J. Am. Chem. Soc. **1998,** *120,* 10409−10415

Ligand-Induced Ring Slippage of η^6- to η^4-Naphthalene. Preparation and Structural Characterization of Ru(η^4-$C_{10}H_8$)(η^4-1,5-C_8H_{12})(L) [L = PMe_3, PEt_3, $P(OMe)_3$] and of Derived Binuclear Complexes Containing Bridging Naphthalene, $Ru_2(\mu$-η^6:η^4-$C_{10}H_8)(\eta^4$-1,5-$C_8H_{12})_2$(L) [L = PEt_3, $P(OMe)_3$]

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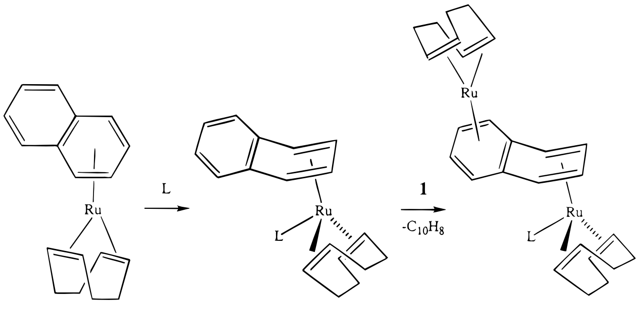
Received March 26, 1998

Abstract: Treatment of (η^6-naphthalene)(η^4-1,5-cyclooctadiene)ruthenium(0), Ru(η^6-$C_{10}H_8$)(η^4-1,5-C_8H_{12}) (**1**), with a slight excess of trimethylphosphine, triethylphosphine, trimethyl phosphite, triethyl phosphite, or *tert*-butyl isocyanide below room temperature gives η^4-naphthalene complexes Ru(η^4-$C_{10}H_8$)(η^4-1,5-C_8H_{12})(L) [L = PMe_3 (**3**), PEt_3 (**4**), $P(OMe)_3$ (**5**), $P(OEt)_3$ (**6**), *t*-BuNC (**7**)], which provide the first examples of the often postulated η^6 to η^4 transformation of naphthalene induced by two-electron donor ligands. The η^4-naphthalene is easily displaced by an excess of the ligands to give RuL_3(η^4-1,5-C_8H_{12}). At room temperature, complex **1** reacts with a deficiency of PMe_3, PEt_3, or $P(OMe)_3$ to give binuclear complexes containing bridging naphthalene, (η^4-1,5-C_8H_{12})Ru(μ-η^6:η^4-$C_{10}H_8$)Ru(η^4-1,5-C_8H_{12})(L) [L = PMe_3 (**8**), PEt_3 (**9**), $P(OMe)_3$ (**10**)]. Single-crystal X-ray studies of complexes **3**, **4**, **5**, **9**, and **10** show the presence in each case of a folded naphthalene ring with a hinge angle of ca. 40°. In **9** and **10** the metal atoms adopt an *anti* arrangement relative to the bridging naphthalene.

Introduction

The coordinated aromatic hydrocarbon in the complex (η^6-naphthalene)(η^4-1,5-cyclooctadiene)ruthenium(0), Ru(η^6-$C_{10}H_8$)-(η^4-1,5-C_8H_{12}), (**1**),[1−3] is labilized in the presence of acetonitrile, thus enabling complex **1** to catalyze the hydrogenation of alkenes,[2] the double bond isomerizations of 1,5-cyclooctadiene and 1-hexene to 1,3-cyclooctadiene and *E*/*Z*-2-hexene, respectively,[4] and the isomerization of allyl ethers and acetals to the corresponding vinyl compounds.[5] In the presence of acetonitrile, naphthalene is displaced from **1** by a wide range of arenes to give the corresponding Ru(η^6-arene)(η^4-1,5-C_8H_{12}) complexes.[1,2] These reactions either do not occur or occur much more slowly in the absence of acetonitrile. It has been suggested[1,2] that acetonitrile promotes the formation of an undetected η^4-naphthalene complex, Ru(η^4-$C_{10}H_8$)(η^4-1,5-C_8H_{12})(NCMe) (**2**), i.e., that acetonitrile acts as an auxiliary ligand to assist in the ring-slippage and ultimate removal of coordinated naphthalene, and complexes of this type containing η^4-1,3-dienes in place of η^4-$C_{10}H_8$ have been isolated.[6] We report here that, by use of certain Group 15 donors in place of acetonitrile, it is possible to isolate and characterize structurally η^4-naphthalene complexes derived from **1**. The chemistry is outlined in Scheme 1.

Scheme 1



1

L = MeCN (**2**) (undetected), PMe_3 (**3**), PEt_3 (**4**), $P(OMe)_3$ (**5**), $P(OEt)_3$ (**6**), *t*-BuNC (**7**)

L = PMe_3 (**8**), PEt_3 (**9**), $P(OMe)_3$ (**10**)

Experimental Section

All operations were carried out under purified nitrogen or argon with use of standard Schlenk techniques. Hydrocarbon and ether solvents were distilled from sodium benzophenone ketyl and CH_2Cl_2 was distilled from CaH_2. The complex Ru(η^6-$C_{10}H_8$)(η^4-1,5-C_8H_{12}) (**1**) was prepared by a published procedure.[2] The NMR spectra were measured on the following spectrometers: Varian Gemini 300 (^{1}H at 300.10 MHz, ^{13}C at 75.43 MHz, and ^{31}P at 121.4 MHz) and Varian XL200 (^{31}P at 80.96 MHz). The chemical shifts (δ) for ^{1}H and ^{13}C are given in ppm referenced to residual solvent signals, those for ^{31}P are reported relative to external 85% H_3PO_4; coupling constants (*J*) are in Hz. The ^{1}H and ^{13}C NMR data for the naphthalene complexes **3**−**10** are collected in Tables 1 and 2, respectively. Mass spectra (EI) were measured at 70 eV on VG Micromass 7070F or Fisons VG Autospec spectrometers. Elemental analyses were performed in-house.

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(1) Vitulli, G.; Pertici, P.; Salvadori, P. *J. Chem. Soc., Dalton Trans.* **1984**, 2255.

(2) Bennett, M. A.; Neumann, H.; Thomas, M.; Wang, X.-Q.; Pertici, P.; Salvadori, P.; Vitulli, G. *Organometallics* **1991**, *10*, 3237.

(3) Crocker, M.; Green, M.; Howard, J. A. K.; Norman, N. C.; Thomas, D. M. *J. Chem. Soc., Dalton Trans.* **1990**, 2299.

(4) Pertici, P.; Uccello Barretta, G.; Burzagli, F.; Salvadori, P.; Bennett, M. A. *J. Organomet. Chem.* **1991**, *413*, 303.

(5) Pertici, P.; Malanga, C.; Giuntoli, A.; Vitulli, G.; Martra, G. *Gazz. Chim. Ital.* **1996**, *126*, 587.

(6) Bennett, M. A.; Wang, X.-Q. *J. Organomet. Chem.* **1992**, *428*, C17.

S0002-7863(98)01027-0 CCC: $15.00

Table 1. ^{1}H NMR Spectroscopic Data for Mononuclear and Binuclear η^4-Naphthalene Ruthenium(0) Complexes[a]

	naphthalene				1,5-cyclooctadiene		
complex	$H^{1,4}$	$H^{2,3}$	$H^{5,8}$	$H^{6,7}$	CH	CH_2	ligand
$Ru(\eta^6\text{-}C_{10}H_8)(\eta^4\text{-}1,5\text{-}C_8H_{12})(PMe_3)$ (**3**)	6.81	6.70	2.88	5.94	2.70 (4H)	2.23 (4H), 1.84 (4H)	1.11 (d, Me, $J_{PH} = 7.5$)
$Ru(\eta^6\text{-}C_{10}H_8)(\eta^4\text{-}1,5\text{-}C_8H_{12})(PEt_3)$ (**4**)	6.74	6.70	3.03	5.97	2.92 (2H), 2.69 (2H)	2.25 (4H), 1.80 (4H)	1.51 (qn, CH_2, $J_{HH} = 7.5$, $J_{PH} = 7.5$), 0.94 (dt, Me, $J_{HH} = 7.5$, $J_{PH} = 13.7$)
$Ru(\eta^6\text{-}C_{10}H_8)(\eta^4\text{-}1,5\text{-}C_8H_{12})\{P(OMe)_3\}$ (**5**)	6.81	6.63	3.09	5.98	3.29 (2H), 2.86 (2H)	2.67 (2H), 2.24 (2H), 1.84 (4H)	3.39 (d, Me, $J_{PH} = 10.8$)
$Ru(\eta^6\text{-}C_{10}H_8)(\eta^4\text{-}1,5\text{-}C_8H_{12})\{P(OEt)_3\}$ (**6**)	6.73	6.61	3.09	5.97	3.33 (2H), 2.86 (2H)	2.76 (2H), 2.27 (2H), 1.88 (4H)	3.89 (CH_2), 1.20 (Me)
$Ru(\eta^6\text{-}C_{10}H_8)(\eta^4\text{-}1,5\text{-}C_8H_{12})(t\text{-}BuNC)$ (**7**)	6.79	6.79	3.16	5.97	3.30 (2H), 2.97 (2H)	2.66 (2H), 2.14 (2H), 1.98 (4H)	1.12 (s, *t*-Bu)
$Ru_2(\mu{-}\eta^6{:}\eta^4\text{-}C_{10}H_8)(\eta^4\text{-}1,5\text{-}C_8H_{12})_2\ (PMe_3)$ (**8**)	4.63	5.30	2.24	5.76	3.43, 2.70−2.55, 2.55−1.65, 2.15		1.14 (d, Me, $J_{PH} = 7.5$)
$Ru_2(\mu\text{-}\eta^6{:}\eta^4\text{-}C_{10}H_8)(\eta^4\text{-}1,5\text{-}C_8H_{12})_2(PEt_3)$ (**9**)	4.63	5.15	2.37	5.83	3.41, 2.74, 2.63−2.24, 2.24−2.00, 1.80−1.60		1.54 (qn, CH_2, $J_{HH} = 7.5$, $J_{PH} = 7.5$), 0.89 (dt, Me, $J_{HH} = 7.5$, $J_{PH} = 14.0$)
$Ru_2(\mu\text{-}\eta^6{:}\eta^4\text{-}C_{10}H_8)(\eta^4\text{-}1,5\text{-}C_8H_{12})_2\{P(OMe)_3\}$ (**10**)	4.62	5.17	2.42	5.81	3.42, 3.06, 2.66, 2.60−2.46, 2.16, 1.82−1.66		3.32 (d, Me, $J_{PH} = 11.5$)

[a] In C_6D_6 at 20 °C, 300 MHz, coupling constants in Hz; naphthalene protons numbered similarly to corresponding carbon atoms in Figures 1 and 2; peaks are multiplets, except where indicated.

Table 2. ^{13}C NMR Spectroscopic Data for Mononuclear and Binuclear η^4-Naphthalene Ruthenium(0) Complexes[a,b]

	naphthalene					1,5-cyclooctadiene		
complex	$C^{1,4}$	$C^{2,3}$	$C^{5,8}$	$C^{6,7}$	$C^{9,10}$	CH	CH_2	ligand
3	122.5 (157)	121.8 (154)	54.0 (150, 2.3)[c]	88.4 (169, 2.9)[c]	144.9, 144.7	71.7 (155, 4.6[c]), 65.1 (151, 6.2[c])	32.6 (129), 30.9 (129)	19.4 (130, 22.4,[c] Me)
4	122.7 (158)	122.1 (155)	54.4 (155)	88.7 (170)	144.5, 144.4	72.0 (156, 4.6[c]), 64.5 (156, 3.5[c])	32.6 (128), 31.6 (124)	17.3 (127, 18.8,[c] CH_2) 8.6 (125, Me)
5	122.3 (156)	121.1 (157)	52.9 (154)	88.6 (173)	144.5, 144.4	73.0 (156, 6.5[c]), 68.3 (156, 9.2[c])	32.3 (127), 31.1 (126)	50.9 (139, 5.1,[c] Me)
6	122.7	121.6	53.6	89.1	144.5, 144.4	73.1, 68.2	32.8, 31.4	60.2 (CH_2), 16.7 (Me)
7	122.3 (156)	120.5 (151)	53.6 (156)	88.3 (170)	145.0, 144.9	72.4 (150), 69.4 (155)	33.4 (132), 31.9 (135)	31.2 (136)
8	81.0	85.4	50.2	89.1	112.7	72.4[d] (4.4[c]), 65.7[d] (6.7[c]), 62.5[e]	35.0,[e] 32.7,[d] 31.0[d]	20.6 (22.1,[c] Me)
9	80.5	85.5	50.1	89.2	112.1	72.3[d](3.9[c]), 64.6[d](6.8[c]), 62.5[e]	35.0,[e] 32.1,[d] 30.8[d]	18.0 (18.7,[c] CH_2), 8.4 (Me)
10	80.3	84.7	49.0	88.9 (3.4[c])	115.8	73.2[d] (5.8[c]), 68.2[d] (9.1[c]), 62.5[e]	35.0,[e] 32.1,[d] 30.8[d]	50.8 (4.6[c])

[a] In C_6D_6 at 20 °C, 75.4 MHz; naphthalene carbon atoms numbered as in Figures 1 and 2. [b] Coupling constants (Hz) in parentheses are $^{1}J_{CH}$, except where indicated. [c] $J_{P-C.}$ [d] $1,5\text{-}C_8H_{12}$ attached to $Ru(\eta^4\text{-}C_{10}H_8)$. [e] $1,5\text{-}C_8H_{12}$ attached to $Ru(\eta^6\text{-}C_{10}H_8)$.

Preparations. (a) (1,5-Cyclooctadiene)(naphthalene)(trimethylphosphine)ruthenium(0), $Ru(\eta^4\text{-}C_{10}H_8)(\eta^4\text{-}1,5\text{-}C_8H_{12})(PMe_3)$ (3). A 0.36 M solution of trimethylphosphine in hexane (1.53 mL, 0.55 mmol) was added by syringe to a solution of complex **1** (185 mg, 0.55 mmol) in 1:1 toluene/hexane (20 mL), which was stirred while being maintained at −10 to −4 °C. The mixture was allowed to stand at this temperature for 3 h and filtered through Celite. The filtrate was concentrated in vacuo to ca. half the volume under reduced pressure and set aside at −20 °C for 1−2 d. The yellow crystals of **3** were washed with cold hexane (2 mL) and dried in vacuo. The yield was 61%. $^{31}P\{^{1}H\}$ NMR (C_6D_6, 25 °C) δ 2.1. EI-MS (70 eV): *m/z* 338.0 (M − PMe_3), 76.0 (PMe_3). Anal. Calcd for $C_{21}H_{29}PRu$: C, 61.00; H, 7.07; P, 7.49. Found: C, 60.83; H, 7.73; P, 8.06.

The complexes $Ru(\eta^4\text{-}C_{10}H_8)(\eta^4\text{-}1,5\text{-}C_8H_{12})(L)$ [L = PEt_3 (**4**), $P(OMe)_3$ (**5**), $P(OEt)_3$ (**6**), and *t*-BuNC (**7**)] were prepared similarly as yellow or yellow-brown solids in yields of ca. 70%, 79%, 40%, and 34%, respectively. **4**: $^{31}P\{^{1}H\}$ NMR (C_6D_6, 25 °C) δ 25.4. EI-MS (70 eV): *m/z* 338.0 (M − PEt_3), 118.0 (PEt_3). Anal. Calcd for $C_{24}H_{35}PRu$: C, 63.27; H, 7.74; P, 6.80. Found: C, 63.02; H, 8.02; P, 6.92. **5**: $^{31}P\{^{1}H\}$ NMR (C_6D_6 or toluene-d_8, 25 °C) δ 172.6. EI-MS (70 eV): *m/z* 338 {M − $P(OMe)_3$}, 124.0 {$P(OMe)_3$}. Anal. Calcd for $C_{21}H_{29}O_3PRu$: C, 54.65; H, 6.33; P, 6.72. Found: C, 55.13; H, 6.38; P, 6.59. **6**: $^{31}P\{^{1}H\}$ NMR (C_6D_6, 25 °C) δ 165.6. **7**: Anal. Calcd for $C_{23}H_{29}NRu$: C, 63.01; H, 7.08; N, 3.20. Found: C, 62.76; H, 7.28; N, 3.46.

(b) Bis(1,5-cyclooctadiene)(μ-naphthalene)(triethylphosphine)diruthenium(0), $(\eta^4\text{-}1,5\text{-}C_8H_{12})Ru(\mu\text{-}\eta^6{:}\eta^4\text{-}C_{10}H_8)Ru(\eta^4\text{-}1,5\text{-}C_8H_{12})(PEt_3)$ (9). (i) A 0.36 M solution of triethylphosphine in hexane (1.06 mL, 0.385 mmol) was added by syringe to a solution of complex **1** (185 mg, 0.55 mmol) in hexane (30 mL) and the mixture was stirred at room temperature for ca. 24 h. The solvent was removed under reduced pressure and the solid residue was extracted with hexane (3 × 1.5 mL) at room temperature, the reddish supernatant liquid being removed by cannulation. The solid residue containing the crude product was dissolved in toluene/hexane (1:8), concentrated in vacuo, and set aside at −20 °C to give yellow crystals of **9**. These were washed with a few milliliters of cold hexane and dried in vacuo. The yield was 38−58%.

(ii) A freshly prepared sample of complex **4** (60 mg, 0.13 mmol) was dissolved in toluene-d_8 (2 mL) and set aside in an NMR tube that was shielded from light. After ca. 47 h, when ca. 80% of **4** had disappeared as shown by ^{1}H NMR spectroscopy, the solution was concentrated in vacuo and set aside in a dry ice bath to give yellow-brown crystals of **9**. The supernatant liquid was removed by cannulation and the crystals were washed by decantation with hexane (2 × 1 mL) at −60 °C. The yield was 12 mg (28%). $^{31}P\{^{1}H\}$ NMR (C_6D_6, 25 °C) δ 24.6. Anal. Calcd for $C_{32}H_{47}PRu_2$: C, 57.81; H, 7.13; P, 4.66. Found: C, 57.62; H, 7.37; P, 4.74.

(c) Bis(1,5-cyclooctadiene)(μ-naphthalene)(trimethyl phosphite)diruthenium(0), $(\eta^4\text{-}C_8H_{12})Ru(\mu\text{-}\eta^6{:}\eta^4\text{-}C_{10}H_8)Ru(\eta^4\text{-}1,5\text{-}C_8H_{12})\{P(OMe)_3\}$ (10). (i) A hexane solution of **1** was treated with trimethyl phosphite (mol ratio Ru:P = 1:0.6) as described for **9** (method (i)). The mixture was concentrated under reduced pressure and transferred to an alumina column (neutral, activity III). The third band eluted with CH_2Cl_2/toluene (1:2) was evaporated to dryness. Recrystallization from toluene/hexane (1:10) at −20 °C over a period of 1−2 d gave yellow crystals of **10** in 50% yield.

(ii) A freshly prepared sample of complex **5** (100 mg, 0.22 mmol) in toluene (5 mL) was set aside in darkness for ca. 60 h. The clear yellow solution was filtered, concentrated in vacuo, and set aside in a dry ice bath to give yellow crystals of **10**, which were washed with hexane (3 × 1 mL) at −60 °C. The yield was 15−30%. ^{31}P{^{1}H} NMR (C_6D_6 or toluene-d_8) δ 173.6. Anal. Calcd for $C_{29}H_{41}O_3PRu_2$: C, 51.93; H, 6.16. Found: C, 51.43; H, 6.11.

(d) Bis(1,5-cyclooctadiene)(μ-naphthalene)(trimethylphosphine)-diruthenium(0), (η^4-1,5-C_8H_{12})Ru(μ-η^6:η^4-$C_{10}H_8$)Ru(η^4-1,5-C_8H_{12})-(PMe_3) (8). This was obtained in 31% yield as air-sensitive, yellow crystals from the reaction of PMe_3 with **1** after purification by chromatography and recrystallization as described for **10** (method (i)). The compound is indefinitely stable under argon at −20 °C. It was identified by its ^{1}H and ^{13}C NMR spectra (Tables 1 and 2). ^{31}P{^{1}H} NMR (C_6D_6, 25 °C) δ 0.0.

(e) (1,5-Cyclooctadiene)tris(trimethylphosphine)ruthenium(0), Ru(η^4-1,5-C_8H_{12})(PMe_3)$_3$ (11). Trimethylphosphine (233 μL, 2.7 mmol) was added by syringe to a solution of **1** (300 mg, 0.89 mmol) in hexane (30 mL) at room temperature. The resulting brown solution was allowed to stand for 4 h and filtered. The filtrate was concentrated to ca. 6 mL volume in vacuo and cooled overnight in a dry ice bath to give the crude product as a brown solid (267 mg, 46%). Recrystallization from hexane at −78 °C gave a yellow crystalline solid, which was washed with ether (2 × 1 mL) at −60 °C and dried in vacuo at 0 °C. The yield was 146 mg (28%). At room temperature, the solid smelt of trimethylphosphine and satisfactory elemental analyses could not be obtained. ^{1}H NMR (C_6D_6, 25 °C) δ 2.66 (br s, 12H, =CH and CH_2), 1.21 (m, 27H, Me); ^{13}C{^{1}H} NMR (C_6D_6, 25 °C) δ 64.27 (J_{CH} = 148.0, J_{CP} = 3.3, =CH), 35.85 (J_{CH} = 122.0, J_{CP} = 2.3, CH_2), 23.61 (m, J_{CH} = 125.1, Me); ^{31}P{^{1}H} NMR (C_6D_6, 25 °C) δ −4.5; EI-MS (70 eV) *m/z* 360 (M − PMe_3), 282 (M − 2PMe_3), 76 (PMe_3).

The complexes RuL_3(η^4-1,5-C_8H_{12}) [L = P(OMe)$_3$ (**13**), P(OEt)$_3$ (**14**), and *t*-BuNC (**15**)] were prepared similarly as air-sensitive, yellow-brown solids (**13**, **14**) or a pale yellow powder (**15**) in yields of 41%, 34%, and 65%, respectively. Satisfactory elemental analyses could not be obtained owing to loss of L at room temperature. **13**: ^{1}H NMR (C_6D_6, 25 °C) δ 3.66 (br s, 31H, =CH, Me), 2.85 (br s, 4H, CH_2), 2.57 (br s, 4H, CH_2). ^{13}C NMR (C_6D_6, 25 °C) δ 69.6 (d, J_{CH} = 150, J_{CP} = 4.8, =CH), 50.9 (J_{CH} = 143, Me), 35.0 (t, J_{CH} = 119, J_{CP} = 3.0, CH_2); ^{31}P{^{1}H} NMR (C_6D_6, 25 °C) δ 166.6. **14**: ^{1}H NMR (C_6D_6, 25 °C) δ 4.16 (m), 3.61 (br s), 2.91 (br s), 1.31 (m) with relative intensities ca. 6:1:1:9; ^{13}C NMR (C_6D_6, 25 °C) δ 69.9 (J_{CH} = 155.1, =CH), 59.7 (J_{CH} = 142, CH_2 of P(OEt)$_3$), 35.1 (J_{CH} = 127, CH_2 of C_8H_{12}), 16.7 (J_{CH} = 125, Me). ^{31}P{^{1}H} NMR (C_6D_6, 25 °C) δ 161.4. **15**: ^{1}H NMR (C_6D_6) δ 3.79 (m, 4H, =CH), 2.86 (m, 4H, CH_2), 2.74 (m, 4H, CH_2), 1.31 (s, 27H, *t*-Bu). ^{13}C NMR (C_6D_6) δ 179.6 (CN*C*Me), 69.86 (d, J_{CH} = 121.9, CH_2 of C_8H_{12}), 31.47 (q, J_{CH} = 126.6, CNC*Me*).

Addition of triethylphosphine (36 μL, 0.27 mmol) to a solution of **1** (30 mg, 0.09 mmol) in benzene-d_6 caused an immediate change of color from orange to yellow brown. The ^{31}P NMR spectrum showed initially a peak at δ 25.4 due to **4**, which was replaced slowly by a singlet at δ 15.6; the ^{1}H NMR spectrum contained broad signals in the region δ 3.0−1.0. The complex, which is assumed to be Ru(PEt$_3$)$_3$-(η^4-1,5-C_8H_{12}) (**12**), could not be isolated because it decomposed even before all of **1** had reacted.

Replacement of PEt$_3$ in 4 by P(OMe)$_3$. A 0.036 M solution of **4** in C_6D_6 contained in a 5 mm NMR tube at 20 °C was treated with known volumes of P(OMe)$_3$ from a microsyringe. The reaction was monitored by following the disappearance of the signal at δ 3.03 due to $H^{5,8}$ of **4** and the appearance of the corresponding resonance at δ 3.39 due to **5**. Good first-order plots were obtained, the pseudo first-order rate constant being 0.06 min^{-1} independent of the concentration of P(OMe)$_3$ (0.05, 0.10, and 0.15 M).

X-ray Crystallography. Crystals of complexes **3**, **4**, **5**, **9**, and **10** were grown from solutions in toluene−hexane at −20 °C. Data were collected in a $\theta-2\theta$ scan mode on a Rigaku AFC6R diffractometer at 213 K with use of Cu Kα radiation (λ = 1.51478 Å). Lattice parameters were determined by least-squares analysis of the setting angles of 25 reflections 90.48° < 2θ < 109.98° for **3**, 98.64° < 2θ < 99.85° for **4**, 94.91° < 2θ < 99.22° for **5**, 99.51° < 2θ < 99.22° for **9**, and 106.58° < 2θ < 109.77° for **10**. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located from difference maps and held fixed for **3**, refined for **4**, **5**, and **9**, and refined only for the naphthalene ring in the case of **10**. All calculations were performed by use of the teXsan Structure Analysis package[7] and included an empirical absorption correction in each case.[8] Neutral atom scattering factors were taken from Cromer and Waber.[9] Anomalous dispersion effects were included in F_{calc}.[10] The values of $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley;[11] values of the mass attenuation coefficients were taken from Creagh and Hubbell.[12] The structures were solved by Patterson and difference Fourier techniques (DIRDIF 92, PATTY)[13] and were refined by full-matrix least-squares analysis, the function minimized being $\Sigma w(|F_o| - |F_c|)^2$. Other details are collected in Table 3.

Results

Treatment of Ru(η^6-$C_{10}H_8$)(η^4-1,5-C_8H_{12}) (**1**) with one or slightly more than one equivalent of trimethylphosphine, triethylphosphine, trimethyl phosphite, triethyl phosphite, or *tert*-butyl isocyanide in toluene or hexane below room temperature gives the corresponding η^4-naphthalene complexes Ru(η^4-$C_{10}H_8$)(η^4-1,5-C_8H_{12})(L) [L = PMe_3 (**3**), PEt$_3$ (**4**), P(OMe)$_3$ (**5**), P(OEt)$_3$ (**6**), or *t*-BuNC (**7**)] as yellow, crystalline solids in yields of 30−70%. The more bulky P-donors PPh$_3$, P-*i*-Pr$_3$, and P-*t*-Bu$_3$ do not react with **1** in benzene-d_6 over a period of 2 days at room temperature. Under similar conditions, the ligands PMe$_2$Ph, PMePh$_2$, and P(OPh)$_3$ give an unidentified mixture of products; there was no evidence for the formation of a η^4-$C_{10}H_8$ complex in these cases. Complexes **3**−**6** are stable as solids at room temperature under argon, and solid **3** is even moderately stable to air, but the *tert*-butyl isocyanide complex **7** decomposes to a sticky oil within an hour at room temperature.

The η^4-naphthalene formulation is based on the ^{1}H and ^{13}C NMR spectra of the complexes, which are listed in Tables 1 and 2, respectively, and on single-crystal X-ray structural analyses of complexes **3**−**5** (see Figure 1 for the molecular structure of **3**, discussed below). For example, the ^{1}H NMR spectrum of the *tert*-butyl isocyanide complex **7** shows a mirror-image, AA′BB′ pair of four-line 2H multiplets at δ 5.97 and 3.16, which can be assigned to the inner and terminal protons, $H^{6,7}$ and $H^{5,8}$, respectively, of η^4-$C_{10}H_8$; the chemical shift difference of ca. 3 ppm between them is similar to those observed in TaH(η^4-$C_{10}H_8$)(dmpe)$_2$,[14] [Cr(CO)$_3$(η^4-$C_{10}H_8$)]$^{2-}$,[15] [Mn(CO)$_3$(η^4-$C_{10}H_8$)]$^-$,[16] Fe(η^6-C_6Me_6)(η^4-$C_{10}H_8$),[17] Fe{P(OMe)$_3$)}$_3$(5-8η-1,4-Me$_2C_{10}H_6$),[18] and Rh(η^5-C_5H_5)(η^4-$C_{10}H_8$),[19] and the increased shielding (ca. 1 ppm) of $H^{5,8}$ in **7** relative to that in the η^6-$C_{10}H_8$ complex **1** is characteristic of η^4-1,3-dienes.

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[7] *teXsan: Single-Crystal Structure Analysis Software*; Molecular Structure Corp.: The Woodlands, TX, 1985 and 1992.

[8] North, A. C. T.; Phillips, D. C.; Mathews, F. S. *Acta Crystallogr., Sect. A* **1968**, *24*, 351.

[9] Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.

[10] Ibers, J. A.; Hamilton, W. C. *Acta Crystallogr.* **1964**, *17*, 781.

[11] Creagh, D. C.; McAuley, W. J. *International Tables for Crystallography*; Kluwer Academic: Boston, MA, 1992; Vol. C, p 219.

[12] Creagh, D. C.; Hubbell, J. H. *International Tables for Crystallography*; Kluwer Academic: Boston, MA, 1992; Vol. C, p 200.

[13] Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; Garcia-Granda, S.; Gould, R. O.; Smits, J. M. M.; Smykalla, C. The DIRDIF-92 Program System. Technical Report of the Crystallography Laboratory, University of Nijmegen: Nijmegen, The Netherlands, 1992.

[14] Albright, J. O.; Datta, S.; Dezube, B.; Kouba, J. K.; Marynick, D. S.; Wreford, S. S.; Foxman, B. M. *J. Am. Chem. Soc.* **1979**, *101*, 611.

[15] Rieke, R. D.; Henry, W. P.; Arney, J. S. *Inorg. Chem.* **1987**, *26*, 420.

[16] Thompson, R. L.; Lee, S.; Rheingold, A. L.; Cooper N. J. *Organometallics* **1991**, *10*, 1657.

[17] Brodt, C.; Niu, S.; Pritzkow, S.; Stephan, M.; Zenneck, U. *J. Organomet. Chem.* **1993**, *459*, 283.

Table 3. Crystal and Refinement Data for Ru(η^4-$C_{10}H_8$)(η^4-1,5-C_8H_{12})(L) [L = PMe_3 (**3**), PEt_3 (**4**), $P(OMe)_3$ (**5**)] and Ru_2(μ-η^6:η^4-$C_{10}H_8$)(η^4-1,5-C_8H_{12})$_2$(L) [L = PEt_3 (**9**), $P(OMe)_3$ (**10**)]

	3	**4**	**5**	**9**	**10**
(a) Crystal Data					
chemical formula	$C_{21}H_{29}PRu$	$C_{24}H_{35}PRu$	$C_{21}H_{29}O_3PRu$	$C_{32}H_{47}O_3PRu_2$	$C_{29}H_{41}O_3PRu_2$
fw	413.50	455.58	461.50	664.84	670.75
cryst syst	orthorhombic	monoclinic	monoclinic	triclinic	triclinic
space group	*Pca*2$_1$ (No. 29)	*P*2$_1$/*n* (No. 14)	*P*2$_1$/*c* (No. 14)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
crystal color, habit	pale, irregular	yellow, prism	pale yellow, prism	yellow-red, irregular	yellow, cuboid
a, Å	17.098(3)	12.065(3)	13.350(2)	7.829(1)	7.476(2)
b, Å	6.584(4)	13.607(2)	7.425(3)	12.432(1)	12.352(3)
c, Å	32.224(4)	12.739(2)	19.847(3)	14.859(3)	14.708(3)
α, deg				95.69(1)	99.10(2)
β, deg		93.48(2)	98.53(1)	100.00(1)	98.50(2)
γ, deg				99.515(10)	97.96(2)
V, Å^3	3627(1)	2087.4(6)	1945.5(8)	1392.5(4)	1307.9(6)
Z	8	4	4	2	2
ρ_{calc}, g cm^{-3}	1.514	1.450	1.576	1.586	1.703
μ[Cu *K*α], cm^{-1}	77.91	68.22	74.52	94.60	101.70
cryst dimens, mm	0.18 × 0.04 × 0.16	0.08 × 0.04 × 0.18	0.24 × 0.18 × 0.16	0.28 × 0.20 × 0.08	0.20 × 0.20 × 0.30
F(000)	1712	952	952	684	684
(b) Data Collection and Processing					
ω-scan width	1.20 + 0.30 tan θ	1.00 + 0.30 tan θ	1.00 + 0.30 tan θ	1.00 + 0.30 tan θ	1.40 + 0.30 tan θ
scan rate, deg min^{-1} [a]	8	32	32	16	32
2θ_{max}, deg	120.2	120.2	120.0	120.3	120.1
no. of unique data	3162	3279	3148	4143	3895
no. of data refined	2589 [$I > 3\sigma(I)$]	2864 [$I > 3\sigma(I)$]	2417 [$I > 3\sigma(I)$]	3957 [$I > 3\sigma(I)$]	3292 [$I > 3\sigma(I)$]
no. of variables	413	376	351	505	349
min, max corr	0.66−1.00	0.72−1.00	0.66−1.00	0.44−1.00	0.54−1.00
(c) Structure Analysis and Refinement					
weighting scheme *w*	$4F_o^2/[\sigma^2(F_o^2) + (0.014F_o^2)^2]$	$4F_o^2/[\sigma^2(F_o^2) + (0.008F_o^2)^2]$	$4F_o^2/[\sigma^2(F_o^2) + (0.009\ F_o^2)^2]$	$4F_o^2/[\sigma^2(F_o^2) + (0.026\ F_o^2)^2]$	$4F_o^2/[\sigma^2(F_o^2) + (0.010F_o^2)^2]$
R	0.025	0.034	0.039	0.037	0.033
R$_w$	0.029	0.038	0.042	0.049	0.036
GOF	1.60	2.88	2.20	2.85	2.20

[a] Weak reflections were scanned up to four times and counts were accumulated.

A 4H multiplet centered at δ 6.79 is due to protons H^{1-4} of the uncoordinated ring, and a 9H singlet at δ 1.12 is due to the *tert*-butyl protons of the added ligand. The resonances arising from the olefinic protons of 1,5-cyclooctadiene appear as a pair of 2H multiplets at δ 3.30 and 2.97, while the methylene protons give rise to three multiplets at δ 2.66 (2H), 2.14 (2H), and 1.98 (4H). The ^{1}H NMR spectroscopic features of η^4-$C_{10}H_8$ and η^4-1,5-C_8H_{12} in complexes **3**−**6** are similar to those in **7**, except that the terminal protons $H^{5,8}$ show more complex multiplets owing to coupling with ^{31}P, and protons $H^{1,4}$ and $H^{2,3}$ in the uncoordinated ring of naphthalene appear as a pair of 2H multiplets in the region δ 6.7. The ^{13}C NMR spectra of **3**−**7** are consistent with the ^{1}H NMR spectra and resemble those of other η^4-$C_{10}H_8$ complexes;[14−19] for example, **7** shows signals at δ 88.3 and 53.6 due to carbon atoms $C^{6,7}$ and $C^{5,8}$ of the coordinated ring of naphthalene as well as signals at δ 122.3 and 120.5 due to carbon atoms C^{1-4} of the uncoordinated ring. There is a pair of resonances at δ 72.4 and 69.4 due to the olefinic carbon atoms of 1,5-cyclooctadiene and a pair at δ 33.4 and 31.9 due to the methylene carbon atoms. The carbon atoms at the ring junction, $C^{9,10}$, are shifted slightly to higher frequency (ca. 10 ppm) relative to those in free naphthalene and are ca. 40 ppm to higher frequency of those in η^6-naphthalene complexes such as **1**, indicating that these carbon atoms are not coordinated to the metal atom. Similar trends are evident for the ring junction carbon atoms (C^{3a}, C^{7a}) in η^5- and η^3-indenyl complexes.[20,21] The fact that there are two olefinic ^{1}H and ^{13}C resonances, two methylene carbon resonances, and three or four methylene proton resonances due to 1,5-cyclooctadiene clearly indicates that complexes **3**−**7** have a less symmetrical

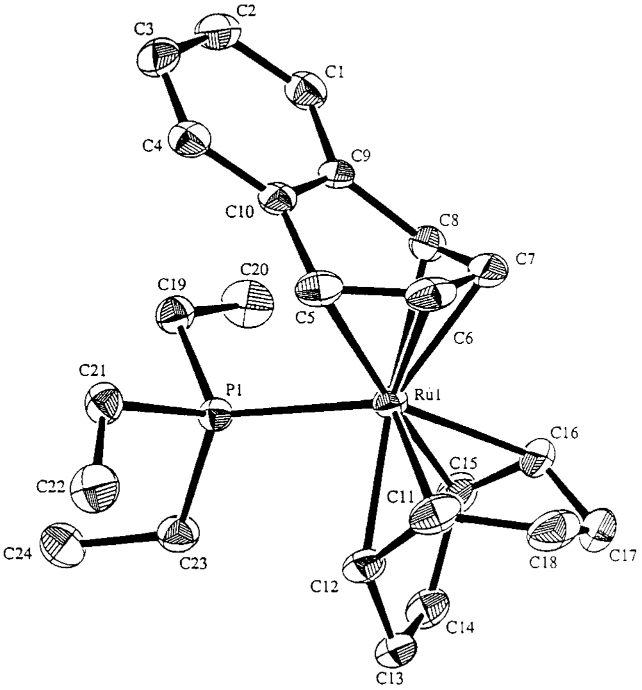

Figure 1. Molecular structure of Ru(η^4-$C_{10}H_8$)(η^4-1,5-C_8H_{12})(PEt_3) (**4**) with atom labeling (hydrogen atoms omitted); ellipsoids show 50% probability levels.

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(18) Schäufele, H.; Hu, D.; Pritzkow, S.; Zenneck, U. *Organometallics* **1989**, *8*, 396.

(19) Müller, J.; Gaede, P.; Hirsch, C.; Qiao, C. *J. Organomet. Chem.* **1994**, *472*, 329.

(20) Kohler, F. H. *Chem. Ber.* **1974**, *107*, 570.

(21) Baker, R. T.; Tulip, T. H. *Organometallics* **1986**, *5*, 839.

structure than Ru(η^6-$C_{10}H_8$)(η^4-1,5-C_8H_{12}) (**1**), and the appearance of two signals for the protons and carbon atoms of the coordinated naphthalene ring suggests that there is a mirror plane between $H^{5,6}$ and $H^{8,7}$. All the data are therefore consistent with a square pyramidal geometry for complexes **3**−**7**, with the 1,5-cyclooctadiene and η^4-naphthalene occupying the basal sites and the added ligand L in the axial site.

Although there is no evidence from the ^{31}P NMR spectrum for the presence of free PEt_3 in solutions of **4**, the coordinated PEt_3 is readily replaced at room temperature by trimethyl phosphite to give complex **5**. The rate of reaction is first order in **4** and independent of the concentration of $P(OMe)_3$, consistent with an initial, rate-determining dissociation of PEt_3 from **4**. More detailed studies were not undertaken because **4** and **5** undergo further reactions with PEt_3 and $P(OMe)_3$.

If complex **1** is treated in hexane with a deficiency of trimethylphosphine, triethylphosphine, or trimethyl phosphite (mol ratio 1 to 0.6−0.8) at room temperature over 24 h, the main products, isolated in 30−60% yield, are crystalline, yellow, binuclear compounds of the general formula (η^4-1,5-C_8H_{12})-Ru(μ-η^6:η^4-$C_{10}H_8$)Ru(η^4-1,5-C_8H_{12})(L) [L = PMe_3 (**8**), PEt_3 (**9**), and $P(OMe)_3$ (**10**)], in which one ring of naphthalene is η^4-bonded to a Ru(L)(η^4-1,5-C_8H_{12}) fragment while the other is η^6-bonded to a Ru(η^4-1,5-C_8H_{12}) fragment. This structural formulation is based on the ^1H and ^{13}C NMR spectra, which are listed in Tables 1 and 2, respectively, and on single-crystal X-ray structural analyses of complexes **9** and **10**, which also establish the *anti* arrangement of the metal atoms. The ^1H NMR spectra of complexes **8**−**10** contain two pairs of 2H multiplets, one at δ ca. 5.8 and 2.4 due to $H^{6,7}$ and $H^{5,8}$ of the η^4-ring, the other at δ ca. 4.6 and 5.2 due to $H^{1,4}$ and $H^{2,3}$ of the η^6-ring. Correspondingly, the ^{13}C NMR spectra of **8**−**10** show three resonances at δ ca. 115, 85, and 80 arising from the η^6-ring, similar to those observed for the η^6-ring in Ru(η^6-$C_{10}H_8$)(η^4-1,5-C_8H_{12}) (**1**),[2] together with a pair of resonances at δ ca. 90 and 50 assignable to $C^{6,7}$ and $C^{5,8}$ of the η^4-ring.

Complexes **9** and **10** have also been isolated in low yield from the decomposition of solutions of the corresponding mononuclear complexes, **4** and **5**, in toluene at room temperature over ca. 24 h in the strict absence of air. The corresponding binuclear complexes containing PMe_3 (**8**), $P(OEt)_3$, and *t*-BuNC could be detected by NMR spectroscopy from similar reactions but they could not be isolated. The decomposition of the mononuclear $P(OMe)_3$ complex **5** (ca. 0.06 M) in toluene-d_8 at 20 °C was studied semiquantitatively by monitoring the peaks due to naphthalene and 1,5-cyclooctadiene in the ^1H NMR spectrum. The main products identified were Ru(η^6-$C_{10}H_8$)-(η^4-1,5-C_8H_{12}) (**1**), free naphthalene, the dinuclear complex **10**, and Ru(η^4-1,5-C_8H_{12}){$P(OMe)_3$}$_3$ (see below). During the first few hours, the amounts of **1** and **10** increased simultaneously; the concentration of **1** then reached a maximum and remained almost constant while the concentration of **10** continued to increase until the ratio of **10** to **1** was ca. 4:1. After ca. 60 h, general decomposition of **10** to Ru(η^4-1,5-C_8H_{12}){$P(OMe)_3$}$_3$, naphthalene, and other unidentified products became evident. When the same experiment was carried out in the presence of **1** (0.02 M), more than 80% of **5** had disappeared after 18 h to give **10** as the main product, the process being accompanied by a steady decrease in the concentration of **1**. Thus **1** can provide the Ru(η^4-1,5-C_8H_{12}) fragment that coordinates to the uncoordinated aromatic ring of **5**.

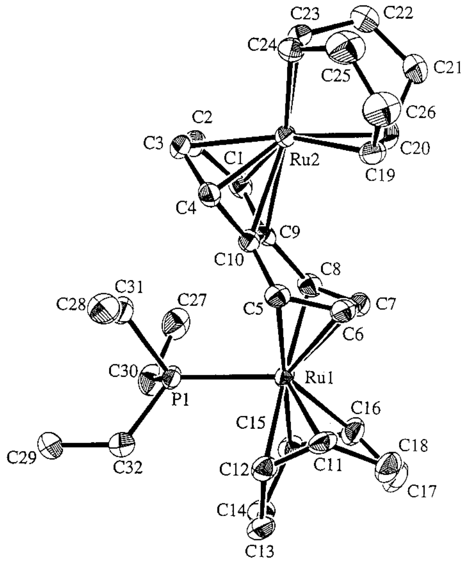

Figure 2. Molecular structure of $Ru_2(\mu^6:\eta^4\text{-}C_{10}H_8)(\eta^4\text{-}1,5\text{-}C_8H_{12})_2(PEt_3)$ (**9**) with atom labeling (hydrogen atoms omitted); ellipsoids show 50% probability levels.

Reaction of complexes **3**−**7** with 2 mol equiv of the appropriate ligands, or of complex **1** with 3 mol equiv of the ligands, causes complete displacement of the naphthalene to give the complexes RuL_3(η^4-1,5-C_8H_{12}) [L = PMe_3 (**11**), PEt_3 (**12**), $P(OMe)_3$ (**13**), $P(OEt)_3$ (**14**), and *t*-BuNC (**15**)]. With the exception of **12**, these can be isolated as solids at low temperature in 30−50% yield, but they decompose (even under argon) and readily lose ligand at room temperature; consequently, satisfactory elemental analyses could not be obtained. The known complexes $M(CO)_3$(η^4-1,5-C_8H_{12}) (M = Ru, Os)[22] also decompose readily, even at −20 °C under nitrogen. The ^1H NMR spectra of **14** and **15** show resonances due to 1,5-C_8H_{12} at δ 3.8−3.6 (4H), 2.9−2.8 (4H), and 2.7−2.6 (4H) together with signals characteristic of $P(OEt)_3$ and *t*-BuNC, respectively. The ^{13}C NMR spectra of **11**, **13**, **14**, and **15** contain resonances typical of coordinated 1,5-C_8H_{12} at δ ca. 70 (=CH) and 35 (CH_2), and complexes **11** − **14** also show the expected singlet ^{31}P NMR resonances.

X-ray Structural Analysis. The molecular structures of the triethylphosphine complexes **4** and **9** illustrated in Figures 1 and 2 are representative. Important bond lengths in **3**−**5** are listed in Table 4; those in **9** and **10** appear in Table 5. In all five complexes, the naphthalene ligand is folded at the terminal diene carbon atoms C(5) and C(8) as a consequence of the Ru-η^4-$C_{10}H_8$ interaction. The hinge angle [42.1°, 40.9° (**3**) (two independent molecules); 41.5°(**4**); 41.2°(**5**); 39.4°(**9**); 39.2°(**10**)] is clearly almost independent of the Group 15 donor and is only slightly reduced when the additional ruthenium atom is present on the aromatic ring. The angles are similar to those reported for other η^4-naphthalene complexes, e.g., TaCl(η^4-$C_{10}H_8$)(dmpe) (43°) (dmpe = $Me_2PCH_2CH_2PMe_2$),[14] Ru(η^6-C_6Me_6)(η^4-$C_{10}Me_8$) (41.5°, 43.3°),[23] Fe(η^6-C_6Me_6)(η^4-$C_{10}H_8$) (34°),[17] Fe{$P(OMe)_3$}$_3$(5-8η-1,4-$Me_2C_{10}H_6$) (41°),[18] [$N(PPh_3)_2$][$Mn(CO)_3$-(η^4-$C_{10}H_8$)] (37.1°),[16] Rh(η^5-C_5H_5)(η^4-$C_{10}H_8$) (34.8°, 36.1°),[19] [K(15-crown-5)$_2$]$_2$[Ti(η^4-$C_{10}H_8$)$_2$($SnMe_3$)$_2$] (31.0°, 35.4°),[24] and [K(15-crown-5)$_2$]$_2$ [Zr(η^4-$C_{10}H_8$)$_3$] (37.1°, 32.4°, 38.4°),[25] and for other η^4-arene complexes, e.g., Ru(η^6-C_6Me_6)(η^4-C_6Me_6) (42.8°)[26] and Rh(η^5-C_5Me_5)(η^4-C_6Me_6) (41.8°).[27] In both the

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[22] Deeming, A. J.; Ullah, S.; Domingos, A. J. P.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc., Dalton Trans.* **1974**, 2093.

[23] Hull, J. W., Jr.; Gladfelter, W. L. *Organometallics* **1984**, *3*, 605.

[24] Ellis, J. E.; Blackburn, D. W.; Yuen, P.; Jang, M. *J. Am. Chem. Soc.* **1993**, *115*, 11616.

[25] Jang, M.; Ellis, J. E. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1973.

[26] Huttner, G.; Lange, S. *Acta Crystallogr., Sect. B* **1972**, *28*, 2049.

Table 4. Selected Interatomic Distances (Å) for Ru(η^4-$C_{10}H_8$)(η^4-1,5-C_8H_{12})(L) [L = PMe_3 (**3**),[a] PEt_3 (**4**),[b] $P(OMe)_3$ (**5**)[c]]

	3	4	5		3	4	5
Ru−C(5)	2.258(6) (A) 2.246(8) (B)	2.271(5)	2.208(6)	Ru−C(6)	2.192(6) (A) 2.152(7) (B)	2.184(4)	2.173(6)
Ru−C(7)	2.179(7) (A) 2.153(7) (B)	2.166(5)	2.190(6)	Ru−C(8)	2.205(7) (A) 2.255(6) (B)	2.223(4)	2.264(6)
Ru−C(11)	2.221(8) (A) 2.160(7) (B)	2.171(4)	2.195(6)	Ru−C(12)	2.247(7) (A) 2.210(6) (B)	2.239(4)	2.211(6)
Ru−C(15)	2.201(7) (A) 2.219(7) (B)	2.209(5)	2.230(6)	Ru−C(16)	2.217(7) (A) 2.149(7) (B)	2.174(4)	2.210(6)
C(5)−C(6)	1.43(1) (A) 1.43(1) (B)	1.421(7)	1.447(9)	C(5)−C(10)	1.49(1) (A) 1.49(1) (B)	1.478(6)	1.480(8)
C(6)−C(7)	1.41(1) (A) 1.39(1) (B)	1.389(7)	1.389(9)	C(7)−C(8)	1.44(1) (A) 1.42(1) (B)	1.432(7)	1.440(9)
C(8)−C(9)	1.488(10) (A) 1.47(1) (B)	1.479(6)	1.481(8)	C(9)−C(10)	1.397(10) (A) 1.40(1) (B)	1.409(6)	1.395(8)
C(11)−C(12)	1.39(1) (A) 1.39(1) (B)	1.397(7)	1.391(9)	C(15)−C(16)	1.41(1) (A) 1.44(1) (B)	1.407(7)	1.382(8)

[a] Ru−P 2.363(2) (A), 2.403(2) (B); P−C(19) 1.792(10) (A), 1.841(8) (B); P−C(20) 1.819(9) (A), 1.841(9) (B); P−C(21) 1.838(8) (A), 1.836(8) (B). [b] Ru−P 2.412(1); P−C(19) 1.837(4); P−C(21) 1.849(5); P−C(23) 1.844(5); C(19)−C(20) 1.517(7); C(21)−C(22) 1.514(7); C(23)−C(24) 1.524(7). [c] Ru−P 2.322(2); P−O(1) 1.623(4); P−O(2) 1.608(4); P−O(3) 1.597(4); O(1)−C(19) 1.424(9); O(2)−C(20) 1.424(8); O(3)−C(21) 1.446(8).

Table 5. Selected Interatomic Distances (Å) for Ru_2(μ-η^6:η^4-$C_{10}H_8$)(η^4-1,5-C_8H_{12})$_2$(L) [L = PEt_3 (**9**),[a] $P(OMe)_3$ (**10**)[b]]

	9	10		9	10
Ru(1)−C(5)	2.280(4)	2.239(5)	Ru(1)−C(6)	2.183(4)	2.178(5)
Ru(1)−C(7)	2.174(4)	2.183(6)	Ru(1)−C(8)	2.248(4)	2.236(6)
Ru(1)−C(11)	2.192(4)	2.203(5)	Ru(1)−C(12)	2.242(4)	2.251(5)
Ru(1)−C(15)	2.227(4)	2.217(5)	Ru(1)−C(16)	2.191(4)	2.194(5)
Ru(2)−C(1)	2.266(4)	2.249(6)	Ru(2)−C(2)	2.265(4)	2.256(6)
Ru(2)−C(3)	2.214(4)	2.212(6)	Ru(2)−C(4)	2.215(4)	2.214(6)
Ru(2)−C(9)	2.318(4)	2.326(5)	Ru(2)−C(10)	2.326(4)	2.329(5)
Ru(2)−C(19)	2.118(4)	2.120(5)	Ru(2)−C(20)	2.142(5)	2.138(5)
Ru(2)−C(23)	2.126(4)	2.120(5)	Ru(2)−C(24)	2.129(5)	2.127(5)
C(5)−C(6)	1.439(6)	1.433(8)	C(5)−C(10)	1.479(6)	1.472(7)
C(6)−C(7)	1.393(7)	1.394(8)	C(7)−C(8)	1.419(6)	1.430(8)

[a] Ru−P 2.417(1); P−C(30) 1.856(5); P−C(31) 1.818(5); P−C(32) 1.863(6); C(27)−C(30) 1.500(8); C(28)−C(31) 1.526(7); C(29)−C(32) 1.532(7). [b] Ru−P 2.315(1); P−O(1) 1.633(4); P−O(2) 1.590(4); P−O(3) 1.605(4); C(27)−O(1) 1.401(7); C(28)−O(3) 1.439(7); C(29)−O(2) 1.445(7).

mononuclear and binuclear complexes, the Ru−C distances to the outer carbon atoms of the η^4-$C_{10}H_8$ unit, C(5) and C(8), are in the range 2.20−2.27 Å and are 0.03−0.10 Å greater than the distances to the inner carbon atoms, C(6) and C(7); this feature is also apparent in the structures of the other η^4-$C_{10}H_8$ complexes cited above. There is no significant difference between the distances to corresponding carbon atoms for the mononuclear and binuclear complexes. Possibly as a consequence of the presence of the strongly electron-donating Group 15 donors, the Ru−C separations to the inner and outer carbon atoms in all five complexes are generally 0.03−0.05 Å greater than the corresponding distances in Ru(η^6-C_6Me_6)(η^4-$C_{10}Me_8$).[23] In the more precisely determined structures of **4**, **5**, **9**, and **10**, there is a slight but distinct long−short−long trend in the C−C distances of the η^4-$C_{10}H_8$ unit. In all five complexes, the coordination geometry about the ruthenium atom bearing the η^4-$C_{10}H_8$ unit is approximately square pyramidal and is similar to that observed in related ruthenium(0) complexes, e.g., Ru{$P(OMe)_3$}(η^4-1,3,5-C_8H_{10})(η^4-1,5-C_8H_{12}),[28] Ru(L)(1-4η-C_8H_8)(1,2,5,6-η-C_8H_8) (L = CO, *t*-BuNC, PMe_3),[29] and Ru{$P(OMe)_3$}(*E,E*-$MeO_2CCH{=}CHCH{=}CHCO_2Me$)$_2$.[30] In **9** and **10**, the second six-membered ring is bound to a Ru(η^4-1,5-C_8H_{12}) fragment in an unsymmetrical η^6 mode similar to that observed in Ru(η^6-$C_{10}H_8$)(η^4-1,5-C_8H_{12}) (**1**),[3] the carbon atoms at the ring junction [C(9), C(10)] being significantly further (ca. 2.33 Å) from Ru(2) than are the remaining carbon atoms C(1)−C(5) (2.21−2.27 Å). The distortion differs from that observed in the benzene ring of Ru(η^6-C_6H_6)(η^4-1,5-C_8H_{12}), which has a shallow boat conformation.[31] The 1,5-C_8H_{12} ligands in all five complexes adopt the usual twist-boat conformation. The Ru(1)−C (1,5-C_8H_{12}) distances in the binuclear complexes **9** and **10** fall in the same range (2.19−2.25 Å) as those in the mononuclear complexes **3**−**5**. The Ru(2)−C distances in **9** and **10** are significantly less (2.12−2.14 Å), and are similar to those in Ru(η^6-C_6H_6)(η^4-1,5-$C_{10}H_{12}$).[31] The difference may be another consequence of the presence of the strong σ-donor Group 15 ligand attached to Ru(1).

The Ru−P distances in the mononuclear and binuclear trimethyl phosphite complexes [2.322(2) Å in **5**, 2.315(1) Å in **10**] are significantly less than those in the corresponding trialkylphosphine complexes [2.363(2) and 2.403(2) Å in independent molecules of **3**, 2.412(1) Å in **4**, 2.417(1) Å in **9**], consistent with the greater π-acceptor ability of the phosphite and higher σ-character in its Ru−P bond. A similar trend has been observed in the chromium(0) complexes $Cr(CO)_5L$ [L = $P(OPh)_3$, PPh_3].[32]

Discussion

η^6-Arene complexes, especially of C_6Me_6 and polycyclic aromatic hydrocarbons, are well established and can often be made by two-electron reduction of η^6-arene complexes of d^6 metal ions, e.g., Ru(η^6-C_6Me_6)(η^4-C_6Me_6) from [Ru(η^6-C_6Me_6)$_2$]$^{2+}$,[33,34] Ru(η^6-C_6Me_6)(η^4-$C_{10}Me_8$) from [Ru(η^6-C_6Me_6)(η^6-$C_{10}Me_8$)]$^{2+}$,[23] Rh(η^5-C_5Me_5)(η^4-C_6Me_6) from [Rh(η^5-C_5Me_5)(η^6-C_6Me_6)]$^{2+}$,[25] [$Cr(CO)_3$(η^4-arene)]$^{2-}$ from $Cr(CO)_3$(η^6-arene) (arene = $C_{10}H_8$, C_6H_6),[15,35] and [$Mn(CO)_3$(η^4-$C_{10}H_8$)]$^-$ from [$Mn(CO)_3$(η^6-$C_{10}H_8$)]$^+$.[16] The isolation of the η^4-naphthalene

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(27) Bowyer, W. J.; Merkert, J. W.; Geiger, W. E.; Rheingold, A. L. *Organometallics* **1989**, *8*, 191.

(28) Pertici, P.; Vitulli, G.; Porzio, W.; Zocchi, M.; Barili, P.; Deganello, G. *J. Chem. Soc., Dalton Trans.* **1983**, 1553.

(29) Bennett, M. A.; Neumann, H.; Willis, A. C.; Ballantini, V.; Pertici, P.; Mann, B. E. *Organometallics* **1997**, *16*, 2868.

(30) McKinney, R. J.; Colton, M. C. *Organometallics* **1986**, *5*, 1080.

(31) Schmid, H.; Ziegler, M. L. *Chem. Ber.* **1976**, *109*, 132.

(32) Plastas, H. J.; Stewart, J. M.; Grim, S. O. *Inorg. Chem.* **1973**, *12*, 265.

(33) Fischer, E. O.; Elschenbroich, C. *Chem. Ber.* **1970**, *103*, 162.

(34) Darensbourg, M. Y.; Muetterties, E. L. *J. Am. Chem. Soc.* **1978**, *100*, 7425.

(35) Leong, V. S.; Cooper, N. J. *J. Am. Chem. Soc.* **1988**, *110*, 2644.

complexes Ru(η^4-$C_{10}H_8$)(η^4-1,5-C_8H_{12})(L) (**3**−**7**) from Ru(η^6-$C_{10}H_8$)(η^4-1,5-C_8H_{12}) provides a rare example of the transformation from η^6- to η^4-arene coordination induced by addition of two-electron donor ligands. The only other established case for a coordinated arene appears to be the reaction of the tridentate ligand $MeSi(CH_2PMe_2)_3$ with Fe(η^6-C_6H_6)$(PMe_3)_2$ to give Fe(η^4-C_6H_6){$MeSi(CH_2PMe_2)_3$}.[36,37] There is evidence from IR spectra for an intermediate, possibly $Cr(CO)_3$(THF)(η^4-$C_{10}H_8$), in the displacement of naphthalene from $Cr(CO)_3$(η^6-$C_{10}H_8$) in THF;[38] this intermediate may also play a role in both intramolecular haptotropic and intermolecular arene exchange of $Cr(CO)_3$(η^6-$C_{10}H_8$) in THF.[39] However, there was no evidence from extended Hückel MO calculations for a *tetrahapto* intermediate in the ring slippage of $Cr(CO)_3$(η^6-$C_{10}H_8$), and an exocyclic *dihapto* intermediate was found to be energetically more favorable.[40,41] In this context, it is of interest to make a comparison with η^5-indenylmetal complexes, which undergo ligand replacement more readily than their η^5-cyclopentadienyl analogues, presumably via intermediates of lower hapticity.[42,43] Although η^3-indenyl and η^3-cyclopentadienyl complexes are known, reactions of η^5-indenyl complexes with ligands commonly lead to η^1-indenyl complexes as the first isolated products,[44,45] e.g., $Re(CO)_3$(η^5-C_9H_7) with PMe_3 gives $Re(CO)_3(PMe_3)_2$(η^1-C_9H_7), the presumed η^3-indenyl intermediate being undetectable. Some exceptions to this behavior are known, two of which occur with electron-rich complexes of later transition elements similar to the naphthalene complexes reported here. Thus, coordinated cyclooctene is displaced from Ir(η^5-C_9H_7)$(C_8H_{14})_2$ by ligands L(PMe_3,PMe_2Ph) to give Ir(η^3-C_9H_7)L_3,[46] and $[Fe(\eta^5\text{-}C_9H_7)(CO)_2]^-$ adds CO to give $[Fe(\eta^3\text{-}C_9H_7)(CO)_3]^-$.[47] A few cases are known involving compounds of the earlier transition elements, e.g., the reaction of V(η^5-C_9H_7)$_2$ with CO to give V(η^5-C_9H_7)(η^3-C_9H_7)$(CO)_2$,[48] and of $[M(\eta^5\text{-}C_9H_7)(CO)_2L_2]^+$ (M = Mo, W; L = NCMe, $HCONMe_2$) with an excess of L or other N-donors to give $[M(\eta^3\text{-}C_9H_7)(CO)_2L_3]^+$;[49] the last reaction appears not to occur with π-acceptor ligands such as isocyanides or tertiary phosphines.[50]

In conclusion, we believe that complexes **3**−**7** are good models for an intermediate in the stepwise replacement of η^6-naphthalene from a metal center. As expected, the η^4-naphthalene is easily displaced, not only by tertiary phosphines and *tert*-butyl isocyanide, but also by a range of 1,3-dienes and heterodienes; these reactions will be reported in full in a later paper. Further, the ready formation of the μ-η^6:η^4-naphthalene complexes **8**−**10** demonstrates the ability of the free aromatic ring in compounds **3**−**5** to bind a second transition metal fragment, in this case Ru(η^4-1,5-C_8H_{12}). A few heterobimetallic complexes containing μ-η^6:η^4-naphthalene are known, e.g., (η^6-C_6H_6)Ru(μ-η^4:η^6-$C_{10}Me_8$)$Cr(CO)_3$[23] and (η^5-C_5H_5)M(μ-η^6:η^4-$C_{10}H_8$)CoH{$R_2P(CH_2)_nPR_2$} (M = V, Cr; R = $CHMe_2$, C_6H_{11}; $n = 1-3$),[51] and it may be possible to make additional examples of this class by treatment of compounds **3**−**5** with the appropriate transition metal reagents.

Acknowledgment. We thank Professor A. D. Rae for helpful discussions about the X-ray structure of compound **3**.

Supporting Information Available: Crystallographic data, atomic coordinates and equivalent isotropic displacement parameters, anisotropic displacement parameters, interatomic distances and angles for non-hydrogen atoms, torsion angles for non-hydrogen atoms, interatomic distances, angles, and torsion angles for hydrogen atoms, and selected least-squares planes for complexes **3**, **4**, **5**, **9**, and **10**, together with a possible modulated approach to the description of the X-ray crystal structure of compound **3** (166 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

JA981027+

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(36) Boncella, J. M.; Green, M. L. H.; O'Hare, D. *J. Chem. Soc., Chem. Commun.* **1986**, 618.

(37) Boncella, J. M.; Green, M. L. H. *J. Organomet. Chem.* **1987**, *325*, 217.

(38) Eden, Y.; Fraenkel, D.; Cais, M.; Halevi, E. A. *Isr. J. Chem.* **1976−1977**, *15*, 223.

(39) Kündig, E. P.; Desobry, V.; Grivet, C.; Rudolph, B.; Spichiger, S. *Organometallics* **1987**, *6*, 1173.

(40) Albright, T. A.; Hofmann, P.; Hoffmann, R.; Lillya, C. P.; Dobosh, P. A. *J. Am. Chem. Soc.* **1983**, *105*, 3396.

(41) Howell, J. A. S.; Ashford, N. S.; Dixon, D. T.; Kola, J. C.; Albright, T. A.; Kang, S. K. *Organometallics* **1991**, *10*, 1852.

(42) O'Connor, J. M.; Casey, C. P. *Chem. Rev.* **1987**, *87*, 307 and references therein.

(43) Basolo, F. *New J. Chem.* **1994**, *18*, 19 and references therein.

(44) Casey, C. P.; O'Connor, J. M. *Organometallics* **1985**, *4*, 384.

(45) Foo, T.; Bergman, R. G. *Organometallics* **1992**, *11*, 1811.

(46) Merola, J.; Kacmarcik, R. T.; Van Engen, D. *J. Am. Chem. Soc.* **1986**, *108*, 329.

(47) Forschner, T. C.; Cutler, A. R.; Kullnig, R. K. *Organometallics* **1987**, *6*, 889.

(48) Kowalewski, R. M.; Rheingold, A. L.; Trogler, W. C.; Basolo, F. *J. Am. Chem. Soc.* **1986**, *108*, 2460.

(49) Ascenso, J. R.; Gonçalves, I. S.; Herdtweck, E.; Romão, C. C. *J. Organomet. Chem.* **1996**, *508*, 169.

(50) Calhorda, M. J.; Gamelas, C. A.; Gonçalves, I. S.; Herdtweck, E.; Romão, C. C.; Veiros, L. F. *Organometallics* **1998**, *17*, 2597.

(51) Jonas, K. *Pure Appl. Chem.* **1990**, *62*, 1169.