(CD_3)_2CO$ |
| $[CN(2,6\text{-}Me_2C_6H_3)]_3$ | 65.1 | 98.1 | 35.8 | 20.8 | 58.8 | 101.7 | 34.0 | 26.8 | this work | $(CD_3)_2CO$ |
| $\eta^6\text{-}C_8H_{10}{}^b$ | 79.6 | 88.4 | 40.9 | 20.0 | 45.0 | 95.5 | 35.4 | 27.7 | this work | $(CD_3)_2CO$ |
| 1-3:5-6-η-$C_8H_{11}$ | 62.4 | 87.6 | 35.3 | 22.5 | 38.9 | 76.7 | 36.7 | 27.3 | 4 | $C_6D_6$ |
| $\eta^6\text{-}C_6H_5BF_3{}^c$ | 75.5 | 83.3 | 30.5 | 23.3 | 35.5 | 86.4 | 39.5 | 32.3 | 17 | $CD_3NO_2$ |

[a] In ppm relative to $Me_4Si$; $^1J(CH)$ (Hz) values in parentheses. [b] Signals for $C_9$–$C_{16}$ were at 101.2, 99.9, 97.6, 95.7*, 95.0, 94.9*, 36.1*, and 28.2* ppm. The asterisks denote exchange-broadened resonances. [c] Corrected from previously reported by addition of 5.9 ppm.

**Table III. $^1H$ Chemical Shifts for $[Ru(1\text{-}3{:}5,6\text{-}\eta\text{-}C_8H_{11})L_3]^{+\,a}$**

| $L_3$ | $H_1$ | $H_2$ | $H_3$ | $H_4$ | $H_4$ | $H_5$ | $H_6$ | $H_7$ | $H_7$ | $H_8$ | $H_8$ | solv |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $(CN\text{-}t\text{-}Bu)_3$ | 3.95 | 3.93 | 3.55 | 2.96 | 2.93 | 3.16 | 4.55 | 2.33 | 2.27 | 2.05 | 1.80 | $CDCl_3$ |
| $[CN(2,6\text{-}Me_2C_6H_3)]_3$ | 4.70 | 4.79 | 4.21 | 3.33 | 3.33 | 3.97 | 5.38 | 2.88 | 2.55 | 2.36 | 2.21 | $(CD_3)_2CO$ |
| $\eta^6\text{-}C_8H_{10}$ | 4.19 | 3.69 | 3.87 | 3.05 | 2.62 | 3.14 | 5.44 | 2.54 | 2.54 | 1.76 | 1.35 | $CD_2Cl_2$ |
| $\eta^6\text{-}C_6H_5BF_3{}^b$ | 5.28 | 3.84 | 4.13 | 2.95 | 2.54 | 3.19 | 4.70 | 2.41 | 2.29 | 2.00 | 1.48 | $CD_2Cl_2$ |

[a] In ppm relative to $Me_4Si$. [b] $J(H\text{–}H)$ (Hz): $J(1,2) = 7.6$, $J(1,8) = 9.7$, $J(1,8') = 6.6$, $J(2,3) = 6.8$, $J(3,4) = 9.4$, $J(3,4') = 5.4$, $J(4,4') = 14.0$, $J(4,5) = 9.2$, $J(4',5) = 7.8$, $J(5,6) = 7.8$, $J(6,7) = 6.4$, $J(6,7') = 1.5$, $J(7,7') = 15.1$, $J(7,8) = 9.8$, $J(7,8') = 12.9$, $J(7',8) = 1.5$, $J(7',8') = 6.4$, $J(8.8') = 14.1$.

**Table IV. $^{13}C$ and $^1H$ Chemical Shifts for $[Ru(1\text{-}5\text{-}\eta\text{-}C_8H_{11})L_3]^{+\,a}$**

| L | $C_1$ | $C_2$ | $C_3$ | $C_4$ | $C_5$ | $H_1$ | $H_2$ | $H_3$ | $H_4$ | $H_{5exo}$ | $H_{5endo}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $AsMePh_2$ | 99.2 | 86.2 | 52.8 | 27.1 | 18.2 | 7.05 t | 4.79 t | 2.89 m | 1.38 d, 0.68 t | 0.79 d | 0.08 q |
| $AsMe_2Ph$ | 99.0 | 86.8 | 50.8 | 26.0 | 20.2 | 6.39 t | 4.59 t | 2.73 m | ≃1.50, 0.87 t | ≃0.89 | 0.09 q |
| $PMe_2Ph$ | 98.5 (167) | 91.0 (159) | 56.0 (147) | 23.6 (127) | 19.1 | 6.0 t | 4.7 t | 2.4 m | ..., 0.48 t | 0.85 d | 0.16 q |
| $P(OMe)_3$ | 99.0 | 94.4 | 53.2 | 26.1 | 19.4 | 6.27 t | 4.77 t | 3.48 m | 2.03, 1.72 t | 1.16 d | 0.34 q |

[a] In ppm relative to $Me_4Si$ for $(CD_3)_2CO$ solutions. Abbreviations: d, doublet; t, triplet; q, quartet; m, multiplet; ..., obscured by other resonances. In parentheses $^1J(CH)$ values (Hz).

poses rapidly (within minutes). Melting points, microanalytical results, and NMR data from $^1H$ and $^{13}C$ studies are given in Tables I–IV. The structures of **2–4** are deduced from their $^1H$ and $^{13}C$ spectra as discussed below.

**NMR Studies.** The $^{13}C$ NMR spectrum established the composition of the cation **2** as $[C_{16}H_{21}Ru]^+$ by showing 16 carbon signals assigned by off-resonance decoupling as 11 CH and 5 $CH_2$ resonances. The absence of any symmetry element was corroborated by the 500-MHz $^1H$ spectrum in $CD_2Cl_2$ solution at 193 K in which only the overlap of two geminal proton signals prevents the identification of a separate multiplet for each of the 21 protons. Figure 1 displays the $^1H$ spectrum with the assignments suggested by $^1H\{^1H\}$ decoupling experiments. The presence of the (1–3:5,6-η-$C_8H_{11}$) ligand was further confirmed by the 500-MHz $^1H$ spectrum of the known[17] complex [Ru(1–3:5,6-η-$C_8H_{11}$)(η⁶-$C_6H_5BF_3$)] which displays (303 K in $CD_2Cl_2$) almost identical multiplets to those assigned to $H_1$ to $H_8$ of **2**. To assist with further characterization of this unusual ligand, a full iterative calculation of the spin system was performed. The observed and calculated spectra are given in Figure 2 and the coupling constants in Table III. Marked changes in the chemical shifts of $H_1$ and $H_6$ (Table III) suggest that the replacement of triene by arene ligand induces some conformational change in the 1–3:5,6-η-$C_8H_{11}$ ring system. The same protons show the greatest variation in chemical shift with temperature (Figure 1).

As the temperature of the solution of **2** in $CD_2Cl_2$ is raised from 193 K, the $^1H$ multiplets broaden and shift to varying degrees and then resharpen so that at 303 K the spectrum consists once more of the multiplets of the 1–3:5,6-η-$C_8H_{11}$ ligand, but most of the remaining ten signals still show substantial exchange broadening. $^1H\{^1H\}$ experiments were, therefore, uninformative in elucidating the structure of the second ring at room temperature, and although at higher temperatures (343 K in acetone or dimethylsulphoxide) the low-field resonances sharpen to recognizable multiplets, the four methylene resonances remain broad until decomposition temperatures. The $^{13}C$ spectrum shows analogous changes with temperature, the 16 sharp signals of **2** in $CD_2Cl_2$ at 193 K are replaced at 303 K by 16 signals of somewhat different chemical shifts. Throughout the intermediate temperatures complex broadening and collapse of signals occur, but it proved impossible to correlate the lines of the 193 K spectrum with those of the 303 K spectrum.

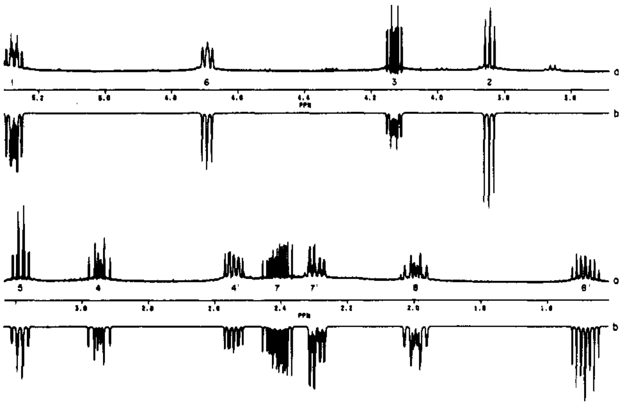

**Figure 2.** 500-MHz $^1H$ NMR spectra of [Ru(1–3:5,6-η-$C_8H_{11}$)(η⁶-$C_6H_5BF_3$)]: (a) observed and (b) calculated.

A significant clue to the nature of the fluxional process is given by the $^1H$ chemical shift of a methylene proton of the cyclooctatriene moiety which is changed from a value of –0.8 ppm at 193 K to 0.2 ppm at 303 K. This proton can be assigned to $H_{16'}$ [H(18B) of the crystal structure], and the high-field position in the low-temperature spectrum is ascribed to the position this proton is constrained to in the shielding region above the triene system. If a simple conformational change about the $CH_2$–$CH_2$ bond is responsible for the observed changes in the spectra, it would move the $H_{16'}$ proton from the shielding region and

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[17] Ashworth, T. V.; Nolte, M. J.; Reiman, R.; Singleton, E. *J. Chem. Soc., Chem. Commun.* 1977, 937.

an averaging of the chemical shifts would result in the downfield shift observed at higher temperatures. In an attempt to produce a fully resolved fast-exchange spectrum a solution of 2 in acetone-$d_6$ at 328 K was recorded at 300 MHz. The $^1$H spectrum is substantially better resolved than the 500-MHz spectrum, and $^1$H-decoupling experiments suggest that the 1,3,5-cyclooctatriene moiety persists in the higher temperature form; in particular, decoupling of the $H_{16'}$ multiplet perturbs only one olefin signal so isomerization to the 1,3,6-triene system can be excluded.

The $^{13}$C assignments for the (1–3:5,6-$\eta$-$C_8H_{11}$) moiety based on selective $^{13}C\{^1H\}$ experiments in acetone-$d_6$ solution at 303 K are given in Table II together with the data for other complexes containing this ligand. [In our hands $CD_3NO_2$ has a $^{13}$C chemical shift of 63.2 ppm relative to internal $Me_4Si$ and not the value of 57.3 ppm quoted in reference works and used as secondary reference in our earlier report.[17]] The complexes $[Ru(1–3:5,6-\eta-C_8H_{11})(CNR)_3]^+$ are nonfluxional, and the analyses and assignments of $^1$H and $^{13}$C spectra were made unexceptionally with the aid of $^1H\{^1H\}$ and selective $^{13}C\{^1H\}$ decoupling. The $^{13}$C values (Table II) show a very consistent pattern of strong shielding of the nuclei $C_3$, $C_4$, and $C_5$, and there is also a modest but noticeable increase in the $^1J$(CH) values for these carbons (**3**, R = *t*-Bu). Explanations of $^{13}$C shielding changes based on electron density arguments have been discouraged in recent years, but although it is clear that correlations with total electron *density* are inappropriate, calculations by Seidman and Maciel[18] have suggested that changes in electron *distribution* could be responsible for the observed shieldings in simple organic systems. Certainly, the increased $^1J$(CH) values, which can be more firmly ascribed to increased s character of the C–H bonds, suggest that greater $\pi$-bonding to the metal occurs from this region. However, even $^1J$(CH) values may respond to other factors such as the deviation of the protons from the plane of the allyl system. The $H_5$ proton is consistently at rather high field for $sp^2$ hybridization (ca. 3.2 ppm in $CDCl_3$ solutions), but the remarkable shielding of 1.1 ppm found[4] in $[Ru(1–3:5,6-\eta-C_8H_{11})_2]$ is not reproduced.

The $[Ru(1–5-\eta-C_8H_{11})L_3]PF_6$ complexes, like the $[Ru(1–3:5,6-\eta-C_8H_{11})(CNR)_3]PF_6$ systems, are coordinatively saturated and do not display the richness of fluxional processes of the agostic $[Ru(1–3-\eta-C_8H_{13})L_3]^+$ counterparts.[9] Room-temperature $^1$H and $^{13}$C parameters are summarized in Table IV. The spectra reflect the ligand symmetry, and $^1H\{^1H\}$ experiments, starting with the simple triplet of the central allyl proton, substantiated the assignment of the proton multiplets allowing assignment of the $^{13}$C signals by subsequent $^{13}C\{^1H\}$ decoupling. At 500 MHz the $^1$H spectra show a characteristic pattern of multiplets (1 H, d; 2 H, t; 1 H, q) slightly deshielded from $Me_4Si$ which decoupling experiments indicate to be due to the $H_{5exo}$, $H_{4\alpha}$, and $H_{5endo}$ protons (suffix with respect to metal), respectively, where $H_{4\alpha}$ is the proton with an approximately $\gamma$-anti disposition to $H_{5endo}$. In contrast to our observed $^1$H NMR spectrum of **5** [L = $P(OMe)_3$], Tkatchenko et al. have reported[14] a more complicated $^1$H NMR spectrum for their product of the same reaction. The assignment of a 1–3:5,6-$\eta$-$C_8H_{11}$ group from their reported results must be viewed with considerable skepticism since a resonance at $\delta$ 7.45, 2.0 ppm to lower field than any signal reported in Table III, is observed.

**X-ray Structures. $[Ru(1–3:5,6-\eta-C_8H_{11})(1,3,5-\eta^6-cyclooctatriene)]PF_6$.** The molecular structure of 2 (Figure 3) shows that the cyclooctadienyl ligand is 1–3:5,6-$\eta$-bonded to the $Ru(1,3,5-\eta^6-C_8H_{10})^+$ moiety. Thus the allyl function occupies two sites and the alkene function the third site of one face of a distorted octahedral coordination geometry. The remaining three coordination sites are occupied by the triene system of the cyclooctatriene ligand. The two ligands are oriented such that the two methylene groups of the cyclooctatriene ligand are adjacent to the alkene function of the cyclooctadienyl ligand.

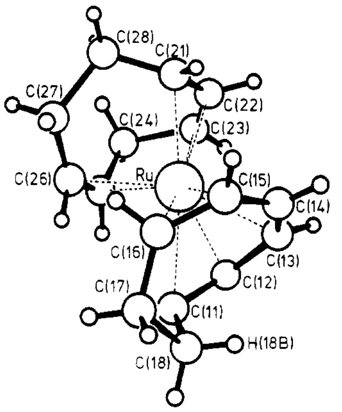

**Figure 3.** A perspective view of the cation of 2 showing the atom numbering scheme.

As the cyclooctadienyl ligand is coordinated to Ru by two separate functions, the ligand, of necessity, "wraps around" the metal atom, and thus the alkene function is endo (with respect to Ru) to the plane of the allyl function. To accommodate this somewhat strained conformation, the $sp^3$ carbon atoms adjacent to the allyl function [C(24) and C(28)] are not coplanar with that function but lie 0.32 (2) and 0.69 (2) Å respectively exo to this plane. The allyl function is not symmetrically bound to ruthenium: the Ru–C(23) distance is ca. 0.25 (4) Å longer than those to C(21) and C(22). This may be due partly to the conformation adopted by the ligand and partly to give sufficient clearance to the noncoordinated methylene group C(24), the single methylene connecting the allyl and alkene functions. A similar asymmetry in the coordination of the allyl function was found in the structure of $[Ru(1–3:5,6-\eta-C_8H_{11})(\eta^6-C_6H_5BPh_3)]$[17] but not in the structure of $[Ru(1–3:5,6-\eta-C_8H_{11})(\eta^6-C_6H_5BF_3)]$ where the allyl function appears to be symmetrically coordinated.[17]

Steric strain is also induced in accommodating the six $sp^2$ and two $sp^3$ carbon atoms of the cyclooctatriene ligand in a $C_8$ ring. Because of this, the six $sp^2$ carbon atoms of the triene system are not all coplanar. In particular, C(11) lies 0.45 (5) Å exo to the least-squares plane of the other five atoms [C(12)–C(16)] which are approximately coplanar with a largest deviation of 0.07 (5) Å from the least-squares plane. As expected, the two noncoordinated $sp^3$ carbon atoms lie exo to the plane of the triene system and, as mentioned above in the NMR section, one of the methylene hydrogen atoms, H(18B), is directed over the triene system and lies 1.86 (6) Å from the $C_6$ least-squares plane of this system. Thus, if this solid-state conformation of the ligand is retained at low temperature in solution, the observed high-field shift of this proton's resonance in the $^1$H NMR spectrum can be explained.

**$[Ru(1–5-\eta-C_8H_{11})(PMe_2Ph)_3]PF_6$.** The molecular structure of 4 (L = $PMe_2Ph$) (Figure 4) shows that the cyclooctadienyl ligand is 1–5-$\eta$-bonded to the $Ru(PMe_2Ph)_3^+$ moiety. The three phosphine ligands are mutually cis (P–Ru–P angles = 90.9 (1)–99.3 (1)°) and thus occupy one face of a distorted octahedral coordination

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[18] Seidman, K.; Maciel, G. E. *J. Am. Chem. Soc.* **1977**, *99*, 659.

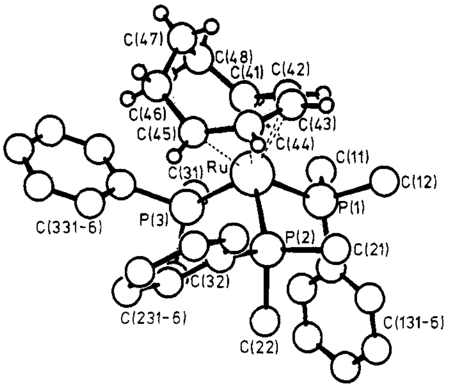

**Figure 4.** A perspective view of the cation of 4 (L = $PMe_2Ph$) showing the atom numbering scheme.

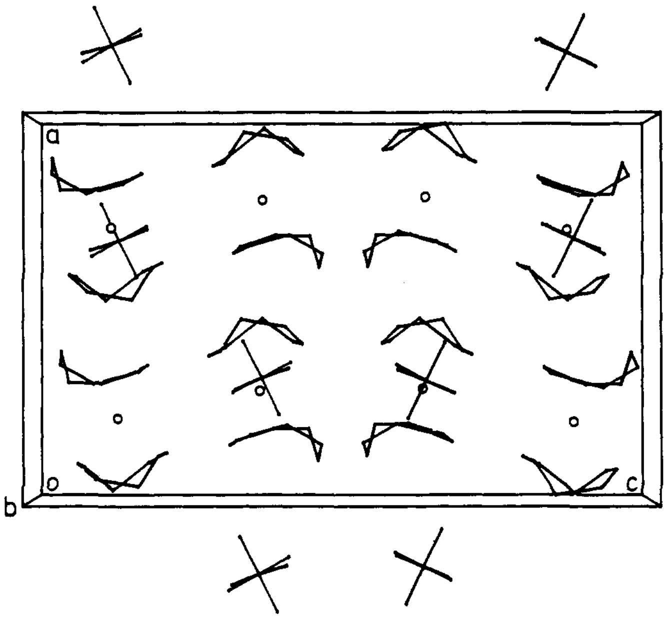

**Figure 5.** The unit cell contents for 2 viewed down the *b* axis.

geometry. The remaining three coordination positions are occupied by the 1–5-$\eta$-bonded carbon atoms of the cyclooctadienyl ligand. P(1) and P(2) are approximately trans to one or another of the outer carbon atoms of the $\eta^5$-bonded function with P(1)–Ru–C(45) = 168.5 (2)° and P(2)–Ru–C(41) = 170.7 (2)°, whereas P(3) is very approximately trans to the central C(43), but, with P(3)–Ru–C(43) = 151.9 (2)°, the deviation from linearity of P–Ru–C is much greater than for P(1) and P(2).

The five coordinated carbon atoms of the cyclooctadienyl ligand are approximately coplanar with a largest deviation of 0.04 (7) Å from the least-squares plane and the three noncoordinated carbon atoms are exo (with respect to Ru) to this plane (Figure 3). Of the five ruthenium–carbon bond distances those to C(42) and C(44) are the shortest with the distance to the central C(43) being ca. 0.04 (1) Å longer and those to the outer C(41) and C(45) being the longest by ca. 0.10 (1) Å. A similar trend in M–C distances was observed for the $\eta^5$-bicyclo[5.1.0]octadienyl ligand in [Ru($\eta^5$-$C_8H_9$)$L_3$]$PF_6$ (L = $PMe_2Ph$[10] and P-$(OMe)_2Ph$[13]) and the $\eta^5$-cyclooctatrienyl ligand in [Ru(1–5-$\eta$-$C_8H_9$)(1,3,5-$C_6H_3Me_3$)]$PF_6$.[19] In contrast, for the $\eta^5$-cyclooctadienyl ligand in [Zr($\eta^5$-$C_8H_{11}$){1,2-$C_2H_4$-$(PMe_2)_2$}$_2$H] all the M–C distances are approximately equal.[5] In our preliminary communication[11] structural

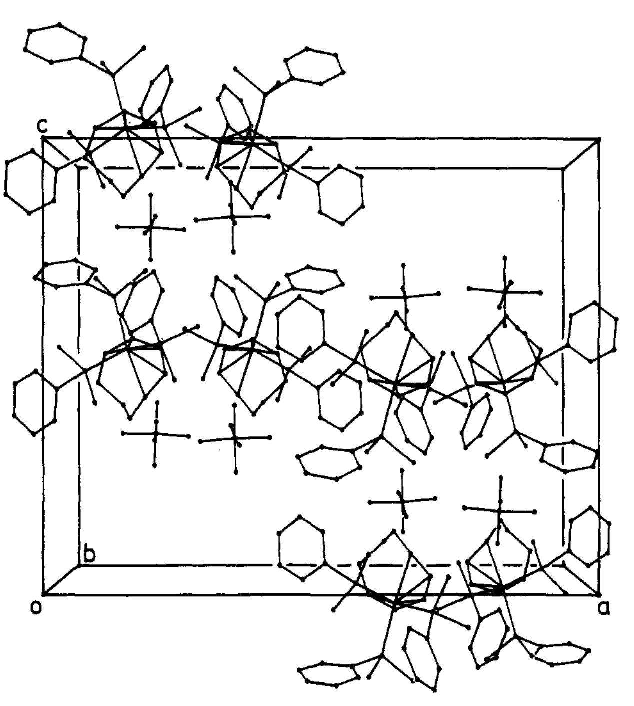

**Figure 6.** The unit cell contents for 4 (L = $PMe_2Ph$) viewed down the *b* axis.

comparisons were also made with a complex described by Blackborow et al.[20] as [Cr(1–5-$\eta$-$C_8H_{11}$)H$(PF_3)_3$]. On closer examination, however, we find the NMR data better explained by an $\eta^4$-structure with an additional agostic C–H···Cr interaction. The published structural parameters, particularly the ring C–C–C angles, also suggest only four unsaturated carbon atoms. The fifth "coordinated" carbon atom, C(3), is significantly further from the chromium atom than the other four, and it is a hydrogen atom bonded to this carbon that we suggest is involved in coordination.

## Discussion

**Formation of [Ru(1–3:5,6-$\eta$-$C_8H_{11}$)($\eta^6$-cyclooctatriene)]$PF_6$.** The reaction of 1 with excess cyclooctatetraene is a convenient route to 2. The reaction requires transfer of two hydrogen atoms to a cyclooctatetraene molecule that ultimately coordinates as the $\eta^6$-cyclooctatriene ligand. The transferred hydrogen atoms come, most likely, from the hydride ligand and a $C_3$ hydrogen atom of the cod ligand. Although an intramolecular mechanism for the hydrogen transfer was not proved, the role of solvent participation could be excluded from the observation that deuterium incorporation in 2 was not found when the reaction was carried out in deuteriated acetone. The formation of 2 may be compared to the reaction of [$ReH_5(PPh_3)_2$] with cyclooctatetraene which initially produces[21] the cyclooctatriene complex [$ReH_3$-($\eta^4$-$C_8H_{10}$)$(PPh_3)_2$]. A plausible reaction pathway is outlined in Scheme II.

The reaction pathway illustrated requires the formation of a Ru(IV) intermediate. Few Ru(IV) derivatives in general, and no bis(allyl) complexes derived from cyclic $C_8$ rings in particular, have been reported. Recently, however, the Ru(IV) compound [Ru($\eta^5$-$C_5H_5$)(1–3:5–7-$\eta$-$C_8H_{10}$)]$PF_6$, closely related to one of the proposed inter-

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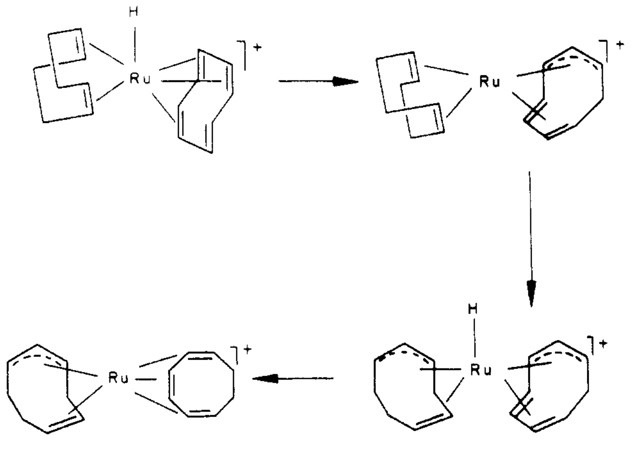
(19) Bennett, M. A.; Matheson, T. W.; Robertson, G. B.; Smith, A. K.; Tucker, P. A. *Inorg. Chem.* **1981**, *20*, 2353.

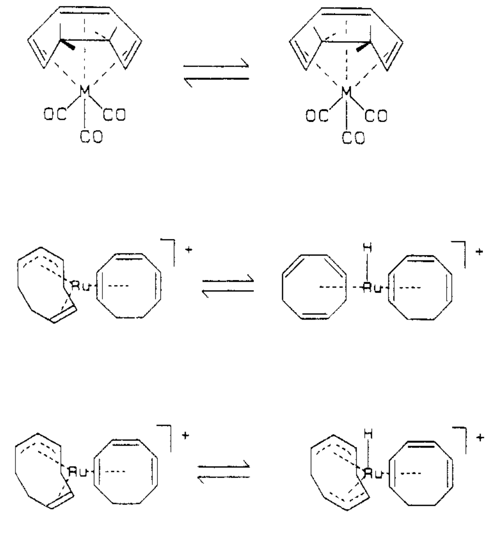
(20) Blackborow, J. R.; Eady, C. R.; Grevels, F.-W.; Koerner von Gustorf, E. A.; Scrivanti, A.; Wolfbeis, O. S. *J. Chem. Soc. Dalton Trans.* **1981**, 661.

(21) Trimarchi, M. C. L.; Green, M. A.; Huffman, J. C.; Caulton, K. G. *Organometallics* **1985**, *4*, 514.

**Scheme II. Mechanism for the Formation of $[\mathrm{Ru}(1\text{-}3{:}5,6\text{-}\eta\text{-}C_8H_{11})(\eta^6\text{-}1,3,5\text{-cyclooctatriene})]^+$ from $[\mathrm{RuH(cod)}(NH_2NMe_2)_3]^+$ and $C_8H_8$**



**Scheme III. Possible Fluxional Processes of 2**



mediates, has been synthesized[22] in this laboratory, as a relatively stable and well-characterized material. This compound is slowly converted to the Ru(II) species $[\mathrm{Ru}(\eta^5\text{-}C_5H_5)(\eta^6\text{-}1,3,5\text{-}C_8H_{10})]PF_6$ over a period of days.

The NMR studies of 2 show that the compound is fluxional, and although line broadening prevents complete assignment of the $^1$H NMR signals at high temperatures, both species contain the 1–3:5,6-$\eta$-cyclooctadienyl ligand. Although a conformational twist of the cyclooctatriene ligand most readily explains the variable-temperature spectra (see earlier), the fluxional process could involve rotation of the cyclooctatriene ligand as proposed earlier[23] to explain the fluxional properties of complexes of this ligand. Although either of the two above mechanisms seems intuitively the most likely, alternative processes involving reversible hydrogen transfer from the 1–3:5,6-$\eta$-cyclooctadienyl group cannot be ruled out (Scheme III). Complex 2 is related to the neutral complexes $[\mathrm{Ru}(1\text{-}3{:}5,6\text{-}\eta\text{-}C_8H_{11})_2]$[4] (I), $[\mathrm{Ru(cod)}(\eta^6\text{-cyclooctatriene})]$[3] (II), and $[\mathrm{Ru}(1\text{-}5\text{-}\eta\text{-}C_8H_{11})_2]$[4] (III) via hydride abstraction. These neutral $\mathrm{RuC_{16}H_{22}}$ isomers are interconvertible, via proposed hydride intermediates, in the sequence I → II → III. In contrast, no evidence for the formation of isomers of 2 containing the 1–5-$\eta$-$C_8H_{11}$ ligand was obtained, and this is the main objection to proposing a hydrogen-transfer process to explain the fluxional behavior of 2.

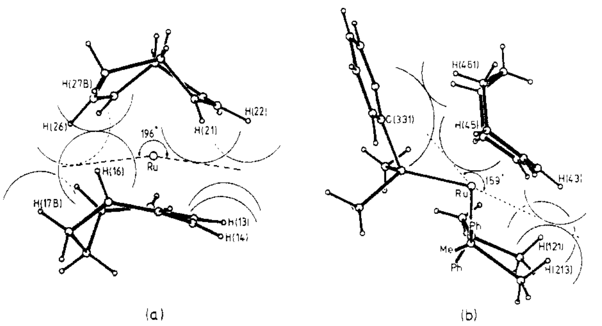


**Figure 7.** Views of the cations of (a) 2 and (b) 4 showing the estimated cone angles for the two forms of the cyclooctadienyl ligand. The arcs represent the van der Waals radii for selected atoms.

**Reactions of 2.** Displacement of the cyclooctatriene ligand in 2 by donor ligands gives complexes 3 and 4 which respectively contain the 1–3:5,6-$\eta$- and 1–5-$\eta$-$C_8H_{11}$ ligands. Complexes 3 may be compared with the much studied cation $[\mathrm{Ru}(1\text{-}3{:}5,6\text{-}\eta\text{-}C_8H_{11})(CO)_3]^+$ which is accessible via hydride abstraction from zerovalent $[\mathrm{Ru(cod)(CO)_3}]$ by $[\mathrm{Ph_3C}]^+$[14] or by replacement of the triene ligand in 2 with carbon monoxide.

The substitution reaction of 2 with phosphorus donor ligands is accompanied by isomerization of the cyclooctadienyl ligand from the 1–3:5,6-$\eta$- to the 1–5-$\eta$-form. That the driving force for this ligand isomerization arises from steric effects can be seen by comparison of the different volumes of space which the two forms of the cyclooctadienyl ligand occupy (Figure 7). The 1–3:5,6-$\eta$-cyclooctadienyl ligand in 2, of necessity, "wraps around" the Ru atom, thus occupying a considerably greater portion of the coordination sphere of the metal than a 1–5-$\eta$-cyclooctadienyl ligand. The volume of space required for coordination of the three phosphorus donor ligands would lead to excessive steric repulsions with the 1–3:5,6-$\eta$-$C_8H_{11}$ ligand, and hence the alternative conformation is adopted. These considerations add further doubt that substitution of the $\eta^6$-ligand of 2 by $\mathrm{P(OMe)_3}$ would lead to $[\mathrm{Ru}(1\text{-}3{:}5,6\text{-}\eta\text{-}C_8H_{11})\{P(OMe)_3\}_3]PF_6$ as reported[14] earlier.

While it is apparent in this particular case that steric effects dominate, in other systems the reason for the preference of one form over another is not always clear. For example, from the results reported here and the formation of $[\mathrm{Ru}(1\text{-}3{:}5,6\text{-}\eta\text{-}C_8H_{11})(\eta^6\text{-}C_6H_5BX_3)]$ (X = Ph or F),[16] it is tempting to infer that good $\pi$-acceptors such as CO, CNR, and arenes prefer the unsymmetric coordination mode. Yet the reaction of $[\mathrm{Ru(H_2O)_6}]^{2+}$ with 1,3-cyclooctadiene and arenes[24] and protonation of $[\mathrm{Ru(cod)}(\eta^6\text{-cot})]$ in the presence of arenes[16] yield $[\mathrm{Ru}(1\text{-}5\text{-}\eta\text{-}C_8H_{11})(\mathrm{arene})]^+$, whereas reaction of $[\mathrm{Ru(cod)(C_6H_6)}]$ with $[\mathrm{Ph_3C}]^+$ yields[14] $[\mathrm{Ru}(1\text{-}3{:}5,6\text{-}\eta\text{-}C_8H_{11})(C_6H_6)]^+$. From these results and the conversion[4] of $[\mathrm{Ru}(1\text{-}3{:}5,6\text{-}\eta\text{-}C_8H_{11})_2]$ into $[\mathrm{Ru}(1\text{-}5\text{-}\eta\text{-}C_8H_{11})_2]$ mentioned earlier, we conclude that the 1–3:5,6-$\eta$-$C_8H_{11}$ ligand is accessible through specific preparative routes (e.g. stereospecific hydrogen transfer from a coordinated cycloocta-1,5-diene) only if the remaining ligands are sterically compact.

## Conclusions

We have demonstrated that hydrogen-transfer processes can occur in cationic complexes of ruthenium(II), thus

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[22] Albers, M. O.; Liles, D. C.; Robinson, D. J.; Singleton, E. *J. Chem. Soc., Chem. Commun.* **1986**, 1102.

[23] Deganello, G. *Transition Metal Complexes of Cyclic Polyolefins*; Academic: New York, 1979; p 390.

[24] Stebler-Röthlisberger, M.; Salzer, A.; Bürgi, H. B.; Lüdi, A. *Organometallics* **1986**, *5*, 298.

**Table V. Fractional Coordinates (×10$^4$) and Isotropic Temperature Factors (Å$^2$ × 10$^3$) for 2**

| | $x/a$ | $y/b$ | $z/c$ | $U$ |
|---|---|---|---|---|
| Ru | 2103 (1) | 2468 (3) | 1316 (1) | 61 (1)[a] |
| C(11) | 3077 (18) | 3350 (19) | 533 (10) | 91 (8) |
| C(12) | 3042 (23) | 3966 (22) | 1088 (12) | 79 (8) |
| C(13) | 3346 (18) | 2477 (21) | 1668 (11) | 75 (8) |
| C(14) | 3510 (12) | 2143 (16) | 1792 (7) | 55 (6) |
| C(15) | 3271 (14) | 1116 (17) | 1480 (9) | 48 (5) |
| C(16) | 3018 (28) | 977 (23) | 880 (12) | 104 (11) |
| C(17) | 3526 (24) | 1266 (21) | 330 (11) | 138 (12) |
| C(18) | 3885 (13) | 2688 (26) | 396 (7) | 87 (7) |
| C(21) | 1086 (19) | 1649 (20) | 1962 (10) | 63 (7) |
| C(22) | 1201 (13) | 2717 (25) | 2122 (8) | 83 (7) |
| C(23) | 961 (26) | 3794 (26) | 1846 (13) | 114 (11) |
| C(24) | 218 (17) | 3814 (22) | 1258 (12) | 93 (8) |
| C(25) | 816 (21) | 3274 (24) | 780 (12) | 74 (8) |
| C(26) | 893 (17) | 2111 (22) | 651 (10) | 78 (9) |
| C(27) | 482 (25) | 1129 (26) | 899 (13) | 134 (12) |
| C(28) | 254 (16) | 1136 (20) | 1624 (9) | 71 (6) |
| P | 6831 (4) | 2427 (13) | 1327 (3) | 73 (5)[a] |
| F(1) | 7239 (22) | 1473 (13) | 1756 (9) | 87 (13)[a] |
| F(2) | 7026 (32) | 3368 (14) | 1805 (10) | 140 (19)[a] |
| F(3) | 6568 (32) | 3408 (21) | 888 (11) | 120 (22)[a] |
| F(4) | 6428 (29) | 1491 (23) | 849 (11) | 134 (20)[a] |
| F(5) | 7812 (10) | 2192 (18) | 1041 (7) | 125 (13)[a] |
| F(6) | 5827 (10) | 2711 (39) | 1620 (7) | 161 (19)[a] |

[a] Equivalent isotropic temperature factor, defined as the geometric mean of the diagonal elements of the diagonalized matrix of U(*ij*).

extending the scope of this reaction beyond the neutral complexes studied earlier.[1-4] The cation 2 is a fluxional species that can only be unequivocally characterized by high-field NMR (500 MHz for $^1$H) at low temperature. High-field NMR studies have also clearly differentiated between 1-5-$\eta$-cyclooctadienyl and 1-3:5,6-$\eta$-cyclooctadienyl groups and indicate that the technique could well solve the problems of assignments of protonated cyclooctatetraene complexes. For example, Bennett et al.[19] have reviewed the six different forms of the $C_8H_9$ moiety that have been proposed for protonated cyclooctatetraene complexes and comment that "this bewildering array of results have been based solely on necessarily complex NMR spectra". Further, these authors find little resemblance between spectra reported for various complexes containing 1-3:6,7-$\eta$-$C_8H_9$. Our findings with the $C_8H_{11}$ moiety are more encouraging for the use of NMR, albeit at very high field, for structure determination of such compounds. Although the more frequent occurrence of exchange-broadening spectra could be a problem, it seems reasonable to expect that in many cases the mere inspection of the multiplets will be sufficient. The preference for one isomer over the other can be ascribed to both steric and electronic factors, although the larger proportion of the coordination sphere required by the 1-3:5,6-$\eta$-$C_8H_{11}$ ligand suggests that, in the presence of ligands with bulky groups *close to* the coordination sphere, the 1-5-$\eta$-isomer will be preferred. The mechanistic course of the reactions is complex; thus the reactions are not general.

**Table VI. Bond Length (Å) and Angles (deg) for 2**

| | | | |
|---|---|---|---|
| Bond Lengths | | | |
| Ru–C(11) | 2.41 (2) | Ru–C(12) | 2.17 (3) |
| Ru–C(13) | 2.18 (2) | Ru–C(14) | 2.22 (2) |
| Ru–C(15) | 2.23 (2) | Ru–C(16) | 2.30 (3) |
| Ru–C(21) | 2.21 (2) | Ru–C(22) | 2.20 (2) |
| Ru–C(23) | 2.46 (3) | Ru–C(25) | 2.31 (3) |
| Ru–C(26) | 2.26 (2) | C(11)–C(12) | 1.42 (3) |
| C(11)–C(18) | 1.36 (3) | C(12)–C(13) | 1.47 (3) |
| C(13)–C(14) | 1.54 (3) | C(14)–C(15) | 1.39 (3) |
| C(15)–C(16) | 1.40 (3) | C(16)–C(17) | 1.45 (3) |
| C(17)–C(18) | 1.67 (4) | C(21)–C(22) | 1.26 (3) |
| C(21)–C(28) | 1.48 (3) | C(22)–C(23) | 1.40 (4) |
| C(23)–C(24) | 1.66 (4) | C(24)–C(25) | 1.48 (3) |
| C(25)–C(26) | 1.34 (3) | C(26)–C(27) | 1.35 (4) |
| C(27)–C(28) | 1.66 (3) | P–F(1) | 1.54 (2) |
| P–F(2) | 1.53 (2) | P–F(3) | 1.52 (2) |
| P–F(4) | 1.60 (2) | P–F(5) | 1.506 (13) |
| P–F(6) | 1.55 (2) | | |
| Bond Angles | | | |
| C(11)–Ru–C(12) | 35.7 (8) | C(11)–Ru–C(13) | 67.9 (8) |
| C(12)–Ru–C(13) | 39.5 (8) | C(11)–Ru–C(14) | 86.7 (7) |
| C(12)–Ru–C(14) | 74.5 (9) | C(13)–Ru–C(14) | 40.8 (8) |
| C(11)–Ru–C(15) | 90.4 (7) | C(12)–Ru–C(15) | 98.4 (9) |
| C(13)–Ru–C(15) | 74.9 (8) | C(14)–Ru–C(15) | 36.3 (7) |
| C(11)–Ru–C(16) | 72.1 (9) | C(12)–Ru–C(16) | 98.3 (7) |
| C(13)–Ru–C(16) | 96.3 (11) | C(14)–Ru–C(16) | 67.6 (9) |
| C(15)–Ru–C(16) | 35.8 (8) | C(11)–Ru–C(21) | 173.9 (8) |
| C(12)–Ru–C(21) | 147.9 (9) | C(13)–Ru–C(21) | 117.8 (9) |
| C(14)–Ru–C(21) | 99.1 (8) | C(15)–Ru–C(21) | 93.2 (8) |
| Cn16)–Ru–C(21) | 108.4 (9) | C(11)–Ru–C(22) | 148.4 (9) |
| C(12)–Ru–C(22) | 115.0 (10) | C(13)–Ru–C(22) | 94.0 (8) |
| C(14)–Ru–C(22) | 96.2 (7) | C(15)–Ru–C(22) | 110.4 (8) |
| C(16)–Ru–C(22) | 137.9 (10) | C(21)–Ru–C(22) | 33.3 (9) |
| C(11)–Ru–C(23) | 116.8 (8) | C(12)–Ru–C(23) | 91.0 (10) |
| C(13)–Ru–C(23) | 90.1 (10) | C(14)–Ru–C(23) | 114.3 (9) |
| C(15)–Ru–C(23) | 141.6 (9) | C(16)–Ru–C(23) | 170.6 (11) |
| C(21)–Ru–C(23) | 62.5 (7) | C(22)–Ru–C(23) | 34.3 (9) |
| C(11)–Ru–C(25) | 83.0 (9) | C(12)–Ru–C(25) | 91.3 (11) |
| C(13)–Ru–C(25) | 125.0 (9) | C(14)–Ru–C(25) | 165.5 (8) |
| C(15)–Ru–C(25) | 153.4 (9) | C(16)–Ru–C(25) | 118.3 (10) |
| C(21)–Ru–C(25) | 91.6 (10) | C(22)–Ru–C(25) | 87.4 (8) |
| C(23)–Ru–C(25) | 62.3 (10) | C(11)–Ru–C(26) | 89.7 (8) |
| C(12)–Ru–C(26) | 114.3 (10) | C(13)–Ru–C(26) | 153.7 (8) |
| C(14)–Ru–C(26) | 156.4 (8) | C(14)–Ru–C(26) | 120.6 (9) |
| C(16)–Ru–C(26) | 89.2 (10) | C(21)–Ru–C(26) | 84.3 (8) |
| C(22)–Ru–C(26) | 99.0 (8) | C(23)–Ru–C(26) | 88.0 (10) |
| C(25)–Ru–C(26) | 34.1 (7) | Ru–C(11)–C(12) | 62.9 (13) |
| Ru–C(11)–C(18) | 113 (2) | C(12)–C(11)–C(18) | 119 (2) |
| Ru–C(12)–C(11) | 81.4 (14) | Ru–C(12)–C(13) | 70.7 (14) |
| C(11)–C(12)–C(13) | 126 (2) | Ru–C(13)–C(12) | 70 (2) |
| Ru–C(13)–C(14) | 71.0 (13) | C(12)–C(13)–C(14) | 124 (2) |
| Ru–C(14)–C(13) | 68.2 (13) | Ru–C(14)–C(15) | 72.0 (10) |
| C(13)–C(14)–C(15) | 133 (2) | Ru–C(15)–C(14) | 71.7 (10) |
| Ru–C(15)–C(16) | 75 (2) | C(14)–C(15)–C(16) | 130 (2) |
| Ru–C(16)–C(15) | 69.2 (13) | Ru–C(16)–C(17) | 117 (2) |
| C(15)–C(16)–C(17) | 133 (3) | C(16)–C(17)–C(18) | 106 (2) |
| C(11)–C(18)–C(17) | 108 (2) | Ru–C(21)–C(22) | 73 (2) |
| Ru–C(21)–C(28) | 108 (22) | C(22)–C(21)–C(28) | 128 (3) |
| Ru–C(22)–C(21) | 74 (2) | Ru–C(22)–C(23) | 82.9 (14) |
| C(21)–C(22)–C(23) | 132 (2) | Ru–C(23)–C(22) | 62.8 (13) |
| Ru–C(26)–C(24) | 91 (2) | C(22)–C(23)–C(24) | 120 (2) |
| C(23)–C(24)–C(25) | 104 (2) | Ru–C(25)–C(24) | 102 (2) |
| Ru–C(25)–C(26) | 71 (2) | C(24)–C(25)–C(26) | 127 (3) |
| Ru–C(26)–C(25) | 75 (2) | Ru–C(26)–C(27) | 100 (2) |
| C(25)–C(26)–C(27) | 132 (3) | C(26)–C(27)–C(28) | 119 (2) |
| C(21)–C(28)–C(27) | 111 (2) | F(1)–F–F(2) | 88.8 (7) |
| F(1)–P–F(3) | 173 (2) | F(2)–P–F(3) | 90 (2) |
| F(1)–P–F(4) | 95 (2) | F(2)–P–F(4) | 170 (2) |
| F(3)–P–F(4) | 87.8 (7) | F(1)–P–F(5) | 79.9 (14) |
| F(2)–P–F(5) | 105 (2) | F(3)–P–F(5) | 94 (2) |
| F(4)–P–F(5) | 85 (2) | F(1)–P–F(6) | 101 (2) |
| F(2)–P–F(6) | 73 (2) | F(32)–P–F(6) | 85 (2) |
| F(4)–P–F(6) | 97 (2) | F(5)–P–F(6) | 178 (2) |

## Experimental Section

**General Data.** Solvents were dried and distilled under nitrogen before use. Reactions and recrystallizations were performed under nitrogen, and filtrations of the crude products were carried out in air. Melting points were determined on a Kofler hot-stage apparatus and are corrected. Variable-temperature $^1$H and $^{13}$C spectra were recorded on Bruker WM 500 and AM 300 spectrometers using standard pulse methods. Temperatures quoted were read from the copper–constantin thermocouple. Calculations of the 500-MHz $^1$H spectrum of Figure 2 were performed with the program PANIC provided with the Aspect 2000 computer. Two separately calculated eight-spin systems were considered, and the resulting spectra were co-added to give the calculated spectrum of Figure 2. Elemental analyses were carried out at NCRL, CSIR, Pretoria. The complexes [RuH(cod)($NH_2NMe_2$)$_3$]Y (Y = $PF_6$ or

**Table VII. Fractional Coordinates (×10$^4$; ×10$^5$ for Ru and P; ×10$^3$ for H) and Equivalent Isotropic Temperature Factors (Å$^2$ × 10$^3$; ×10$^4$ for Ru) for 4 (L = PMe$_2$Ph)$^a$**

| | *x*/*a* | *y*/*b* | *z*/*c* | *U*(eq) | | *x*/*a* | *y*/*b* | *z*/*c* | *U*(eq) |
|---|---|---|---|---|---|---|---|---|---|
| Ru | 13717 (2) | 26979 (3) | 53982 (3) | 258 (3) | H(111) | 249 (3) | 147 (5) | 454 (4) | 67 (9)$^b$ |
| P(1) | 20423 (8) | 15221 (13) | 55109 (11) | 37 (1) | H(112) | 358 (3) | 72 (5) | 475 (4) | 67 (9)$^b$ |
| C(11) | 2317 (4) | 1049 (7) | 4698 (6) | 57 (6) | H(113) | 206 (3) | 66 (5) | 442 (4) | 67 (9)$^b$ |
| C(12) | 2711 (4) | 1898 (7) | 5896 (6) | 56 (6) | H(121) | 290 (3) | 243 (5) | 567 (4) | 67 (9)$^b$ |
| C(131) | 1906 (3) | 496 (5) | 6009 (4) | 38 (5) | H(122) | 290 (3) | 142 (5) | 591 (4) | 67 (9)$^b$ |
| C(132) | 1570 (4) | −172 (6) | 5728 (5) | 49 (5) | H(123) | 270 (3) | 212 (5) | 635 (4) | 67 (9)$^b$ |
| C(133) | 1455 (4) | −936 (6) | 6102 (7) | 62 (7) | H(132) | 147 (4) | −14 (6) | 532 (4) | 67 (9)$^b$ |
| C(134) | 1687 (11) | −1043 (11) | 6765 (13) | 74 (11) | H(133) | 117 (3) | −133 (5) | 580 (4) | 67 (9)$^b$ |
| C(135) | 2007 (5) | −402 (8) | 7056 (6) | 69 (8) | H(134) | 170 (7) | −127 (9) | 679 (9) | 67 (9)$^b$ |
| C(136) | 2124 (4) | 367 (6) | 6671 (5) | 52 (6) | H(135) | 211 (3) | −60 (5) | 753 (4) | 67 (9)$^b$ |
| P(2) | 11189 (7) | 25578 (12) | 65873 (9) | 30 (1) | H(136) | 240 (3) | 69 (5) | 684 (4) | 67 (9)$^b$ |
| C(21) | 1709 (4) | 2794 (6) | 7180 (4) | 45 (5) | H(221) | 198 (2) | 226 (4) | 724 (3) | 39 (6)$^b$ |
| C(22) | 855 (6) | 1484 (6) | 6967 (7) | 41 (6) | H(212) | 159 (3) | 297 (4) | 762 (3) | 39 (6)$^b$ |
| C(231) | 569 (3) | 3324 (5) | 6902 (3) | 32 (4) | H(213) | 187 (3) | 339 (4) | 707 (3) | 39 (6)$^b$ |
| C(232) | 5 (3) | 3114 (5) | 6807 (4) | 37 (4) | H(221) | 57 (3) | 112 (4) | 674 (3) | 39 (6)$^b$ |
| C(233) | −430 (4) | 3665 (6) | 7032 (4) | 47 (5) | H(222) | 83 (3) | 155 (4) | 749 (3) | 39 (6)$^b$ |
| C(234) | −283 (5) | 4450 (6) | 7366 (5) | 50 (6) | H(223) | 92 (5) | 176 (6) | 695 (6) | 39 (6)$^b$ |
| C(235) | 271 (4) | 4676 (6) | 7477 (4) | 47 (5) | H(232) | −10 (3) | 262 (4) | 661 (3) | 39 (6)$^b$ |
| C(236) | 696 (4) | 4122 (5) | 7239 (4) | 43 (5) | H(233) | −93 (3) | 348 (4) | 689 (3) | 39 (6)$^b$ |
| P(3) | 6414 (8) | 18513 (12) | 48935 (10) | 32 (1) | H(234) | −54 (3) | 480 (4) | 753 (4) | 39 (6)$^b$ |
| C(31) | 216 (3) | 1061 (5) | 5413 (5) | 42 (5) | H(235) | 35 (3) | 522 (4) | 770 (3) | 39 (6)$^b$ |
| C(32) | 860 (4) | 1092 (6) | 4193 (4) | 43 (5) | H(236) | 102 (3) | 426 (4) | 737 (4) | 39 (6)$^b$ |
| C(331) | 67 (3) | 2462 (4) | 4472 (3) | 27 (4) | H(311) | −11 (3) | 76 (4) | 509 (3) | 52 (7)$^b$ |
| C(332) | 18 (3) | 2541 (5) | 3757 (4) | 37 (4) | H(312) | −4 (3) | 138 (4) | 571 (3) | 52 (7)$^b$ |
| C(333) | −409 (3) | 3027 (5) | 3448 (4) | 45 (5) | H(313) | 46 (3) | 61 (4) | 561 (3) | 52 (7)$^b$ |
| C(334) | −812 (4) | 3424 (6) | 3856 (5) | 50 (6) | H(321) | 109 (3) | 58 (4) | 432 (3) | 52 (7)$^b$ |
| C(335) | −787 (3) | 3351 (5) | 4590 (5) | 47 (5) | H(322) | 56 (3) | 97 (4) | 388 (4) | 52 (7)$^b$ |
| C(336) | −355 (3) | 2873 (5) | 4879 (4) | 40 (4) | H(323) | 113 (3) | 151 (4) | 391 (3) | 52 (7)$^b$ |
| C(41) | 1682 (3) | 3049 (5) | 4299 (4) | 39 (4) | H(332) | 26 (3) | 221 (4) | 347 (3) | 52 (7)$^b$ |
| C(42) | 2062 (3) | 3337 (5) | 4822 (4) | 38 (5) | H(333) | −44 (3) | 305 (4) | 291 (3) | 52 (7)$^b$ |
| C(43) | 1951 (3) | 3874 (5) | 5413 (5) | 37 (5) | H(334) | −105 (3) | 375 (5) | 372 (4) | 52 (7)$^b$ |
| C(44) | 1406 (4) | 4125 (5) | 5650 (4) | 35 (4) | H(335) | −103 (3) | 361 (5) | 488 (4) | 52 (7)$^b$ |
| C(45) | 880 (3) | 4017 (5) | 5295 (4) | 36 (4) | H(336) | −34 (3) | 277 (4) | 544 (3) | 52 (7)$^b$ |
| C(46) | 721 (3) | 4451 (5) | 4624 (5) | 41 (5) | H(41) | 189 (2) | 249 (4) | 400 (3) | 41 (6)$^b$ |
| C(47) | 1197 (4) | 4568 (6) | 4091 (4) | 48 (6) | H(42) | 245 (3) | 308 (4) | 485 (3) | 41 (6)$^b$ |
| C(48) | 1368 (4) | 3675 (6) | 3810 (4) | 42 (5) | H(43) | 224 (3) | 398 (4) | 575 (3) | 41 (6)$^b$ |
| P(4) | 33601 (11) | 35772 (18) | 33470 (14) | 59 (2) | H(44) | 137 (3) | 428 (4) | 612 (3) | 41 (6)$^b$ |
| F(11) | 4030 (4) | 3446 (7) | 3357 (5) | 110 (3)$^b$ | H(45) | 58 (3) | 404 (4) | 557 (3) | 41 (6)$^b$ |
| F(12) | 2699 (4) | 3675 (8) | 3266 (5) | 110 (3)$^b$ | H(461) | 42 (3) | 418 (4) | 441 (3) | 41 (6)$^b$ |
| F(13) | 3304 (5) | 2619 (9) | 3663 (7) | 154 (5)$^b$ | H(462) | 57 (3) | 499 (4) | 472 (3) | 41 (6)$^b$ |
| F(14) | 3428 (5) | 4567 (8) | 3145 (7) | 142 (4)$^b$ | H(471) | 150 (3) | 483 (4) | 432 (3) | 41 (6)$^b$ |
| F(15) | 3389 (6) | 3280 (10) | 2576 (8) | 169 (5)$^b$ | H(472) | 109 (3) | 485 (4) | 374 (3) | 41 (6)$^b$ |
| F(16) | 3342 (5) | 3953 (8) | 4093 (6) | 143 (4)$^b$ | H(481) | 161 (3) | 383 (4) | 344 (3) | 41 (6)$^b$ |
| F(21) | 3380 (6) | 4228 (11) | 2646 (9) | 78 (5)$^b$ | H(482) | 104 (3) | 336 (4) | 361 (3) | 41 (6)$^b$ |
| F(22) | 3322 (9) | 3001 (16) | 4060 (12) | 118 (7)$^b$ | | | | | |
| F(23) | 3593 (9) | 2796 (14) | 2861 (11) | 125 (7)$^b$ | | | | | |
| F(24) | 2928 (12) | 4232 (17) | 3760 (15) | 165 (9)$^b$ | | | | | |
| F(25) | 3950 (10) | 4027 (16) | 3656 (12) | 148 (9)$^b$ | | | | | |
| F(26) | 2816 (11) | 3056 (18) | 3056 (13) | 162 (10)$^b$ | | | | | |

[a] *U*(eq) is defined as the geometric mean of the diagonal elements of the diagonalized matrix of U(*ij*). The site occupation factors for F(11)–F(16) and F(21)–F(26) are 0.67 (2) and 0.33 (2) respectively. [b] Isotropic temperature factor.

BPh$_4$) and [RuH(cod)L$_3$]PF$_6$ (L = PMe$_2$Ph or AsMePh$_2$) were prepared according to the literature methods.[9,12] The ligands were obtained commercially (Strem) and were not purified further, except that cyclooctatetraene was distilled prior to use.

**Preparation of the Ruthenium Complexes. [Ru(1-3:5,6-η-C$_8$H$_{11}$)(η$^6$-1,3,5-cyclooctatriene)]PF$_6$.** Cyclooctatetraene (0.5 mL, excess) was added to a methanol solution (10 mL) of [RuH(cod)(NH$_2$NMe$_2$)$_3$]PF$_6$ (1 g, 1.9 mmol) and the solution refluxed for 30 min. The yellow solid that separated from solution was filtered off and washed with diethyl ether; yield 0.3–0.5 g (34–57%).

**[Ru(1-3:5,6-η-C$_8$H$_{11}$)(η$^6$-1,3,5-cyclooctatriene)]BPh$_4$.** Cyclooctatetraene (0.3 mL, excess) was added to a methanol solution (10 mL) of [RuH(cod)(NH$_2$NMe$_2$)$_3$]BPh$_4$ (1 g, 1.4 mmol) and the solution refluxed for 30 min. The yellow solid that separated from solution was filtered off and washed with diethyl ether; yield 0.54 g (61%).

[Ru(1-5-η-C$_8$H$_{11}$){P(OMe)$_3$}$_3$]PF$_6$, [Ru(1-5-η-C$_8$H$_{11}$)(PMe$_2$Ph)$_3$]PF$_6$, and [Ru(1-5-η-C$_8$H$_{11}$)(AsMePh$_2$)$_3$]PF$_6$ were obtained in good yield in the following three ways ([Ru(1-5-η-C$_8$H$_{11}$)(AsMe$_2$Ph)$_3$]PF$_6$ was obtained only by method III).

**Method I.** cod (excess) was added to a suspension of [RuH(cod)L$_3$]PF$_6$ (L = PMe$_2$Ph or AsMePh$_2$) in methanol (ca. 10 mL) and the mixture refluxed for 24 or 4 h, respectively. The solid that separated from solution was filtered off and washed with diethyl ether.

**Method II**: the same procedure as outlined in method I using dioxane as solvent. The reaction time is ca. 10 min.

**Method III.** Ligand [L = PMe$_2$Ph, AsMe$_2$Ph, AsMePh$_2$, and P(OMe)$_3$] (3 mmol) was added to a suspension of [Ru(1-3:5,6-η-C$_8$H$_{11}$)(η$^6$-1,3,5-cyclooctatriene)]PF$_6$ (0.5 g, 1.1 mmol) in methanol (ca. 10 mL) and the mixture refluxed for ca. 2 h. The solid that separated from solution was filtered off and washed with diethyl ether.

**[Ru(1-3:5,6-η-C$_8$H$_{11}$)(CN-*t*-Bu)$_3$]PF$_6$.** [Ru(1-3:5,6-η-C$_8$H$_{11}$)(η$^6$-1,3,5-cyclooctatriene)]PF$_6$ (0.5 g, 1.1 mmol) and *tert*-butyl isocyanide (0.4 mL) were stirred in acetone (10 mL) at room temperature for 18 h. The orange solution was taken to dryness. A cream solid was obtained on crystallizing the oil from acetone–ethanol; yield 0.2 g (30%).

**Table VIII. Bond Lengths (Å) and Selected Bond Angles (deg) for 4 (L = $PMe_2Ph$)**

Bond Lengths

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Ru–P(1) | 2.374 (2) | Ru–P(2) | 2.356 (2) | C(11)–H(111) | 0.81 (8) | C(11)–H(112) | 0.79 (8) |
| Ru–P(3) | 2.343 (2) | Ru–C(41) | 2.283 (8) | C(11)–H(113) | 1.00 (7) | C(12)–H(121) | 1.01 (7) |
| Ru–C(42) | 2.182 (8) | Ru–C(43) | 2.226 (7) | C(12)–H(122) | 0.84 (8) | C(12)–H(123) | 0.93 (8) |
| Ru–C(44) | 2.191 (7) | Ru–C(45) | 2.297 (7) | C(132)–H(132) | 0.81 (7) | C(133)–H(133) | 1.06 (7) |
| P(1)–C(11) | 1.823 (11) | P(1)–C(12) | 1.827 (10) | C(134)–H(134) | 0.35 (13) | C(135)–H(135) | 0.99 (8) |
| P(1)–C(131) | 1.834 (8) | C(131)–C(132) | 1.383 (12) | C(136)–H(136) | 0.88 (8) | C(21)–H(211) | 1.03 (6) |
| C(131)–C(136) | 1.377 (12) | C(132)–C(133) | 1.375 (14) | C(21)–H(212) | 0.93 (7) | C(21)–H(213) | 1.00 (6) |
| C(133)–C(134) | 1.39 (3) | C(134)–C(135) | 1.34 (3) | C(22)–H(221) | 0.97 (6) | C(22)–H(222) | 1.02 (7) |
| C(135)–C(136) | 1.39 (2) | P(2)–C(21) | 1.826 (9) | C(22)–H(223) | 0.44 (9) | C(232)–H(232) | 0.86 (6) |
| P(2)–C(22) | 1.868 (11) | P(2)–C(231) | 1.831 (7) | C(233)–H(233) | 1.25 (6) | C(234)–H(234) | 0.86 (7) |
| C(231)–C(232) | 1.379 (10) | C(231)–C(236) | 1.388 (11) | C(35)–H(235) | 0.95 (6) | C(236)–H(236) | 0.83 (6) |
| C(232)–C(233) | 1.382 (11) | C(233)–C(234) | 1.380 (12) | C(31)–H(311) | 1.08 (7) | C(31)–H(312) | 0.96 (7) |
| C(234)–C(235) | 1.37 (2) | C(235)–C(236) | 1.376 (13) | C(31)–H(313) | 0.96 (7) | C(32)–H(321) | 0.97 (7) |
| P(3)–C(31) | 1.840 (8) | P(3)–C(32) | 1.826 (9) | C(32)–H(322) | 0.94 (7) | C(32)–H(323) | 1.04 (7) |
| P(3)–C(331) | 1.821 (6) | C(331)–C(332) | 1.375 (10) | C(322)–H(332) | 0.93 (7) | C(333)–H(333) | 1.04 (7) |
| C(331)–C(336) | 1.402 (10) | C(332)–C(333) | 1.375 (11) | C(334)–H(334) | 0.79 (7) | C(335)–H(335) | 0.89 (7) . |
| C(333)–C(334) | 1.363 (12) | C(334)–C(335) | 1.406 (14) | C(336)–H(336) | 1.08 (7) | C(41)–H(41) | 1.12 (6) |
| C(335)–C(336) | 1.362 (11) | C(41)–C(42) | 1.407 (11) | C(42)–H(42) | 1.00 (6) | C(43)–H(43) | 0.96 (6) |
| C(41)–C(48) | 1.516 (11) | C(42)–C(43) | 1.408 (11) | C(44)–H(44) | 0.92 (6) | C(45)–H(45) | 0.88 (6) |
| C(43)–C(44) | 1.412 (11) | C(44)–C(45) | 1.422 (11) | C(46)–H(461) | 0.91 (6) | C(46)–H(462) | 0.91 (6) |
| C(45)–C(46) | 1.485 (11) | C(46)–C(47) | 1.524 (12) | C(47)–H(471) | 0.92 (6) | C(47)–H(472) | 0.84 (7) |
| C(47)–C(48) | 1.495 (12) | P(4)–F(11) | 1.589 (10) | C(48)–H(481) | 0.94 (6) | C(48)–H(482) | 0.99 (6) |
| P(4)–F(12) | 1.572 (10) | P(4)–F(13) | 1.562 (14) | | | | |
| P(4)–F(14) | 1.539 (12) | P(4)–F(15) | 1.54 (2) | | | | |
| P(4)–F(16) | 1.531 (12) | P(4)–F(21) | 1.66 (2) | | | | |
| P(4)–F(22) | 1.61 (2) | P(4)–F(23) | 1.59 (2) | | | | |
| P(4)–F(24) | 1.62 (3) | P(4)–F(25) | 1.65 (2) | | | | |
| P(4)–F(26) | 1.59 (3) | | | | | | |

Bond Angles

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| P(1)–Ru–P(2) | 90.9 (1) | P(1)–Ru–P(3) | 97.2 (1) | C(31)–P(3)–C(331) | 99.0 (3) | C(32)–P(3)–C(331) | 101.4 (4) |
| P(2)–Ru–P(3) | 99.3 (1) | P(1)–Ru–C(41) | 92.3 (2) | P(3)–C(331)–C(322) | 122.9 (5) | P(3)–C(331)–C(336) | 120.1 (5) |
| P(2)–Ru–C(41) | 170.2 (2) | P(3)–Ru–C(41) | 89.0 (2) | C(332)–C(311)–C(336) | 117.0 (6) | C(331)–C(332)–C(333) | 122.1 (7) |
| P1)–Ru–C(42) | 82.8 (2) | P(2)–Ru–C(42) | 135.4 (1) | C(332)–C(333)–C(334) | 11997 (8) | C(333)–C(334)–C(335) | 120.4 (8) |
| P(3)–Ru–C(42) | 125.2 (2) | C(41)–Ru–C(42) | 36.6 (3) | C(334)–C(335)–C(336) | 118.3 (8) | C(331)–C(336)–C(335) | 122.4 (7) |
| P(1)–Ru–C(43) | 100.2 (2) | P(2)–Ru–C(43) | 102.3 (2) | Ru–C(41)–C(42) | 67.8 (4) | Ru–C(41)–C(48) | 123.4 (5) |
| P(3)–Ru–C(43) | 151.9 (2) | C(41)–Ru–C(43) | 68.5 (3) | C(42)–C(41)–C(48) | 123.9 (7) | Ru–C(42)–C(41) | 75.6 (4) |
| C(42)–Ru–C(43) | 37.2 (3) | P(1)–Ru–C(44) | 132.7 (2) | Ru–C(42)–C(43) | 73.1 (4) | C(41)–C(42)–C(43) | 128.7 (7) |
| P(2)–Ru–C(44) | 83.4 (2) | P(3)–Ru–C(44) | 130.1 (2) | Ru–C(43)–C(42) | 69.7 (4) | Ru–C(43)–C(44) | 70.0 (4) |
| C(41)–Ru–C(44) | 88.0 (3) | C(42)–Ru–C(44) | 69.9 (3) | C(42)–C(43)–C(44) | 125.3 (7) | Ru–C(44)–C(43) | 72.7 (4) |
| C(43)–Ru–C(44) | 37.3 (3) | P(1)–Ru–C(45) | 168.5 (2) | Ru–C(44)–C(45) | 75.6 (4) | C(43)–C(44)–C(45) | 127.5 (7) |
| P(2)–Ru–C(45) | 91.8 (2) | P(3)–Ru–C(45) | 93.4 (2) | Ru–C(45)–C(44) | 67.5 (4) | Ru–C(45)–C(46) | 125.2 (5) |
| C(41)–Ru–C(45) | 83.4 (3) | C(42)–Ru–C(45) | 87.5 (3) | C(44)–C(45)–C(46) | 125.6 (7) | C(45)–C(46)–C(47) | 116.0 (7) |
| C(43)–Ru–C(45) | 68.3 (3) | C(44)–Ru–C(45) | 36.8 (3) | C(46)–C(47)–C(48) | 109.5 (7) | C(41)–C(48)–C(47) | 117.6 (7) |
| Ru–P(1)–C(11) | 116.5 (3) | Ru–P(1)–C(12) | 112.4 (3) | F(11)–P(4)–F(12) | 174.7 (6) | F(11)–P(4)–F(13) | 88.0 (6) |
| C(11)–P(1)–C(12) | 99.0 (5) | Ru–P(1)–C(131) | 123.4 (2) | F12)–P(4)–F(13) | 92.3 (6) | F(11)–P(4)–F(14) | 91.0 (6) |
| C(11)–P(1)–C(131) | 100.2 (4) | C(12)–P(1)–C(131) | 101.5 (4) | F(12)–P(4)–F(14) | 89.3 (6) | F(13)–P(4)–F(14) | 171.7 (7) |
| P(1)–C(131)–C(132) | 120.2 (6) | P(1)–C(131)–C(136) | 121.9 (6) | F(11)–P(4)–F(15) | 86.1 (6) | F(12)–P(4)–F(15) | 88.7 (6) |
| C(132)–C(131)–C(136) | 117.8 (8) | C(131)–C(132)–C(133) | 120.9 (9) | F(13)–P(4)–F(15) | 96.2 (8) | F(14)–P(4)–F(15) | 91.9 (7) |
| C(312)–C(133)–C(134) | 119.4 (11) | C(133)–C(134)–C(135) | 121 (2) | F(11)–P(4)–F(16) | 93.6 (6) | F(12)–P(4)–F(16) | 91.7 (6) |
| C(134)–C(135)–C(136) | 118.9 (14) | C(131)–C(136)–C(135) | 121.8 (9) | F(13)–P(4)–F(16) | 88.6 (7) | F(14)–P(4)–F(16) | 83.2 (7) |
| Ru–P(2)–C(21) | 112.8 (3) | Ru–P(2)–C(22) | 122.3 (4) | F(15)–P(4)–F(16) | 175.2 (7) | F(21)–P(4)–F(22) | 176.0 (10) |
| C(21)–P(2)–C(22) | 100.3 (5) | Ru–P(2)–C(231) | 116.0 (2) | F(21)–P(4)–F(23) | 87.2 (10) | F(22)–P(4)–F(23) | 96.8 (11) |
| C(21)–P(2)–C(231) | 102.3 (4) | C(22)–P(2)–C(231) | 100.2 (5) | F(21)–P(4)–F(24) | 93.2 (11) | F(22)–P(4)–F(24) | 82.9 (12) |
| P(2)–C(231)–C(232) | 119.7 (5) | P(2)–C(231)–C(236) | 122.6 (6) | F(23)–P(4)–F(24) | 161.2 (12) | F(21)–P(4)–F(25) | 91.5 (10) |
| C(232)–C(231)–C(236) | 117.7 (7) | C(231)–C(232)–C(233) | 122.5 (7) | F(22)–P(4)–F(25) | 87.9 (11) | F(23)–P(4)–F(25) | 102.5 (11) |
| C(232)–C(233)–C(234) | 117.8 (8) | C(233)–C(234)–C(235) | 121.4 (9) | F(24)–P(4)–F(25) | 96.2 (13) | F(21)–P(4)–F(26) | 92.4 (11) |
| C(234)–C(235)–C(236) | 119.7 (8) | C(231)–C(236)–C(235) | 120.9 (8) | F(22)–P(4)–F(26) | 88.5 (12) | F(23)–P(4)–F(26) | 73.9 (12) |
| Ru–P(3)–C(31) | 121.7 (3) | Ru–P(3)–C(32) | 115.5 (3) | F(24)–P(4)–F(26) | 87.3 (13) | F(25)–P(4)–F(26) | 174.6 (13) |
| C(31)–P(3)–C(32) | 98.5 (4) | Ru–P(3)–C(331) | 117.1 (2) | | | | |

**[Ru(1-3:5,6-η-$C_8H_{11}$)(CNxylyl)$_3$]PF$_6$.** [Ru(1-3:5,6-η-$C_8H_{11}$)(η$^6$-1,3,5-cyclooctatriene)]PF$_6$ (0.3 g, 0.7 mmol) and xylyl isocyanide (0.27 g, 2.1 mmol) were stirred in acetone (10 mL) at room temperature for 18 h. A beige solid was obtained from the brown solution on addition of ethanol. The solid was filtered off and washed with diethyl ether; yield 0.17 g (33%).

**X-ray Structure Determination of 2.** Pale yellow rectangular-prismatic crystals of the complex were grown from dichloromethane/ethanol solution. A crystal of dimension 0.30 × 0.17 × 0.07 mm, coated with cyanoacrylate glue to protect it from atmospheric decomposition, was used for the structure determination.

**Crystal data**: $C_{16}H_{21}F_6PRu$, $M_r$ 459.38; orthorhombic, space group $C222_1$, $a$ = 13.620 (2) Å, $b$ = 11.222 (2) Å, $c$ = 22.421 (3) Å, $U$ = 3427 (2) Å$^3$, $Z$ = 8, $D_{calcd}$ = 1.781 Mg m$^{-3}$, $F(000)$ = 1840, Mo $K\alpha$ radiation, λ = 0.710 69 Å, $\mu$(Mo K$\alpha$) = 0.947 mm$^{-1}$, $T$ = 275 K.

The unit-cell dimensions were determined by a least-squares fit to the positions of 25 reflections with 7.52 ⩽ $\theta$ ⩽ 15.57°, and intensity measurements were made by using an Enraf-Nonius CAD4F four-cycle diffractometer with graphite-crystal-monochromatized Mo $K\alpha$ radiation. A total of 1704 reflections with 3 ⩽ $\theta$ ⩽ 25° in the octant $+h$, $+k$, $+l$ were measured by using $\omega/2\theta$ scan mode with a variable scan speed: maximum −0.055° s$^{-1}$ in $\omega$, maximum time 60 s/reflection, and a scan width of (0.46 + 0.77 tan $\theta$)° in $\omega$ (the scan width parameters were obtained by a least-squares fit to the observed peak widths of 10 reflections with varying $\theta$ values). The scan width was extended by 25% on each side for background measurements. Three standard reflections (423, 427, 10,0,0) were measured every 60 min and showed no significant variations. Semiempirical absorption corrections,[25] based on $\phi$-scans of five reflections, were applied to the data; corrections: maximum 0.9957, minimum 0.9461, average 0.9740. A total of 994 reflections with $F_o \geqslant 4\sigma(F_o)$ were used in the refinement. The high proportion of weak reflections made the choice of the correct space group problematical. However, a solution was eventually found for space group $C222_1$, and subsequent satisfactory refinement supported this choice of space group. The structure was solved by normal heavy-atom methods and was refined by full-matrix weighted least-squares [$w = \sigma^{-2}(F_o)$ (based on counting statistics), the function minimized was $\sum w(|F_o| - |F_c|)^2$] with use of SHELX.[26] Complex neutral-atom scattering factors[27] were used for all atoms. Owing to the paucity of reliable data, anisotropic temperature factors were refined only for the ruthenium atom and the $PF_6$ anion. All hydrogen atoms were added in calculated positions ($d_{C-H} = 0.95$ Å). A separate common isotropic temperature factor was refined for the hydrogen atoms of each ligand. The refinement converged with $R = 0.0673$ and $R_w = 0.0528$. A total of 139 parameters were refined giving an observation to parameter ratio of 7.15. A final difference electron density map showed no significant residual features: $\delta\rho_{max}$ 0.60 e Å$^{-3}$ (close to Ru); $\delta\rho_{min}$ −0.53 e Å$^{-3}$. An equivalent refinement of the alternative enantiomorph gave $R = 0.678$, $R_w = 0.0532$, and no significant differences in the observed bond lengths and angles for the structure. The final atom coordinates and anisotropic (or equivalent isotropic) temperature factors are given in Table V; bond lengths and bond angles are given in Table VI. Listings of observed and calculated structure factors, calculated hydrogen atom coordinates, anisotropic temperature factors, and equations of least-squares planes are available as supplementary material. Figure 3 is a perspective view of the cation, and Figure 5 shows the unit cell contents.

**X-ray Structure Determination of 4 (L = $PMe_2Ph$).** Colorless rectangular-prismatic crystals of the complex were grown from dichloromethane/ethanol solution. A crystal of dimensions 0.19 × 0.18 × 0.16 mm was used for the structure determination.

**Crystal data**: $C_{32}H_{44}F_6P_4Ru$, $M_r$ 767.66; orthorhombic, space group *Pbca*, $a = 23.553$ (4) Å, $b = 14.965$ (2) Å, $c = 19.085$ (3) Å, $U = 6727$ (3) Å$^3$, $Z = 8$, $D_{calcd} = 1.516$ Mg m$^{-3}$, $F(000) = 3152$, Mo $K\alpha$ radiation, $\lambda = 0.71069$ Å, $\mu(\text{Mo } K\alpha) = 0.628$ mm$^{-1}$, $T = 275$ K.

The unit cell determination and intensity measurements were carried out by using a Philips PW1100 four-circle diffractometer with graphite-crystal-monochromatized Mo $K\alpha$ radiation. A total of 5245 reflections with $3 \leqslant \theta \leqslant 23°$ in the octant $+h, +k, +l$ were measured by using the $\omega/2\theta$ scan mode with a scan speed of 0.0344° s$^{-1}$ in $\omega$ and a scan width of 0.86° in $\omega$. Stationary background measurements were made at each end of the scan for (scan time)/2. Three standard reflections (424, 526, 10,4,2) were measured every 60 min and showed no significant variations. A total of 3242 reflections with $F_o \geqslant 4\sigma(F_o)$ were used in the refinement of the structure; no absorption corrections were applied to the data. The structure was solved by normal heavy-atom methods and was refined by blocked-matrix weighted least-squares procedures[$w = \sigma^{-2}(F_o)$ (based on counting statistics); the function minimized was $\sum w(|F_o| - |F_c|)^2$] with use of SHELX.[26] Complex neutral-atom scattering factors[27] were used for all atoms. Anisotropic temperature factors were refined for all non-fluorine or hydrogen atoms. The fluorine atoms of the $PF_6$ anion were found to be disordered, and two orientations for the anion were observed. Two sets of coordinates for the fluorine atoms were refined along with a site occupation factor (sof) for each set. The two sof's were, however, constrained to sum to 1.0. Individual isotropic temperature factors were refined for each partial fluorine atom. All hydrogen atom positions were located by using difference maps and were refined by using four common isotropic temperature factors. The refinement converged with $R = 0.0531$ and $R_w = 0.0461$. A total of 519 parameters were refined giving an observation to parameter ratio of 6.25. A final difference electron density map showed no significant residual features: $\delta\rho_{max}$, 0.67 e Å$^{-3}$ (close to the $PF_6$ anion); $\delta\rho_{min}$ −0.63 e Å$^{-3}$. The final atom coordinates and equivalent isotropic temperature factors are given in Table VII; bond lengths and bond angles are given in Table VIII. Listings of observed and calculated structure factors, anisotropic temperature factors, and equations of least-squares planes are available as supplementary material. Figure 4 is a perspective view of the molecule, and Figure 6 shows the unit cell contents.

**Registry No.** **2**·$PF_6$, 99040-71-8; **2**·$BPh_4$, 107799-51-9; **3**·$PF_6$ (R = *t*-Bu), 99085-60-6; **3**·$PF_6$ (R = 2,6-$Me_2C_6H_3$), 99085-62-8; **4**·$PF_6$ (L = $P(OMe)_3$), 99039-06-2; **4**·$PF_l$ (L = $PMe_2Ph$), 99039-04-0; **4**·$PF_6$ (L = $AsMePh_2$), 99040-69-4; **4**·$PF_6$ (L = $AsMe_2Ph$), 107799-53-1; $[RuH(cod)(NH_2NMe_2)_2]PF_l$, 64722-25-4; $[RuH(cod)(NH_2NMe_2)_3]BPh_4$, 65390-74-1; $[RuH(cod)(PMe_2Ph)_3]PF_6$, 61003-34-7; $[RuH(cod)(AsMePh_2)_3]PF_6$, 91127-98-9; $AsMe_2Ph$, 696-26-4; $AsMePh_i$, 945-48-2; *tert*-butyl isocyanide, 7188-38-7; xylyl isocyanide, 2769-71-3; cyclooxtatetraene, 629-20-9.

**Supplementary Material Available:** Tables of calculated hydrogen coordinates for **2** and anisotropic temperature factors and equations of least-squares planes for **2** and **4** (L = $PMe_2Ph$) (6 pages); listings of observed and calculated structure factors for **2** and **4** (L = $PMe_2Ph$) (19 pages). Ordering information is given on any current masthead page.

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