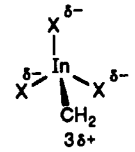
triphenylphosphonium or tmen derivatives show that ylid formation results in only a slight deshielding of the CH_2 protons relative to those in X_2InCH_2X, so that there is clearly little change in the electron density at the CH_2 site on ylid formation.

The structural results show that ylid formation is accompanied (or followed) by halide transfer, so that, whatever the ground state, the products are in fact derivatives of the formal structure



The synthetic consequences of the electronic structures and reactivities of these X_2InCH_2X species will be discussed elsewhere.

Acknowledgment. This work was supported in part by Operating Grants (to D.G.T.) from the Natural Sciences and Engineering Research Council of Canada. C.P. thanks the Universidade Federal da Paraiba for a leave of absence and the Conselho Nacional de Desenvolvimento Cientifico e Tecnologico, Brazil, for financial support for the early stages of this work at UFPb.

Supplementary Material Available: Tables of hydrogen atom coordinates and anisotropic temperature factors (5 pages); tables of calculated and observed structure factors (24 pages). Ordering information is given on any current masthead page.

Synthesis and Fluxional Behavior of Protonated 1,3-Diene Complexes of Ruthenium(0), Osmium(0), Rhodium(I), and Iridium(I) Containing 2,3-Dimethylene-5,6,7,8-dibenzobicyclo[2.2.2]octane (ddbo, $C_{18}H_{14}$). Single-Crystal X-ray Study of the Agostic Complex $[Ru(C_{18}H_{15})(\eta\text{-}C_6H_3Me_3)]PF_6$

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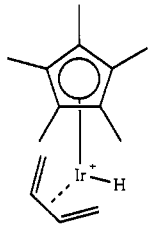
The 1,3-diene 2,3-dimethylene-5,6,7,8-dibenzobicyclo[2.2.2] octane (ddbo, $C_{18}H_{14}$, **6**) forms complexes $Ir(\eta\text{-}C_5H_5)(C_{18}H_{14})$ (**7**), $M(\eta\text{-}C_5Me_5)(C_{18}H_{14})$ [M = Rh (**8**), Ir (**9**)], and $M(\eta\text{-}1,3,5\text{-}C_6H_3Me_3)(C_{18}H_{14})$ [M = Ru (**10**), Os (**11**)], which react with aqueous HPF_6 or triflic acid to give fluxional monoprotonated cations $[Ir(\eta\text{-}C_5H_5)(C_{18}H_{15})]^+$ (**14**), $[Rh(\eta\text{-}C_5Me_5)(C_{18}H_{15})]^+$ (**12**), $[Ru(\eta\text{-}C_6H_3Me_3)(C_{18}H_{15})]^+$ (**13**), and $[Os(\eta\text{-}C_6H_3Me_3)(C_{18}H_{15})]^+$ (**15**). Crystals of **13**·PF_6 are orthorhombic, space group $P2_12_12_1$, with a = 14.243 (2) Å, b = 13.554 (2) Å, c = 12.894 (2) Å, and Z = 4. The structure was solved by heavy-atom methods and refined by least-squares analysis to R = 0.034 and R_w = 0.043 for 2020 unique observed reflections. The $C_{18}H_{15}$ moiety is bound to a (η^6-mesitylene)ruthenium unit through a η^3-enyl linkage [Ru–C(1) = 2.180 (8) Å, Ru–C(2) = 2.196 (7) Å, Ru–C(17) = 2.148 (7) Å] and a two-electron, three-center interaction Ru–H(18C)–C(18) to the terminal methyl group of the butenyl moiety [Ru–C(18) = 2.357 (9) Å, C(18)–H(18C) = 0.98 (8) Å, Ru–H(18C) = 1.81 (8) Å, ∠C(17)–C(18)–H(18C) = 108 (5)°, ∠C(18)–H(18C)–Ru = 112 (6)°]. The NMR (^1H, ^{13}C) spectra of the rhodium complex **12** at −60 °C are consistent with a similar ground-state agostic η^3-methallyl structure, but unexpectedly, the ^1H NMR spectrum of **13** at −100 °C resembles that expected for a hydrido (1,3-diene) structure. It is suggested that in **13** reversible C–H bond cleavage occurs more easily than M–H bond cleavage, whereas **12** shows the more usual reverse behavior. The NMR and IR spectra of **14** show this complex to have a hydrido 1,3-diene structure; the same is probably true for **15**, although a η^3-methallyl structure with a strong agostic interaction cannot be excluded. Treatment of **13** and **15** with *tert*-butyl isocyanide causes irreversible hydride transfer to ddbo, giving $[M(\eta\text{-}C_6H_3Me_3)(C_{18}H_{15})(CN\text{-}t\text{-}Bu)]PF_6$ [M = Ru (**17**), Os (**16**)].

It has been shown[1] that protonation of 1,3-diene complexes of the type $Ir(\eta\text{-}C_5Me_5)$(diene) and $Os(\eta\text{-}1,3,5\text{-}C_6H_3Me_3)$(diene) (diene = 1,3-cyclohexadiene or 2,3-dimethylbutadiene) with strong acids containing poorly coordinating anions gives cationic hydrido diene complexes **1** and **2**. These are fluxional only above room temperature owing to reversible migration of the hydride ligand between the metal atom and the diene. Similar protonation of the rhodium(I) complexes $Rh(\eta\text{-}C_5Me_5)$(1,3-diene) gives highly fluxional species whose ^1H and ^{13}C NMR spectra at low temperature are consistent with an agostic structure **3** similar to those established by single-crystal X-ray and



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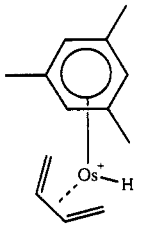

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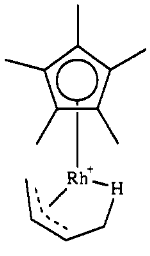
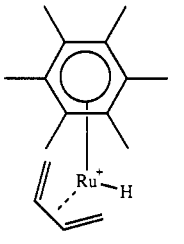


3

neutron diffraction studies of $Fe\{P(OMe)_3\}_3(\eta^3\text{-}C_8H_{13})$[2] and $Mn(CO)_3(\eta^3\text{-}C_6H_8CH_3)$.[3,4] With increasing temperature, two independent processes occur in which first the M–H and then the C–H bonds are cleaved reversibly, as illustrated for the case of an acyclic 1,3-diene in Figure 1. The behavior resembles that of $Mn(CO)_3(\eta^3\text{-}C_6H_9)$[3] although the activation energies for the cationic rhodium system are clearly lower. The monoprotonated $Ru(\eta\text{-}C_6R_6)$(1,3-diene) (R = H, Me) complexes are also highly fluxional, but the patterns of the low-temperature ^1H and ^{13}C NMR spectra more closely resemble those expected for a hydrido 1,3-diene complex 4, analogous to 2, and are at first sight inconsistent with an agostic structure 5, analogous to 3. Unfortunately, the protonated ruthenium compounds derived from 1,3-cyclohexadiene or 2,3-dimethylbutadiene could not be obtained in a form suitable for single-crystal X-ray analysis, and we therefore turned to analogous complexes formed by a bulkier 1,3-diene, viz. 2,3-dimethylene-5,6,7,8-dibenzobicyclo[2.2.2]octane, $C_{18}H_{14}$ (6) (Chart I). The results are reported in this paper.



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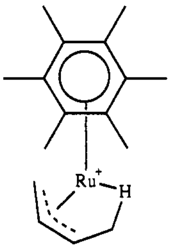

5 (R = H, Me)

Experimental Section

Proton NMR spectra were measured on Varian HA100, Jeol FX200, Bruker CXP200, and Bruker HFX270 instruments with $(CH_3)_4Si$ or CD_2Cl_2 as internal references. Carbon-13 NMR spectra were recorded at 15.04, 50.10, 50.29, and 67.89 MHz on Jeol FX60, Jeol FX200, Bruker CXP200, and Bruker HFX270 spectrometers, respectively. IR spectra were taken on a Perkin-Elmer 683 grating instrument. Mass spectra were recorded at 70 eV on a VG Micromass 7070F instrument. All reactions were carried out under high-purity nitrogen or argon with use of standard Schlenk-tube, inert-atmosphere techniques or in a Vacuum Atmospheres HE-193-1 inert-atmosphere box. Elemental analyses for the new complexes and NMR (^1H, ^{13}C) data for the neutral complexes of ddbo are in Tables I and II, respectively. The labeling of the protons and carbon atoms is as shown in the structural diagrams of 6, 12, and 14–17 (Chart I).

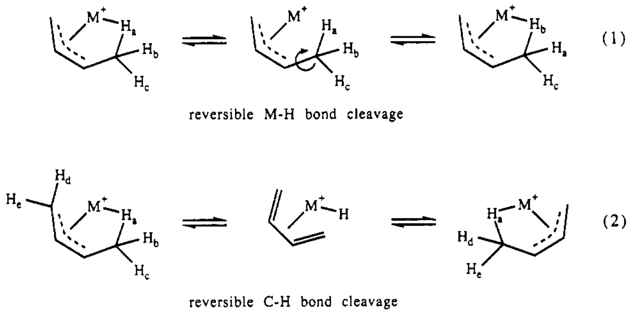

Figure 1. Fluxional processes in an acyclic (1,3-diene)metal complex.

Table I. Elemental Analyses and Mass Spectrometric Data for Complexes Derived from ddbo (6)

complex	calcd, % C	calcd, % H	found, % C	found, % H	m/z[a]
$Ir(\eta\text{-}C_5H_5)(C_{18}H_{14})$ (7)	56.7	3.9	57.1	3.9	488
$Rh(\eta\text{-}C_5Me_5)(C_{18}H_{14})$ (8)	71.8	6.2	72.1	6.4	468
$Ir(\eta\text{-}C_5Me_5)(C_{18}H_{14})$ (9)	60.3	5.2	60.0	5.3	558
$Ru(\eta\text{-}C_6H_3Me_3)(C_{18}H_{14})$ (10)	71.8	5.8	69.9	5.7	452
$Os(\eta\text{-}C_6H_3Me_3)(C_{18}H_{14})$ (11)	60.9	4.9	60.1	5.2	542
$[Rh(\eta\text{-}C_5Me_5)(C_{18}H_{15})]PF_6$ (12)[b]	54.7	4.9	54.7	5.0	
$[Ru(\eta\text{-}C_6H_3Me_3)(C_{18}H_{15})]PF_6$ (13)	54.3	4.6	54.4	4.6	
$[Os(\eta\text{-}C_6H_3Me_3)(C_{18}H_{15})]CF_3SO_3$ (15)[c]	48.7	3.9	49.0	4.2	
$[Os(\eta\text{-}C_6H_3Me_3)(C_{18}H_{15})(t\text{-}BuNC)]PF_6$ (16)[d]	49.9	4.7	50.2	4.9	
$[Ru(\eta\text{-}C_6H_3Me_3)(C_{18}H_{15})(t\text{-}BuNC)]$-$PF_6$ (17)[e]	56.5	5.3	55.6	5.4	

[a] Parent ion. [b] % P: calcd, 5.0; found, 5.0. [c] % F: calcd, 8.25; found, 8.4. [d] % N: calcd, 1.8; found, 1.6. [e] % N: calcd, 2.1; found, 2.0.

Starting Materials. The compounds $[RhCl_2(\eta\text{-}C_5Me_5)]_2$,[5] $[IrCl_2(\eta\text{-}C_5Me_5)]_2$,[6] $[RuCl_2(\eta\text{-}1,3,5\text{-}C_6H_3Me_3)]_2$,[7] $[OsCl_2(\eta\text{-}1,3,5\text{-}C_6H_3Me_3)]_2$,[8] $[IrCl(C_8H_{14})_2]_2$,[9] and $NaC_5H_5{\cdot}MeOCH_2CH_2OMe$ (CpNa·DME)[10] were made by the appropriate literature procedures. 2,3-Dimethylene-5,6,7,8-dibenzobicyclo[2.2.2]octane (ddbo, $C_{18}H_{14}$) (6) was prepared by a four-step procedure starting with the Diels–Alder reaction of anthracene with fumaryl chloride.[11]

Preparation of $Ir(\eta\text{-}C_5H_5)(C_{18}H_{14})$ (7). A slurry of $[IrCl(C_8H_{14})_2]_2$ (750 mg, 0.84 mmol) in dichloromethane (8 mL) was treated with thallium(I) acetylacetonate (530 mg, 1.75 mmol), and the mixture was stirred for 2 h. After filtration to remove a gray sediment, the supernatant liquid was evaporated to dryness to yield a brown solid, $Ir(acac)(C_8H_{14})_2$. This was dissolved in dichloromethane (10 mL), a slight excess of ddbo (400 mg, 1.74 mmol) was added, and the mixture was stirred at room temperature for 4 h. Evaporation to dryness gave a yellow oil that became a brown solid, presumed to be $Ir(C_{18}H_{14})(acac)$, on washing with hexane. This was dissolved in THF (15 mL), and to the stirred solution was added CpNa·DME (330 mg, 1.85 mmol). The dark mixture was stirred at room temperature for 4 h, treated with a few milliliters of water to decompose the excess of NaC_5H_5, and evaporated to dryness in a vacuum. The residue was extracted with toluene (40 mL) and filtered; the extract was concentrated under reduced pressure. Product 7 was obtained as light brown crystals on addition of hexane and cooling overnight in the refrigerator. The yield was 390 mg (50% based on $[IrCl(C_8H_{14})_2]_2$).

Preparation of $M(\eta\text{-}C_5Me_5)(C_{18}H_{14})$ [M = Rh (8), Ir (9)] and $M'(\eta\text{-}C_6H_3Me_3)(C_{18}H_{14})$ [M = Ru (10), Os (11)]. A mixture of $[MCl_2(\eta\text{-}C_5Me_5)]_2$ (M = Rh, Ir) or $[M'Cl_2(\eta\text{-}C_6H_3Me_3)]_2$ (M' = Ru, Os) (ca. 500 mg), anhydrous Na_2CO_3 (500 mg) and ddbo (6) (ca 400 mg, 2- to 3-fold excess) in 2-propanol (20 mL) was heated at 70–80 °C with stirring for 3–4 h. The resulting brown solution was allowed to cool to room temperature and evaporated to dryness in a vacuum. The residue was extracted with hexane

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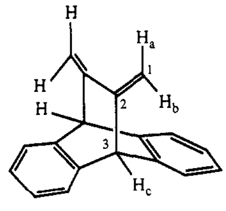
Chart I



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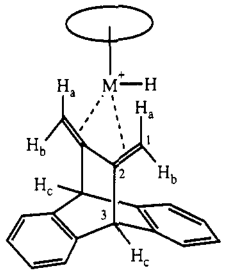
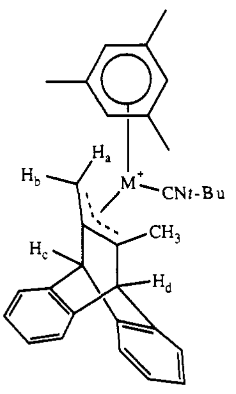
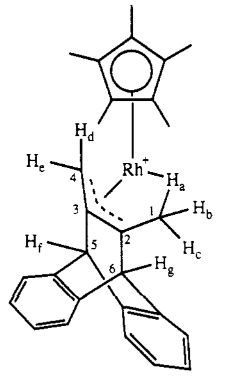


13a (M = Ru; ⬭ = η^6-$C_6H_3Me_3$)
14 (M = Ir; ⬭ = η^5-C_5H_5)
15 (M = Os; ⬭ = η^6-$C_6H_3Me_3$)



16 (M = Os)
17 (M = Ru)



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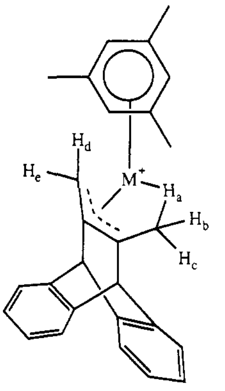
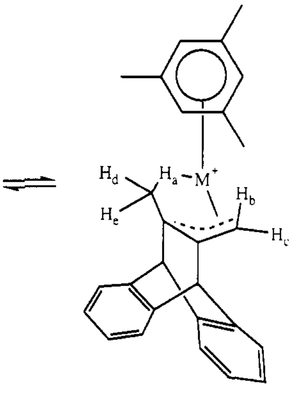


13b



13c (M = Ru)

(2 × 20 mL), and the yellow solution was filtered. Evaporation to dryness gave an oily solid. The compound was purified by chromatography on a column of neutral alumina (grade 1) made up in 60–80 °C petroleum ether and was eluted with ether/petroleum ether (1:4 v/v). Samples for analysis were recrystallized from hexane at -78 °C. Yields were 20% (**8**), 30% (**9**), 65% (**10**), and 50% (**11**).

Protonation of Complexes 7-11. The same general procedure was used in all cases. A solution of the complex (200–300 mg) in ether (10–20 mL) was stirred and treated with a few drops of 60% aqueous HPF_6 or anhydrous CF_3SO_3H. The salts $[Rh(\eta$-$C_5Me_5)(C_{18}H_{15})]PF_6$ (**12**), $[Ru(\eta$-$C_6H_3Me_3)(C_{18}H_{15})]PF_6$ (**13**), $[Ir(\eta$-$C_5H_5)(C_{18}H_{15})]PF_6$ (**14**), and $[Os(\eta$-$C_6H_3Me_3)(C_{18}H_{15})]Y$ (Y = PF_6, CF_3SO_3) (**15**) precipitated immediately. After removal of the supernatant liquid by decantation, the salts were washed with ether and dried in a vacuum. Complexes **12** and **15** could be recrystallized from dichloromethane/ether; **13** was not very soluble in dichloromethane but could be recrystallized from acetone/ether. Data for the complexes are as follows.

12. ^1H NMR (CD_2Cl_2, 270 MHz, 20 °C): δ 7.35–7.15 (m, 8 H, C_6H_4), 4.79 (br, s, 2 H, H_f, H_g), 1.36 (s, 15 H, C_5Me_5). ^1H NMR (CD_2Cl_2, 270 MHz, -60 °C): δ 7.53–7.09 (m, 8 H, C_6H_4), 5.01 (m, 1 H, H_e), 4.87 (s, 1 H, H_f or H_g), 4.65 (s, 1 H, H_g or H_f), 2.93 (m, 1 H, H_d), 1.28 (s, 15 H, C_5Me_5), 1.25 (m, 3 H, H_a, H_b, H_c). ^{13}C NMR (CD_2Cl_2, 50 MHz, -60 °C): 143.6, 141.6, 128.4, 126.9, 126.6, 125.9, 124.1, 123.3, 122.8 (C_6H_4), 103.4 (J_{RhC} = 1 Hz, C^3), 100.1 (J_{RhC} = 7.7 Hz, C_5Me_5), 71.0 (J_{CH} = 165 Hz, J_{RhC} = 9.0 Hz, C^4), 66.5 (J_{RhC} = 10.7 Hz, C^2), 53.0 (J_{CH} ca. 130 Hz, partly obscured by CD_2Cl_2 resonance, C^5 or C^6), 48.6 (J_{CH} = 130 Hz, C^6 or C^5), 14.9 (J_{CH} = 129 Hz, C^1), 8.8 (J_{CH} = 129 Hz, C_5Me_5).

13. ^1H NMR (CD_2Cl_2, 200 MHz, 20 °C): δ 7.41–7.10 (m, 8 H, C_6H_4), 5.03 (s, 3 H, C_6H_3), 4.96 (s, 2 H, H_f, H_g), 2.10 (s, 9 H, $C_6H_3Me_3$), -1.13 (m, 5 H, H_a, H_b, H_c, H_d, H_e). ^1H NMR (CD_2Cl_2, 200 MHz, -100 °C): 7.13 (m, 8 H, C_6H_4), 4.89 (s, 5 H, H_f, H_g, C_6H_3), 2.45 (br m, 2 H, H_e, H_c), 1.92 (s, 9 H, $C_6H_3Me_3$), -0.50 (br m, 2 H, H_b, H_d), -10.26 (br s, 1 H, H_a). ^{13}C NMR (CD_3NO_2, 50 MHz, 20 °C): 146.0, 127.8, 127.5, 125.8, 125.7 (C_6H_4), 105.8 (C_3Me_3), 101.1 (C^2, C^3), 89.6 (C_3H), 52.9 (C^5, C^6), 19.6 ($C_6H_3Me_3$), 19.2 (br, C^1, C^4).

14. ^1H NMR (CD_2Cl_2, 270 MHz, 20 °C): δ 7.5–7.1 (m, 8 H, C_6H_4), 5.22 (s, 7 H, H_c, C_5H_5), 1.63 (br m, 5 H, H_a, H_b, IrH). ^1H NMR (CD_2Cl_2, 270 MHz, -40 °C): 7.5–7.1 (m, 8 H, C_6H_4), 5.23 (s, 2 H, H_c), 4.24 (d, 2 H, J = 1.6 Hz, H_b), 2.31 (m, 2 H, H_a), -15.55 (s, 1 H, IrH). ^{13}C NMR (CD_2Cl_2, 68 MHz, -60 °C): δ 146.0, 144.5, 142.6, 141.3, 128–122 (C_6H_4), 113.1 (C^2), 87.1 (J = 189 Hz, C_5H_5), 49.8 (J = 146 Hz, C^3), 28.0 (J = 167 Hz, C^1). IR (KBr): 2185 cm^{-1} [m, ν(IrH)].

15. ^1H NMR (CD_2Cl_2, 200 MHz, -80 °C): δ 7.45–7.04 (m, 8 H, C_6H_4), 5.08 (br m, 2 H, H_c), 5.00 (s, 3 H, C_6H_3), 3.45 (d, 2 H, J = 3Hz, H_b), 2.28 (s, 9 H, $C_6H_3Me_3$), 1.48 (poorly resolved t, J = 3Hz, H_a), -13.53 (s, 1 H, OsH). ^{13}C NMR (CD_2Cl_2, 50 MHz, -20 °C): δ 143.7, 143.3, 126.9, 126.6, 125.1, 124.9 (C_6H_4), 106.6 (C^2), 106.4 (C_3Me), 89.3 (J = 174 Hz, C_3H), 50.7 (J = 145 Hz, C^3), 21.0 (J = 162 Hz, C^1), 19.4 (J = 130 Hz, $C_6H_3Me_3$).

Reaction of $[Os(\eta$-$C_6H_3Me_3)(C_{18}H_{15})]PF_6$ (15) with *tert*-Butyl Isocyanide. A solution of **15** (210 mg, 0.31 mmol) in dichloromethane (10 mL) was treated with *t*-BuNC (50 μL, 1 equiv). The yellow solution darkened somewhat. After 1 h solvent was removed under reduced pressure to give a yellow oily solid. This was washed with hexane and recrystallized from CH_2Cl_2/hexane and acetone/ether to give $[Os(\eta$-$C_6H_3Me_3)(C_{18}H_{15})(t$-$BuNC)]PF_6$ (**16**) as a yellow solid in ca. 50% yield. ^1H NMR (CD_2Cl_2, 200 MHz): δ 7.44–6.90 (m, C_6H_4), 5.32 (s, C_6H_3), 4.68 (s, H_c or H_d), 4.55 (s, H_d or H_c), 3.90 (d, J = 2.7 Hz, H_b), 2.41 (d, J = 2.9 Hz, H_a), 2.28 (s, $C_6H_3Me_3$), 1.42 (s, *t*-Bu), 1.38 (s, CH_3 of methallyl).

The corresponding ruthenium complex $[Ru(\eta$-$C_6H_3Me_3)(C_{18}H_{15})(t$-$BuNC)]PF_6$ (**17**) was prepared similarly from a solution of **13** (250 mg, 0.42 mmol) in CH_2Cl_2 (20 mL) and *t*-BuNC (51 μL). The product precipitated on addition of ether as a pale yellow oil that solidified on scratching and was recrystallized twice from CH_2Cl_2/ether. The yield was 185 mg (65%). ^1H NMR (CD_2Cl_2, 200 MHz): δ 7.4–6.9 (m, C_6H_4), 5.32 (s, C_6H_3), 4.74 (s, H_c or H_d), 4.64 (s, H_d or H_c), 3.66 (d, J = 2.9 Hz, H_b), 2.22 (d, J = 2.7 Hz, H_a), 2.15 (s, $C_6H_3Me_3$), 1.20 (s, CH_3 of methallyl).

Crystallography. Crystallographic data are as follows. $C_{27}H_{27}RuPF_6$ (**13**), fw 597.5, orthorhombic, space group $P2_12_12_1$,

Table II. ^{1}H and ^{13}C Chemical Shifts (δ) and Coupling Constants (J) for Neutral Complexes of ddbo (6)[a]

	^{1}H					^{13}C				
	η^6-arene, η^5-C_5H_5, or η^5-C_5Me_5	ddbo				η^6-arene, η^5-C_5H_5, or η^5-C_5Me_5	ddbo			
complex		Ar	Ha	H_b	H_c		Ar	C^1	C^2	C^3
Ir(η-C_5H_5)-($C_{18}H_{14}$) (7)[b]	4.57 (s)	7.35–6.98 (m)	0.13 (d, J = 2.2)	2.94 (d, J = 2.2)	4.61 (s)	76.5	125.7, 125.5, 124.3, 122.6	18.9	93.5	51.7
Rh(η-C_5Me_5)-($C_{18}H_{14}$) (8)[c]	1.65 (s)	7.2–6.8 (m)	0.62 (m)	1.94 (m)	4.53 (s)	94.8 (d, C_5, J_{RhC} = 5.9), 11.1 (Me)	147.6, 144.8, 125.2, 123.8, 123.2	34.0 (J_{RhC} = 16.1)	94.8	52.9
Ir(η-C_5Me_5)-($C_{18}H_{14}$) (9)[c]	1.67 (s)	7.2–6.8 (m)	0.25 (d, J = 1.8)	2.18 (d, J = 1.9)	4.49 (s)	88.9 (C_5), 11.0 (Me)	147.3, 144.5, 125.1, 125.0, 123.7, 123.4	22.0	88.9	52.3
Ru(η-$C_6H_3Me_3$)-($C_{18}H_{14}$) (10)[d]	4.54 (s, C_6H_3), 1.78 (s, Me)	7.3–6.9 (m)	0.11 (d, J = 2.0)	2.02 (d, J = 1.8)	4.46 (s)	85.5 (J_{CH} = 160, CH), 20.0 (J_{CH} = 126, Me)	147.5, 146.2, 125.0, 124.8, 123.8, 123.2	27.8 (J_{CH} = 150, 158)	90.2	53.4 (J_{CH} = 142)
Os(η-$C_6H_3Me_3$)-($C_{18}H_{14}$) (11)[e]	4.43 (s, C_6H_3), 1.89 (s, Me)	7.3–6.8 (m)	0.09 (d, J = 2.5)	2.34 (d, J = 2.5)	4.40 (s)	77.2 (J_{CH} = 167, CH), 20.1 (J_{CH} = 128)	147.0, 145.6, 125.1, 124.7, 123.8, 123.2	19.4 (J_{CH} = 149, 160)	81.5	53.6 (J_{CH} = 141)

[a] Coupling constants are in Hz; those without suffix are J_{HH}; labeling of protons and carbon atoms is as shown in 6. [b] CD_2Cl_2, 200 MHz (^{1}H), 50 MHz (^{13}C). [c] C_6D_6, 200 MHz (^{1}H), 50 MHz (^{13}C). [d] C_6D_6, 100 MHz (^{1}H), 15 MHz (^{13}C). [e] C_6D_6, 100 MHz (^{1}H), 50 MHz (^{13}C).

a = 14.243 (2) Å, b = 13.554 (2) Å, c = 12.894 (2) Å, V_c = 2489.2 Å^3, T = 22 ± 1 °C, ρ_{calcd} = 1.59 g cm^{-3}, ρ_{obsd} = 1.59 (1) g cm^{-3}, Z = 4, μ(Cu Kα) = 62.7 cm^{-1}. Diffraction-quality crystals were grown by vapor diffusion (acetone/ether) under a nitrogen atmosphere. Reflection intensities were measured with a Philips PW1100 diffractometer operating in θ–2θ scan mode [2° min^{-1} in 2θ, 2 × 10 s backgrounds at extremes, Cu Kα radiation, graphite monochromator, $+h$, $+k$, $+l$, $3 < 2\theta < 120°$, 3 standards (800, 080, 008) every 120 min, 2% degradation, 2132 unique reflections, 2020 observed ($I > 3\sigma$), T = 295 (2) K, specimen crystal dimensions 0.14 × 0.12 × 0.16 × 0.30 mm perpendicular to bounding forms {101}, {$\bar{2}$01}, {011}, and {0$\bar{1}$1}]. Quoted unit cell dimensions are from least-squares analysis of setting angles for 12 carefully centered, well-dispersed reflections with $37 < 2\theta < 47°$ (Picker FACS-1 diffractometer, λ = 0.709 26 Å).

The reflection data were corrected for crystal degradation[12] and for specimen absorption effects,[13] and the structure was solved by conventional Patterson and Fourier techniques. Refinement was accomplished by full-matrix least-squares analysis on F (SHELX 76)[18] with reflection weights $w = [\sigma^2(F_o) + 0.002F_o^2]^{-1}$. All hydrogen atoms except for one atom on one methyl group could be observed in difference Fourier maps. Phenyl hydrogen atoms were included in the scattering model at computed sites, and their coordinates were not refined. Methyl hydrogen atoms were included and refined as rigid methyl group components (all C–H = 0.95 Å). Global group thermal parameters were specified for (1) methyl hydrogen atoms of the arene ligand, (2) aromatic hydrogen atoms of the arene ligand, and (3) aromatic hydrogen atoms of the olefinic ligand. For the butenyl and bridgehead hydrogen atoms of the olefinic ligand both coordinates and individual parameters were refined. Atomic scattering factors and anomalous dispersion corrections supplied by SHELX[13] were used for P, F, C, and H, and values from ref 14 were used for Ru. At convergence R = 0.034, R_w = 0.043, $-0.45 < \Delta\rho < 0.56$ e Å^{-3}, maximum Δ/σ = 0.09, and extinction coefficient x (in $F_c^{corr} = F_c - 0.0001xF_c^2$) = 0.0022. The enantiomeric structure has R_w = 0.065 and can be rejected with better than 99.9% confidence.[15] Final atomic coordinates, together with estimated standard errors, and equivalent isotropic thermal parameters are listed in Table III. Listings of hydrogen atom parameters, anisotropic thermal parameters, and observed and calculated structure factor amplitudes have been included in the supplementary material.

Results and Discussion

The starting diene complexes were made by standard procedures. Treatment of the cyclooctene iridium(I) acetylacetonato complex Ir(acac)(C_8H_{14})$_2$ with ddbo (6) completely displaced cyclooctene to give a compound presumed to be Ir(acac)($C_{18}H_{14}$), which reacted with C_5H_5Na to give Ir(η-C_5H_5)($C_{18}H_{14}$) (7) as a slightly air-sensitive yellow solid. The complexes M(η-C_5Me_5)($C_{18}H_{14}$) [M = Rh (8), Ir (9)] and M′(η-$C_6H_3Me_3$)($C_{18}H_{14}$) [M′ = Ru (10), Os (11)] were made by heating the appropriate metal dichloride dimer, [MCl$_2$(η-C_5Me_5)]$_2$ or [M′Cl$_2$(η-$C_6H_3Me_3$)]$_2$, with the diene and 2-propanol in the presence of anhydrous Na_2CO_3.[1]

The ^{1}H NMR spectra of complexes 7–11 show a pair of doublets at δ ca. 0.1–0.2 and ca. 2–3 (J ca 2 Hz) due to the inner and outer diene protons H_a and H_b. The shielding of ca. 5 ppm for H_a in the complexes relative to the free diene is characteristic of this type of compound. The remaining resonances are a singlet at δ ca. 4.5 due to the bridgehead protons H_c and multiplets in the usual aromatic region; these change little on coordination.

In the ^{1}H-coupled ^{13}C NMR spectra of 7–11 the resonance due to the outer carbon atoms C^1 appears as a doublet of doublets (J ca. 150, 160 Hz) at ca. 80 ppm to low frequency of the corresponding resonance in 6 and the

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Table III. Atomic Coordinates[a] and Equivalent Isotropic Thermal Parameters (Å^2)[b,c] for $[Ru(C_{18}H_{15})(\eta\text{-}C_6H_3Me_3)]PF_6$ (13)

atom	x/a	y/b	z/c	U_{eq}
Ru	0.1466 (0)	0.2397 (0)	−0.1218 (0)	0.034
P	0.3805 (2)	0.3140 (2)	0.4297 (2)	0.067
C(1)	0.0365 (7)	0.2936 (7)	−0.0188 (8)	0.055
C(2)	0.0653 (5)	0.1988 (5)	0.0164 (6)	0.040
C(3)	0.0986 (6)	0.1701 (6)	0.1248 (7)	0.045
C(4)	0.1914 (5)	0.1176 (5)	0.1179 (6)	0.038
C(5)	0.2712 (6)	0.1378 (7)	0.1762 (7)	0.061
C(6)	0.3473 (7)	0.0809 (8)	0.1639 (8)	0.069
C(7)	0.3494 (6)	0.0045 (8)	0.0965 (7)	0.073
C(8)	0.2690 (6)	−0.0199 (6)	0.0371 (7)	0.056
C(9)	0.1911 (5)	0.0387 (5)	0.0492 (6)	0.039
C(10)	0.0965 (5)	0.0228 (6)	−0.0036 (6)	0.042
C(11)	0.0261 (5)	0.0115 (6)	0.0847 (6)	0.047
C(12)	−0.0347 (6)	−0.0669 (7)	0.1010 (7)	0.065
C(13)	−0.0931 (7)	−0.0654 (9)	0.1869 (10)	0.079
C(14)	−0.0908 (7)	0.0111 (10)	0.2555 (9)	0.090
C(15)	−0.0304 (7)	0.0911 (8)	0.2404 (8)	0.077
C(16)	0.0265 (5)	0.0906 (6)	0.1549 (6)	0.048
C(17)	0.0688 (5)	0.1205 (5)	−0.0533 (5)	0.039
C(18)	0.0216 (7)	0.1307 (9)	−0.1569 (7)	0.060
C(19)	0.2974 (5)	0.2412 (5)	−0.0854 (6)	0.041
C(20)	0.2602 (5)	0.3377 (5)	−0.0724 (6)	0.044
C(21)	0.2137 (5)	0.3834 (6)	−0.1557 (7)	0.050
C(22)	0.2001 (5)	0.3342 (6)	−0.2512 (6)	0.050
C(23)	0.2391 (5)	0.2391 (6)	−0.2612 (6)	0.048
C(24)	0.2920 (5)	0.1931 (6)	−0.1828 (6)	0.043
C(201)	0.2707 (8)	0.3886 (7)	0.0298 (8)	0.069
C(221)	0.1446 (7)	0.3805 (8)	−0.3371 (8)	0.076
C(241)	0.3377 (7)	0.0926 (6)	−0.1981 (7)	0.064
F(1)	0.4158 (9)	0.2267 (8)	0.3660 (9)	0.218
F(2)	0.3559 (13)	0.3613 (10)	0.3263 (9)	0.286
F(3)	0.3416 (12)	0.3977 (8)	0.4885 (9)	0.244
F(4)	0.3978 (11)	0.2635 (11)	0.5319 (7)	0.235
F(5)	0.4719 (9)	0.3485 (17)	0.4271 (16)	0.395
F(6)	0.2846 (9)	0.2721 (17)	0.4239 (12)	0.311
H(1A)	0.057 (6)	0.347 (6)	0.016 (6)	0.04 (2)
H(1B)	−0.021 (5)	0.297 (5)	−0.062 (5)	0.03 (2)
H(3)	0.104 (6)	0.216 (6)	0.153 (6)	0.05 (3)
H(10)	0.092 (4)	−0.030 (4)	−0.053 (4)	0.01 (1)
H(18A)	−0.048 (5)	0.163 (5)	−0.151 (5)	0.04 (2)
H(18B)	0.028 (6)	0.082 (6)	−0.207 (7)	0.06 (3)
H(18C)	0.047 (6)	0.190 (6)	−0.191 (6)	0.05 (2)

[a] Coordinates of constrained H atoms have been deposited as supplementary material. [b] $U_{eq} = {}^1/_3\sum_i(U_{ii})$. [c] Actual values for H atoms.

equivalent bridgehead carbon atoms give one doublet at δ ca. 50. The NMR spectra thus confirm that **7**–**11** are symmetrical half-sandwich complexes.

Treatment of $Rh(\eta\text{-}C_5Me_5)(C_{18}H_{14})$ (**8**) with HPF_6 causes immediate precipitation of a dark green solid of empirical formula $[Rh(\eta\text{-}C_5Me_5)(C_{18}H_{15})]PF_6$ (**12**). Although the elemental analyses are satisfactory, the green color may be due to an impurity, because the corresponding protonated 2,3-dimethylbutadiene complex is orange;[1] attempts to purify the compound by recrystallization were unsuccessful. At −60 °C the ^1H NMR spectrum of **12** shows six resonances due to the dienyl group. Just distinguishable from the C_5Me_5 singlet at δ 1.28 is a three-proton singlet at δ 1.25 assigned to the protons H_a, H_b, and H_c of the agostic methyl group. These are exchanging rapidly owing to reversible cleavage of Rh–H_a and rotation about the C^1–C^2 bond (process 1 in Figure 1). There are also two singlets at δ 2.93 and 5.01 due to the terminal η^3-allyl protons H_d and H_e and two singlets at δ 4.87 and 4.65 due to inequivalent bridgehead protons H_f and H_g. These data show that the dienyl group is bound unsymmetrically to the metal and are consistent with an agostic η^3-enyl structure. In agreement, the ^{13}C NMR spectrum of **12** at −60 °C shows a quartet due to the carbon atom C^1 of the agostic methyl group at δ 14.9 (J = 129 Hz) and a pair of doublets due to the inequivalent bridgehead carbon atoms C^5 and C^6 at δ 48.6 and 53.0. The terminal allylic carbon atom C^4 gives a doublet of triplets at δ 71.0 (J_{CH} = 165 Hz, J_{RhH} = 9.0 Hz), and the resonances due to the inner carbon atoms C^2 and C^3 at δ 66.5 and 103.4 also show small couplings to ^{103}Rh (10.7 and 1 Hz, respectively).

On warming of the samples to 20 °C the multiplets due to H_d and H_e and the singlet due to $H_{a,b,c}$ collapse, while the singlets due to the bridgehead protons H_f and H_g merge into a broad two-proton resonance at δ 4.79. The aromatic proton multiplets also simplify somewhat. This behavior is attributed to reversible C–H bond cleavage via a hydrido diene intermediate (process 2 in Figure 1), which leads to an apparent plane of symmetry through the diene. We were unable to freeze out the faster fluxional process 1 in which the Rh–H_a bond is cleaved reversibly. At −100 °C the three-proton singlet at δ 1.25 is almost obscured by the C_5Me_5 singlet, which moves to slightly lower frequency on cooling.

Reaction of $Ru(\eta\text{-}C_6H_3Me_3)(C_{18}H_{14})$ (**10**) with HPF_6 gives a yellow monoprotonated salt $[Ru(\eta\text{-}C_6H_3Me_3)(C_{18}H_{15})]PF_6$ (**13**) that is air-stable as a solid but air-sensitive in solution. Complex **10** is regenerated when **13** is treated with aqueous Na_2CO_3. At 20 °C the ^1H NMR spectrum of **13** shows, in addition to the arene resonances, a five-proton multiplet at δ −1.13, a two-proton singlet due to the bridgehead protons at δ 4.96, and an eight-proton multiplet due to the aromatic protons at δ 7.4–7.1. On cooling, the five-proton multiplet collapses, and at −100 °C, three broad peaks appear at δ 2.45 (2 H), −0.50 (2 H), and −10.26 (1 H); the rest of the spectrum remains unchanged except for slight shifts to low frequency in the η-arene resonances. This spectrum clearly differs from that of the rhodium complex **12** and, at first sight, is consistent with fluxional hydrido diene structure **13a**, the peaks being assigned as follows: δ −10.26 (RuH), −0.50 (H_a), 2.45 (H_b), 4.89 (H_c). The single-crystal X-ray study discussed below shows, however, that in the solid state the compound adopts the η^3-enyl agostic structure **13b**, similar to that postulated for the rhodium complex **12**. Two possible explanations for this apparent discrepancy are (1) complex **13** has a different structure in solution at −100 °C from that in the solid state or (2) the η^3-enyl agostic structure is retained in solution but, in contrast to **12**, C–H bond cleavage (process 2) occurs more rapidly than M–H bond cleavage (process 1). If process 2 is still fast at −100 °C, the time-averaged structure will be represented by the intermediate in that process, i.e. the hydrido diene. Both explanations imply that structures **13a** and **13b** differ very little in energy.

The behavior of the ^1H NMR spectrum of **13** with temperature is similar to that observed for the complexes $[RuH(\eta\text{-}C_6R_6)(1,3\text{-cyclohexadiene})]^+$ (R = H, Me),[1] and studies of the ^{13}C NMR spectra of these species at low temperature suggest that the second explanation is correct, although limiting spectra cannot be achieved even at −100 °C. Unfortunately, complex **13** is not sufficiently soluble in suitable solvents for ^1H-coupled ^{13}C NMR spectra to be obtained at low temperature. The IR spectrum of **13** shows no band in the 2000-cm^{-1} region assignable to ν(RuH), either in the solid state or in solution. This evidence also supports the second explanation, but it is not conclusive because metal–hydride bands are often weak and may escape detection.

We assume that the η^3-enyl agostic structure found in solid **13** is retained in solution and that there is a rapid equilibrium on the NMR time scale at −100 °C between species **13b** and **13c** as a result of making and breaking of the C–H_a bond. The ^1H NMR spectrum at −100 °C is then assigned as follows: δ −10.26 (RuH_a), −0.50 [H_b, H_d (average)], 2.45 [H_c, H_e (average)]. At 20 °C, Ru–H bond breaking also takes place rapidly on the NMR time scale, and together the two processes cause H_a, H_b, H_c, H_d, and H_e to become equivalent.

Treatment of complex **10** with DPF_6 gives a yellow solid whose ^1H NMR spectrum at 20 °C is similar to that of **13** but contains additional singlets at δ −1.28, −1.47, −1.66, and −1.89 corresponding to the incorporation of one, two, three, and four deuterium atoms. This observation shows that an agostic hydrido complex takes part in the fast-exchange process,[3,16] but it does not necessarily indicate that the ground-state structure is agostic.

When $Ir(\eta\text{-}C_5H_5)(C_{18}H_{14})$ (**7**) is treated with HPF_6, the monoprotonated salt $[Ir(\eta\text{-}C_5H_5)(C_{18}H_{15})]PF_6$ (**14**) precipitates immediately as a light brown solid whose IR spectrum shows a sharp band at 2185 cm^{-1} assigned to ν(IrH). This compound could not be obtained analytically pure, but its variable-temperature ^1H and ^{13}C NMR spectra suggest that it is a fluxional hydrido diene complex. At 20° C, the ^1H NMR spectrum shows a seven-proton singlet at δ 5.22, due to overlap of the singlets due to the bridgehead protons H_c and C_5H_5, and a five-proton multiplet at δ 1.63 due to the average of H_a, H_b, and IrH. On cooling, the latter resonance collapses, and at −40 °C a limiting spectrum containing three resonances at δ 4.24 (2 H, H_b), 2.31 (2 H, H_a), and −15.55 (1 H, IrH) is observed. At −40 °C the resonances due to H_c appear as a singlet at δ 5.23 and are distinguishable from the C_5H_5 singlet. The ^{13}C NMR spectrum at −60 °C shows a triplet at δ 28.0 (J = 167 Hz) due to C^1, a doublet at δ 49.8 (J = 146 Hz) due to C^3, and a singlet at δ 113.1 due to C^2.

Protonation of $Os(\eta\text{-}C_6H_3Me_3)(C_{18}H_{14})$ (**11**) with either HPF_6 or CF_3SO_3H gives the cation $[Os(\eta\text{-}C_6H_3Me_3)(C_{18}H_{15})]^+$ (**15**); only the triflate salt could be obtained analytically pure. Unlike all other protonated (arene)(1,3-diene)osmium(II) cations we have examined,[1] **15** shows no ν(OsH) band in the 2100-cm^{-1} region of the IR spectrum. Its variable-temperature ^1H and ^{13}C NMR spectra are, however, similar to those of the ruthenium and iridium compounds, **13** and **14**. The ^1H NMR spectrum at 20 °C shows, in addition to the η-mesitylene resonances, a complex multiplet at δ 7.4–7.0 due to the C_6H_4 protons and a singlet at δ 5.15 due to the bridgehead protons. On cooling of the sample to 0° C, three additional broad resonances appear at ca. δ 3.4 (2 H), 1.5 (2 H), and −13.5 (1 H), and these become well-resolved at −40 °C. As in the case of **13** and **14**, this spectrum is consistent with a fluxional hydrido 1,3-diene structure, but the possibility of an agostic η^3-enyl structure in which C–H bond cleavage is occurring more rapidly than M–H bond cleavage (as in **13**) cannot be excluded. At −80 °C the singlet at δ 5.15 due to the bridgehead protons is broad, an observation that might suggest that process 2 is beginning to freeze out. The other signals, however, remain sharp at −80 °C; the resonance at δ 3.45 is a doublet (J = 3 Hz) and that at δ 1.48 is a poorly resolved triplet, indicative of a weak three-bond coupling with the hydride. The ^{13}C NMR spectrum at −20 °C is similar to that of the iridium complex **14**.

Treatment of **15** with 1 equiv of *tert*-butyl isocyanide gives quantitatively a yellow η^3-methallyl complex $[Os(\eta\text{-}C_6H_3Me_3)(\eta^3\text{-}C_{18}H_{15})(t\text{-BuNC})]PF_6$ (**16**) formed by irreversible transfer of hydride to the coordinated diene. The η^3-allyl fragment is characterized by a three-proton singlet at δ 1.38 due to the methyl group and two one-proton doublets at δ 2.41 and 3.90 due to the terminal protons H_a and H_b. As expected, the bridgehead protons are inequivalent. The presence of coordinated *t*-BuNC is evident from a nine-proton singlet at δ 1.42. The corresponding ruthenium complex $[Ru(\eta\text{-}C_6H_3Me_3)(\eta^3\text{-}C_{18}H_{15})(t\text{-BuNC})]PF_6$ (**17**) is obtained similarly from **13** and *tert*-butyl isocyanide.

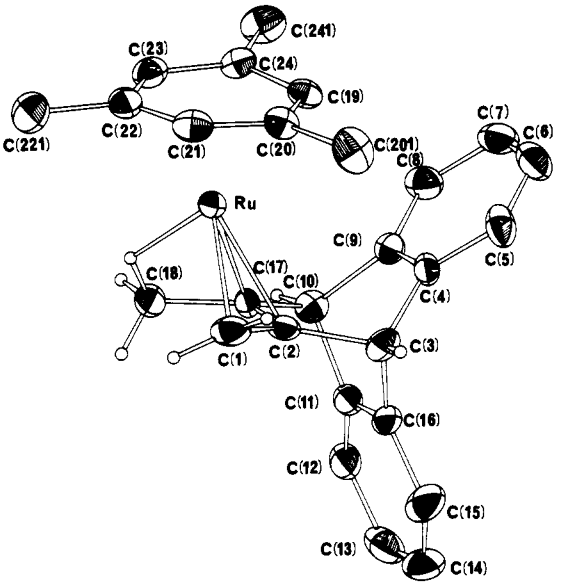

Figure 2. Structure and atom nomenclature for $[Ru(\eta\text{-}C_6H_3Me_3)(C_{18}H_{15})]^+$ (**13**), with 50% ellipsoids.

Table IV. Selected Bond Distances (Å) and Interbond Angles (deg) for $[Ru(C_{18}H_{15})(\eta\text{-}C_6H_3Me_3)]PF_6$ (13)

Ru–C(1)	2.180 (8)	C(10)–C(17)	1.523 (10)
Ru–C(2)	2.196 (7)	C(10)–H(10)	0.96 (6)
Ru–C(17)	2.148 (7)	C(11)–C(12)	1.386 (11)
Ru–C(18)	2.357 (9)	C(11)–C(16)	1.403 (11)
Ru–C(19)	2.200 (7)	C(12)–C(13)	1.385 (14)
Ru–C(20)	2.188 (7)	C(13)–C(14)	1.363 (16)
Ru–C(21)	2.214 (7)	C(14)–C(15)	1.397 (15)
Ru–C(22)	2.238 (7)	C(15)–C(16)	1.369 (11)
Ru–C(23)	2.230 (7)	C(17)–C(18)	1.501 (11)
Ru–C(24)	2.304 (7)	C(18)–H(18A)	1.09 (7)
Ru–H(18C)	1.81 (8)	C(18)–H(18B)	0.93 (8)
C(1)–C(2)	1.423 (10)	C(18)–H(18C)	0.98 (8)
C(1)–H(1A)	0.90 (8)	C(19)–C(20)	1.421 (10)
C(1)–H(1B)	0.99 (7)	C(19)–C(24)	1.417 (10)
C(2)–C(3)	1.526 (11)	C(20)–C(21)	1.406 (11)
C(2)–C(17)	1.392 (10)	C(20)–C(201)	1.495 (11)
C(3)–C(4)	1.503 (10)	C(21)–C(22)	1.414 (11)
C(3)–C(16)	1.538 (11)	C(22)–C(23)	1.410 (11)
C(3)–H(3)	0.72 (8)	C(22)–C(221)	1.499 (12)
C(4)–C(5)	1.390 (10)	C(23)–C(24)	1.407 (11)
C(4)–C(9)	1.388 (10)	C(24)–C(241)	1.523 (10)
C(5)–C(6)	1.340 (13)	P–F(1)	1.526 (9)
C(6)–C(7)	1.352 (14)	P–F(2)	1.521 (10)
C(7)–C(8)	1.416 (13)	P–F(3)	1.473 (9)
C(8)–C(9)	1.373 (10)	P–F(4)	1.505 (10)
C(9)–C(10)	1.525 (10)	P–F(5)	1.385 (9)
C(10)–C(11)	1.525 (10)	P–F(6)	1.481 (14)
C(1)–C(2)–C(3)	127.8 (7)	C(18)–C(17)–C(10)	124.8 (7)
C(1)–C(2)–C(17)	119.5 (7)	C(18)–C(17)–C(2)	119.2 (8)
C(3)–C(2)–C(17)	112.7 (6)	C(10)–C(17)–C(2)	113.6 (6)
C(2)–C(3)–C(4)	109.9 (6)	C(17)–C(10)–C(9)	107.1 (6)
C(2)–C(3)–C(16)	101.7 (6)	C(17)–C(10)–C(11)	103.4 (6)
C(4)–C(3)–C(16)	105.7 (6)	C(9)–C(10)–C(11)	105.2 (6)

Structure of $[Ru(\eta\text{-}C_6H_3Me_3)(C_{18}H_{15})]PF_6$ (13).

The cation exhibits approximate mirror symmetry and comprises a (η^6-mesitylene)ruthenium unit attached via both a η^3-enyl interaction and a three-center two-electron Ru–

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[16] Brookhart, M.; Green, M. L. H.; Wong, L.-L. *Prog. Inorg. Chem.* **1988**, *36*, 1 and references cited therein.

H–C bond to a butenyl moiety derived by protonation of the 1,3-diene (Figure 2). Selected bond distances and interbond angles are given in Table IV. The geometry of the Ru–mesitylene moiety is similar to that found in $[Ru(\eta\text{-}C_6H_3Me_3)(1,5\text{-}\eta\text{-}C_8H_9)]PF_6$ (**18**) and $[Ru(\eta\text{-}C_6H_3Me_3)(1\text{-}3{:}6\text{-}7\text{-}\eta\text{-}C_8H_9)]PF_6$ (**19**)[17] (values in braces). The arene ring is just significantly nonplanar [Δ(max) = 0.044 (5) Å] in a twist-boat conformation, the ruthenium atom lies 1.72 Å {1.74, 1.74 Å} from the mean plane, and the Ru–C(arene) distances are in the range 2.191 (7)–2.304 (7) Å {2.218 (6)–2.266 (3) Å}. The methyl substituents are each bent slightly away from the C_6 mean plane toward the metal atom [Δ = 0.02 (1)–0.11 (1) Å]; surprisingly, the structures of **18** and **19** do not show this feature. The dihedral angle between the C_6 plane of the arene ligand and the C_4 plane of the butenyl moiety is 11°; that between the C_6 and the C_3 η-enyl plane is 13°. The Ru–C(η-enyl) distances [Ru–C(1) = 2.180 (8) Å, Ru–C(2) = 2.196 (7) Å, Ru–C(17) = 2.148 (7) Å] are similar to those found in the closely related agostic species $[Ru\{P(OMe)Ph_2\}_3(\eta^3\text{-}C_8H_{13})]PF_6$ (**20**) [2.246 (7), 2.216 (8), 2.197 (8) Å][18] and $[Ru(PMe_2Ph)_3(\eta^3\text{-}C_4H_7)]PF_6$ (**21**) [2.26 (2), 2.17 (2), 2.14 (2) Å].[19,20]

The Ru–C(18) distance [2.357 (9) Å] is greater than that expected for a metal–carbon σ-bond but is entirely consistent with the presence of a two-electron, three-center (agostic) interaction, Ru-H(18C)–C(18). It is significantly less than the metal–carbon distance reported for the agostic interaction in the η^3-cyclooctenyl ruthenium complex **20** [2.592 (9) Å][18] but is within experimental error of that found in the more closely related η^3-butenyl complex **21** [2.38 (2) Å].[19] Similar values are also found in the η^3-cyclooctenyl iron complex $Fe\{P(OMe)_3\}_3(\eta^3\text{-}C_8H_{13})$ (**22**) [2.362 (2) Å][2] and in $Mn(CO)_3(\eta^3\text{-}C_6H_8CH_3)$ (**23**) [2.301 (2) Å][3]. Direct evidence for a C–H–M interaction in each of the complexes **20**, **22**, and **23** follows from the known locations of the agostic hydrogen atoms. Likewise, in **13**, all hydrogen atoms except for one atom in one methyl group were observable in difference syntheses and coordinates of all five hydrogen atoms of the C_4H_5 enyl unit (along with those of the bridgehead hydrogen atoms) refined to yield acceptable geometric parameters. Relevant values for the C(18)–H(18C)–Ru moiety are C(18)–H(18C) = 0.98 (8) Å, Ru–H(18C) = 1.81 (8) Å, ∠C(17)–C(18)–H(18C) = 108 (5)°, and ∠C(18)–H(18C)–Ru = 112 (6)°. The observed Ru–H(18C) distance is within experimental error of the minimum internuclear separation (1.79 Å; C–H = 1.08 Å assumed) allowed by the known metal and ligand atom coordinates. To achieve this result requires methyl group C(18) to be so oriented as to bring H(18C) to near coplanarity with Ru, C(17), and C(18), and that orientation is confirmed by the torsion angles C(2)–C(17)–C(18)–Ru [62.9 (6)°], C(2)–C(17)–C(18)–H(18C) [55 (5)°], and C(2)–C(17)–C(18)–H average [61 (+0, 120, 180) ± 14°]. For this geometry the value computed for r_{bp} [$=d_{bp} - r_M$, where d_{bp} is the metal to C–H bond-pair distance and r_M is the metal atom covalent radius] is 0.42 Å and for H [the internuclear C–H–Ru bond angle] is 109°. Crabtree et al.[21] have proposed that r_{bp} provides a useful measure of the strength of an agostic interaction, and by that criterion the interaction in complex **13** is one of the strongest yet observed. The interaction in complex **21**, which has a calculated minimum internuclear Ru–H separation of 1.85 Å, is probably only marginally weaker. The strong interactions in **13** and **21** are clearly favored by the torsional flexibility about the C–C(methyl) bond and, perhaps more importantly, by the fact that the geometries of the coordinated and free ligands (including the methyl group orientation) are likely to be little different.

The C(1)–C(2) and C(2)–C(17) bond lengths [1.42 (1), 1.39 (1) Å] are consistent with the enyl formulation and indicate substantial delocalization over the allylic framework. In contrast, the C(17)–C(18), C(17)–C(10), and C(2)–C(3) distances [1.50 (1), 1.52 (1), 1.53 (1) Å] all agree well with the 1.51 Å distance expected for a C(sp^2)–C(sp^3) bond. Presumably in order to accommodate the agostic hydrogen atom H(18C) in the coordination sphere of the metal atom and in the C(17), C(18), Ru plane, carbon atom C(18) is displaced by –0.33 (1) Å from the C(1), C(2), C(17) enyl plane; the Ru atom is +1.61 Å from the plane. The bridgehead carbon atoms C(3) and C(10) are also slightly out-of-plane [+0.06 (1), –0.07 (1) Å], and a small degree of angle strain is apparent at those centers [opening ∠C(2)–C(3)–C(4) and ∠C(9)–C(10)–C(17), average 108.5°, at the expense of ∠C(2)–C(3)–C(16) and ∠C(11)–C(10)–C(17), average 102.6°]. Distances and angles elsewhere in the $C_{18}H_{15}$ ligand are uniformly unexceptional as are those in the PF_6 anion. There are just two interion contacts that are appreciably shorter than the normal van der Waals separation [H(7)–F(5) = 2.38 Å, H(20A)–F(3) = 2.61 Å].

Conclusions

The NMR behavior of complexes of 2,3-dimethylene-5,6,7,8-dibenzobicyclo[2.2.2]octane (ddbo) with $M(\eta\text{-}C_5R_5)$ (M = Rh, Ir) and M′(arene) (M′ = Ru, Os) resembles that of the corresponding 2,3-dimethylbutadiene and 1,3-cyclohexadiene complexes.[1] It seems reasonable to assume, therefore, that the protonated (arene)ruthenium complexes of these dienes also have agostic η^3-enyl structures. In complex **13** the agostic interaction is apparently so strong, i.e. the approach to a hydrido 1,3-diene structure is sufficiently close, that the activation energy for reversible cleavage of the C–H bond in these complexes is less than that for cleavage of the M–H bond. In contrast, for complex **21**, with Ru–H minimum (and r_{bp} minimum) only 0.06 Å greater than for **13**, the opposite behavior is observed. Thus ruthenium occupies an interesting intermediate position between iridium, osmium, and other 5d elements on the one hand, which tend to form hydrido 1,3-diene structures, and rhodium and most of the 3d elements on the other, which form agostic η^3-enyl structures in which M–H bond rupture precedes C–H bond cleavage. This intermediate behavior of ruthenium has also recently been observed in the case of the 2,4-dimethylpentadienyl complex $[RuH(\eta^5\text{-}C_7H_{11})_2]^+$, whose dynamic NMR behavior was interpreted in terms of a hydrido dienyl structure containing a weak Ru–H···C interaction with a terminal methylene group.[22]

Supplementary Material Available: Listings of hydrogen atom parameters, anisotropic thermal parameters, crystal data, and data collection and refinement details (4 pages); a table of observed and calculated structure factor amplitudes (12 pages). Ordering information is given on any current masthead page.

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