New ruthenium carboxylate complexes having a 1-5-.eta.5-cyclooctadienyl ligand

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New Ruthenium Carboxylate Complexes Having a 1–5-η^5-Cyclooctadienyl Ligand

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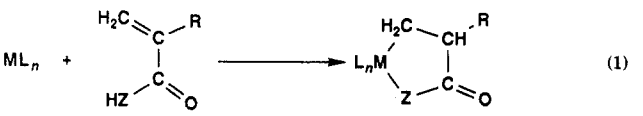
Reaction of 3-butenoic acid with Ru(cod)(cot) (cod = 1-2-η^2:5-6-η^2-cyclooctadiene; cot = 1–6-η^6-cyclooctatriene) in the presence of PMe_3 gives a new ruthenium(II) complex formulated as Ru(1–5-η^5-C_8H_{11})($\eta^1(O)$,$\eta^2(C,C')$-$OCOCH_2CH{=}CH_2$)(PMe_3) (1). X-ray crystallography revealed its structure as having a piano-stool coordination around the ruthenium center. Crystals of 1 are tetragonal, space group $P4_32_12$, with a = 12.559 (3) Å, c = 20.455 (4) Å, and Z = 8. The structure calculation converged to R = 0.053 and R_w = 0.054 for 1208 reflections with $F_o > 3\sigma(F_o)$. ^1H and $^{13}C\{^1H\}$ NMR spectra of 1 agree well for the structure with the allyl entity of the carboxylate π-bonded through the C=C double bond to ruthenium. Reaction of acetic acid with Ru(cod)(cot) gives an acetate complex formulated as Ru(1–5-η^5-C_8H_{11})(OCOMe)(1–4-η^4-C_8H_{12}) (2), which reacts further with 2 equiv of PMe_3 to give Ru(1–5-η^5-C_8H_{11})(OCOMe)(PMe_3)$_2$ (3). Complexes 2 and 3 were characterized by means of NMR spectroscopy.

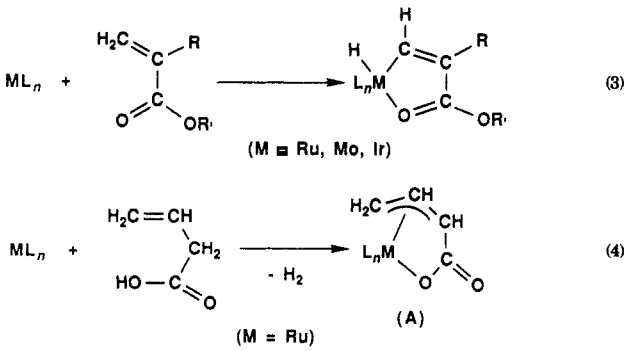
Introduction

Recently, increasing attention has been given to reactions of transition-metal complexes with functionalized olefins such as unsaturated carboxylic acids, their esters and amides, and unsaturated amines and phosphines.[2-8] In certain cases simple π-coordination takes place, whereas in other cases activation of vinylic or allylic C—H bonds or insertion of the C=C double bond into the metal–hydrogen or metal–carbon bond occurs. These reaction pathways are strongly influenced by the nature of the substrate, the steric and/or electronic character of the auxiliary ligand, and the valency of the metal center. Some representative reactions are summarized in Schemes I–III. Since some of these complexes having cyclic structures undergo reaction with CO or Br_2 to release cyclization products such as lactones, and cyclic anhydrides and imides of dicarboxylic acids,[2,5,9-11] they can be regarded as intermediates in the carbonylative cyclization of unsaturated carboxylic acids and their derivatives catalyzed by cobalt and palladium complexes.[12]

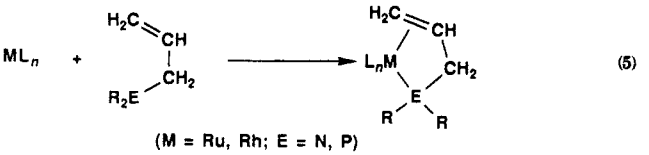
Scheme I. Type I: Transfer of an OH or NH Hydrogen to the C=C Double Bond in the Substrate To Give Metallacyclic Compounds[2,3]



Scheme II. Type II: Complex Formation through C—H Bond Activation of the Substrate[4-6]



Scheme III. Type III: Coordination of a Substrate through π-Bonding of the Olefinic Group[7,8]



Previously we observed that reaction of Ru(cod)(cot) (cod = 1-2-η^2:5-6-η^2-cyclooctadiene; cot = 1–6-η^6-cyclooctatriene) with 3-butenoic acid in the presence of PPh_3 gave a Ru(II) complex formulated as $(Ph_3P)_2Ru(\eta^1(O),\eta^3(C,C',C'')$-$OCOCH{-}CH{-}CH_2)$ accompanied by liberation of cyclooctadiene isomers (Scheme II; eq 4, type

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Table I. Crystal Data and Details of Structure Determination for Complex 1

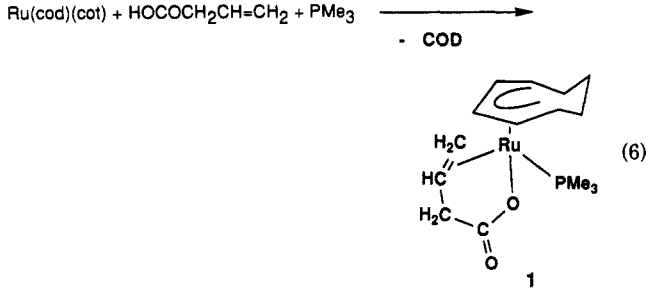
formula	$C_{15}H_{25}O_2PRu$
mol wt	369.41
cryst syst	tetragonal
space group	$P4_32_12$
a, Å	12.559 (3)
c, Å	20.455 (4)
V, Å^3	3226.3
Z	8
μ, cm^{-1}	10.47
$F(000)$	1520
D_{cal}, g cm^{-3}	1.522
cryst size, mm	0.2 × 0.2 × 0.3
2θ range, deg	3.0–50.0
scan rate, deg min^{-1}	4
hkl ranges (h < k)	$0 < h < 14$, $0 < k < 24$, $0 < l < 14$
no. of unique rflns	1609
no. of rflns used ($F_o > 3\sigma(F_o)$)	1208
R	0.053
R_w	0.054
q[a]	0.036

[a] Parameter q in $w = [\sigma^2(F_o) + q^2(F_o)^2]^{-1}$.

II).[5] The reaction involves activation of the allylic C–H bond in 3-butenoic acid by the ruthenium center. However, similar reaction of Ru(cod)(cot) with 3-butenoic acid in the presence of PMe_3 ligand caused formation of a different type of ruthenium carboxylate complex having an olefinic group π-coordinated in a manner similar to type III (Scheme III). Here we show the structure of this new complex determined by means of X-ray crystallography as well as NMR spectroscopy. Reaction of Ru(cod)(cot) with acetic acid is also described in relation to the formation mechanism of the complex having a π-coordinated olefinic group and the carboxylate group.

Results and Discussion

Preparation of Ru(1-5-η⁵-C_8H_{11})(η¹(*O*),η²(*C*,*C*′)-OCOCH$_2$CH=CH$_2$)(PMe$_3$) (1). Ru(cod)(cot) reacts with 3-butenoic acid in the presence of PMe_3 at room temperature to give a complex formulated as Ru(1-5-η⁵-C_8H_{11})(η¹(*O*),η²(*C*,*C*′)-OCOCH$_2$CH=CH$_2$)(PMe$_3$) (1).



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Complex 1 is practically insoluble in many common organic solvents such as toluene, CH_2Cl_2, acetone, and Et_2O and sparingly soluble in THF.

Previously we reported that the reaction of Ru(cod)(cot) with 3-butenoic acid in the presence of 2 equiv of PPh_3 gave the ruthenium complex Ru(η¹(*O*),η³(*C*,*C*′,*C*″)-OCOCH–CH–CH$_2$)(PPh$_3$)$_2$, which has two PPh_3 ligands and an η³-2-propenecarboxylate ligand. This reaction involves ruthenium-promoted activation of O—H and C—H bonds in the unsaturated carboxylic acid accompanied by hydrogenation of the cyclooctatriene ligand to cyclooctadiene, which is eliminated from the complex during the reaction. In reaction 6 formation of a similar ruthenium complex with an η³-2-propenecarboxylate ligand is not observed even when 2 equiv of PMe_3 to 1 equiv of Ru(cod)(cot) is used.

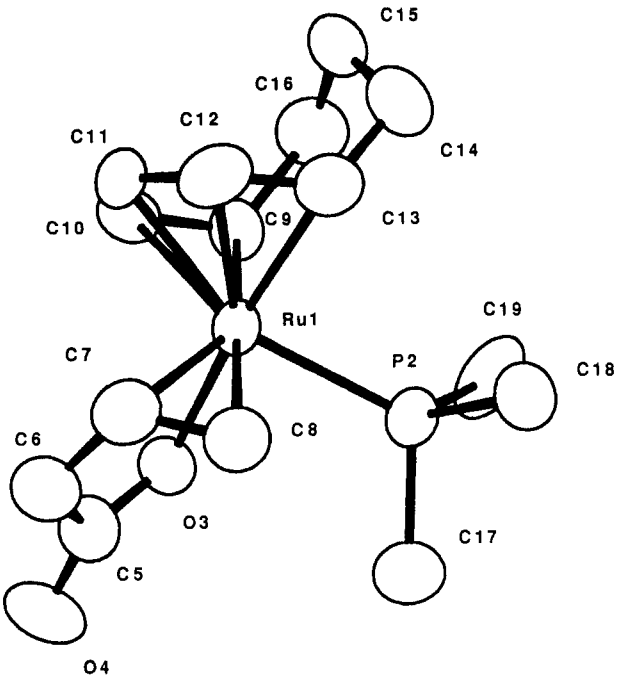

Figure 1. ORTEP drawing of Ru(η⁵-C_8H_{11})(η¹(*O*),η²(*C*,*C*′)-OCOCH$_2$CH=CH$_2$)(PMe$_3$) (1) showing 50% probability ellipsoids.

Table II. Selected Bond Distances and Angles[a]

	Distances (Å)		
Ru1–P2	2.346 (3)	Ru1–O3	2.106 (8)
Ru1–C7	2.201 (14)	Ru1–C8	2.217 (14)
Ru1–C9	2.182 (12)	Ru1–C10	2.161 (13)
Ru1–C11	2.221 (14)	Ru1–C12	2.134 (11)
Ru1–Cl3	2.180 (15)	C5–O3	1.28 (2)
C5–O4	1.24 (2)	C5–C6	1.49 (2)
C6–C7	1.50 (2)	C7–C8	1.37 (2)
	Angles (deg)		
P2–Ru1–O5	84.8 (2)	P2–Ru1–C7	115.6 (4)
P2–Ru1–C8	82.6 (4)	O3–Ru1–C7	77.9 (4)
O3–Ru1–C8	88.8 (4)	C7–Ru1–C8	36.2 (5)
O3–C5–O4	123.9 (1.3)	O3–C5–C6	115.3 (1.2)
O4–C5–C6	120.5 (1.4)	C5–C6–C7	114.7 (1.2)
C6–C7–C8	124.2 (1.3)	C6–C7–Ru1	106.9 (1.0)
C8–C7–Ru1	72.5 (8)	C7–C8–Ru1	71.3 (8)

[a] Standard deviations are in parentheses.

Crystal Structure of Complex 1. Single crystals of complex 1 obtained by recrystallization from THF were subjected to X-ray crystallographic analysis. Figure 1 shows the molecular structure of 1. Tables I and II summarize the crystal data and details of the measurement and selected bond distances and angles, respectively. 1 has a piano-stool coordination around the ruthenium center, which is bonded to a η⁵-cyclooctadienyl ligand, PMe_3, and a η¹(*O*),η²(*C*,*C*′)-3-butenecarboxylate ligand. The five coordinated carbon atoms in the cyclooctadienyl ligand are essentially planar, and the ruthenium–carbon bond distances are in the range 2.13–2.22 Å, a range similar to those for [RuH(1-5-η⁵-C_8H_{11})$_2$]BF$_4$ and [Ru(1-5-η⁵-C_8H_{11})-(PMe$_2$Ph)$_3$]BF$_4$.[13,14] Bond distances between ruthenium and the carbons in the olefinic group in the carboxylate ligand are 2.20 and 2.22 Å. The values are similar to those in π-coordinated olefin complexes of ruthenium(0) and ruthenium(II).[8,15,16]

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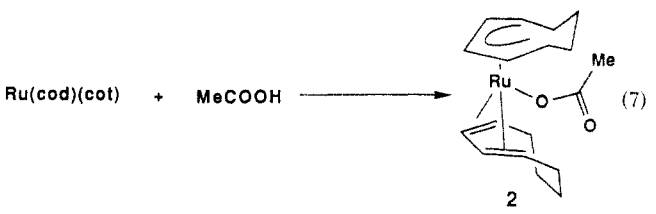
IR and NMR Spectra of Complex 1. The IR spectrum of complex **1** in a KBr disk shows strong bands at 1642 and 1610 cm^{-1}, which can be assigned to ν_{as}(COO) and ν_s(COO) vibrations.

The $^{13}C\{^1H\}$ NMR spectrum of **1** shows 12 signals that are assignable to carbon atoms in the cyclooctadienyl and carboxylate ligands. The signal at 179.9 ppm is due to the COO carbon atom of the carboxylate ligand. Complex **1** enriched with ^{13}C at the COO position has been prepared by reaction of Ru(cod)(cot) with [1-^{13}C]-3-butenoic acid in the presence of PMe_3. The $^{13}C\{^1H\}$ NMR spectrum shows a doublet at 37.9 ppm due to the methylene carbon adjacent to the carbonyl group with a ^{13}C–^{13}C coupling of 51 Hz. The other carbon signals are assigned unambiguously on the basis of an off-resonance spectrum and a ^1H–^{13}C COSY spectrum.

The ^1H NMR spectrum of **1** shows signals that agree well with the proposed structure, although coupling constants of some of the signals are not unequivocally determined due to their overlapping with each other. Assignment of the signals is based on the ^1H–^1H COSY spectrum. A signal at 0.20 ppm is assigned to the endo methylene hydrogen of the CH_2 group at the center of three CH_2 groups in the cyclooctadienyl ligand. The extremely high magnetic field position is probably due to a shielding effect by π-electrons in the η^5-cyclooctadienyl ligand. A similar high-field shift of a methylene hydrogen due to magnetic anisotropy of the η^5-pentadienyl plane has been also observed in the ^1H NMR spectrum of Ru(η^5-C_8H_{11})$_2$.[17] Coupling constants between the hydrogen atoms of the allyl group in the carboxylate ligand are similar to those of the corresponding hydrogen atoms in 3-butenoic acid.

Preparation and Characterization of Complexes 2 and 3. Reaction of Ru(cod)(cot) with acetic acid gives the complex Ru(1–5-η^5-C_8H_{11})(OCOMe)(1–4-η^4-C_8H_{12}) (**2**) in 53% yield. ^1H and ^{13}C NMR spectra of **2** respectively



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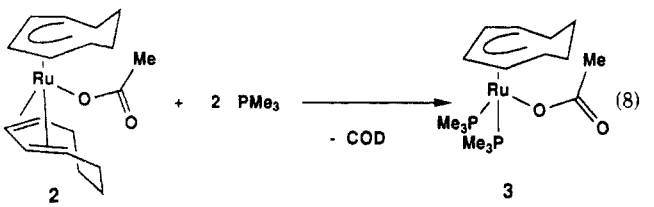
show signals due to vinylic hydrogens and vinylic carbons at reasonable positions. Most of the vinylic carbon signals in the $^{13}C\{^1H\}$ NMR spectrum and signals of vinylic hydrogens in the ^1H NMR spectrum of **2** are assigned on the basis of ^1H–^1H and ^1H–^{13}C COSY spectra as well as a ^1H-gated-decoupled ^{13}C NMR spectrum. The following spectroscopic features indicate the presence of the 1,3-cyclooctadiene ligand, which is considered to be formed through a hydrogen shift of the 1,5-cyclooctadiene ligand in the starting complex. Signals due to the vinylic hydrogens of the cyclooctadiene ligand are observed at 3.23 (H_j), 4.69 (H_i), 2.5 (H_p), and 3.33 (H_o) ppm, respectively (see Experimental Section for designation of protons), although the obtained chemical shift of the third signal is not accurate due to its overlapping with the signal of CH_2 hydrogens. The ^1H–^1H COSY spectrum clearly indicates the ^1H–^1H coupling in H_j–H_i, H_i–H_p, and H_p–H_o pairs of the hydrogen atoms.

^1H and ^{13}C NMR signals due to methylene carbons and hydrogens of the cyclooctadienyl and cyclooctadiene ligands are not unequivocally assigned due to overlapping of the signals in the ^1H NMR spectra.

Previously Chaudret and his co-workers investigated the reaction of Ru(cod)(cot) with HBF_4 and observed initial protonation of the ruthenium center to give a cationic hydride ruthenium(II) complex formulated as [RuH(1–6-η^6-C_8H_{10})(1–4-η^4-C_8H_{12})]BF_4, which was transformed into the isomeric complex [Ru(1–5-η^5-C_8H_{11})(1–4-η^4-C_8H_{12})]BF_4 through formation of [RuH(1–5-η^5-C_8H_{11})$_2$]BF_4 followed by migration of the hydride ligand into a cyclooctadienyl ligand.[18] Reaction 7 is also considered to proceed through initial protonation of the ruthenium center of Ru(cod)(cot) followed by hydride migration into the cyclooctatriene ligand. However, it is not clear whether the reaction proceeds through a cationic intermediate in a manner similar to the reaction of Ru(cod)(cot) with HBF_4 or through a neutral intermediate such as RuH(OCOMe)(1–4-η^4-C_8H_{10})(1–4-η^4-C_8H_{12}).

Complex **2** reacts with 2 equiv of PMe_3 to give the complex Ru(1–5-η^5-C_8H_{11})(OCOMe)(PMe_3)$_2$ (**3**) in 58% yield. The ^1H NMR spectrum of **3** shows signals due to



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vinylic hydrogens at 5.84, 4.35, and 2.98 ppm in a peak area ratio of 1:2:2. The $^{13}C\{^1H\}$ NMR spectrum shows three signals due to the corresponding CH carbons of the cyclooctadienyl ligand. The peak positions are quite similar to those of the corresponding carbons in Ru(1–5-η^5-C_8H_{11}).[19]

Mechanism of Formation of Complex 1. Two reaction pathways are possible for formation of complex **1** by reaction of Ru(cod)(cot) with 3-butenoic acid in the presence of PMe_3 ligand. One involves initial protonation of the complex by the acid to give a carboxylate complex with a η^5-cyclooctadienyl ligand as in reaction 7 followed by coordination of a PMe_3 ligand and the olefinic group of the carboxylate ligand. Another pathway involves formation of a PMe_3-coordinated ruthenium(0) complex such as Ru(PMe_3)(1–4-η^4-C_8H_{12})(1–4-η^4-C_8H_{10}),[20] which undergoes further reaction with 3-butenoic acid to give complex **2**. Reactions 7 and 8 seem to support the former mechanism, although we do not have sufficient experimental data to exclude the latter one.

Reaction of Ru(cod)(cot) with 3-butenoic acid in the presence of PPh_3 gives Ru(η^1(*O*),η^3(*C*,*C*′,*C*″)-OCOCH-CH-CH$_2$)(PPh_3)$_2$ (A) as shown previously.[5] Formation of two different complexes depending on the nature of tertiary phosphine ligands is intriguing and may be explained as follows. The reaction with the PPh_3 ligand may involve an intermediate ruthenium complex having a π-coordinated olefinic group such as Ru(1–5-η^5-C_8H_{11})(η^1-(*O*),η^2(*C*,*C*′)-OCOCH$_2$CH=CH$_2$)(PPh_3). This intermediate is sterically much less stable than **1**, which has the compact PMe_3 ligand, and can be converted into A (reaction 4)

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through ruthenium-promoted abstraction of the allylic hydrogen followed by elimination of cyclooctadiene ligand under the reaction conditions.

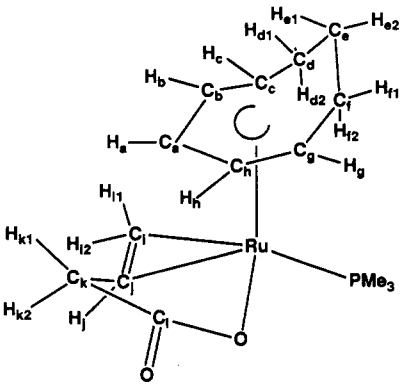
Experimental Section

All the manipulations of the complexes were carried out under nitrogen or argon. Ru(cod)(cot)[17,19] and 3-butenoic acid[21] were prepared according to the literature. [1-^{13}C]-3-Butenoic acid was similarly prepared from Na^{13}CN purchased from CEA.

Elemental analyses were carried out by Dr. M. Tanaka of our laboratory by using a Yanagimoto Type MT-2 CHN autocorder. IR spectra were recorded on a JASCO IR 810 spectrophotometer. NMR spectra were recorded on JEOL FX-100 and GX-500 spectrometers by Dr. Y. Nakamura and A. Kajiwara.

Preparation of Ru(1-5-η⁵-C_8H_{11})(η¹(*O*),η²(*C*,*C'*)-$OCOCH_2CH{=}CH_2$)(PMe_3) (1). To a THF (1 mL) solution of Ru(cod)(cot) (210 mg, 0.67 mmol) and PMe_3 (53 mg, 0.70 mmol) was added 3-butenoic acid (58 mg, 0.67 mmol) at room temperature. The initially formed yellow solution gradually changed to orange on stirring. After 1 h a yellow solid precipitated. It was filtered, washed with cold THF several times, and dried in vacuo; yield 130 mg, 53%. Anal. Calcd for $C_{15}H_{25}O_2PRu$: C, 48.8; H, 6.8. Found: C, 49.0; H, 7.1.

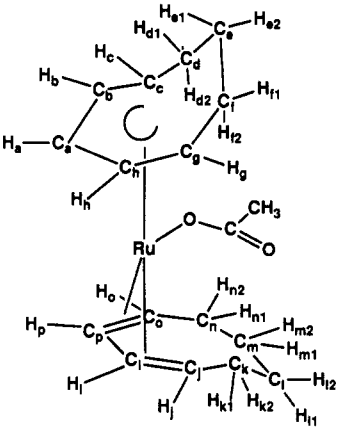
A similar reaction of Ru(cod)(cot), PMe_3, and 3-butenoic acid in a 1:2:1 ratio gave complex 1 in a 42% yield.



^{1}H NMR (500 MHz at 25 °C in THF-d_8; in ppm referred to the $CD_2CD\mathit{H}CD_2$ signal of the solvent (3.58 ppm)): 6.89 (H_a, t, $J(H_aH_b) = J(H_aH_h) = 7$ Hz), 4.55 (H_h, t, $J(H_hH_a) = J(H_hH_g) = 7$ Hz), 4.15 (H_j, dtt, $J(H_jH_{i1}) = 11$ Hz, $J(H_jH_{i2}) = J(H_jH_{k2}) = 8$ Hz, $J(H_jH_{k1}) = J(H_jP) = 3$ Hz), 3.28 (H_g, dt, $J(H_gH_h) = 8$ Hz, $J(H_gH_{f1}) = J(H_gH_{f2}) = 4$ Hz), 2.65 (H_{k2}, dd, $J(H_{k2}H_{k1}) = 17$ Hz, $J(H_{k2}H_j) = 8$ Hz), 2.402 (H_c, m), 2.20 (H_b, dd, $J(H_bH_a) = 6$ Hz, $J(H_bH_c) = 3$ Hz), 2.00–2.10 (H_{f1}, H_{i1}, H_{k1}), 1.75–1.85 (H_{d1}, H_{f2}, m), 1.54 (H_{d2}, tt, $J(H_{d2}H_{d1}) = J(H_{d2}H_{e1}) = 14$ Hz, $J(H_{d2}H_{e2}) = J(H_{d2}H_c) = 3$ Hz), 1.22 (H_{i2}, d, $J(H_{i2}H_j) = 8$ Hz), 1.15 (H_{e2}, doublet of quintets, $J(H_{e2}H_{e1}) = 14$ Hz, $J(H_{e2}H_{d1}) = J(H_{e2}H_{d2}) = J(H_{e2}H_{f1}) = J(H_{e2}H_{f2}) = 3$ Hz), 0.20 (H_{e1}, triplet of quartets, $J(H_{e1}H_{e2}) = J(H_{e1}H_{d2}) = J(H_{e1}H_{f2}) = 14$ Hz, $J(H_{e1}H_{d1}) = J(H_{e1}H_{f1}) = 3$ Hz). ^{13}C{^{1}H} NMR (125 MHz at 25 °C in THF-d_8; in ppm referred to the center of the $-CD_2O$ signal of the solvent (25.3 ppm)): 179.9 (C_l, s), 112.1 (C_a, d, $J(C_aP) = 11$ Hz), 97.4 (C_h, s), 80.1 (C_b, s), 63.43 (C_j, s), 56.8 (C_c, s), 53.9 (C_g, s), 52.2 (C_i, d, $J(C_iP) = 7$ Hz), 37.9 (C_k, s), 27.5 (C_f, s), 26.8 (C_d, s), 20.7 (C_e, s), 15.0 ($P(\mathit{C}H_3)_3$, d, $J(CP) = 29$ Hz). ^{31}P{^{1}H} NMR (40 MHz at 25 °C in THF-d_8; in ppm referred to external 85% H_3PO_4): 8.1 (s).

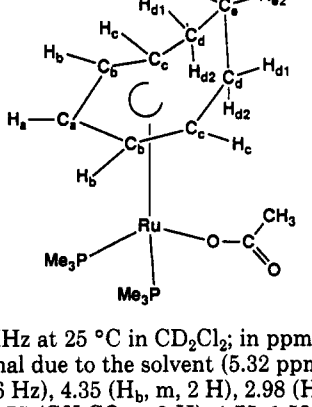
Preparation of Ru(1-5-η⁵-C_8H_{11})(OCOMe)(1-4-η⁴-C_8H_{12}) (2). To an Et_2O (6 mL) solution of Ru(cod)(cot) (339 mg, 1.07 mmol) was added acetic acid (64 mg, 1.07 mmol) at room temperature. Stirring the solution at this temperature caused a change in color of the solution from yellow to red. After 2 h the solution was cooled to −20 °C to give 2 as an orange-yellow solid, which was filtered, washed with Et_2O, and dried in vacuo; yield 213 mg, 53%. Anal. Calcd for $C_{18}H_{26}O_2Ru$: C, 57.6; H, 6.9. Found: C, 57.4; H, 7.1.

(21) (a) Rietz, E. *Organic Syntheses*; Wiley: New York, 1955; Collect. Vol. III, p 851. (b) Supniewski, J. V.; Salzberg, P. L. *Organic Syntheses*; Wiley: New York, 1932; Collect. Vol. I, p 46.



^{1}H NMR (500 MHz at −40 °C in THF-d_8; in ppm referred to $CD_2CD\mathit{H}CD_2$ signal of the solvent (3.58 ppm)): 5.60 (H_b, dd, $J(H_bH_a) = 3$ Hz, $J(H_bH_c) = 8$ Hz), 5.25 (H_c, dt, $J(H_cH_b) = 8$ Hz, $J(H_cH_{d1}) = J(H_cH_{d2}) = 10$ Hz), 4.79 (H_a, dd, $J(H_aH_b) = 3$ Hz, $J(H_aH_h) = 8$ Hz), 4.69 (H_i, dd, $J(H_iH_j) = 7$ Hz, $J(H_iH_p) = 3$ Hz), 4.35 (H_h, t, $J(H_hH_g) = J(H_hH_a) = 8$ Hz), 4.03 (H_g, dt, $J(H_gH_h) = 8$ Hz, $J(H_gH_{f1}) = J(H_gH_{f2}) = 10$ Hz), 3.33 (H_o, dd, $J(HH) = 6$ and 3 Hz), 3.23 (H_j, dt, $J(H_jH_i) = 7$ Hz, $J(H_jH_{k1}) = J(H_jH_{k2}) = 8$ Hz), 1.84 ($C\mathit{H}_3CO$, s). Assignment of the signals due to CH_2 hydrogens is not feasible due to overlapping of the signals. The signal due to H_p is overlapped with those of CH_2 hydrogens. Approximate peak positions have been obtained from a ^{1}H–^{1}H correlation spectrum as 2.5 ppm. ^{13}C{^{1}H} NMR (125 MHz at −40 °C in THF-d_8; in ppm referred to the center of the $-CD_2O$ signal of the solvent (25.3 ppm)): 183.4 (COO), 135.9 (C_b), 126.4 (C_c), 106.3 (C_h), 90.1 (C_j), 86.0 (C_a), 84.9 (C_i), 81.4 (C_p), 74.0 (C_o), 58.8 (C_g), 37.1, 34.2, 29.5, 26.7, 26.4, 25.8, 25.3 (C_d–C_f, C_k–C_n), 24.8 ($\mathit{C}H_3CO$). Assignment of the signals due to CH_2 carbons from a ^{1}H–^{13}C correlation spectrum is not feasible due to overlapping of the signals of the CH_2 hydrogens in the ^{1}H NMR spectrum. The signal at 25.3 ppm is overlapped with those of the solvent. The peak position has been obtained from the ^{1}H-gated-decoupled ^{13}C NMR spectrum.

Preparation of Ru(1-5-η⁵-C_8H_{11})(OCOMe)(PMe_3)$_2$ (3). To a THF (3 mL) solution of complex 2 (103 mg, 0.27 mmol) was added PMe_3 (46 mg, 0.60 mmol) at room temperature. The color of the solution immediately changed from orange to light yellow. After 2 h the solvent was removed under reduced pressure to give complex 3 as a white solid, which was washed with Et_2O and then with hexane and dried in vacuo; yield 67 mg, 58%. Anal. Calcd for $C_{16}H_{32}O_2P_2Ru$: C, 45.8; H, 7.6. Found: C, 45.3; H, 8.7.



^{1}H NMR (270 MHz at 25 °C in CD_2Cl_2; in ppm referred to the center of the signal due to the solvent (5.32 ppm)): 5.84 (H_a, t, 1 H, $J(H_aH_b) = 6$ Hz), 4.35 (H_b, m, 2 H), 2.98 (H_c, m, 2 H), 2.15 (CH_2, m, 2 H), 1.75 ($C\mathit{H}_3CO$, s, 3 H), 1.75–1.58 (CH_2, m, 3 H), 1.36–1.29 ($P(C\mathit{H}_3)_3$, br, 18 H), 0.51 (H_{e1}, triplet of quartets, 1 H, $J(H_{e1}H_{e2}) = J(H_{e1}H_{d1}) = 14$ Hz, $J(H_{e1}H_{d2}) = 3$ Hz). ^{13}C{^{1}H} NMR (54 MHz at 25 °C in CD_2Cl_2; in ppm referred to the center of the solvent peak (53.8 ppm)): 171.0 ($COCH_3$), 98.7 (C_a), 92.9 (C_b), 54.4 (C_c), 27.0 (C_d), 20.8 (C_e), 20.2 (CH_3CO), 20–19 ($P(\mathit{C}H_3)_3$, br). ^{31}P{^{1}H} NMR (40 MHz at 25 °C in CD_2Cl_2; in ppm referred to external H_3PO_4): −6.5 (s).

X-ray Crystallography. Crystals of 1 suitable for X-ray crystallography were grown in THF at −20 °C. Lattice constants

were determined by a least-squares calculation of 2θ values of 25 reflections with $19° < 2\theta < 22°$. Intensities were collected on a Rigaku AFC-5 four-cycle automated diffractometer by using Mo Kα radiation (λ = 0.71068 Å). Detailed conditions for the data collection are summarized in Table I. No absorption correction was applied.

Calculations were carried out with the program system CRYSTAN on a FACOM A-70 computer. The structure was solved by a combination of direct methods (SAPI85) and Fourier techniques. Full-matrix least-squares calculations were used with anisotropic temperature factors for all non-hydrogen atoms. Hydrogen atoms were located at idealized positions with isotropic temperature factors, and their parameters were not refined.

Systematic absences of reflections ($h00$, $h = 2n$; $0k0$, $k = 2n$; $00l$, $l = 4n$) indicated space group $P4_12_12$ or its enantiomorph $P4_32_12$. As least-squares calculations with the latter space group showed better convergence ($R = 0.052_6$ and $R_w = 0.054_1$) than calculations with the former space group ($R = 0.054_3$ and $R_w = 0.056_1$), structure calculations were carried out with $P4_32_12$.

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Registry No. **1**, 127355-85-5; **2**, 127355-86-6; **3**, 127355-87-7; Ru(cod)(cot), 127382-91-6; 3-butenoic acid, 625-38-7.

Supplementary Material Available: Tables S1 and S2 (fractional coordinates and temperature factors of **1**) and Table S3 (bond distances and angles) (6 pages); Table S4 (observed and calculated structure factors) (6 pages). Ordering information is given on any current masthead page.

^{207}Pb CP MAS NMR Study of Hexaorganyldiplumbanes

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Lead-207 CP MAS NMR spectra have been obtained for the series of hexaorganyldiplumbanes Pb_2R_6 (R = phenyl, *o*-tolyl, *m*-xylyl, mesityl, cyclohexyl). These data will be discussed in relation to the respective solution-state ^{207}Pb NMR spectra and to the complementary information available from crystallographic studies. The ^{207}Pb shielding tensor components will be considered both qualitatively and quantitatively. Three triorganyllead halides have also been examined, and chemical shift data are reported for them.

Introduction

For some not so obvious reasons the ^{207}Pb nucleus in organolead compounds has so far attracted very little attention for high-resolution solid-state NMR studies. There are only a few reports on ^{207}Pb CP MAS studies in the literature,[1-6] although solid-state ^{207}Pb NMR spectroscopy can be expected to become an extremely useful analytical tool in the field of organolead chemistry, on the grounds of what is known from solution-state ^{207}Pb NMR studies.[7]

Especially with organolead(IV) compounds with mainly covalent bonds there are no experimental difficulties in obtaining good-quality ^{207}Pb CP MAS spectra. In this light, the hexaorganyldiplumbanes are ideal candidates for a ^{207}Pb CP MAS study: (i) the symmetrically substituted diplumbanes Pb_2R_6 are reasonably stable compounds, (ii) the X-ray crystal structures of $Pb_2(phenyl)_6$[8] and $Pb_2(cyclohexyl)_6$[9] are known, (iii) most of these compounds are soluble enough to obtain solution-state ^{207}Pb NMR data for comparison purposes, and (iv) recently, the scalar coupling constant $^1J(^{207}Pb^{207}Pb)$ in diplumbanes has attracted the attention of NMR spectroscopists.[10]

In this paper we present a series of ^{207}Pb CP MAS spectra of some hexaorganyldiplumbanes, Pb_2R_6 (R = phenyl, cyclohexyl, *o*-tolyl, *m*-xylyl, mesityl), together with the respective solution-state ^{207}Pb NMR data. During the course of this investigation it became highly desirable to have further crystallographic information on $Pb_2(o\text{-tolyl})_6$.

Table I. ^{207}Pb NMR Data for Hexaorganyldiplumbanes and Related Compounds[a]

	$\delta(^{207}Pb)$/ppm	
compd	soln	solid (half-height width/Hz)
$Pb_2(phenyl)_6$ (I)	−79.8	−131.8 (250)
		+14.5 (140)
$Pb_2(cyclohexyl)_6$ (II)	+80.2	+140.6 (100)
$Pb_2(o\text{-tolyl})_6$ (III)	−88.7	−83.9 (500)
$Pb_2(p\text{-tolyl})_6$[b] (IV)	−77.6	−95
		−66
$Pb_2(m\text{-xylyl})_6$ (V)	−91.2	−92.7 (500)
$Pb_2(mesityl)_6$ (VI)	−154.5	−141.3 (500)
		−154.1 (500)
$Pb(o\text{-tolyl})_4$	−166.3[d]	−159.2 (250)
$(cyclohexyl)_3PbCl$	+381.6[d]	+321 (500)
$(cyclohexyl)_3PbBr$	+409[d]	*c*
$(mesityl)_3PbI$	−356.8[d]	−350 ± 2 (1600)

[a] Conditions are given in the Experimental Section. $\delta(^{207}Pb)$ for the solid state is accurate to ±0.5 ppm, unless stated otherwise. [b] Data from ref 1. [c] No ^{207}Pb CP MAS spectrum obtained; the failure is possibly due to excessive line broadening as a consequence of residual (^{207}Pb, $^{79/81}$Br) dipolar interactions in the solid state and/or due to $^{79/81}$Br relaxation effects on the cross-polarization experiment. [d] Saturated $CDCl_3$ solution at room temperature.

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