do not correlate directly with the results discussed here, however, because the study of Fe(I) was of collisionally activated adducts. Of the three decomposition pathways for the Cu(I)/octyne adducts, hydride abstraction is not observed for Fe(I)/octynes, and propargylic insertion occurs more readily than remote functionalization. The percentage of propargylic insertion products increases as the triple bond is moved across the octyne skeleton, whereas the percentage of remote functionalization decreases.[49] This is similar to the trend observed for the Cu(I) systems.

Preliminary results obtained in this laboratory by collisional activation indicate that the [Cu^+/octyne] adducts need little additional energy to open a multiplicity of new reaction modes. Additional work with the collisionally activated decompositions of the adducts studied here should provide more insight into the interesting reactivity of Cu(I).

Acknowledgment. This work was supported by funds from the National Science Foundation (CHE-9017250), the Deutsche Forschungsgemeinschuft, and the Volkswagen-Stifung.

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[49] Only the products of the remote functionalization and propargylic insertion pathways were considered when the percent calculations were made.

General Route to the "Half-Open" Metallocenes C_5Me_5Ru(pentadienyl) and C_5Me_5Ru(diene)Cl. X-ray Structures of an Optically Active Half-Open Metallocene and of a Dimetallic Ruthenabenzene Complex

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Received November 4, 1991

Treatment of $[C_5Me_5RuCl_2]_n$ (1) with various acyclic and cyclic diolefins in the presence of zinc powder leads to the "half-open" metallocenes C_5Me_5Ru(pentadienyl), to C_5Me_5Ru(diolefin) chloro compounds, or to cationic complexes with an η^6 ligand, depending on the stereochemistry and substitution pattern of the starting diolefin. An X-ray crystallographic analysis of optically active C_5Me_5Ru(dimethylnopadienyl) (11; $[\alpha]_{589} = -250.6°$), which crystallizes from methanol in the monoclinic space group $P2_1$ with $a = 9.214$ (4) Å, $b = 17.593$ (8) Å, $c = 13.115$ (6) Å, $\beta = 101.55$ (4)°, and $Z = 4$, reveals the coordination of the C_5Me_5Ru moiety from the sterically less hindered side of the tricyclic ligand. The half-open metallocene $C_5Me_5Ru(2,4\text{-}C_7H_{11})$ (2; $2,4\text{-}C_7H_{11} = \eta^5$-2,4-dimethylpentadienyl) can be protonated with HBF_4, yielding $[C_5Me_5Ru(H)(C_7H_{11})]BF_4$, which has a dynamic structure on the NMR time scale. **2** can also be lithiated; the site of lithiation could be determined by quenching experiments with $MeOD/CH_3COOD$. **2** reacts with $[C_5H_5Ru(CH_3CN)_3]PF_6$ to yield the dimetallic complex $[C_5H_5Ru(\mu\text{-}2,4\text{-}C_7H_9)Ru(C_5Me_5)(CH_3CN)]PF_6$ (**19**). **19** crystallizes from propionic anhydride in the orthorhombic space group *Pnma*, with $a = 13.274$ (2) Å, $b = 11.865$ (2) Å, $c = 16.578$ (3) Å, and $Z = 4$ and displays an η^6 coordination of a ruthenabenzene unit to C_5H_5Ru. The substitution of the diolefin and/or chloro ligand in C_5Me_5Ru(2-methyl-(*E*)-pentadiene)Cl (**7**) in a range of solvents and under mild conditions is a rapid and facile process. Mono- and bidentate ligands (Br, CO, CH_3, $P(OMe)_3$, cod) substitute the diolefin, the chloro ligand, or both, depending on reaction conditions, to produce the complex $C_5Me_5RuL_2X$, $[C_5Me_5RuL_3]^+$, or $[C_5Me_5RuL_2L']^+$. All compounds are obtained in high yield and have been characterized by a combination of elemental analyses and spectroscopic methods (IR, ^1H and ^{13}C NMR, MS).

Introduction

The chemistry of "open" and "half-open" metallocenes, that is of metal complexes with pentadienyl ligands, was largely left unexplored for a long time, in contrast to the vigorous development in the chemistry of related cyclopentadienyl or allyl complexes. Recent research, however, confirmed earlier predictions on the stability of metal–pentadienyl compounds and their chemical and catalytic properties.[1,2] This is largely due to the work of Ernst and co-workers. Two general synthetic routes to such complexes emerged from their research, namely the metathetical pathway of reacting lithium, potassium, or tin pentadienyl derivatives with transition-metal halides and the reductive method employing either $RuCl_3 \cdot nH_2O$ or Na_2OsCl_6, zinc powder, and an appropriate diolefin ligand, based on the general procedure developed by Vitulli.[3]

Both methods are somewhat restricted, as the absence or presence of additional methyl substituents in the organic ligand very often is crucial for synthetic success,[2] and the handling of the pyrophoric and reactive alkali-metal pentadienyl derivatives requires considerable synthetic skill. The reductive route, on the other hand, suffers from unpredictable yields, possibly owing to the uncertain and variable nature of the commercial starting material

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(3) Pertici, P.; Vitulli, G.; Paci, M.; Porri, L. *J. Chem. Soc., Dalton Trans.* **1980,** 1961.

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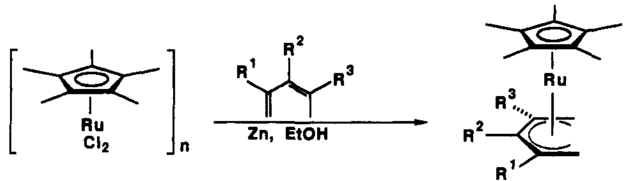
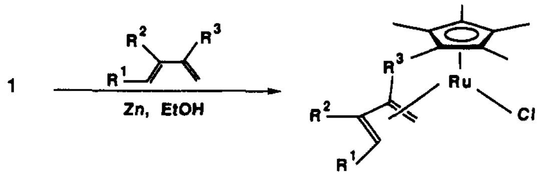
Scheme I



2 $R^1 = R^3 = CH_3$, $R^2 = H$
3 $R^1 = R^2 = R^3 = H$
4 $R^1 = R^3 = H$, $R^2 = CH_3$
5 $R^1 = CH_3$, $R^2 = R^3 = H$

Scheme II



6 $R^1 = CH_3$, $R^2 = R^3 = H$
7 $R^1 = R^3 = CH_3$, $R^2 = H$
8 $R^1 = R^2 = CH_3$, $R^3 = H$

"$RuCl_3 \cdot nH_2O$". The introduction of functional groups, in particular, has not yet been demonstrated at all by either method.

Herein we report a general high-yield synthetic route to half-open metallocenes of ruthenium of the type C_5Me_5Ru(pentadienyl) as well as some studies on their reactivity.

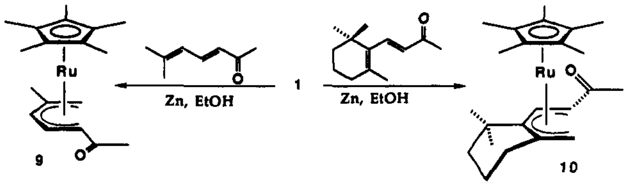
Discussion

Preparation of Complexes. Rybinskaya et al., in their report on the synthesis of triple-decker complexes of the iron triad, describe a very efficient and simple synthesis of $C_5Me_5RuC_5H_5$ from $[C_5Me_5RuCl_2]_n$, zinc powder, and cyclopentadiene.[4] Considering that cyclopentadiene is just another conjugated diolefin with an *endo*-methylene group, this method suggested to us that other cyclic or acyclic diolefins with appropriate methylene or methyl groups should also undergo a similar reaction, giving half-open metallocenes.

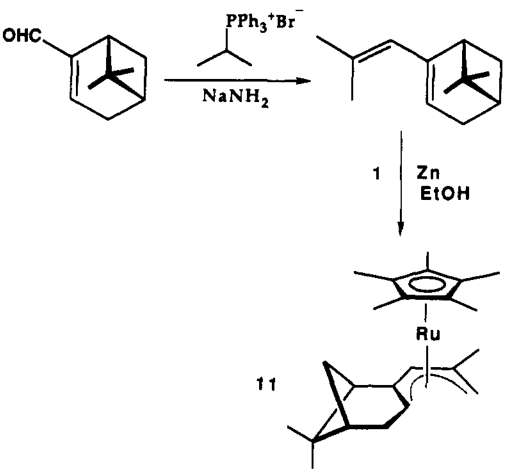
The most commonly used organic starting material for open metallocenes is 2,4-dimethyl-1,3-pentadiene, which is easily prepared in larger quantities and is the precursor for the symmetrical 2,4-dimethylpentadienyl ligand (2,4-C_7H_{11}). Reacting this with $[C_5Me_5RuCl_2]_n$ (**1**) and zinc powder in ethanol indeed gave $C_5Me_5Ru(2,4\text{-}C_7H_{11})$ (**2**) as pale yellow crystals in 95% yield. The complex is soluble in most common organic solvents, air-stable in the solid state over longer periods, and sublimable under high vacuum. The reaction sequence seems to be quite general, as all diolefins tested having a (*Z*)-methyl group undergo this reaction, giving the corresponding dienyl complexes **2–5** in virtually quantitative yields (Scheme I). Complex **2** has been described previously.[5]

When, as in the case of pentadiene, 2-methylpentadiene, and 3-methylpentadiene, commercial samples of the diolefin consisted of a mixture of *E* and *Z* isomers, these samples could still be employed and also gave good yields of the dienyl complex. A second product, however, invariably formed as orange needles, easily separable from the dienyl complex owing to its different solubility. This turned out to be a complex of general formula C_5Me_5Ru((*E*)-diolefin)Cl. Using the pure *E* isomer produced this type of complex exclusively, again in almost quantitative yields (Scheme II).

Scheme III



Scheme IV



These results suggested that all diolefins react with $[C_5Me_5RuCl_2]_n$ and zinc powder in a similar manner, forming the primary products C_5Me_5Ru(diolefin)Cl, which then, in the case of (*Z*)-olefins, undergo spontaneous β-elimination, followed by reductive elimination of HCl. In the case of pure 2-methyl-1,3-(*E*)-pentadiene, prolonged reaction times with a large excess of ligand also gave 85% yield of the dienyl complex **5**, indicating that an additional mechanism for slow *E*/*Z* isomerization also existed. Under the regular conditions (2-fold excess of ligand, 1 h reaction time), only the (*E*)-diolefin chloro complex **7** was formed in 94% yield.

As these reactions proceeded under very mild conditions, we assumed that the presence of functional groups in the diolefin ligand might not be a serious obstacle. This proved to be the case, as treatment of **1** with 2-methyl-2,4-heptadien-6-one or the natural product β-ionone gave the functionalized pentadienyl complexes **9** and **10** in good yields. A common feature of both ligands again is a methyl group that, with loss of a proton, can be incorporated into a U-shaped dienyl ligand (Scheme III). Complexes **9** and **10** to our knowledge are the first half-open metallocenes bearing a functional group.

As the last example for an acyclic diolefin, we also investigated the reaction of **1** with an optically active diolefin. The diolefin dimethylnopadiene was prepared from the natural product (−)-myrtenal by Wittig olefination. Reaction under the same conditions as before produced reasonable yields of the optically active pentadienyl complex **11**. No trace of the other possible diastereomer was detectable by NMR spectroscopy, even in the raw product. This result is in agreement with the chemistry of the optically active diolefin ligand (+)-nopadiene, whose coor-

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[4] Kudinov, A. R.; Rybinskaya, M. I.; Struchnov, Yu. T.; Yanovskii, A. I.; Petrovskii, P. V. *J. Organomet. Chem.* **1987**, *336*, 187.

[5] (a) Cox, D. N.; Roulet, R. *J. Chem. Soc., Chem. Commun.* **1989**, 175. (b) Kreindlin, A. Z.; Petrovskii, P. V.; Rybinskaya, M. I. *Bull. Acad. Sci. USSR, Div. Chem. Sci.* (*Engl. Transl.*) **1987**, 1772. (c) A reviewer (R. D. Ernst) has advised us that complexes **2–5** can also be obtained by a different route: Trakarnpruk, W.; Arif, A. M.; Ernst, R. D. *Organometallics*, in press.

Table I. Summary of Crystal Data and Details of the Intensity Collection and Refinement for 11 and 19

	19[a]	11
	Crystal Data	
empirical formula	$C_{24}H_{32}NF_6PRu_2$	$C_{23}H_{34}Ru$
color, habit	red cube	yellow prism
cryst size, mm	0.4 × 0.3 × 0.25	0.52 × 0.34 × 0.29
cryst syst	orthorhombic	monoclinic
space group	*Pnma*	$P2_1$
unit cell dimens		
a, Å	13.274 (2)	9.124 (4)
b, Å	11.865 (2)	17.593 (8)
c, Å	16.578 (3)	13.115 (6)
β, deg		101.55 (4)
V, $Å^3$	2610.9 (7)	2062.5 (17)
Z	4	4
fw	681.6	411.6
density (calcd), Mg/m^3	1.734	1.325
abs coeff, mm^{-1}	1.250	0.746
$F(000)$	1360	864
	Data Collection	
diffractometer used	Siemens R3m/V	
radiation	Mo Kα (λ = 0.71073 Å)	
temp, K	211	238
monochromator	highly oriented graphite crystal	
2θ range, deg	4.0–58	4.0–55.0
scan type	ω	Wyckoff
scan speed, deg/min	variable; 2.00–15.00 in ω	variable; 2.25–14.65 in ω
scan range (ω), deg	1.40	1.20
bkgd measmt	stationary crystal and stationary counter at beginning and end of scan, each for 25% of total scan time	
std rflns	3 measd every 97 rflns	
index ranges	$0 \le h \le 18$, $0 \le k \le 16$, $0 \le l \le 22$	$0 \le h \le 11$, $0 \le k \le 22$, $-17 \le l \le 16$
no. of rflns collected	3141	5195
no. of indep rflns	2958 (R_{int} = 1.48%)	4926 (R_{int} = 4.42%)
no. of obsd rflns	2509 ($F > 6.0\sigma(F)$)	4419 ($F > 6.0\sigma(F)$)
abs cor	N/A	
	Solution and Refinement	
system used	Siemens SHELXTL PLUS (Micro VAX II)	
solution	direct methods	
refinement method	full-matrix least squares	
quantity minimized	$\sum w(F_o - F_c)^2$	
abs confign	N/A	
extinction cor	N/A	
H atoms	located out of diff map and refined isotropically	Riding model, refined isotropic U
weighting scheme	unit weights	
final R indices (obsd data), %	R = 2.88, R_w = 2.96	R = 5.16, R_w = 5.64
R indices (all data), %	R = 3.64, R_w = 4.30	R = 5.83, R_w = 6.11
goodness of fit	1.67	1.88
largest and mean Δ/σ	0.223, 0.002	0.005, 0.001
data to param ratio	10.5:1	10.1:1
largest diff peak, e/$Å^3$	0.59	1.42
largest diff hole, e/$Å^3$	−0.59	−0.81

[a] Reflections 020, 002, 122, and 111 not used for least-squares calculations.

dinating behavior we had previously investigated.[6] In the majority of cases, this ligand and its functionalized derivatives reacted with complete diastereoselectivity to produce only one transition-metal complex, thereby opening a direct route toward the synthesis and investigation of optically active diolefin complexes. Complex 11 seems to be the first example of an optically active half-open sandwich molecule (Scheme IV).

We were also able to grow single crystals of complex 11 by slowly cooling a saturated methanolic solution to 4 °C. Selected bond lengths are listed in Table III and bond angles in Table IV. The solid-state structure analysis of 11 confirms the coordination of the C_5Me_5Ru moiety from the sterically less hindered side of the dienyl ligand. The relative orientation of the two ligands is such that the methyl groups of the pentamethylcyclopentadienyl ligand and the bridge carbon atom C(18) and the methyl carbon atom C(20) of the dienyl ligand assume a staggered conformation, thereby minimizing the steric interaction of their hydrogen atoms. This is in contrast to the structure of C_5H_5Ru(dimethylpentadienyl) reported by Ernst,[7] which showed an almost ideally eclipsed conformation. Sterical interactions of the two bulky ligands are also most likely responsible for a pronounced bending of the two ligand planes defined by the C_5Me_5 ligand and the dienyl group (Figure 1). They form an angle of 13.9 and 14.5°, respectively, for the two independent molecules in the unit cell. A similar ring tilt was also observed for the complex C_5Me_5Rh(nopadiene),[6] where an angle of 11.6° was found. A considerable variation in Ru–C as well as C–C bond lengths is evident with regard to the dienyl ligand, but there seems to be no easily explained trend of bond length alterations, especially when both molecules in the unit cell are compared. Such trends have been inferred from structures of more symmetrical half-open and open sandwich molecules.[7]

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(7) Gleiter, R.; Hyla-Kryspin, I.; Ziegler, M. L.; Sergeson, G.; Green, J. C.; Stahl, L.; Ernst, R. D. *Organometallics* **1989**, *8*, 298.

Table II. Atom Coordinates (×10^5) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^4) for 11

	x	y	z	U(eq)^a
Ru(1)	36 414 (8)	24 330	55 660 (5)	346 (2)
C(1)	37 423 (167)	21 204 (74)	39 382 (105)	544 (42)
C(2)	49 961 (162)	18 392 (87)	46 610 (110)	569 (46)
C(3)	58 212 (110)	24 067 (84)	51 768 (82)	474 (31)
C(4)	51 233 (144)	31 101 (89)	47 585 (97)	526 (39)
C(5)	38 454 (141)	29 362 (69)	39 876 (92)	492 (38)
C(6)	25 991 (201)	16 823 (101)	31 566 (113)	933 (72)
C(7)	54 267 (207)	9 756 (73)	47 724 (123)	843 (67)
C(8)	73 275 (122)	23 408 (110)	59 282 (104)	846 (58)
C(9)	57 680 (187)	38 931 (80)	49 939 (147)	830 (69)
C(10)	28 894 (176)	34 900 (90)	32 510 (107)	857 (63)
C(11)	37 226 (132)	15 519 (63)	67 639 (90)	516 (39)
C(12)	22 708 (138)	15 900 (66)	61 467 (96)	495 (40)
C(13)	15 140 (133)	22 570 (54)	60 130 (90)	454 (36)
C(14)	20 217 (104)	30 199 (65)	63 448 (70)	363 (28)
C(15)	34 822 (102)	31 270 (70)	69 671 (74)	420 (30)
C(16)	38 923 (128)	39 745 (67)	72 337 (98)	581 (42)
C(17)	25 879 (158)	45 096 (63)	68 360 (107)	654 (49)
C(18)	20 233 (156)	43 464 (63)	56 729 (99)	606 (46)
C(19)	10 692 (118)	37 165 (62)	60 306 (78)	442 (32)
C(20)	15 544 (155)	9 017 (64)	55 688 (109)	674 (50)
C(21)	11 037 (135)	42 177 (63)	70 256 (84)	531 (38)
C(22)	10 232 (140)	38 024 (75)	80 517 (85)	601 (43)
C(23)	−1 614 (166)	48 004 (75)	68 427 (102)	759 (54)
Ru(2)	74 923 (8)	30 665 (6)	7 552 (6)	387 (2)
C(24)	72 451 (126)	30 380 (111)	23 635 (80)	630 (43)
C(25)	65 314 (161)	37 213 (92)	18 635 (113)	614 (48)
C(26)	53 110 (141)	35 001 (72)	10 760 (91)	491 (39)
C(27)	52 535 (137)	27 070 (78)	10 788 (95)	557 (42)
C(28)	64 177 (158)	24 288 (109)	18 761 (109)	645 (48)
C(29)	85 060 (151)	30 056 (143)	33 249 (83)	1117 (77)
C(30)	68 974 (218)	45 531 (95)	22 070 (137)	1016 (80)
C(31)	41 860 (169)	40 268 (89)	4 203 (110)	797 (58)
C(32)	39 722 (160)	22 228 (103)	4 371 (140)	975 (78)
C(33)	66 199 (240)	15 888 (97)	22 247 (150)	1093 (93)
C(34)	93 162 (143)	38 521 (70)	6 699 (104)	600 (45)
C(35)	82 399 (148)	38 789 (69)	−2 717 (103)	516 (42)
C(36)	77 947 (111)	32 046 (59)	−8 627 (82)	428 (33)
C(37)	82 249 (109)	24 532 (76)	−5 327 (70)	395 (28)
C(38)	92 441 (126)	22 659 (65)	4 077 (84)	480 (38)
C(39)	94 693 (143)	13 941 (69)	6 387 (84)	545 (40)
C(40)	85 172 (148)	9 238 (71)	−2 224 (97)	560 (43)
C(41)	69 165 (130)	11 927 (64)	−4 575 (94)	561 (40)
C(42)	74 451 (124)	17 843 (61)	−11 731 (83)	455 (33)
C(43)	74 899 (154)	46 292 (61)	−6 620 (99)	642 (47)
C(44)	86 734 (129)	11 795 (60)	−13 190 (79)	492 (35)
C(45)	80 730 (162)	5 921 (66)	−21 586 (92)	697 (48)
C(46)	101 675 (141)	13 375 (74)	−15 131 (102)	653 (47)

^{a} Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table III. Selected Bond Lengths (Å) for 11

Ru(1)–C(1)	2.224 (14)	Ru(1)–C(2)	2.148 (16)
Ru(1)–C(3)	2.151 (11)	Ru(1)–C(4)	2.223 (15)
Ru(1)–C(5)	2.293 (13)	Ru(1)–C(11)	2.198 (12)
Ru(1)–C(12)	2.174 (13)	Ru(1)–C(13)	2.159 (13)
Ru(1)–C(14)	2.213 (11)	Ru(1)–C(15)	2.235 (11)
C(1)–C(2)	1.421 (19)	C(1)–C(5)	1.439 (18)
C(1)–C(6)	1.518 (20)	C(2)–C(3)	1.348 (19)
C(2)–C(7)	1.569 (20)	C(3)–C(4)	1.448 (20)
C(3)–C(8)	1.527 (14)	C(4)–C(5)	1.415 (16)
C(4)–C(9)	1.505 (21)	C(5)–C(10)	1.519 (18)
C(11)–C(12)	1.409 (16)	C(13)–C(14)	1.457 (15)
C(12)–C(13)	1.355 (15)	C(12)–C(20)	1.507 (17)
C(14)–C(15)	1.429 (12)	C(14)–C(19)	1.511 (15)
C(15)–C(16)	1.560 (17)	C(17)–C(21)	1.515 (19)
C(16)–C(17)	1.525 (17)	C(21)–C(23)	1.526 (18)
C(17)–C(18)	1.536 (18)	C(18)–C(19)	1.539 (17)
C(19)–C(21)	1.570 (15)	C(21)–C(22)	1.546 (16)

Table IV. Selected Bond Angles (deg) for 11

C(1)–Ru(1)–C(2)	37.9 (5)	C(1)–Ru(1)–C(3)	63.2 (5)
C(2)–Ru(1)–C(3)	36.6 (5)	C(1)–Ru(1)–C(4)	61.9 (5)
C(2)–Ru(1)–C(4)	61.7 (6)	C(3)–Ru(1)–C(4)	38.6 (5)
C(1)–Ru(1)–C(5)	37.1 (5)	C(2)–Ru(1)–C(5)	61.9 (5)
C(3)–Ru(1)–C(5)	63.1 (4)	C(4)–Ru(1)–C(5)	36.5 (4)
C(1)–Ru(1)–C(11)	120.6 (5)	C(2)–Ru(1)–C(11)	96.4 (5)
C(3)–Ru(1)–C(11)	104.7 (5)	C(4)–Ru(1)–C(11)	141.4 (5)
C(5)–Ru(1)–C(11)	157.0 (4)	C(1)–Ru(1)–C(12)	107.8 (5)
C(2)–Ru(1)–C(12)	107.3 (5)	C(3)–Ru(1)–C(12)	133.9 (5)
C(4)–Ru(1)–C(12)	168.5 (5)	C(5)–Ru(1)–C(12)	137.4 (4)
C(11)–Ru(1)–C(12)	37.6 (4)	C(1)–Ru(1)–C(13)	115.9 (5)
C(2)–Ru(1)–C(13)	136.7 (5)	C(3)–Ru(1)–C(13)	170.3 (5)
C(4)–Ru(1)–C(13)	150.7 (4)	C(5)–Ru(1)–C(13)	122.7 (4)
C(11)–Ru(1)–C(13)	66.9 (4)	C(12)–Ru(1)–C(13)	36.4 (4)
C(1)–Ru(1)–C(14)	135.9 (4)	C(2)–Ru(1)–C(14)	173.3 (4)
C(3)–Ru(1)–C(14)	148.7 (5)	C(4)–Ru(1)–C(14)	119.7 (5)
C(5)–Ru(1)–C(14)	114.8 (4)	C(11)–Ru(1)–C(14)	85.9 (4)
C(12)–Ru(1)–C(14)	70.9 (4)	C(13)–Ru(1)–C(14)	38.9 (4)
C(1)–Ru(1)–C(15)	161.1 (4)	C(2)–Ru(1)–C(15)	149.2 (4)
C(3)–Ru(1)–C(15)	115.0 (4)	C(4)–Ru(1)–C(15)	104.2 (5)
C(5)–Ru(1)–C(15)	124.2 (4)	C(11)–Ru(1)–C(15)	78.2 (4)
C(12)–Ru(1)–C(15)	87.0 (4)	C(13)–Ru(1)–C(15)	69.2 (4)
C(14)–Ru(1)–C(15)	37.5 (3)	C(1)–C(2)–C(7)	123.6 (12)
C(2)–C(1)–C(5)	106.3 (11)	C(2)–C(1)–C(6)	128.8 (13)
C(5)–C(1)–C(6)	124.5 (12)	C(1)–C(2)–C(3)	111.8 (13)
C(3)–C(2)–C(7)	124.5 (12)	C(2)–C(3)–C(4)	106.5 (10)
C(3)–C(4)–C(5)	108.8 (12)	C(2)–C(3)–C(8)	127.4 (14)
C(4)–C(3)–C(8)	125.5 (13)	C(3)–C(4)–C(9)	125.4 (11)
C(5)–C(4)–C(9)	125.2 (13)	C(4)–C(5)–C(10)	127.0 (12)
C(1)–C(5)–C(4)	106.6 (11)	C(10–C(5)–C(10)	126.0 (11)
Ru(1)–C(11)–C(12)	70.3 (7)	Ru(1)–C(12)–C(20)	126.5 (10)
Ru(1)–C(12)–C(13)	71.2 (7)	C(11)–C(12)–C(13)	120.8 (10)
C(19)–C(21)–C(23)	111.0 (9)	C(11)–C(12)–C(20)	120.9 (10)
C(13)–C(12)–C(20)	118.2 (10)	Ru(1)–C(13)–C(12)	72.4 (8)
Ru(1)–C(13)–C(14)	72.5 (6)	C(12)–C(13)–C(14)	129.5 (10)
Ru(1)–C(12)–C(11)	72.1 (7)	Ru(1)–C(14)–C(13)	68.5 (7)
Ru(1)–C(14)–C(15)	72.1 (6)	C(13)–C(14)–C(15)	119.8 (10)
Ru(1)–C(14)–C(19)	130.8 (7)	C(13)–C(14)–C(19)	122.3 (8)
C(15)–C(14)–C(19)	117.9 (10)	Ru(1)–C(15)–C(14)	70.4 (6)
Ru(1)–C(15)–C(16)	130.9 (8)	C(14)–C(15)–C(16)	114.1 (9)
C(15)–C(16)–C(17)	112.2 (9)	C(19)–C(21)–C(22)	117.5 (9)
C(16)–C(17)–C(18)	107.9 (11)	C(17)–C(18)–C(19)	86.0 (9)
C(16)–C(17)–C(21)	113.4 (10)	C(14)–C(19)–C(21)	108.3 (8)
C(18)–C(17)–C(21)	88.1 (9)	C(18)–C(19)–C(21)	86.0 (8)
C(17)–C(21)–C(22)	120.2 (10)	C(14)–C(19)–C(18)	109.7 (9)
C(22)–C(21)–C(23)	106.7 (11)	C(17)–C(21)–C(19)	85.6 (9)
C(17)–C(21)–C(23)	114.8 (10)		

By way of summary *it can* be stated that the ligand dimethylnopadiene shows a clear π-facial selectivity of complex formation, very similar to its congeners (+)-nopadiene[6] and the related cyclopentadienyl ligand described by Paquette.[8] The bulky dimethylmethylene bridge in the fused ring system very effectively prevents coordination from the "wrong" side of the ligand, thereby opening a direct route to the synthesis of a variety of optically active metal π-complexes. A complexation from the sterically more hindered side, while not impossible and in several cases observed,[6,8] will always have to be accompanied by a severe distortion of the ligand.

As the first example for the general method of synthesis outlined above was cyclopentadiene, a cyclic diolefin with an *endo*-methylene group, other cyclic diolefins were also investigated by us. 1,3- and 1,4-cyclohexadiene both gave the well-known cationic $[C_5Me_5Ru(\eta^6\text{-benzene})]^+$ complex (**12**).[4] Likewise, cycloheptatriene only produced the cation $[C_5Me_5Ru(\eta^6\text{-cycloheptatriene})]^+$ (**13**). 1,3-Cyclooctadiene, on the other hand, gave two products, namely the cationic species $[C_5Me_5Ru(\eta^6\text{-1,3,5-cyclooctatriene}]^+$ (**14**) as well as the neutral dienyl complex $C_5Me_5Ru(\eta^5\text{-cyclooctadienyl})$ (**15**).

The reaction of **1** with either cyclic or acyclic diolefins bearing (*Z*)-methyl or -methylene groups in the presence of a reducing agent therefore emerges as a general high-yield route to half-open ruthenocene derivatives,

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(8) Paquette, L. A.; Moriarty, K. J.; McKinney, J. A.; Rogers, R. D. *Organometallics* **1989**, *8*, 1707.

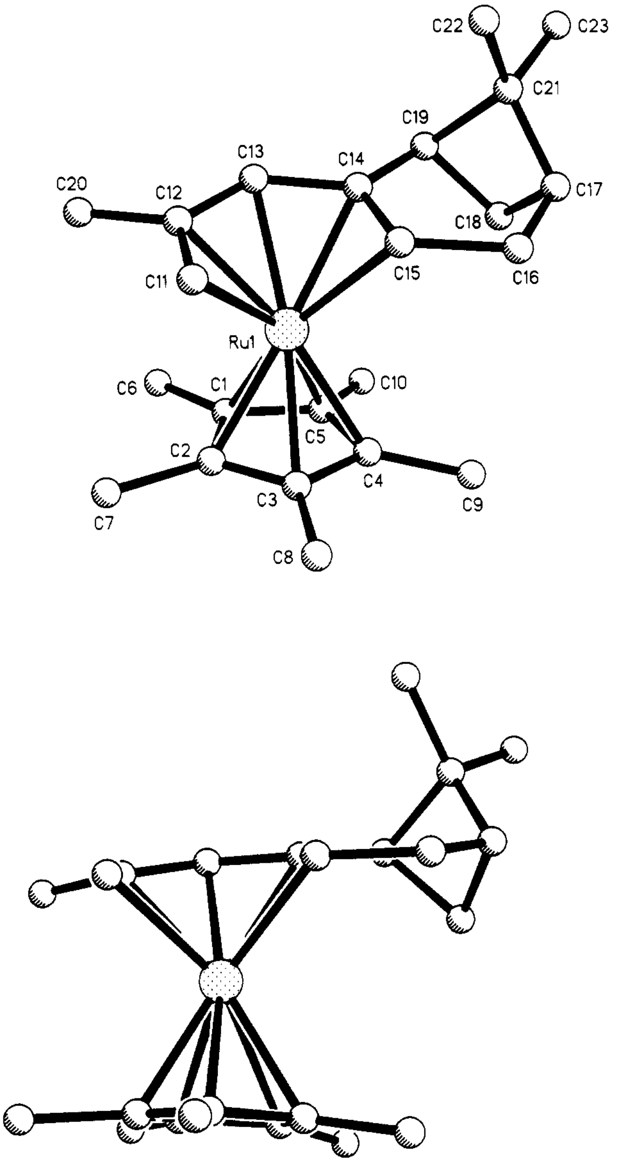


Figure 1. Molecular structure and crystallographic numbering scheme for $C_5Me_5RuC_{13}H_{19}$ (11). The crystallographic labeling scheme is arbitrary and different from the numbering used for assignment of ^{13}C NMR spectra.

C_5Me_5Ru(diolefin) chloro compounds, or cationic complexes with an η^6 ligand.

Reactivity of C_5Me_5(2,4-dimethylpentadienyl)ruthenium. Comparatively little is as yet known about the reactivity of open metallocenes, in contrast to the well-explored chemistry of metallocenes. As the half-open metallocenes appear to possess higher stability than their open analogues, we hoped to be able to show some general trends as far as their electrophilic or nucleophilic reactivities were concerned. The C_5Me_5 complexes appear to be more suitable for this than their C_5H_5 counterparts recently prepared by Ernst,[7] as the permethylated ligand is not expected to react itself in any way, apart from acting as a stabilizing force.

It had already been pointed out by Ernst that protonation of $C_5H_5RuC_7H_{11}$ afforded a stable product and proceeded much more readily than the protonation of ruthenocene.[7] The latter does not form an isolable product at all, the protonated species only being detectable in highly acidic solution by its proton NMR spectrum.

Treatment of 2 with HBF_4/propionic anhydride instantaneously gave the protonated complex **16**, precipitable by cold ether as a pale yellow solid in almost quantitative yields. The ^1H NMR spectrum at room temperature

$$C_5Me_5Ru(2,4\text{-}C_7H_{11}) + HBF_4 \rightarrow \underset{\mathbf{16}}{[C_5Me_5Ru(H)(2,4\text{-}C_7H_{11})]BF_4}$$

showed, apart from sharp singlets for the methyl groups of both ligands and a singlet at 5.97 ppm for the proton at C-3, one common, very broad signal centered at −0.8 ppm for the four terminal hydrogens of the dienyl ligand and the additional proton. When the temperature was lowered, this signal disappeared and at −80 °C three new sharp resonances in the ratio of 2:2:1 were detected at 2.45 ppm (doublet of doublets), −0.25 ppm (doublet of doublets), and −9.9 ppm (five-line signal) (Figure 2). This spectrum was very similar to the one reported by Ernst for the protonated species $[C_5H_5Ru(H)(2,4\text{-}C_7H_{11})]BF_4$ at low temperatures. In essence, the protonated complex appears to have a metal hydride ground state and at ambient temperatures shows fluxional behavior involving the hydride ligand and the terminal hydrogens at C-1 and C-5 of the pentadienyl ligand (see also ref 28).

The dynamic behavior observed for the protonated complex is in fact very reminiscent of a system described

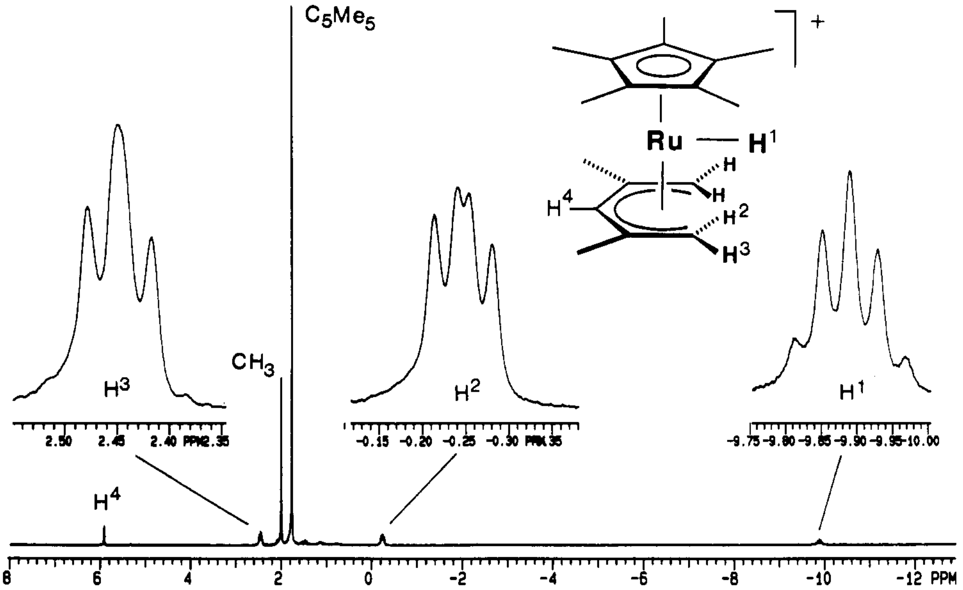
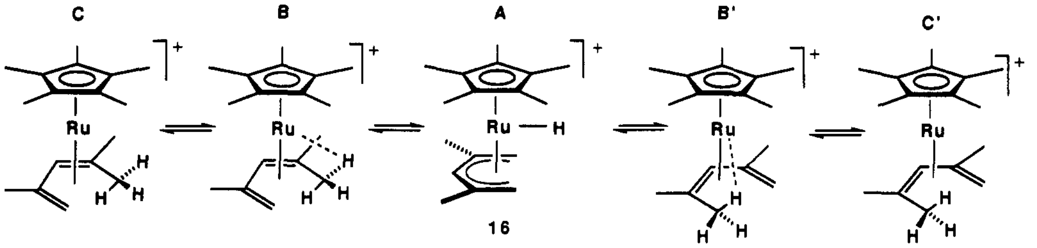


Figure 2. ^1H NMR spectrum for $[C_5Me_5Ru(H)(2,4\text{-}C_7H_{11})]^+$ at −80 °C.

Scheme V



by us recently, namely the protonated diolefin complexes $[C_5R_5M(H)(diene)]^+$ (R = H, CH_3; M = Co, Rh, Ir), where by low-temperature NMR spectroscopy the iridium complex was shown to have a metal hydride ground state, while for the cobalt and rhodium complexes agostic ground states could be identified.[9] The dynamic behavior at room temperature, however, was very similar for all complexes and a common mechanism for hydrogen exchange could be postulated for these complexes involving hydride (A), agostic (B), and unsaturated $16e^-$ (C) species in equilibrium.

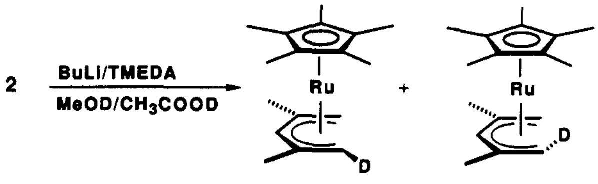
Formulating the same mechanism for the dynamic behavior of **16**, we envisage three similar species, the hydride complex (A), the agostic species (B, B′), and the unsaturated $16e^-$ diolefin complex (C, C′), in rapid equilibrium. The process C $\rightleftharpoons$ C′ then corresponds to a 1,5-hydrogen shift exchanging hydrogens from both ends of the diene ligand, while the process B $\rightleftharpoons$ C is best described as a hindered methyl rotation, equilibrating the three terminal hydrogens at one end, which would be inequivalent in a static agostic structure (Scheme V). These processes have indeed been observed separately under favorable conditions in other systems[10,11] and also in our own work on the protonated diolefin complexes of the cobalt triad.[9] C, C′ and B, B′ are enantiomeric pairs that interconvert by these processes through the hydride species, which has a plane of symmetry bisecting the C_5Me_5 and the dienyl ligand as well as the M–H bond. The participation of the unsaturated $16e^-$ diolefin species is also confirmed by the behavior of **16** toward Lewis bases such as CO. Short exposure to CO gas immediately transforms **16** to the complex $[C_5Me_5Ru(CO)(2,4\text{-}C_7H_{12})]^+$ (**17**), the proton now being irreversibly bound to the terminal carbon. This reactivity

$$[C_5Me_5Ru(H)(2,4\text{-}C_7H_{11})]BF_4 + CO \rightarrow \underset{\mathbf{17}}{[C_5Me_5Ru(CO)(2,4\text{-}C_7H_{12})]BF_4}$$

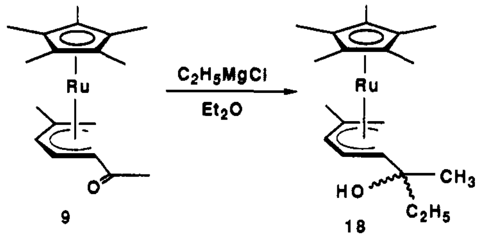
again closely matches that of the protonated diolefin complexes mentioned above, where, irrespective of the observed ground state of the protonated species, CO addition immediately formed $[C_5R_5M(CO)(allyl)]^+$ complexes (R = H, CH_3; M = Co, Rh, Ir) in virtually quantitative yields.[9] This method appears to be a very convenient way of converting complexes with η^x-π-bonded ligands into their cationic counterparts with η^{x-1} ligands.

While the protonation of **2** proceeded readily and quantitatively to give a stable product, we were unable to effect other electrophilic additions or substitutions. Various attempts at acetylation or formylation of **2** under conditions normally successful with metallocenes or diolefin complexes failed to give any stable products. Reagents used, among others, were acetyl chloride/$AlCl_3$, acetic anhydride/$AlCl_3$, acetic anhydride/H_3PO_4, and methylformamide/$POCl_3$.

Scheme VI



Scheme VII



Ferrocene and ruthenocene are known to be readily metalated by *n*-butyllithium, a route that, coupled with subsequent reactions, allows a wide range of substitutions to be carried out at the cyclopentadienyl rings. Metalation of **2** with 2.5 equiv of *n*-BuLi and 1.2 equiv of TMEDA, however, proceeded only very slowly, the metalated product separating after 3 days as pyrophoric orange-red crystals. To determine the site of metalation, the reaction mixture was then quenched with MeOD/CH_3COOD. The ^{13}C NMR spectrum showed that only the two terminal methylene carbons of the pentadienyl ligand had been deuterated, the product being an equal mixture of the monodeuterated *syn* and *anti* isomers (Scheme VI). Reaction of the metalated intermediate with DMF did not lead to the formation of any stable formylated product, so that this route also does not look promising for the introduction of functional groups into the pentadienyl moiety.

As we were able to synthesize functionalized dienyl complexes by the direct method, the reason for the failure of the electrophilic substitution route cannot be seen in the lack of stability of the final products, but possibly in competing redox reactions and subsequent decomposition under the reaction conditions. Thus, C_5Me_5Ru(2-methyl-6-oxoheptadienyl) (**9**), prepared by reaction of $[C_5Me_5RuCl_2]_n$ with (*E*)-2-methyl-2,4-heptadien-6-one, not only forms in good yields (64%) but appears to be no less stable than the other half-open metallocenes. Attempts, however, to reduce the ketone group were unsuccessful with $NaBH_4$ (no reaction) or $LiAlH_4$ (decomposition). Only reaction with EtMgCl led to the stereospecific formation of one tertiary alcohol product, **18**, which was characterized by a ^{13}C NMR spectrum. Further attempts at purification by chromatography again led to decomposition (Scheme VII). It therefore seems doubtful whether half-open or open metallocenes will ever have an organic chemistry as rich as that of their closed analogues, as at

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[9] Buchmann, B.; Piantini, U.; von Philipsborn, W.; Salzer, A. *Helv. Chim. Acta* **1987**, *70*, 1487.

[10] Michael, G.; Kaub, J.; Kreiter, C. G. *Chem. Ber.* **1985**, *118*, 3944.

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Table V. Atom Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3) for 19

	x	y	z	U(eq)[a]
Ru(1)	8168 (1)	2500	4427 (1)	37 (1)
Ru(2)	6085 (1)	2500	4360 (1)	24 (1)
C(1)	7017 (3)	3697 (3)	4734 (2)	34 (1)
C(2)	7656 (3)	3585 (3)	5417 (2)	43 (1)
C(3)	7915 (4)	2500	5722 (3)	47 (1)
C(4)	8202 (4)	4590 (5)	5765 (3)	72 (1)
C(5)	9697 (3)	3097 (5)	4175 (3)	76 (1)
C(6)	9078 (4)	3441 (6)	3554 (4)	95 (1)
C(7)	8683 (5)	2500	3165 (5)	98 (2)
C(8)	4453 (4)	2500	3941 (3)	36 (1)
C(9)	3533 (5)	2500	4473 (4)	63 (1)
C(10)	4927 (3)	3475 (3)	3633 (2)	36 (1)
C(11)	4623 (4)	4678 (4)	3773 (3)	66 (1)
C(12)	5737 (3)	3115 (3)	3138 (2)	38 (1)
C(13)	6363 (4)	3868 (5)	2615 (3)	68 (1)
N(1)	5528 (3)	2500	5503 (2)	32 (1)
C(14)	5135 (4)	2500	6116 (3)	35 (1)
C(15)	4624 (5)	2500	6888 (3)	53 (1)
P(1)	11593 (2)	2500	6348 (1)	86 (1)
F(1)	11461 (5)	2500	5421 (3)	193 (2)
F(2)	11787 (4)	2500	7265 (3)	117 (1)
F(3)	12450 (3)	3434 (4)	6234 (3)	124 (1)
F(4)	10754 (3)	3382 (5)	6453 (3)	162 (1)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

least some of the more promising synthetic routes for functionalization seem to be unproductive.

Formation and X-ray Structure of a Dimetallic Ruthenabenzene Complex. It is now generally accepted that triple-decker complexes with cyclopentadienyl or similar cyclic ligands should achieve maximum stability when having a 30-valence-electron (VE) shell. This is also supported by molecular orbital calculations.[12] Nevertheless, the first, and for a long time the only, triple-decker complex with cyclopentadienyl rings, the well-known $[Cp_3Ni_2]^+$ prepared by us almost two decades ago,[13] is an exception to this rule, having 34 valence electrons. Attempts to prepare the 30-VE analogues of the iron triad were unsuccessful for a long time. Only in 1987 did Rybinskaya and co-workers show that the inclusion of pentamethylcyclopentadienyl ligands for the bridging position was essential to obtain stable products such as $[CpRuC_5Me_5RuC_5Me_5]^+$.[4] This result prompted us to investigate whether similar triple-decked species, with either a C_5Me_5 or a pentadienyl ligand occupying the central bridging position, could be obtained from 2 by the now well-established "stacking" procedures.

On treatment of 2 with the labile precursor $[CpRu(CH_3CN)_3]PF_6$, we indeed observed the formation of the dimetallic product 19 with analytical formula $[C_{24}H_{32}NRu_2]PF_6$ in a slow reaction. Proton NMR spectra showed that apparently two hydrogens of the pentadienyl ligand has been lost in the reaction. Two hydrogen atoms resonated at very low field (10.3 ppm) and these were, according to heteronuclear 2D experiments, directly bonded to carbon atoms resonating at 178 ppm in the ^{13}C NMR spectrum. As we were unable to elucidate the structure of 19 from spectroscopic and analytical data alone, an X-ray structural analysis was also undertaken. Crystals were grown from a saturated solution of 19 in propionic anhydride slowly cooled to −20 °C. Bond lengths are listed in Table VI and bond angles in Table VII.

The structure of 19 (Figure 3) can roughly be described as that of a dimetallic "ruthenabenzene" complex. While the CpRu unit, introduced through the addition of $[CpRu(CH_3CN)_3]^+$, is now η^6-bonded to the metallabenzene unit in a symmetrical fashion, the C_5Me_5Ru moiety has tilted by 90° and ruthenium has inserted into two terminal C–H bonds, now forming one part of a six-membered heterocycle. An additional CH_3CN ligand is also coordinated to this ruthenium atom, bringing the overall electron count to 34 valence electrons.

Table VI. Bond Lengths (Å) for 19

Ru(1)–Ru(2)	2.767 (1)	Ru(1)–C(1)	2.146 (3)
Ru(1)–C(2)	2.193 (4)	Ru(1)–C(3)	2.173 (5)
Ru(1)–C(5)	2.190 (5)	Ru(1)–C(6)	2.192 (7)
Ru(1)–C(7)	2.202 (8)	Ru(1)–C(1A)	2.146 (3)
Ru(1)–C(2A)	2.193 (4)	Ru(1)–C(5A)	2.190 (5)
Ru(1)–C(6A)	2.192 (7)	Ru(2)–C(1)	1.983 (3)
Ru(2)–C(8)	2.276 (5)	Ru(2)–C(10)	2.269 (4)
Ru(2)–C(12)	2.202 (3)	Ru(2)–N(1)	2.034 (4)
Ru(2)–C(1A)	1.983 (3)	Ru(2)–C(10A)	2.269 (4)
Ru(2)–C(12A)	2.202 (3)	C(1)–C(2)	1.420 (5)
C(2)–C(3)	1.425 (5)	C(2)–C(4)	1.510 (7)
C(3)–C(2A)	1.425 (5)	C(5)–C(6)	1.379 (8)
C(5)–C(5A)	1.416 (12)	C(6)–C(7)	1.392 (8)
C(7)–C(6A)	1.392 (8)	C(8)–C(9)	1.507 (8)
C(8)–C(10)	1.412 (5)	C(8)–C(10A)	1.412 (5)
C(10)–C(11)	1.502 (6)	C(10)–C(12)	1.418 (5)
C(12)–C(13)	1.497 (6)	C(12)–C(12A)	1.459 (7)
N(1)–C(14)	1.142 (6)	C(14)–C(15)	1.448 (8)
P(1)–F(1)	1.546 (6)	P(1)–F(2)	1.541 (5)
P(1)–F(3)	1.598 (4)	P(1)–F(4)	1.538 (5)
P(1)–F(3A)	1.598 (4)	P(1)–F(4A)	1.538 (5)

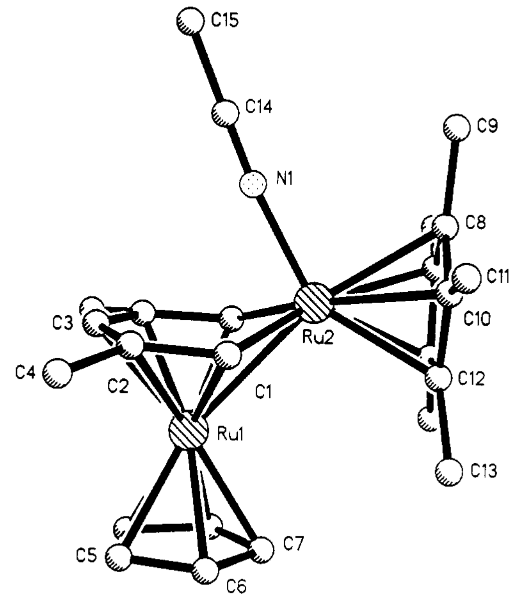

Figure 3. Molecular structure and crystallographic numbering scheme for $[(C_5H_5)Ru(\mu\text{-}C_7H_9)Ru(C_5Me_5)(CH_3CN)]PF_6$ (19) (PF_6 anion not shown).

It cannot be excluded that the primary product of the reaction is indeed a triple-decked species with a central pentadienyl ligand (that might be referred to as a "one-third open" triple decker), which then by insertion of ruthenium into the two terminal C–H bonds, reductive elimination of H_2, and addition of CH_3CN gives the final product (Scheme VIII). It has in fact been observed that mass spectra of half-open metallocenes show prominent peaks corresponding to loss of H_2, and a similar conversion of a monomeric pentadienyl precursor to a dimetallic metallabenzene species has been previously described in one case.[14]

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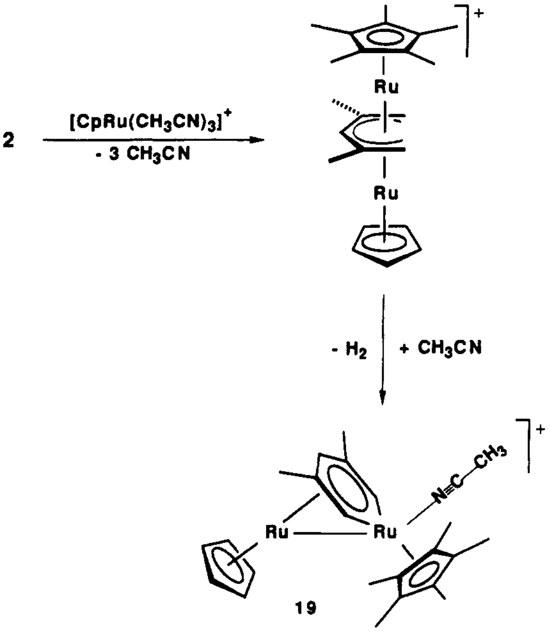
(13) Werner, H.; Salzer, A. *Synth. Inorg. Met.-Org. Chem.* **1972**, *2*, 239.

(14) Kralik, M. S.; Rheingold, A. L.; Ernst, R. D. *Organometallics* **1987**, *6*, 2612.

Table VII. Bond Angles (deg) for 19

Ru(2)–Ru(1)–C(1)	45.5 (1)	Ru(2)–Ru(1)–C(2)	73.8 (1)	C(12)–Ru(2)–C(1A)	131.0 (1)	N(1)–Ru(2)–C(1A)	86.3 (1)
C(1)–Ru(1)–C(2)	38.2 (1)	Ru(2)–Ru(1)–C(3)	83.4 (2)	Ru(1)–Ru(2)–C(10A)	134.3 (1)	C(1)–Ru(2)–C(10A)	162.5 (1)
C(1)–Ru(1)–C(3)	69.9 (1)	C(2)–Ru(1)–C(3)	38.1 (1)	C(8)–Ru(2)–C(10A)	36.2 (1)	C(10)–Ru(2)–C(10A)	61.3 (2)
Ru(2)–Ru(1)–C(5)	156.7 (1)	C(1)–Ru(1)–C(5)	119.4 (2)	C(12)–Ru(2)–C(10A)	62.5 (1)	N(1)–Ru(2)–C(10A)	104.3 (1)
C(2)–Ru(1)–C(5)	103.9 (2)	C(3)–Ru(1)–C(5)	109.4 (2)	C(1A)–Ru(2)–C(10A)	102.9 (1)	Ru(1)–Ru(2)–C(12A)	104.3 (1)
Ru(2)–Ru(1)–C(6)	121.6 (2)	C(1)–Ru(1)–C(6)	102.2 (2)	C(1)–Ru(2)–C(12A)	131.0 (1)	C(8)–Ru(2)–C(12A)	61.3 (1)
C(2)–Ru(1)–C(6)	111.5 (2)	C(3)–Ru(1)–C(6)	137.6 (2)	C(10)–Ru(2)–C(12A)	62.5 (1)	C(12)–Ru(2)–C(12A)	38.7 (2)
C(5)–Ru(1)–C(6)	36.7 (2)	Ru(2)–Ru(1)–C(7)	105.8 (2)	N(1)–Ru(2)–C(12A)	141.3 (1)	C(1A)–Ru(2)–C(12A)	100.5 (1)
C(1)–Ru(1)–C(7)	116.5 (2)	C(2)–Ru(1)–C(7)	143.8 (1)	C(10A)–Ru(2)–C(12A)	36.9 (1)	Ru(1)–C(1)–Ru(2)	84.0 (1)
C(3)–Ru(1)–C(7)	170.8 (2)	C(5)–Ru(1)–C(7)	62.0 (2)	Ru(1)–C(1)–C(2)	72.7 (2)	Ru(2)–C(1)–C(2)	123.7 (3)
C(6)–Ru(1)–C(7)	36.9 (2)	Ru(2)–Ru(1)–C(1A)	45.5 (1)	Ru(1)–C(2)–C(1)	69.1 (2)	Ru(1)–C(2)–C(3)	70.2 (3)
C(1)–Ru(1)–C(1A)	82.8 (2)	C(2)–Ru(1)–C(1A)	89.5 (1)	C(1)–C(2)–C(3)	120.8 (4)	Ru(1)–C(2)–C(4)	127.0 (3)
C(3)–Ru(1)–C(1A)	69.9 (1)	C(5)–Ru(1)–C(1A)	156.7 (2)	C(1)–C(2)–C(4)	121.2 (4)	C(3)–C(2)–C(4)	117.5 (4)
C(6)–Ru(1)–C(1A)	152.3 (2)	C(7)–Ru(1)–C(1A)	116.5 (2)	Ru(1)–C(3)–C(2)	71.7 (2)	Ru(1)–C(3)–C(2A)	71.7 (2)
Ru(2)–Ru(1)–C(2A)	73.8 (1)	C(1)–Ru(1)–C(2A)	89.5 (1)	C(2)–C(3)–C(2A)	129.2 (5)	Ru(1)–C(5)–C(6)	71.7 (3)
C(2)–Ru(1)–C(2A)	71.9 (2)	C(3)–Ru(1)–C(2A)	38.1 (1)	Ru(1)–C(5)–C(5A)	71.1 (1)	C(6)–C(5)–C(5A)	107.2 (4)
C(5)–Ru(1)–C(2A)	128.3 (2)	C(6)–Ru(1)–C(2A)	164.6 (2)	Ru(1)–C(6)–C(5)	71.6 (4)	Ru(1)–C(6)–C(7)	71.9 (4)
C(7)–Ru(1)–C(2A)	143.8 (1)	C(1A)–Ru(1)–C(2A)	38.2 (1)	C(5)–C(6)–C(7)	109.4 (6)	Ru(1)–C(7)–C(6)	71.1 (4)
Ru(2)–Ru(1)–C(5A)	156.7 (1)	C(1)–Ru(1)–C(5A)	156.7 (2)	Ru(1)–C(7)–C(6A)	71.1 (4)	C(6)–C(7)–C(6A)	106.6 (7)
C(2)–Ru(1)–C(5A)	128.3 (2)	C(3)–Ru(1)–C(5A)	109.4 (2)	Ru(2)–C(8)–C(9)	126.4 (4)	Ru(2)–C(8)–C(10)	71.7 (2)
C(5)–Ru(1)–C(5A)	37.7 (3)	C(6)–Ru(1)–C(5A)	61.8 (2)	C(9)–C(8)–C(10)	125.0 (2)	Ru(2)–C(8)–C(10A)	71.7 (2)
C(7)–Ru(1)–C(5A)	62.0 (2)	C(1A)–Ru(1)–C(5A)	119.4 (2)	C(9)–C(8)–C(10A)	125.0 (2)	C(10)–C(8)–C(10A)	110.0 (4)
C(2A)–Ru(1)–C(5A)	103.9 (2)	Ru(2)–Ru(1)–C(6A)	121.6 (2)	Ru(2)–C(10)–C(8)	72.1 (2)	Ru(2)–C(10)–C(11)	125.8 (3)
C(1)–Ru(1)–C(6A)	152.3 (2)	C(2)–Ru(1)–C(6A)	164.6 (2)	C(8)–C(10)–C(11)	127.1 (4)	Ru(2)–C(10)–C(12)	68.9 (2)
C(3)–Ru(1)–C(6A)	137.6 (2)	C(5)–Ru(1)–C(6A)	61.8 (2)	C(8)–C(10)–C(12)	107.5 (3)	C(11)–C(10)–C(12)	125.4 (4)
C(6)–Ru(1)–C(6A)	61.3 (4)	C(7)–Ru(1)–C(6A)	36.9 (2)	Ru(2)–C(12)–C(10)	74.1 (2)	Ru(2)–C(12)–C(13)	127.8 (3)
C(1A)–Ru(1)–C(6A)	102.2 (2)	C(2A)–Ru(1)–C(6A)	111.5 (2)	C(10)–C(12)–C(13)	125.2 (4)	Ru(2)–C(12)–C(12A)	70.7 (1)
C(5A)–Ru(1)–C(6A)	36.7 (2)	Ru(1)–Ru(2)–C(1)	50.5 (1)	C(10)–C(12)–C(12A)	107.5 (2)	C(13)–C(12)–C(12A)	126.7 (3)
Ru(1)–Ru(2)–C(8)	164.6 (1)	C(1)–Ru(2)–C(8)	133.6 (1)	Ru(2)–N(1)–C(14)	174.2 (4)	N(1)–C(14)–C(15)	179.2 (6)
Ru(1)–Ru(2)–C(10)	134.3 (1)	C(1)–Ru(2)–C(10)	102.9 (1)	F(1)–P(1)–F(2)	177.0 (3)	F(1)–P(1)–F(3)	87.9 (3)
C(8)–Ru(2)–C(10)	36.2 (1)	Ru(1)–Ru(2)–C(12)	104.3 (1)	F(2)–P(1)–F(3)	89.9 (2)	F(1)–P(1)–F(4)	91.7 (3)
C(1)–Ru(2)–C(12)	100.5 (1)	C(8)–Ru(2)–C(12)	61.3 (1)	F(2)–P(1)–F(4)	90.5 (3)	F(3)–P(1)–F(4)	93.3 (2)
C(10)–Ru(2)–C(12)	36.9 (1)	Ru(1)–Ru(2)–N(1)	109.0 (1)	F(1)–P(1)–F(3A)	87.9 (3)	F(2)–P(1)–F(3A)	89.9 (2)
C(1)–Ru(2)–N(1)	86.3 (1)	C(8)–Ru(2)–N(1)	86.4 (2)	F(3)–P(1)–F(3A)	87.8 (3)	F(4)–P(1)–F(3A)	178.9 (3)
C(10)–Ru(2)–N(1)	104.3 (1)	C(12)–Ru(2)–N(1)	141.3 (1)	F(1)–P(1)–F(4A)	91.7 (3)	F(2)–P(1)–F(4A)	90.5 (3)
Ru(1)–Ru(2)–C(1A)	50.5 (1)	C(1)–Ru(2)–C(1A)	91.5 (2)	F(3)–P(1)–F(4A)	178.9 (3)	F(4)–P(1)–F(4A)	85.7 (4)
C(8)–Ru(2)–C(1A)	133.6 (1)	C(10)–Ru(2)–C(1A)	162.5 (1)	F(3A)–P(1)–F(4A)	93.3 (2)		

Scheme VIII



Several structural features of the complex merit some further comment. A crystallographic mirror plane bisects the cation as well as the PF_6 anion, the atoms C(3), Ru(1), Ru(2), C(7), and C(8) as well as P(1), F(1), and F(2) lying on this plane. As a consequence, the pentadienyl part of the ruthenabenzene and the cyclopentadienyl ligand adopt a staggered conformation, in contrast to the case for the half-open metallocene $CpRuC_7H_{11}$.[7] The Cp and C_5Me_5 ligands are in two planes perpendicular to each other. The bond lengths within the former pentadienyl ligand are almost identical, indicating a high degree of delocalization. The Ru–Ru distance of 2.676 Å is on the order of a normal single metal–metal bond. Noteworthy are the short distances Ru(2)–C(1) and Ru(2)–C(1A). At 1.983 Å they are considerably shorter than the value expected for Ru–C single bonds (2.05–2.19 Å)[15] and almost fall within the range of Ru=C double bonds (1.83–1.94 Å). The C(1)–Ru(2)–C(1A) angle is 91.5° and is similar to that found in other heterobenzenes, e.g. stibabenzene (C–Sb–C = 93°, C–Sb = 2.05 Å).[16] The ruthenium atom is, however, significantly displaced from the plane of the five pentadienyl carbons by 27.2°. This may be due to strong steric interaction between the hydrogen atoms of the Cp and C_5Me_5 rings but may also help to optimize the Ru–Ru bond length. The delocalization of electrons within the ruthenabenzene moiety and the partial metal–carbene character of the Ru–C bonds is apparent from the ^1H and ^{13}C chemical shifts of the terminal CH units, which, as mentioned earlier, occur at very low field. Similar low-field shifts for terminal C–H units are also found in "fly-over" complexes,[17] but not in true triple-decked species, where the doubly coordinated C–H units are strongly shielded and NMR signals are shifted to higher field. The formulation of 19 as either a metallabenzene or as a fly-over complex is therefore largely a question of semantics rather than of any basic difference in bonding modes, the major distinction being that in fly-over complexes, such as $[CpRu(\mu\text{-}C_8H_8)RuCp]^{2+}$,[17] the two terminal carbons are

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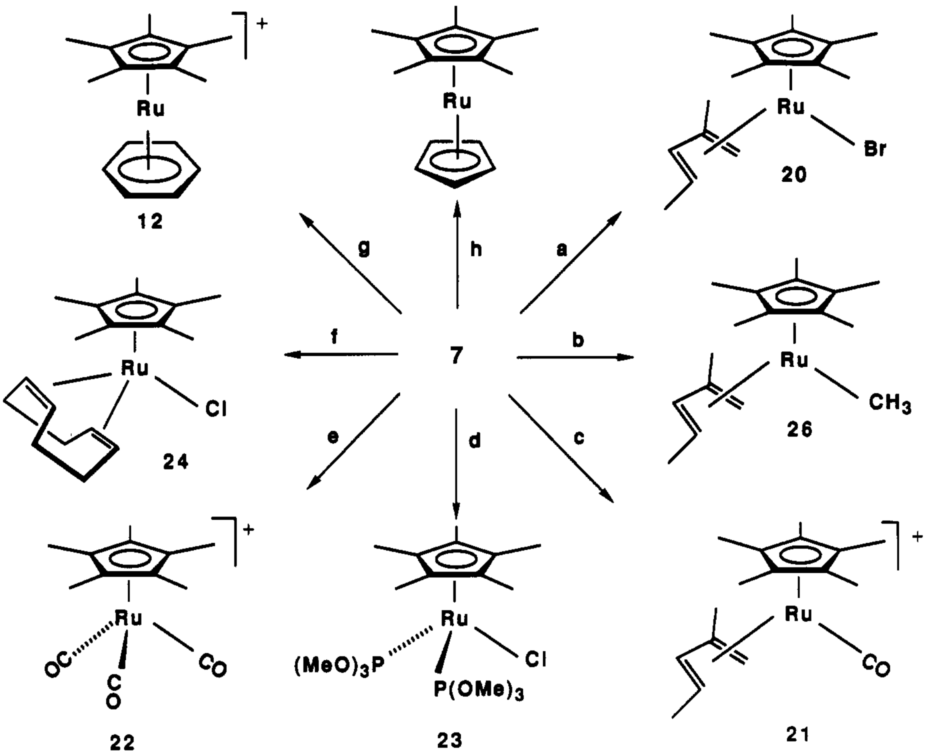
Scheme IX[a]



[a] Legend: (a) LiBr, MeOH; (b) MeMgCl, THF; (c) CO, MeOH; (d) P(OMe)$_3$, THF; (e) CO, AgBF$_4$, acetone; (f) cod, acetone; (g) C$_6$H$_6$, acetone; (h) TlCp, EtOH.

σ-bonded to two different metal atoms and not, as in **19**, to the same metal.

Metallabenzenes are still very rare species, in contrast to the relatively large number of metallacyclopentadienes described in the literature. The only examples, to our knowledge, are an osmabenzene complex described by Roper,[18] an iridabenzene compound made by Bleeke,[19] and a dimetallic molybdabenzene derivative prepared by Ernst.[14] All of these complexes show similar structural and spectroscopic features with a large degree of delocalization within the metallabenzene ring and also the characteristic low-field NMR shifts at the terminal C–H units. The question as to what extent metallabenzenes can be expected to show delocalization has also been addressed in a theoretical paper by Hoffmann[20] (see also ref 19b).

In conclusion, it can be said that the only stable products formed from **2** are those derived from protonation, from lithiation, and from attack by an unsaturated organometallic fragment. We are currently trying to establish whether **2** could also be used as a building block for other bi- or polymetallic species.

Reactivity of C$_5$Me$_5$Ru(diene)Cl Complexes. It has already been described that reaction of [C$_5$Me$_5$RuCl$_2$]$_n$/Zn with diolefins not having terminal (*Z*)-methyl or -methylene groups leads to the formation of C$_5$Me$_5$Ru(diene)Cl complexes in excellent yields. It seemed worthwhile to also explore the reactivity of this type of complex with regard to substitution reactions, as the number of selective routes to C$_5$Me$_5$RuL$_x$ complexes is still small. Previous methods used start from [Ru(nbd)Cl$_2$]$_x$,[21] [C$_5$Me$_5$RuCl$_2$]$_n$,[22] or [C$_5$Me$_5$Ru(CO)$_2$]$_2$[23] and either suffer from low yields or require several steps, especially if, as in the last case, the substitution of both carbonyl ligands is required. C$_5$Me$_5$Ru(diene)Cl appears as a suitable multifunctional starting material, as the diolefin, the halide ligand, or both can in principle be substituted. We found that these substitution reactions indeed occur and can be fine-tuned by variation of temperature, solvent, and halide-abstracting reagent (Scheme IX).

Metathesis of **7** with LiBr in methanol led to the quantitative formation of C$_5$Me$_5$Ru(C$_6$H$_{10}$)Br (**20**). Reaction with CO at room temperature and precipitation with NH$_4$PF$_6$ gave [C$_5$Me$_5$Ru(C$_6$H$_{10}$)CO]PF$_6$ (**21**) in excellent yields, while reaction with CO and AgBF$_4$ under reflux produced [C$_5$Me$_5$Ru(CO)$_3$]$^+$ (**22**) in 89% yield.[23] In less polar solvents, such as THF, the displacement of the diolefin ligand appears to be much more favored, as treatment of **7** with P(OMe)$_3$ gives the neutral product C$_5$Me$_5$Ru{P(OMe)$_3$}$_2$Cl (**23**) exclusively. The diolefinic ligand can also readily be displaced by other diolefins, e.g. by 1,5-cyclooctadiene (cod) to form C$_5$Me$_5$Ru(cod)Cl (**24**). By addition of AgBF$_4$ together with cyclooctadiene, complex **25** with the formula [C$_5$Me$_5$Ru(η^4-C$_8$H$_{12}$)(η^2-C$_8$H$_{12}$)]BF$_4$ is formed, in which one cod ligand is bound by two double bonds and the other by only one. Triolefins such as cycloheptatriene or benzene substitute both diolefin and halide ligands under mild conditions to form [C$_5$Me$_5$Ru(η^6-C$_7$H$_8$)]$^+$ (**13**) and [C$_5$Me$_5$Ru(C$_6$H$_6$)]$^+$ (**12**), respectively. Reaction of **7** with TlCp gave C$_5$Me$_5$RuC$_5$H$_5$[4] in virtually quantitative yields. A similar versatile substitution chemistry has also been described for CpRu(cod)Cl.[24]

Finally, we also substituted the chloro ligand for an alkyl group. Reaction of **7** with CH$_3$MgCl gave pale yellow

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crystals of $C_5Me_5Ru(C_6H_{10})CH_3$ (**26**) in 80% yield. We are currently exploring the chemistry of this interesting molecule.

In conclusion, it can be summarized that reductive treatment of $[C_5Me_5RuCl_2]_n$ with zinc powder in the presence of diolefins provides an elegant entry into the field of half-open sandwich complexes as well as a facile high-yield route for the synthesis of half-sandwich complexes of the general type $C_5Me_5RuL_2X$, $[C_5Me_5RuL_3]^+$, and $[C_5Me_5RuL_2L']^+$.

Experimental Section

$RuCl_3{\cdot}xH_2O$ was purchased from Johnson-Matthey (Ru content 42.12%); $[C_5Me_5RuCl_2]_n$[22] and $[C_5H_5Ru(CH_3CN)_3]^+$[25] were prepared by the published procedures. The ligands 1,3-pentadiene, 2-methyl-1,3-pentadiene, 1,3,5-cycloheptatriene, 1,3-cyclohexadiene, 1,4-cyclohexadiene, 1,3-cyclooctadiene, and β-ionone as well as isopropyltriphenylphosphonium bromide/$NaNH_2$ ("Instant-Ylide") were commercial products of Fluka, 3-methyl-1,3-pentadiene and (−)-myrtenal were purchased from Aldrich, 3-methylcrotonaldehyde was obtained from Merck, and pentamethylcyclopentadiene was purchased from Strem Chemicals. (*E*)-2-Methyl-1,3-pentadiene was prepared by the method of Ernst[26] and 2,4-dimethyl-1,3-pentadiene by the procedure of Jitkow,[27] *using* CH_3Li *instead of* CH_3MgCl.

All operations involving organometallics were carried out under a nitrogen atmosphere by using Schlenk type glassware. Nonaqueous solvents were thoroughly dried and deoxygenated by standard methods. Elemental analyses were carried out by the Analytical Department of the Organic Laboratory of Zürich University. ^1H, $^{13}C\{^1H\}$, and ^1H–^{13}C HETCOR-2D NMR spectra were recorded by using a Varian Gemini 200 instrument at either 200 or 50.3 MHz at ambient temperatures, unless otherwise stated. Mass spectra were obtained on a Finnigan MAT 8230 instrument.

(*E*)-2-Methyl-2,4-heptadien-6-one. A 10% aqueous NaOH solution (100 mL) was added with vigorous stirring to 25 mL of 3-methylcrotonaldehyde, dissolved in acetone (100 mL) and H_2O (400 mL). Stirring was continued for 50 h at room temperature, the solution gradually turning dark yellow. After this solution was extracted three times with 200 mL of ether each time, the collected organic phases were dried over $MgSO_4$ and ether was evaporated under reduced pressure. Distillation of the residue gave 12 g (37%) of slightly yellow (*E*)-2-methyl-2,4-heptadien-6-one, bp 93 °C/15 mm. ^{13}C NMR ($CDCl_3$): δ 197.3 (C-2), 146.3 (C-6), 138.6, 127.4, 123.5 (C-5, C-4, C-3), 26.1, 25.4, 17.7 (C-1, C-7, CH_3).

Synthesis of Dimethylnopadiene. Isopropyltriphenylphosphonium bromide/$NaNH_2$ (Instant-Ylide; 30 g, 69 mmol) was dissolved in THF (300 mL) and the mixture stirred for 1 h. (−)-Myrtenal (10.36 g, 69 mmol) was added and stirring continued for 2 h. The pale yellow suspension was poured on Et_2O/H_2O (200 mL/200 mL), and the ether phase was separated. After several ether extractions, the collected organic phases were washed with 40% aqueous $NaHSO_3$ solution and dried over $NaHCO_3$. After evaporation of most of the solvent, Ph_3PO precipitated and was filtered off. After further evaporation, the oily residue was distilled to give dimethylnopadiene (9.36 g), bp 80–82 °C/10 mm. Anal. Calcd for $C_{13}H_{20}$: C, 88.56; H, 11.43. Found: C, 88.84; H, 11.22. ^{13}C NMR ($CDCl_3$): δ 145.7, 132.6 (C), 126.3, 120.4 (CH), 46.7, 40.4 (CH), 37.5 (C), 31.6, 31.4 (CH_2), 26.5, 26.2, 20.9, 19.6 (CH_3).

Typical Synthesis Using a Diolefin with a (*Z*)-Methyl Group: (Pentamethylcyclopentadienyl)(2,4-dimethylpentadienyl)ruthenium, $(\eta^5\text{-}C_5Me_5)Ru(\eta^5\text{-}2,4\text{-}C_7H_{11})$ (2). $[C_5Me_5RuCl_2]_n$ (1.2 g, 3.9 mmol) and 2,4-dimethyl-1,3-pentadiene (8 mL) were dissolved in ethanol (20 mL), and the mixture was stirred for 3 h. After addition of zinc powder (1 g), stirring was continued for 1 h. The solution was filtered over a fritted disk covered with cotton wool. Solvent was removed in vacuo, and the crystalline residue was taken up in hexane and filtered again over 10 cm of Al_2O_3 (grade IV). After evaporation of the solvent and drying under high vacuum, pale yellow crystals (1.2 g, 95%) remained. Anal. Calcd for $C_{17}H_{26}Ru$: C, 61.6; H, 7.9; Ru, 30.5. Found: C, 61.5; H, 8.0; Ru, 30.4. ^1H NMR (C_6D_6): δ 4.77 (s, 1 H), 2.15 (dd, 2 H, *J* = 2.5, 0.6 Hz), 1.73 (s, 6 H), 1.68 (s, 15 H), 0.34 (dd, 2 H, *J* = 2.5, 0.6 Hz). ^{13}C NMR ($CDCl_3$): δ 91.7 (C-3), 91.2 (C-2), 89.4 (C_5Me_5), 43.8 (C-1), 25.3 (CH_3), 10.4 ($(CH_3)_5$). Mass spectrum (EI; *m*/*e* (relative intensity)): 135 (16), 228 (16), 229 (17), 230 (19), 231 (20), 232 (19), 233 (18), 234 (15), 309 (18), 311 (14), 312 (31), 313 (38), 314 (42), 315 (79), 316 (19), 317 (45), 324 (14), 326 (18), 327 (31), 328 (39), 329 (72), 330 (100), 331 (58), 332 (99), 333 (20), 334 (36).

(Pentamethylcyclopentadienyl)pentadienylruthenium, $(\eta^5\text{-}C_5Me_5)Ru(\eta^5\text{-}C_5H_7)$ (3): same procedure as for **2**, using (*Z*)-1,3-pentadiene; yield 85%. Anal. Calcd for $C_{15}H_{22}Ru$: C, 59.38; H, 7.31. Found: C, 59.54; H, 7.39. ^1H NMR (C_6D_6): δ 4.83 (tt, 1 H, *J* = 5.7, 0.8 Hz), 4.02 (m, 2 H, *J* = 5.6, 8.4, 8.4 Hz), 2.30 (dd, 2 H, *J* = 8.5, 2.3 Hz), 1.73 (s, 15 H), 0.32 (ddd, 2 H, *J* = 8.5, 2.5, 0.8 Hz). ^{13}C NMR ($CDCl_3$): δ 91.5 (C-3), 90.2 (C_5Me_5), 82.5 (C-2), 42.5 (C-1), 10.5 ($(CH_3)_5$).

(Pentamethylcyclopentadienyl)(3-methylpentadienyl)ruthenium, $(\eta^5\text{-}C_5Me_5)Ru(\eta^5\text{-}C_6H_9)$ (4): same procedure as for **2**, using (*Z*)-3-methylpentadiene; yield 82%. Anal. Calcd for $C_{16}H_{24}Ru$: C, 60.54; H, 7.62. Found: C, 60.81; H, 7.54. ^1H NMR (C_6D_6): δ 3.88 (t, 2 H, *J* = 8.0 Hz), 2.30 (dd, 2 H, *J* = 7.7, 2.5 Hz), 1.79 (s, 3 H), 1.64 (s, 15 H), 0.39 (dd, 2 H, *J* = 7.7, 2.5 Hz). ^{13}C NMR ($CDCl_3$): δ 100.6 (C-3), 89.6 (C_5Me_5), 82.8 (C-2), 42.9 (C-1), 21.6 (CH_3), 10.2 ($(CH_3)_5$).

(Pentamethylcyclopentadienyl)(2-methylpentadienyl)ruthenium, $(\eta^5\text{-}C_5Me_5)Ru(\eta^5\text{-}C_6H_9)$ (5): same procedure as for **2**, using (*Z*)-2-methylpentadiene; yield 89%. Anal. Calcd for $C_{16}H_{24}Ru$: C, 60.54; H, 7.62. Found: C, 60.81; H, 7.54. ^1H NMR (C_6D_6): δ 4.79 (d, 1 H, *J* = 5.6 Hz), 3.97 (dt, 1 H, *J* = 5.7, 8.4 Hz), 2.26 (dd, 1 H, *J* = 8.3, 2.5 Hz), 2.20 (d, 1 H, *J* = 2.1 Hz), 1.73 (s, 3 H), 1.70 (s, 15 H), 0.48 (dd, 1 H, *J* = 8.4, 2.5 Hz), 0.38 (d, 1 H, *J* = 2.2 Hz). ^{13}C NMR ($CDCl_3$): δ 92.5 (C-2), 91.5 (C-3), 89.8 (C_5Me_5), 81.6 (C-4), 43.23, 43.17 (C-1, C-5), 25.0 (CH_3), 10.5 ($(CH_3)_5$).

(Pentamethylcyclopentadienyl)(2-methyl-6-oxaheptadienyl)ruthenium, $(\eta^5\text{-}C_5Me_5)Ru(\eta^5\text{-}C_8H_{11}O)$ (9): same method as for **2**, using 2-methyl-2,4-heptadien-6-one. After reaction and filtration, the hexane solution was transferred to a chromatography column, packed with Al_2O_3 (grade IV). A yellow band could be eluted with methanol, which was collected and reduced in volume. Free ligand and solvent were removed under high vacuum, giving crystals after 2 days. Dark yellow crystals were obtained at −80 °C from methanol; yield 0.9 g (64%). Anal. Calcd for $C_{18}H_{26}ORu$: C, 60.14; H, 7.32. Found: C, 60.22; H, 7.48. ^{13}C NMR ($CDCl_3$): δ 204.9 (C-6), 97.1 (C-2), 91.5 (C-3), 90.1 (C_5Me_5), 81.8 (C-4), 56.2 (C-5), 44.8 (C-1), 30.6 (C-7), 24.9 (CH_3), 9.5 ($(CH_3)_5$).

$(\eta^5\text{-}C_5Me_5)Ru(\eta^5\text{-}C_{13}H_{19}O)$ (10): same method and workup as for **9**, using β-ionone; yield 59%. Anal. Calcd for $C_{23}H_{34}ORu$: C, 64.61; H, 8.02. Found: C, 64.43; H, 7.91. ^{13}C NMR ($CDCl_3$): δ 206.2 (C-6), 114.5 (C-3), 94.4 (C-2), 90.1 (C_5Me_5), 77.6 (C-4), 55.4 (C-5), 45.4 (C-1), 39.3, 34.4, 34.2, 18.9 (C-8, C-9, C-10, C-11), 34.7, 30.9, 29.5 (CH_3), 9.7 ($(CH_3)_5$).

$(\eta^5\text{-}C_5Me_5)Ru(\eta^5\text{-}C_{13}H_{19})$ (11): same method as for **2**, using $[C_5Me_5RuCl_2]_n$ (1.68 g, 5.4 mmol) and dimethylnopadiene (9.36 g). After evaporation of the solvent, the residue was taken up in hexane and filtered. Hexane and excess ligand were removed from the filtrate under high vacuum at 50 °C. The oily residue was taken up in hexane and purified by chromatography over grade IV Al_2O_3 (2.5 × 45 cm). A yellow band was collected at first. After evaporation of the solvent, the oily residue was dissolved in warm ethanol (40 mL) and slowly cooled to −30 °C. Pale yellow crystals precipitated, which were separated and dried under vacuum; yield 0.58 g (25.7%). Anal. Calcd for $C_{23}H_{34}Ru$: C, 67.11; H, 8.32. Found: C, 66.87; H, 8.15. $[\alpha]_{589}$ ($CHCl_3$) = −250.6°. ^{13}C NMR ($CDCl_3$): δ 113.2 (C-2), 88.8 (C_5Me_5), 88.8 (C-8), 87.1 (C-9), 48.5, 41.99 (C-1, C-5), 48.1 (C-3), 46.5 (C-10), 38.7 (C-6), 37.2, 28.1 (C-4, C-7), 26.3, 24.5, 21.7 (C-6A, C-6B, C-11), 10.7 ($(CH_3)_5$).

X-ray Diffraction Study of $(\eta^5\text{-}C_5Me_5)Ru(\eta^5\text{-}C_{13}H_{19})$ (11). Crystals were grown by slowly cooling a saturated solution of **11** in methanol to 4 °C. Crystal data and details of the intensity

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collection and refinement are summarized in Table I. Atomic coordinates and equivalent isotropic displacement coefficients are listed in Table II and selected bond lengths and angles in Tables III and IV.

Typical Synthesis Using a Diolefin with an (*E*)-Methyl Group. (Pentamethylcyclopentadienyl)[(*E*)-pentadiene]ruthenium Chloride, $(\eta^5\text{-}C_5Me_5)Ru(\eta^4\text{-}C_5H_7)Cl$ (6). $[C_5Me_5RuCl_2]_n$ (1.2 g, 3.9 mmol) and (*E*)-1,3-pentadiene (5 mL) were dissolved in ethanol (20 mL), and the mixture was stirred for 3 h. After addition of zinc powder (1 g), stirring was continued for 1 h. After filtration and evaporation of solvent and excess ligand, the residue was recrystallized from methanol. Orange crystals precipitated at −30 °C; yield 1.14 g (86%). Anal. Calcd for $C_{15}H_{23}ClRu$: C, 53.01; H, 6.82; Cl, 10.43. Found: C, 52.87; H, 6.60; Cl, 10.51. ^1H NMR ($CDCl_3$): δ 4.07 (dd, 1 H, *J* = 10.3, 5.3 Hz), 3.79 (m, 1 H), 2.93 (dd, 1 H, *J* = 7.6, 1.9 Hz), 2.51 (qd, 1 H, *J* = 6.5, 10.3 Hz), 1.77 (dd, 1 H, *J* = 10.4, 1.9 Hz), 1.47 (d, 3 H, *J* = 6.5 Hz), 1.32 (s, 15 H). ^{13}C NMR ($CDCl_3$): δ 94.5 (d, *J* = 156.4 Hz, C-3), 93.8 (s, C_5Me_5), 87.8 (d, *J* = 166.9 Hz, C-2), 71.6 (d, *J* = 160.4 Hz, C-4), 51.6 (t, *J* = 160.9 Hz, C-1), 16.5 (q, *J* = 129.7 Hz, C-5), 9.0 (q, *J* = 128.5 Hz, $(CH_3)_5$).

(Pentamethylcyclopentadienyl)[(*E*)-2-methylpenta-1,3-diene]ruthenium Chloride, $(\eta^5\text{-}C_5Me_5)Ru(\eta^4\text{-}C_6H_{10})Cl$ (7): same procedure as for 6, using (*E*)-2-methylpenta-1,3-diene; yield 1.29 g (94%). Anal. Calcd for $C_{16}H_{25}RuCl$: C, 54.31; H, 7.12. Found: C, 54.18; H, 7.21. ^1H NMR ($CDCl_3$): δ 4.51 (d, 1 H, *J* = 9.1 Hz), 3.07 (dd, 1 H, *J* = 0.7, 2.1 Hz), 2.04 (q, 1 H, *J* = 7.3 Hz), 1.93 (s, 3 H), 1.62 (s, 15 H), 1.54 (d, 3 H, *J* = 7.3 Hz), 1.37 (dd, 1 H, *J* = 2.1, 0.7 Hz). ^{13}C NMR ($CDCl_3$): δ 102.5 (C-2), 94.1 (C_5Me_5), 92.8 (C-3), 69.9 (C-4), 51.9 (C-1), 20.9, 16.9 (C-5, CH_3), 9.3 ($(CH_3)_5$).

(Pentamethylcyclopentadienyl)[(*E*)-3-methylpenta-1,3-diene]ruthenium Chloride, $(\eta^5\text{-}C_5Me_5)Ru(\eta^4\text{-}C_6H_{10})Cl$ (8): same procedure as for 6, using (*E*)-3-methylpenta-1,3-diene; yield 1.25 g (91%). Anal. Calcd for $C_{16}H_{25}RuCl$: C, 54.31; H, 7.12. Found: C, 54.40; H, 7.16. ^1H NMR ($CDCl_3$): δ 3.86 (dd, 1 H, *J* = 10.2, 8.9 Hz), 2.84 (dd, 1 H, *J* = 8.9, 2.2 Hz), 2.35 (q, 1 H, *J* = 8.1 Hz), 1.50 (s, 3 H), 1.45 (d, 3 H, *J* = 8.1 Hz), 1.40 (dd, 1 H, *J* = 10.2 Hz), 1.31 (s, 15 H). ^{13}C NMR ($CDCl_3$): δ 105.2 (C-3), 93.7 (C_5Me_5), 87.8 (C-2), 67.6 (C-4), 50.5 (C-1), 16.2, 12.9 (C-5, CH_3), 8.6 ($(CH_3)_5$).

Typical Synthesis Using a Mixture of *E* and *Z* Olefins. Synthesis of 3 and 6. The same procedure was used as for 2 or 6, with an isomeric mixture of (*E*)-/(*Z*)-pentadiene (12 mL). After filtration and removal of solvent, an oily residue remained. This was extracted with hexane (30 mL). The hexane solution was chromatographed over Al_2O_3 (grade IV), the pale yellow band being collected and evaporated under reduced pressure. Sublimation at 10^{-2} mm and 70 °C gave yellow crystals of 3 (0.7 g, 58%). The residue, not soluble in hexane, was dissolved in ethanol and recrystallized at −30 °C. After 2 days, orange needles of 6 were recovered and dried (0.4 g, 34%).

Reaction of 1 with 1,3-Cyclohexadiene and Cycloheptatriene: same procedure as for 2, using either 1,3-cyclohexadiene or cycloheptatriene. Recrystallization from ethanol at −30 °C gave $[C_5Me_5Ru(benzene)]^+Cl^-$ (12; 0.89 g, 73%) as white crystals and $[C_5Me_5Ru(cycloheptatriene)]^+Cl^-$ (13; 1.15 g, 81%) as yellow needles. Anal. Calcd for $C_{16}H_{21}ClRu$ (12): C, 54.9; H, 6.05. Found: C, 54.6; H, 5.9. ^{13}C NMR for 12 (CD_3NO_2): δ 98.2 (C_5Me_5), 88.5 (C_6H_6), 10.8 ($(CH_3)_5$). Anal. Calcd for $C_{17}H_{23}ClRu$ (13): C, 56.1; H, 6.37. Found: C, 56.2; H, 6.5. ^{13}C NMR for 13 (CD_3NO_2): δ 100.3 (C_5Me_5), 97.7, 96.0 (C-2–5), 34.2 (C-1,6), 23.8 (C-7), 10.1 ($(CH_3)_5$).

Reaction of 1 with 1,3-Cyclooctadiene: same procedure as for 2, using 1 (1.2 g) and 1,3-cyclooctadiene (10 mL). After the mixture was stirred for 13 h, the solvent and excess ligand were evaporated under reduced pressure and the residue was extracted with hexane (30 mL). The hexane solution was chromatographed over Al_2O_3 (grade IV), and a yellow band was collected. After evaporation of the solvent, yellow crystals of $C_5Me_5Ru(\eta^5\text{-cyclooctadienyl})$ (15) remained (0.57 g, 50%). The residue, insoluble in hexane, was recrystallized from ethanol and cooled to −30 °C, yielding $[C_5Me_5Ru(\eta^6\text{-}1,3,5\text{-cyclooctatriene})]Cl$ (14) as yellow needles (0.34 g, 31%). Anal. Calcd for $C_{18}H_{26}Ru$ (15): C, 62.94; H, 7.6. Found: C, 62.76; H, 7.4. ^{13}C NMR for 15 (C_6D_6): δ 102.5 (C-3), 90.5 (C_5Me_5), 77.5 (C-2,4), 48.7 (C-1,5), 29.3 (C-6,8), 21.8 (C-7), 9.8 ($(CH_3)_5$). Anal. Calcd for $C_{18}H_{25}RuCl$ (14): C, 57.20; H, 6.67. Found: C, 57.31; H, 6.81. ^{13}C NMR for 14 (CD_3NO_2): δ 101.9 (C-3,4), 101.0 (C_5Me_5), 94.5, 93.2 (C-1,2,5,6), 34.5 (C-7,8), 9.4 ($(CH_3)_5$).

Protonation of 2. 2 (0.3 g, 0.9 mmol) was dissolved in 10 mL of propionic anhydride and cooled in an ice bath. HBF_4 (0.2 mL of a 50% aqueous solution), dissolved in 2 mL of propionic anhydride, was added dropwise. Within a few seconds, a yellow precipitate formed. Precipitation was completed by addition of cold ether (−30 °C). After filtration and washing with ether, complex 16 was dried; yield 0.37 g (99%). Anal. Calcd for $C_{17}H_{27}BF_4Ru$: C, 48.69; H, 6.49; F, 18.13. Found: C, 48.94; H, 6.42; F, 17.97. ^1H NMR (CD_2Cl_2, 25 °C): δ 5.97 (s, 1 H), 2.01 (s, 6 H), 1.83 (s, 15 H), −1.00 (broad, 5 H). ^1H NMR (CD_2Cl_2, −80 °C): δ 5.91 (s, 1 H), 2.45 (dd, 2 H, *J* = 5.1, 7.0 Hz), 1.99 (s, 6 H), 1.76 (s, 15 H), −0.25 (dd, 2 H, *J* = 5.1, 8.4 Hz), −9.89 (m, 1 H, *J* = 7.0, 8.4 Hz). ^{13}C NMR (CD_2Cl_2, −80 °C): δ 100.3 (C-2), 98.6 (C_5Me_5), 96.3 (C-3), 32.4 (td, *J* = 156.3, 37 Hz, C-1), 24.8 (CH_3), 9.6 ($(CH_3)_5$).

Reaction of 16 with CO. Complex 16 (0.3 g, 0.7 mmol) was dissolved in CH_2Cl_2 (25 mL), and CO was bubbled through the solution for 2 h. A white, flocculent precipitate formed. The product was precipitated with ether, filtered, washed, and dried; yield of $[C_5Me_5Ru(CO)(C_7H_{12})]BF_4$ (17) 0.32 g (100%). Anal. Calcd for $C_{18}H_{27}BF_4ORu$: C, 48.33; H, 6.08; F, 16.99. Found: C, 48.45; H, 5.94; F, 17.22. ^{13}C NMR ($CDCl_3$): δ 208.8 (CO), 105.0, 95.5 (C-2, C-4), 100.9 (C_5Me_5), 89.4 (C-3), 46.2 (C-1), 29.8, 22.7, 22.0 (CH_3), 9.1 ($(CH_3)_5$).

Metalation and Deuteration of 2. Freshly distilled TMEDA (0.12 mL, 0.8 mmol) was dissolved in hexane (5 mL) and the solution treated dropwise with 1 mL of 1.6 M *n*-BuLi in hexane (1.6 mmol). A solution of 2 (0.2 g, 0.6 mmol) in 10 mL of hexane was added dropwise. After it was stirred for 3 days, the pale yellow solution turned dark red and orange-red crystals separated. This solution was treated at 0 °C with a mixture of CH_3OD (1.5 mL) and CH_3COOD (0.5 mL). The solution turned yellow again. Solvent was evaporated, and the complex was recrystallized from hexane at −80 °C; yield 0.14 g (70%) of $C_5Me_5C_7H_{10}D$. ^{13}C NMR (C_6D_6): δ 91.8 (C-3), 90.9 (C-2,4), 89.1 (C_5Me_5), 44.5 (C-5), 44.3 (t, $J_{C,D}$ = 24.7 Hz, CDH), 44.2 (t, J_{CD} = 24 Hz, CHD), 25.1 (CH_3), 10.1 ($(CH_3)_5$).

Reduction of 9 with EtMgCl. A solution of ethylmagnesium chloride (1.2 mL, 2.4 mmol, 25% in THF) in Et_2O (25 mL) was treated dropwise at −25 °C with a solution of 9 (0.6 g, 1.6 mmol) in Et_2O (15 mL). The solution turned red. After it was slowly warmed to room temperature and subsequently hydrolyzed with NH_4Cl solution, the ether phase was twice extracted with H_2O, dried over $MgSO_4$, and evaporated to leave a yellow oil. This oil solidified to an orange solid of 18 (0.59 g, 63%) after high-vacuum evaporation. Attempted chromatography over Al_2O_3 (grade IV) with hexane led to decomposition. ^{13}C NMR (C_6D_6): δ 92.6 (C-2), 89.4 (C_5Me_5), 87.7 (C-3), 80.2 (C-4), 75.0 (C-5), 72.8 (C-6), 43.9 (C-1), 37.2 (C-7), 29.3, 24.8 (CH_3), 10.9 ($(CH_3)_5$), 9.4 (C-8).

Synthesis of $[(\eta^5\text{-}C_5H_5)Ru(\mu\text{-}(1\text{-}5\text{-}\eta)\text{:}(1,5\text{-}\eta)\text{-}C_7H_9)Ru(CH_3CN)(\eta^5\text{-}C_5Me_5)]PF_6$ (19). 2 (1.2 g, 3.6 mmol) and $[C_5H_5Ru(CH_3CN)_3]PF_6$ (1.6 g, 3.6 mmol) were dissolved in CH_3NO_2 (100 mL), the mixture was stirred at room temperature for 3 days. The dark solution was evaporated to dryness under reduced pressure. The black residue was taken up in acetone and purified by chromatography over Al_2O_3 (grade IV). A brown band was collected and reduced in volume. After addition of ether and cooling to −30 °C, a red-brown precipitate formed (1.2 g, 49%). Anal. Calcd for $C_{24}H_{32}F_6NPRu_2$: C, 42.29; H, 4.73; F, 16.72. Found: C, 42.01; H, 4.55; F, 16.64. ^1H NMR (CD_3NO_2): δ 10.31 (d, 2 H, *J* = 1.4 Hz), 5.47 (t, 1 H, *J* = 1.4 Hz), 5.03 (s, 5 H), 2.30 (s, 6 H), 2.09 (s, 3 H), 1.78 (s, 15 H). ^{13}C NMR (CD_3NO_2): δ 178.5 (C-1), 128.7 (CN), 107.2 (C_5Me_5), 102.2 (C-2,4), 95.6 (C-3), 84.0 (C_5H_5), 27.3 (CH_3), 9.8 ($(CH_3)_5$), 3.4 (CH_3CN). The correlation of ^1H and ^{13}C chemical shifts was determined by a heteronuclear 2D spectrum (HETCOR).

X-ray Diffraction Study of $[(\eta^5\text{-}C_5H_5)Ru(\mu\text{-}(1\text{-}5\text{-}\eta)\text{:}(1,5\text{-}\eta)C_7H_9)Ru(CH_3CN)(\eta^5\text{-}C_5Me_5)]PF_6$ (19). Crystals were grown by cooling a saturated solution of 19 in propionic anhydride to −30 °C for 1 week. Crystal data and details of the intensity collection and refinement are summarized in Table I. Atomic coordinates and equivalent isotropic displacement coefficients are listed in Table V and bond lengths and angles in Tables VI and VII.

Synthesis of (η^5-C_5Me_5)Ru(η^4-C_6H_{10})Br (20). Complex 7 (0.26 g, 0.74 mmol) was dissolved in methanol (40 mL) and treated with LiBr (0.26 g). After 6 h, excess LiBr was filtered off and the orange solution was cooled to −30 °C. Orange crystals separated; yield 0.29 g (100%). Anal. Calcd for $C_{16}H_{25}RuBr$: C, 48.24; H, 6.32. Found: C, 48.12; H, 6.22. ^{13}C NMR ($CDCl_3$): δ 101.5 (C-2), 93.9 (C_5Me_5), 91.6 (C-3), 67.4 (C-4), 49.0 (C-1), 20.7, 16.8 (C-5, C-6), 9.8 ($(CH_3)_5$). Mass spectrum (EI; *m/e* (relative intensity)): 67 (51), 228 (24), 229 (24), 230 (37), 231 (37), 232 (42), 233 (46), 234 (57), 235 (38), 236 (62), 238 (30), 310 (13), 312 (17), 313 (30), 314 (35), 315 (62), 316 (94), 317 (44), 318 (100), 319 (16), 320 (37), 395 (10), 396 (14), 397 (30), 398 (42), 399 (22), 400 (45), 402 (18).

Synthesis of [(η^5-C_5Me_5)Ru(η^4-C_6H_{10})(CO)]PF_6 (21). 7 (0.23 g, 0.65 mmol) was dissolved in methanol (30 mL) and the solution treated with CO for 1 h. After 10 min, the orange color of the solution gradually disappeared. The product was precipitated by addition of NH_4PF_6. Recrystallization from CH_2Cl_2/Et_2O gave 0.25 g (79%) of a white powder. Anal. Calcd for $C_{17}H_{25}F_6OPRu$: C, 41.54; H, 5.13; F, 23.19. Found: C, 41.43; H, 5.01; F, 23.31. ^{13}C NMR (CD_3NO_2): δ 209.7 (CO), 105.8 (C-2), 102.7 (C_5Me_5), 92.1 (C-3), 71.4 (C-4), 46.6 (C-1), 20.7, 17.5 (C-5, C-6), 9.9 ($(CH_3)_5$).

Synthesis of [(η^5-C_5Me_5)Ru$(CO)_3$]BF_4 (22). 7 (0.18 g, 0.51 mmol) was dissolved in methanol and the solution treated with $AgBF_4$ (0.08 g, 0.51 mmol) and refluxed for 6 h under a constant slow stream of CO. The solvent was evaporated, the residue extracted with CH_2Cl_2 (20 mL), and the product precipitated by adding ether and cooling to −80 °C; yield 0.18 g (89%). ^{13}C NMR (CD_3NO_2): δ 193.0 (CO), 107.8 (C_5Me_5), 10.2 ($(CH_3)_5$).

Synthesis of (η^5-C_5Me_5)Ru$\{P(OMe)_3\}_2$Cl (23). 7 (0.3 g, 0.85 mmol) was dissolved in THF (20 mL) and the solution treated with 2.2 equiv of $P(OMe)_3$. The solution was stirred for 3 h and evaporated under reduced pressure. Recrystallization from ethanol/acetone at −30 °C gave 362 mg of orange needles; yield 82%. Anal. Calcd for $C_{16}H_{33}ClP_2O_6Ru$: C, 36.96; H, 6.39. Found: C, 36.74; H, 6.31. ^{13}C NMR ($CDCl_3$): δ 92.73 (C_5Me_5, t, J = 3.2 Hz), 51.51 (CH_3, d, J = 2.5 Hz), 9.0 ($(CH_3)_5$).

Synthesis of (η^5-C_5Me_5)Ru(η^4-C_8H_{12})Cl (24). 7 (0.2 g, 0.56 mmol) was dissolved in acetone (30 mL), treated with 1,5-cyclooctadiene (0.21 mL), and stirred for 5 h at ambient temperature. The solvent was evaporated under reduced pressure and the residue extracted with CH_2Cl_2. After evaporation of CH_2Cl_2, the residue was recrystallized from ethanol (15 mL) at −30 °C, yielding yellow crystals (0.16 g, 75%). ^{13}C NMR ($CDCl_3$): δ 95.4 (s, C_5Me_5), 84.8 (d, J = 154.6 Hz, CH), 83.9 (d, J = 161.2 Hz, CH), 30.7 (t, J = 127.5 Hz, CH_2), 28.4 (t, J = 121.1 Hz, CH_2), 9.2 (q, J = 127.5 Hz, $(CH_3)_5$).

Synthesis of (η^5-C_5Me_5)Ru(η^4-C_8H_{12})(η^2-C_8H_{12})BF_4 (25). 7 (0.2 g, 0.56 mmol) and $AgBF_4$ (0.12 g) were dissolved in acetone (30 mL), and the solution was treated with 1,5-cyclooctadiene (0.25 mL). AgCl precipitated at once. After the mixture was for 4 h, the solvent was evaporated and the residue extracted with CH_2Cl_2. Slow addition of ether and cooling to −80 °C produced yellow crystals after 2 days; yield 0.18 g (60%). ^{13}C NMR (CD_3NO_2): δ 105.7 (C-5′,6′), 102.3 (C_5Me_5), 98.1 (C-1′,2′), 91.1, 90.3 (C-1,2,5,6), 67.8, 63.1 (C-3′,4′,7′,8′), 38.6, 37.6 (C-3,4,7,8), 9.3 ($(CH_3)_5$).

Synthesis of (η^5-C_5Me_5)Ru(η^4-C_6H_{10})CH_3 (26). 7 (0.3 g, 0.85 mmol) was dissolved in ether and the solution treated at 0 °C with methylmagnesium chloride (0.35 mL (1.1 mmol) of a 20% solution in THF) and stirred for 30 min at 0 °C. Stirring was continued for 6 h at room temperature. The solution turned yellow. After evaporation of solvent, the residue was extracted with hexane (10 mL) and the extracts were filtered and cooled to −80 °C. Pale yellow crystals formed after 6 days; yield 0.23 g (80%). Anal. Calcd for $C_{17}H_{28}Ru$: C, 61.22; H, 8.46. Found: C, 61.44; H, 8.35. ^{13}C NMR (CD_3NO_2): δ 94.5 (C_5Me_5), 93.2 (C-2), 87.1 (C-3), 60.7 (C-4), 45.0 (C-1), 21.5, 17.8 (CH_3), 9.6 ($(CH_3)_5$), 6.0 (Ru-CH_3). Mass spectrum (EI; *m/e* (relative intensity)): 165 (14), 227 (24), 228 (28), 229 (30), 230 (37), 231 (46), 232 (39), 233 (52), 234 (37), 235 (46), 236 (34), 237 (32), 238 (10), 239 (11), 297 (11), 298 (16), 299 (20), 300 (30), 301 (27), 302 (29), 303 (10), 309 (18), 310 (14), 311 (23), 312 (31), 313 (52), 314 (65), 315 (99), 316 (83), 317 (100), 318 (62), 319 (70), 320 (19), 322 (23), 328 (37), 329 (42), 330 (55), 331 (75), 332 (59), 333 (89), 334 (50), 335 (80), 336 (36).

Acknowledgment. This work was supported by the Swiss National Science Foundation (Grant No. 20-29821.90). We wish to thank one of the reviewers (R. D. Ernst) for making preprints and unpublished results available.[28]

Registry No. 1, 96503-27-4; 2, 115557-91-0; 2-d_1, 140411-45-6; 3, 139407-22-0; 4, 140411-28-5; 5, 139375-86-3; 6, 126821-63-4; 7, 140411-29-6; 8, 140411-30-9; 9, 140411-31-0; 10, 140411-32-1; 11, 140411-33-2; 12, 116887-49-1; 13, 140411-34-3; 14, 140411-35-4; 15, 131731-09-4; 16, 123635-35-8; 17, 140411-37-6; 18, 140411-38-7; 19, 140411-40-1; 20, 140411-41-2; 21, 140411-43-4; 22, 86853-54-5; 23, 92361-60-9; 24, 92390-26-6; 25, 140438-00-2; 26, 140411-44-5; [$C_5H_5Ru(CH_3CN)_3$]PF_6, 99604-67-8; $P(OMe)_3$, 121-45-9; (*E*)-2-methyl-2,4-heptadien-6-one, 16647-04-4; 3-methylcrotonaldehyde, 107-86-8; dimethylnopadiene, 140411-27-4; isopropyltriphenylphosphonium bromide, 1530-33-2; (−)-myrtenal, 564-94-3; β-ionone, 79-77-6; (*E*)-1,3-pentadiene, 2004-70-8; (*E*)-2−methylpenta-1,3-diene, 926-54-5; (*E*)-3-methylpenta-1,3-diene, 2787-43-1; 1,3-cyclohexadiene, 592-57-4; 1,3-cyclooctadiene, 1700-10-3; propionic anhydride, 123-62-6; ethylmagnesium chloride, 2386-64-3; 1,5-cyclooctadiene, 111-78-4; methylmagnesium chloride, 676-58-4; (*Z*)-3-methylpentadiene, 2787-45-3; (*Z*)-2-methylpentadiene, 1501-60-6; (*Z*)-1,3-pentadiene, 1574-41-0; 2,4-dimethyl-1,3-pentadiene, 1000-86-8.

Supplementary Material Available: Additional tables of bond lengths and angles for 11, tables of anisotropic displacement coefficients and hydrogen coordinates for 11 and 19, and additional structure diagrams of 11 (13 pages). Ordering information is given on any current masthead page.

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[28] Note added in proof: It now appears most likely that complex 16 has an agostic ground state, as an X-ray structural analysis of protonated 4 (Ernst, R. D. Unpublished results) shows an agostic C···H···M bond in the solid state. The NMR spectrum shown in Figure 2 therefore represents the dynamic equilibrium B, B′ and not the hydride structure A.