Registry No. 3, 72954-06-4; 4, 82311-95-3; 6, 91798-57-1; 7, 91798-58-2; 8, 91841-52-0; 10, 91798-59-3; $(Fp)_2$, 12154-95-9; FpI, 12078-28-3; $Fe(CO)(PPh_3)CpI$, 12099-18-2; (1,1′-ferrocenediyl)phenylarsine, 72954-08-6; 1-diphenylarsino-1′-lithioferrocene, 91798-60-6.

Supplementary Material Available: Tables of final anisotropic thermal parameters, bond angles and lengths involving H atoms, torsion angles and calculated and observed structure factor amplitudes (35 pages). Ordering information is given on any current masthead page.

The X-ray Crystal and Molecular Structure of $[Ru(\eta^3\text{-}C_8H_{13})\{P(OMe)Ph_2\}_3][PF_6]$: A Cationic Complex with an Agostic Metal···H···C Interaction

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The X-ray crystal and molecular structure of the complex $[Ru(\eta^3\text{-}C_8H_{13})\{P(OMe)Ph_2\}_3][PF_6]$ has been determined. The crystals are orthorhombic of space group $Pna2_1$ with a = 20.510 (5) Å, b = 12.992 (3) Å, and c = 16.954 (4) Å; R = 0.0478 for 3257 unique reflections. The structure reveals the existence of an agostic Ru···H···C interaction that contains a Ru···H distance of 2.08 (7) Å and a lengthened C–H bond of 1.14 (7) Å. The hydrogen atom occupies the sixth coordination site of a distorted octahedron; the other sites being taken up by the η^3-enyl portion of the cyclooctenyl ligand and the three phosphorus donor ligands (Ru–P bond distances = 2.350 (2), 2.302 (2), and 2.223 (2) Å.) The shortest Ru–P bond is situated trans to the Ru···H interaction. A discussion of the structure in comparison with analogous structures containing an agostic η^3-enyl ligand is presented.

Introduction

We have recently reported[1] the sterically controlled isomerization of the hydrido–diene complexes $[RuH(cod)L_3][PF_6]$ which gave a series of η^3-enyl cations $[Ru(\eta^3\text{-}C_8H_{13})L_3]^+$ analogous with the species $[Fe(\eta^3\text{-}C_8H_{13})\{P(OMe)_3\}_3]^+$.[2] As with the iron complex, the ^1H NMR spectra of the ruthenium compounds all contain a feature characteristic of an agostic M···H–C interaction, viz., an exchange-broadened high field signal due to the two endo hydrogen atoms adjacent to the η^3-enyl functional group, either of which can interact with the metal at any one time. For the complex $[Ru(\eta^3\text{-}C_8H_{13})\{P(OMe)Ph_2\}_3][PF_6]$ (1) it was possible to reach the slow-exchange region of this process at −90 °C using a 500-MHz instrument, indicating that the barrier to exchange is higher for this compound than for the other ruthenium compounds studied. We decided to determine the structure of 1 in order to obtain some insight into the factors giving rise to the higher exchange barrier for 1; e.g., whether it is a function of a stronger M···H–C interaction or of steric repulsions between the bulky $P(OMe)Ph_2$ ligands and the atoms of the cyclooctenyl ligand. Although there are now a number of structural studies of M···H–C interactions,[3] only two are relevant to complex 1. The structures of $[Fe(\eta^3\text{-}C_8H_{13})\{P(OMe)_3\}_3][BF_4]$ (2)[4] and $[Mn(\eta^3\text{-}C_7H_{11})(CO)_3]$ (3)[5] have been thoroughly studied by both X-ray and neutron diffraction methods. In this paper the X-ray structure of 1 is presented and, by comparison with the structures 2 and 3, an estimate of the structural effect of the Ru···H–C interaction is made.

Experimental Section

Orange-brown multifacetted crystals suitable for X-ray examination were grown from dichloromethane–ethanol solution. Unit cell dimensions were determined by least-squares fit to the diffracting positions of 25 reflections measured on a Philips PW 1100 four-circle diffractometer. The intensities of 3557 reflections with $3 \le \theta \le 23°$ in the octant $+h,+k,+l$ were measured by using the ω–2θ scan mode with a scan width of 1.00° in ω and a scan speed of 0.04° s^{-1}. Backgrounds were measured for 12.5 s at each end of the scan. Three reference reflections were measured every 60 min and showed no significant deviations from their mean intensities. No absorption corrections were applied.

Crystal data: $C_{47}H_{52}F_6O_3P_4Ru$; M_r = 1003.9; orthorhombic; space group $Pna2_1$; a = 20.510 (5) Å, b = 12.992 (3) Å, c = 16.954 (4) Å, U = 4517.7 Å^3, D_{calcd} = 1.476 Mg m^{-3} for Z = 4, $F(000)$ = 2064; Mo Kα radiation, λ = 0.710 69 Å, μ(Mo Kα) = 0.482 mm^{-1}. The structure was solved by Patterson and difference electron density synthesis methods and was refined by using SHELX.[6] The z coordinate of the Ru atom was fixed at 0.25 to define the origin. The H atoms of the cyclooctenyl ligand and the methyl groups were located by using a subsequent difference electron density synthesis and were refined. All other H atoms were added in calculated positions (C–H = 0.95 Å). Isotropic temperature factors were refined for the phenyl C atoms, and anisotropic temperature factors were refined for all other non-H atoms. Five common isotropic temperature factors were refined for the H atoms. Least-squares refinement using a weighting scheme $w = 1/\sigma^2(F_o)$ and with the matrix blocked so that in each group of three cycles Ru refined in cycles 1 and 2, the atoms of the ligands containing P(1) or P(2) refined in cycle 1, the atoms of the ligand containing

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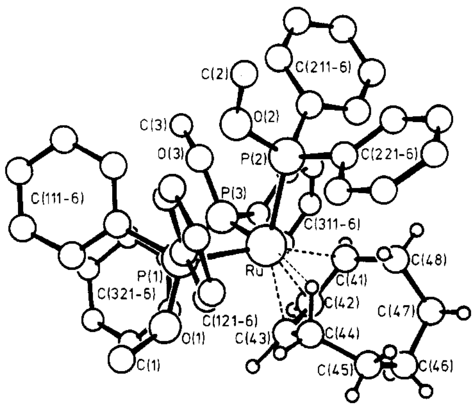

Figure 1. A perspective view of the cation of 1 showing the atom numbering scheme.

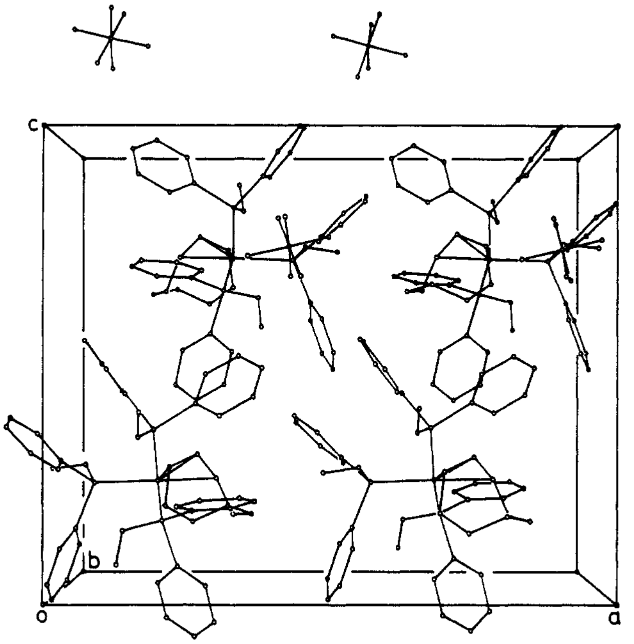

Figure 2. The unit cell of 1 viewed perpendicular to the B face.

P(3) and the C_8H_{13} ligand refined in cycle 2, and the PF_6 anion refined in cycle 3 converged to give R [= $\sum\Delta/\sum F_o$, $\Delta = ||F_o| - |F_c||$] = 0.0478, R_w [= $\sum w\Delta/\sum sF_o$] = 0.0397, and R_G [= $\sum w\Delta^2/\sum wF_o^2$] = 0.0411 for 3257 unique observed reflections. The reductions in R_G at all stages of the refinement were significant at the 99.5% level.[7] Complex neutral atom scattering factors were used for all atoms.[8] In the final cycles of refinement 440 parameters were varied comprising 248 positional parameters, 150 anisotropic temperature factor components, 41 isotropic temperature factors, and 1 overall scale factor.

Results and Discussion

The final atom coordinates and isotropic or equivalent isotropic temperature factors are given in Table I. Selected bond lengths, bond angles and non-bonded distances are given in Table II. (Tables of structure factors and anisotropic temperature factors have been deposited.) Figure 1 is a perspective view of the cation showing the atom numbering scheme, and Figure 2 is a view of the unit cell.

The crystal structure consists of discrete cations and anions (Figure 2) with no unusually short intermolecular distances. The shortest intermolecular distance not involving an H atom is F(2)···C(3) (−x, +y, +z) of 3.12 (1) Å and that involving an H atom is H(213)···H(13) (+x, −y, z) of 2.27 (8) Å. The PF_6 anion has a normal geometry and is reasonably well ordered; however, a number of somewhat large anisotropic temperature factor components for the F atoms indicate either limited disorder or high thermal motion of the anion. A final difference synthesis showed no evidence of gross disorder in this anion.

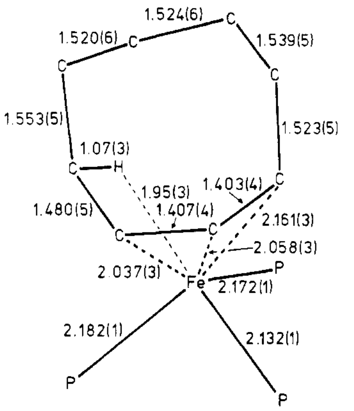

Figure 3. Part of the cation of 2 showing selected bond lengths (Å) taken from the X-ray structure determination.[4]

The coordination geometry around the ruthenium ion is irregular square pyramidal—if only non-hydrogen atoms are considered—with P(3) occupying the axial site, P(1) and P(2) situated in basal sites cis to each other, and the η^3-enyl portion of the cyclooctenyl ligand coordinated across the two remaining basal sites. The bond distances from ruthenium to the basal phosphorus atoms P(1) and P(2) are different, being 2.350 (2) and 2.302 (2) Å, respectively. Both lengths are in the range normally found[9] in ruthenium complexes containing phosphorus donor ligands, and the different values result probably from a combination of steric repulsion and the unsymmetrical coordination of the η^3-C_8H_{13} group (vide infra). In contrast, the Ru–P(3) bond distance of the axial phosphorus ligand is much shorter at 2.223 (2) Å. This value is typical[10] of axial Ru–P lengths in a square pyramidal configuration with 16 valence electrons available for bonding. The coordination geometry is thus broadly similar to that found[4] in the iron complex 2, which is given for comparison in Figure 3 together with pertinent bond distances and angles.

To detect the Ru···H–C interaction, the positions of the hydrogen atoms in the cyclooctenyl ligand were considered. They were directly observable in the difference electron density syntheses (see Experimental Section) and were refined by least squares. The Ru–H(442) distance of 2.08 (7) Å together with the close Ru···C(44) distance of 2.592 (9) Å confirms the existence of a two-electron, three-center bonding interaction in the complex. This hydrogen atom occupies the sixth coordination site of an octahedral configuration as is evident from the bond angles P(1)–Ru–H(442) = 91 (2)°, P(2)–Ru–H(442) = 94 (2)°, and P(3)–Ru–H(442) = 171 (2)°. The Ru–H(442)–C(44) angle of 103 (5)° is comparable to the corresponding angles of 99.42 (2) and 100 (1)° found in 2 and 3, respectively.

Terminal Ru–H bonds are usually in the range 1.60–1.70 Å[9,11] whereas hydrides bridging a ruthenium–ruthenium bond are reported[12] to have longer bonds to ruthenium,

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Table I. Fractional Coordinates (×10^4; ×10^5 for Ru; ×10^3 for H) and Isotropic Temperature Factors (Å^2, ×10^3; ×10^4 for Ru)

	x/a	y/b	z/c	U, Å^2
Ru	18844 (2)	22347 (4)	25000 (0)	252 (2)[a]
P(1)	741 (1)	2317 (1)	2455 (2)	31 (1)[a]
O(1)	510 (2)	3406 (4)	2805 (3)	45 (3)[a]
C(1)	−132 (5)	3866 (8)	2707 (9)	66 (6)[a]
H(11)	−38 (3)	336 (5)	248 (6)	59 (11)
H(12)	−9 (4)	394 (6)	335 (5)	59 (11)
H(13)	−6 (4)	449 (5)	233 (5)	59 (11)
C(111)	203 (3)	1385 (6)	2957 (5)	35 (2)
C(112)	236 (4)	349 (6)	2808 (4)	39 (2)
C(113)	−191 (4)	−335 (7)	3163 (5)	50 (2)
C(114)	−651 (4)	16 (7)	3698 (5)	57 (2)
C(115)	−676 (4)	1046 (7)	3869 (5)	57 (3)
C(116)	−242 (4)	1738 (7)	3518 (5)	48 (2)
C(121)	399 (4)	2353 (6)	1463 (5)	43 (2)
C(122)	171 (4)	1493 (7)	1068 (5)	50 (2)
C(123)	−53 (5)	1546 (8)	294 (6)	67 (3)
C(124)	−41 (5)	2455 (8)	−90 (7)	86 (3)
C(125)	169 (5)	3315 (9)	274 (7)	89 (4)
C(126)	402 (4)	3290 (7)	1061 (5)	61 (3)
P(2)	2028 (1)	810 (1)	1712 (1)	29 (0)[a]
O(2)	1364 (2)	177 (4)	1532 (3)	33 (2)[a]
C(2)	1286 (5)	−469 (8)	861 (6)	55 (6)[a]
H(21)	116 (4)	−13 (6)	34 (5)	59 (11)
H(22)	98 (4)	−98 (6)	91 (5)	59 (11)
H(23)	162 (4)	−70 (7)	71 (6)	59 (11)
C(211)	2602 (3)	−216 (5)	1969 (4)	31 (2)
C(212)	3269 (4)	−26 (6)	2012 (5)	45 (2)
C(213)	3649 (4)	−837 (6)	2194 (5)	52 (2)
C(214)	3471 (4)	−1796 (7)	2301 (5)	57 (3)
C(215)	2808 (4)	−1996 (6)	2258 (5)	50 (2)
C(216)	2372 (4)	−1205 (6)	2104 (5)	46 (2)
C(221)	2285 (4)	1179 (5)	721 (4)	34 (2)
C(222)	2815 (4)	734 (7)	336 (6)	63 (3)
C(223)	2960 (5)	1043 (6)	−451 (7)	82 (3)
C(224)	2577 (5)	1726 (8)	−826 (7)	77 (3)
C(225)	2053 (5)	2144 (7)	−452 (6)	65 (3)
C(226)	1902 (4)	1889 (6)	316 (5)	51 (2)
P(3)	1850 (1)	1346 (2)	3620 (1)	30 (1)[a]
O(3)	1634 (2)	178 (4)	3480 (3)	37 (2)[a]
C(3)	1686 (8)	−670 (9)	4022 (8)	66 (7)[a]
H(31)	186 (6)	−37 (10)	463 (9)	169 (37)
H(32)	212 (6)	−99 (11)	406 (9)	169 (37)
H(33)	163 (9)	−100 (13)	380 (11)	169 (37)
C(311)	2614 (3)	1242 (6)	4178 (5)	34 (2)
C(312)	3056 (4)	491 (7)	3930 (5)	56 (2)
C(313)	3649 (5)	374 (8)	4335 (6)	71 (3)
C(314)	3783 (5)	1009 (7)	4945 (6)	63 (3)
C(315)	3362 (4)	1720 (7)	5197 (6)	60 (3)
C(316)	2770 (4)	1850 (7)	4808 (5)	50 (2)
C(321)	1312 (4)	1860 (6)	4386 (5)	38 (2)
C(322)	1203 (4)	2896 (7)	4428 (6)	63 (3)
C(323)	808 (5)	3312 (9)	5027 (6)	78 (3)
C(324)	534 (5)	2686 (8)	5561 (6)	74 (3)
C(325)	601 (5)	1645 (8)	5525 (7)	79 (3)
C(326)	1016 (5)	1217 (8)	4916 (6)	71 (3)
C(41)	2942 (3)	2683 (6)	2536 (8)	37 (4)[a]
C(42)	2569 (4)	3355 (6)	3034 (5)	32 (4)[a]
C(43)	2024 (4)	3881 (6)	2742 (5)	35 (4)[a]
C(44)	1937 (4)	4051 (7)	1871 (5)	37 (4)[a]
C(45)	2425 (5)	4794 (8)	1482 (7)	55 (6)[a]
C(46)	3086 (5)	4909 (7)	1839 (7)	51 (5)[a]
C(47)	3546 (4)	4015 (7)	1691 (6)	50 (5)[a]
C(48)	3232 (4)	2957 (6)	7141 (6)	42 (4)[a]
H(41)	310 (4)	236 (6)	270 (5)	42 (6)
H(42)	258 (3)	336 (6)	359 (4)	42 (6)
H(43)	171 (3)	435 (6)	320 (4)	42 (6)
H(441)	150 (3)	430 (6)	180 (4)	42 (6)
H(442)	196 (3)	327 (5)	157 (4)	42 (6)
H(451)	249 (4)	469 (6)	97 (5)	42 (6)
H(452)	218 (4)	529 (5)	153 (5)	42 (6)
H(461)	316 (4)	501 (5)	235 (4)	42 (6)
H(462)	324 (3)	547 (5)	165 (4)	42 (6)
H(471)	388 (3)	403 (5)	205 (4)	42 (6)
H(472)	368 (3)	421 (5)	112 (5)	42 (6)
H(481)	358 (4)	248 (5)	163 (4)	42 (6)
H(482)	287 (3)	289 (5)	131 (4)	42 (6)
P(4)	4251 (1)	1720 (2)	7552 (2)	43 (1)[a]
F(1)	4189 (4)	831 (6)	8152 (5)	126 (5)[a]
F(2)	4047 (3)	2519 (5)	8199 (4)	83 (3)[a]
F(3)	4466 (3)	923 (4)	6895 (3)	72 (3)[a]
F(4)	4268 (4)	2583 (6)	6935 (5)	118 (6)[a]
F(5)	3520 (3)	1543 (6)	7347 (5)	135 (5)[a]
F(6)	4961 (2)	1869 (5)	7765 (5)	114 (5)[a]

[a] Equivalent isotropic temperature factor.

Table II. Bond Lengths (Å)

Ru-P(1)	2.350 (2)	Ru-C(41)	2.246 (7)
Ru-P(2)	2.302 (2)	Ru-C(42)	2.216 (8)
Ru-P(3)	2.223 (2)	Ru-C(43)	2.197 (8)
		Ru-H(442)	2.08 (7)
P(1)-O(1)	1.606 (5)	C(41)-C(42)	1.44 (1)
P(2)-O(2)	1.621 (5)	C(42)-C(43)	1.40 (1)
P(3)-O(3)	1.599 (5)	C(43)-C(44)	1.50 (1)
P(1)-C(111)	1.846 (8)	C(44)-C(45)	1.54 (1)
P(1)-C(121)	1.822 (8)	C(45)-C(46)	1.49 (1)
P(2)-C(211)	1.830 (7)	C(46)-C(47)	1.52 (1)
P(2)--C(221)	1.825 (8)	C(47)-C(48)	1.52 (1)
P(3)-C(311)	1.834 (7)	C(48)-C(41)	1.52 (2)
P(3)-C(321)	1.830 (8)	C(41)-H(41)	0.59 (8)
O(1)-C(1)	1.45 (1)	C(42)-H(42)	0.95 (8)
O(2)-C(2)	1.42 (1)	C(43)-H(43)	1.18 (8)
O(3)-C(3)	1.44 (1)	C(44)-H(441)	0.97 (7)
		C(44)-H(442)	1.14 (7)
C(nm1)-C(nm2)	1.38 (1)[a]	C(45)-H(451)	0.88 (8)
C(nm1)-C(nm6)		C(45)-H(452)	0.82 (7)
C(nm2)-C(nm3)	1.40 (2)[a]	C(46)-H(461)	0.89 (8)
C(nm5)-C(nm6)		C(46)-H(462)	0.86 (7)
C(nm3)-C(nm4)	1.36 (2)[a]	C(47)-H(471)	0.93 (7)
C(nm4)-C(nm5)		C(47)-H(472)	1.04 (8)
		C(48)-H(481)	0.95 (7)
C–H(methyl)	0.95 (10)[a]	C(48)-H(482)	1.04 (7)

[a] Mean bond lengths (n = 1, 2, or 3; m = 1 or 2).

in the range 1.70–1.85 Å. Since these values were determined from X-ray data that result in an underestimation[13] of metal–hydride bond lengths, it is reasonable to consider a "true" value for a bridging hydride of between 1.80 and 1.95 Å. On the other hand, the distance between ruthenium and H(442) is likely to be *overestimated* (or, alternatively, an upper limit) because the electron density associated with the hydrogen atom will reside mainly between the C(44) and H(442) atoms. Thus the C(44)–H(442) distance would be underestimated and any lengthening to the "true" value would lead to closer approach of the hydrogen atom to the ruthenium. This phenomenon has been described previously by Cotton[14] and is well illustrated in the case of 2 for which both X-ray and neutron diffraction data are available. The relevant bond lengths are Fe–H (1.95 and 1.874 Å) and C–H (1.07 (3) and 1.164 (3) Å) for the X-ray and neutron data, respectively. The conclusion which must be drawn is that the position of H(442) is consistent with a bonding interaction between the metal and this particular endo-hydrogen atom. Another structural feature that substantiates the agostic interaction is the observation that the C(44)–H(442) bond length (1.14 (7) Å) is probably longer than the other aliphatic C–H bonds that range from 0.84 to 1.04 (7) Å even though the observed difference is not significant. Although

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(13) Reference 12b, p 187.

(14) Cotton, F. A.; La Cour, T.; Stanislowski, A. G. *J. Am. Chem. Soc.* **1974**, *96*, 754.

Table III. Bond Angles (deg)

P(1)–Ru–P(2)	98.4 (1)	P(1)–Ru–C(41)	162.4 (2)	P(1)–Ru–H(442)	91 (2)
P(1)–Ru–P(3)	91.2 (1)	P(1)–Ru–C(42)	128.0 (2)	P(2)–Ru–H(442)	94 (2)
P(2)–Ru–P(3)	94.7 (1)	P(1)–Ru–C(43)	95.3 (2)	P(3)–Ru–H(442)	171 (2)
Ru–P(1)–O(1)	108.8 (2)	Ru–P(2)–C(221)	111.1 (2)	O(2)–P(2)–C(221)	101.7 (3)
Ru–P(2)–O(2)	114.1 (2)	Ru–P(3)–C(311)	116.9 (2)	O(3)–P(3)–C(311)	104.1 (3)
Ru–P(3)–O(3)	112.0 (2)	Ru–P(3)–C(321)	115.8 (3)	O(3)–P(3)–C(321)	106.5 (3)
Ru–P(1)–C(111)	123.5 (2)	O(1)–P(1)–C(111)	103.4 (3)	C(111)–P(1)–C(121)	102.3 (3)
Ru–P(1)–C(121)	114.5 (2)	O(1)–P(1)–C(121)	101.8 (3)	C(211)–P(2)–C(221)	103.0 (3)
Ru–P(2)–C(211)	122.0 (2)	O(2)–P(2)–C(211)	102.5 (3)	C(311)–P(3)–C(321)	100.2 (3)
P(2)–Ru–C(41)	95.7 (3)	P(3)–Ru–C(41)	98.2 (3)	C(41)–Ru–H(442)	77 (2)
P(2)–Ru–C(42)	133.2 (2)	P(3)–Ru–C(42)	90.7 (2)	C(42)–Ru–H(442)	81 (2)
P(2)–Ru–C(43)	151.0 (2)	P(3)–Ru–C(43)	110.5 (2)	C(43)–Ru–H(442)	60 (2)
C(48)–C(41)–C(42)	126.1 (7)	C(43)–C(44)–C(45)	115.9 (7)	C(46)–C(47)–C(48)	114.8 (7)
C(41)–C(42)–C(43)	120.9 (8)	C(44)–C(45)–C(46)	118.6 (9)	C(47)–C(48)–C(41)	115.4 (8)
C(42)–C(43)–C(44)	120.9 (7)	C(45)–C(46)–C(47)	114.9 (8)		
C(43)–C(44)–H(441)	106 (5)	C(45)–C(44)–H(441)	110 (5)	H(441)–C(44)–H(442)	106 (6)
C(43)–C(44)–H(442)	108 (4)	C(45)–C(44)–H(442)	110 (4)	C(44)–H(442)–Ru	103 (5)
P(1)–O(1)–C(1)	126.0 (6)	P(2)–O(2)–C(2)	122.9 (5)	P(3)–O(3)–C(3)	127.7 (6)
P–C–C	122.5 (14)[a,b] 118.6 (12)[a,b]				
C(*nm*2)–C(*nm*1)–C(*nm*6)	118.9 (6)[a]	C(*nm*2)–C(*nm*3)–C(*nm*4)	120.2 (10)[a]	C–C–H (sp^3)[c,d]	108 (7)[a]
C(*nm*1)–C(*nm*2)–C(*nm*3)	119.9 (9)[a]	C(*nm*4)–C(*nm*5)–C(*nm*6)		H–C–H[c,d]	108 (6)[a]
C(*nm*1)–C(*nm*6)–C(*nm*5)		C(*nm*3)–C(*nm*4)–C(*nm*5)	120.8 (12)[a]	C–C–H (sp^2)[c]	117 (5)[a]

[a] Mean bond angles (*n* = 1, 2, or 3; *m* = 1 or 2). [b] For each phenyl group the two P–C–C angles are asymmetric. [c] C_8 ring. [d] Excluding angles at C(44).

Table IV. η^3-Enyl Ligands Bonded to Ru

compd	Ru–C(enyl), Å			ref
$[Ru(\eta^3\text{-}C_3H_5)(NO)(PPh_3)_2]$	2.214	2.130	2.258	16
$[Ru(\eta^3\text{-}C_3H_5)(\eta^6\text{-}C_6H_6)I]$	2.205	2.133	2.207	17
	2.205	2.143	2.209	
$[Ru(\eta^3\text{-}C_3H_5)(\eta^6\text{-}C_6H_6)CN]$	2.188	2.130	2.188	17
$[Ru\{1\text{–}3;6,7\text{-}\eta\text{-}C_8H_8\text{-}8\text{-}(SiMe_3)\}(SiMe_3)(CO)_2]$	2.305	2.195	2.229	18
$[Ru(1\text{–}3;5,6\text{-}\eta\text{-}C_8H_{11})(\eta^6\text{-}C_6H_5BF_3)]$	2.24	2.17	2.29	19
$[Ru_2\text{-}\mu\text{-}\{2',3',7',8'\text{-}\eta;4'\text{–}6'\text{-}\eta\text{-}(4\text{-}C_8H_8SiMe_2C_2H_4SiMe_2)(CO)_5]$	2.263	2.187	2.242	20
$[Ru_2(C_{16}H_{16})(CO)_5]$	2.27	2.21	2.29	21
	2.29	2.18	2.19	
$[Ru(\eta^3\text{-}C_8H_{13})\{P(OMe)Ph_2\}_3]^+$	2.246	2.216	2.197	this work

the estimated error is relatively large compared to the room-temperature X-ray structure of **2** for which the pertinent C–H bond length was 1.07 (3) Å, it is nevertheless an intriguing possibility that the C–H bond may be weaker in **1** than in **2**.

Since the estimated error in the hydrogen atom positions is relatively large (±0.08 Å), it seemed appropriate to validate our assertion by considering other structural aspects that arise because of the Ru···H–C interaction. These are obtained by considering the unsymmetrical coordination of the η^3-enyl moiety and distortions within the cyclooctenyl ring.

The outer carbon atoms of the η^3-enyl functionality are not symmetrically bound to the ruthenium atom. The C(43)–Ru distance of 2.197 (8) Å is significantly shorter (0.049 Å) than the C(41)–Ru distance of 2.246 (7) Å and is slightly shorter than the central C–Ru distance of 2.216 (8) Å, although the latter difference is only 1.7 times its esd. A similar, but more prominent, trend was observed in the structures of **2** and **3**, and it was noted that, in the absence of steric constraints, the allyl ligand in most other allyl complexes is symmetrically bound to the metal with the shortest M–C bond being to the central carbon.[15] Suitable examples of η^3-enyl ligands bonded to ruthenium are given in Table IV.

The unsymmetric coordination of the η^3-enyl portion of the C_8H_{13} ligand is also shown by the following criteria that closely correspond to the distortions found in **2**: (1) C(42) is not symmetrically located with respect to P(1) and P(2) [C(42)–Ru–P(1) = 128.0 (2)°; C(42)–Ru–P(2) = 133.2 (2)°]. (2) The atoms C(41), C(42), and C(43) are all displaced in the same direction from the equatorial plane defined by Ru, P(1), and P(2). The deviations [C(41), 0.41 Å, C(42), 0.20 Å, and C(43) 0.95 Å] are larger by ca. 0.15 Å than found in **2**, and this may be a consequence of the greater steric crowding in the ruthenium complex. (3) The C(48)–C(41)–C(42) angle of 126.1 (7)° differs significantly from the C(42)–C(43)–C(44) angle of 120.8 (7)°. The comparable values in **2** are 127.3 (1) and 118.6 (1)°, respectively.

These observations, together with the close correspondence between the structures **1** and **2**, can be interpreted only in terms of a substantial interaction between

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ruthenium and the C–H bond of interest.

A final consideration is whether steric crowding may hinder the interchange of the pertinent endo hydrogen atoms at the ruthenium coordination site. The X-ray structure gives no evidence that this may be the case. The site exchange of the endo hydrogen atoms of C(44) and C(48) requires movement of these two carbon atoms that do not appear to be restricted in any way by close nonbonded contacts with atoms of the phosphorus donor ligands. The closest contact distances are 3.475 Å between C(44) and P(1) and 3.478 Å between C(48) and C(221) (all other nonbonded contacts are ≥3.60 Å). A translational motion of C(48) toward the ruthenium coordination site will increase this distance, so atom C(221) cannot be considered to hinder the fluxional process. In addition, the groups attached to the phosphorus atoms appear to adopt positions that minimize compressions with the η^3-cyclooctenyl ligand; thus the Ru–P–C angles of the phenyl substituents lying close to the η^3-enyl group have normal angles [114.5 and 111.1° for Ru–P(1)–C(121) and Ru–P(2)–C(221), respectively] whereas Ru–P(1)–C(111) (123.5°) and Ru–P(2)–C(211) (122.0°) have large angles to minimize steric repulsions between the $P(OMe)Ph_2$ ligands.

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Supplementary Material Available: Tables of observed and calculated structure factors and anisotropic temperature factors (15 pages). Ordering information is given on any current masthead page.

Simple Synthesis of Enolate Complexes of Titanocene and Zirconocene. Molecular Structure of $Cp_2Ti(OC_2H_3)_2$

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Lithium enolates, e.g., $LiOC_2H_3$, prepared by the reaction of BuLi with THF, or $LiOCH{=}CMe_2$, prepared from MeLi and $Me_3SiOCH{=}CMe_2$, react readily with Cp_2MXCl (X = Me, Cl; M = Ti, Zr) to give the corresponding enolates $Cp_2M(OCH{=}CR_2)Me$ and $Cp_2M(OCH{=}CR_2)_2$ (R = H, Me). These complexes are thermally quite stable and show no tendency to eliminate aldehyde and form ketene complexes. The crystal structure of $Cp_2Ti(OC_2H_3)_2$ has been determined: orthohombic, *Pbcn*, $a = 14.046$ (4) Å, $b = 6.099$ (2) Å, $c = 14.709$ (5) Å, $V = 1250.1$ (6) Å^3, $Z = 4$, $\rho_{calcd} = 1.39$ g/cm^3. The molecule has crystallographically imposed C_2 symmetry. Important bond distances (Å) and angles (deg) are as follows: Ti—Cp(centroid) = 2.088 (4), Cp—Ti—Cp = 131.2 (1), Ti—O = 1.903 (2), C—O = 1.329 (4), C=C = 1.306 (5), Ti—O—C = 145.5 (2), O—C—C = 128.4 (2).

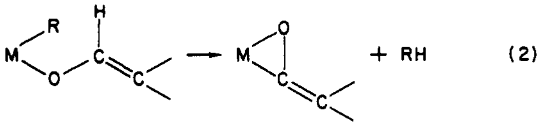
Introduction

Enolate complexes of transition metals are a little studied class of compounds. The enolate ion is potentially ambidentate, capable of binding to metals through oxygen or carbon (eq 1). The mode of binding is expected to

$$M^+ + \{CH_2{=}CH{-}O^- \leftrightarrow {}^-CH_2{-}CH{=}O\} \rightarrow \underset{A}{M{-}O{-}CH{=}CH_2} \text{ or } \underset{B}{M{-}CH_2{-}CH{=}O} \quad (1)$$

depend on the oxophilicity of the metal with M–O bonding predominating for the early transition metals and M–C bonding possibly being favored by the softer, late transition metals.

Furthermore, hydrogen abstraction from an enolate ligand could lead to ketene complexes (eq 2). The ketene



(2)

ligand is a possible precursor to complexes with a bridging methylene functionality whose properties are of interest in connection with CO hydrogenation chemistry.[1] This latter possibility is illustrated by the formation of $Cp^*_2Co_2(\mu\text{-}CH_2)(\mu\text{-}CO)$ from Cp*Li, $CoCl_2$, and $LiOC_2H_3$ ($Cp^* = C_5Me_5$).[2]

Several enolate complexes have been prepared by indirect methods,[3-8] some of which are illustrated in eq 3-8.

Since enolate salts are readily prepared according to eq 9[2,9] and 10,[10,11] we undertook to investigate the reactions of simple enolate ions with metal halides. We here report our results with the metallocene halides Cp_2MXCl (M =

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