(13) R. F. Heck, *J. Am. Chem. Soc.*, **85**, 655 (1963).
(14) M. Basato and A. Poe, *J. Chem. Soc., Dalton Trans.*, 456 (1974).
(15) R. E. Davis, T. A. Dodds, T.-H. Hseu, J. C. Wagnon, T. Devon, J. Tancrede, J. S. McKennis, and R. Pettit, *J. Am. Chem. Soc.*, **96**, 7562 (1974).
(16) The experimental fact that the relevant reaction steps proceed only photochemically in the case of DMB but thermally with DPA may be rationalized by applying qualitative FMO theory.[17] The coordinated alkyne in (L)-$Fe(CO)_3$(DPA) still has one of the degenerate HOMO's available for intramolecular cycloaddition, while the diene in (L)$Fe(CO)_3(1,2\text{-}\eta\text{-DMB})$ uses its Ψ_2 orbital for complexation and therefore cannot undergo the cycloaddition reaction by a thermal pathway.
(17) K. Fukui, *Top. Current Chem.*, **15**, 1 (1970).
(18) H. Kisch, *J. Organomet. Chem.*, **30**, C 25 (1971).
(19) O. Diels and K. Alder, *Justus Liebigs Ann. Chem.*, **490**, 236 (1931); H. D. Scharf and D. Korte, *Chem. Ber.*, **99**, 3925 (1966).
(20) We are indebted to Professor E. Koerner von Gustorf for the loan of this apparatus.
(21) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry", Wiley, New York, N.Y., 1966, p 783; C. G. Hatchard and C. A. Parker, *Proc. R. Soc. London, Ser. A*, **235**, 518 (1956).
(22) H. Hermann, G. Koltzenburg, and D. Schulte-Frohlinde, *Ber. Bunsenges. Phys. Chem.*, **77**, 677 (1973).

Carbon–Hydrogen Bond Activation by Transition Metal Complexes. Oxidative Addition of Alkyl Methacrylate to Ruthenium. The Structure of Hydrido(2-*n*-butoxycarbonylpropenyl-C^1,O)tris(triphenylphosphine)ruthenium(II)

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Abstract: Alkyl methacrylate reacts with dihydridotetrakis(triphenylphosphine)ruthenium(II) via vinylic C–H bond cleavage to give hydrido(2-alkoxycarbonylpropenyl-C^1,O)tris(triphenylphosphine)ruthenium(II), $RuH(CH{=}C(CH_3)C(O)OR)(PPh_3)_3$, accompanied by formation of an equimolar amount of alkyl isobutyrate per mole of the dihydrido complex. A hydridoalkenyl-type structure for the complex was proposed on the basis of chemical reactions, such as the formation of methyl *cis*-β-deuteriomethacrylate on treatment of the complex with DCl, and methylation at the β-position of alkyl methacrylate on treatment with methyl iodide. The low $\nu(C{=}O)$ band ($\sim$1580 cm^{-1}) in its ir spectrum, the presence of a hydride signal in the ^1H NMR spectrum, and the $^{31}P\{^1H\}$ NMR spectrum characteristic of meridional octahedral configuration support the proposed structure. An x-ray study confirmed the structure of hydrido(2-*n*-butoxycarbonylpropenyl-C^1,O)tris(triphenylphosphine)ruthenium(II). This compound crystallizes from tetrahydrofuran–diethyl ether in the space group $C_{2h}{}^6$-$C2/c$ with $a = 29.691\ (8)$ Å, $b = 21.865\ (5)$ Å, $c = 21.245\ (6)$ Å, $\beta = 122.26\ (1)°$, and $Z = 8$. Based on 4801 unique reflections with $F_o{}^2 \geq 3\sigma(F_o{}^2)$ full-matrix, least-squares refinement led to agreement indices (on F) of $R = 0.067$ and $R_w = 0.111$. The structure consists of discrete molecules of the complex in which the ruthenium atom is six-coordinate with distorted octahedral geometry. Three coordination sites are occupied by the phosphine ligands in a meridional arrangement. The alkyl methacrylate ligand is bidentate, bonded to the ruthenium atom via the vinylic carbon and the carboxyl oxygen atoms forming a Ru–C–C–C–O five-membered ring. The vinyl carbon atom is trans to a phosphine ligand and the oxygen atom is trans to the hydrido ligand. The terminal three carbon atoms of the *n*-butyl group of the *n*-butyl methacrylate ligand are disordered making a satisfactory description of their positions difficult. Some relevant metric parameters in the complex are: Ru–C(1), 2.061 (10) Å; Ru–O(1), 2.246 (7) Å; C(1)–C(2), 1.368 (15) Å; C(2)–C(4), 1.442 (15) Å; C(4)–O(1), 1.254 (12) Å; O(1)–Ru–C(1), 75.6 (4)°; Ru–C(1)–C(2), 117.8 (8)°; C(1)–C(2)–C(4), 113.4 (10)°; C(2)–C(4)–O(1), 121.2 (11)°; and C(4)–O(1)–Ru, 111.6 (7)°.

Activation of a C–H bond by a transition metal complex is attracting increasing interest because of its potential utility in synthetic organic chemistry. Oxidative additions involving C–H bond cleavage have been postulated in ethylene dimerization,[2,3] oxidative substitution of an olefin assisted by palladium compounds,[4–7] and in H–D exchange in aliphatic and/or aromatic hydrocarbons catalyzed by tantalum, niobium, iridium,[8,9] platinum,[10–13] titanium,[14,15] rhodium,[16] cobalt,[17] and rhenium compounds.[18] However, unequivocal examples of isolation of the product of oxidative addition involving C–H bond cleavage are relatively limited, except for a few examples of orthometalation and its analogous reactions in which C–H bond cleavage of a coordinated ligand is involved.[19–32] Metalation of a vinylic carbon atom to form metal-sp^2-carbon σ-bonds has been reported for platinum,[33] rhodium,[34] and iridium,[35] all of which involve nitrogen as a donor atom. In the course of our systematic studies on the reaction of dihydridotetrakis(triphenylphosphine)ruthenium (**1**) with various substituted olefins, we found that alkyl methacrylate reacts with **1** via vinylic C–H bond activation to yield hydrido-2-alkoxycarbonylpropenyl-type complexes. The present paper reports in detail the preparation and characterization of these novel compounds with a series of ester-alkyl groups, and the crystallographic determination of the structure of one of these complexes, hydrido(2-*n*-butoxycarbonylpropenyl-C^1,O)tris(triphenylphosphine)ruthenium(II). A preliminary account has been published elsewhere.[36] Isolation of the hydrido carbon-to-metal σ-complexes by the direct oxidative addition involving C–H bond cleavage has also been reported for naphthalene,[19–21] benzene,[37,39–45] *p*-xylene and mesitylene,[38]

Table I. Analyses and Physical Properties of $\overline{\text{RuH(CH=C(CH}_3\text{)C(O}}\text{)OR)(PPh}_3)_3$ (**2**)

Complex R	Appearance	Analyses[a] C %	Analyses[a] H %	Mp[b] (°C)	Yield[c] (%)
Me (**2**a)	Light yellow powder	70.0[d] (71.7)	5.4 (5.4)	211–213	73
Et (**2b**)	Yellow prisms	72.3 (72.0)	5.4 (5.7)	200	83
i-Pr (**2**c)	Yellow needles	72.4 (72.1)	6.3 (5.6)	178–180	25
n-Bu (**2**d)	Yellow prisms	72.8 (72.3)	6.2 (5.7)	165–167	15

[a] Calculated values are in parentheses. [b] With decomposition. [c] Yields are calculated on the basis of the starting dihydrido complex **1**. [d] Good analytical value is not obtainable owing to difficulty in purification of the product (see text).

Table II. Infrared Data for Hydrido-σ-Alkenyl Complexes (cm^{-1})[a]

Complex R[b]	ν(Ru—H)	ν(C=O)
Me (**2a**)	1980 m	1590 s
Et (**2b**)	1980 m	1580 s
i-Pr (**2c**)	1960 m	1580 s
n-Bu (**2d**)	1960 m	1580 s

[a] KBr disk. Intensity abbreviations: s, strong; m, medium. [b] Designation of R is as indicated in Table I.

and other olefins.[39-45] However, this paper presents, we believe, the first crystallographic evidence for oxidative addition involving vinylic C–H bond cleavage.

Experimental Section

All manipulations were carried out under nitrogen or under a vacuum. Solvents were dried in the usual manner, distilled, and stored under nitrogen. Analysis of evolved gas was carried out by mass spectrometry and gas chromatography after collecting gases fractionally using a Toepler pump, by which the volumes of gases were also measured. Analyses of liquid products were carried out by GC-mass spectroscopy (JEOL JNS-100 GC-mass spectrometer) and gas chromatography (Shimadzu Model GC-3BT). Infrared spectra were recorded on an Hitachi EPI-G3 spectrometer using KBr pellets prepared under an inert atmosphere. Measurement of NMR spectra obtained on a JEOL PS-100 spectrometer was carried out by Mr. Y. Nakamura.[1a] ^{1}H NMR signals are referred to tetramethylsilane and ^{31}P{^{1}H} NMR signals to triphenylphosphine (downfield positive). Microanalyses were carried out by Mr. T. Saito[1a] using a Yanagimoto CHN Autocorder Type MT-2.

Dihydridotetrakis(triphenylphosphine)ruthenium(II), $RuH_2(PPh_3)_4$,[46] **1**, and its deuterido analogue, $RuD_2(PPh_3\text{-}d_6)_4$[47,48] were prepared by the methods reported previously. Commercially available methyl, ethyl, isopropyl, and *n*-butyl methacrylates and methyl iodide were used after distillation over CaH_2 in vacuo. Ethyl *cis*-β-deuteriomethacrylate was synthesized from methylacetylene, nickel carbonyl, and ethanol-d_1, according to the method described in the literature.[49]

Reaction of 1 with Methyl Methacrylate. Excess methyl methacrylate (15.0 ml) was introduced to complex **1** (1.185 g, 1.03 mmol) by trap-to-trap distillation. After a day at room temperature, a light yellow precipitate (**2a**) was formed, which was filtered off, washed with *n*-hexane, and dried under vacuum. Because of the difficulty in separating the resulting complex from the polymer formed, a reliable analytical value could not be obtained (Table I). Pouring the yellow solution into acidic methanol caused precipitation of poly(methyl methacrylate), which was identified after filtration, washing with methanol, and drying under vacuum (yield, 0.11%). Thermolysis of complex **2a** (413 mg, 0.418 mmol) at 200° liberated 0.345 mmol of methyl methacrylate (83%).

Reaction of 1 with Ethyl Methacrylate. Ethyl methacrylate (3.0 ml) was added to complex **1** (861 mg, 0.748 mmol) by trap-to-trap distillation. After a day at room temperature a yellow precipitate was separated from the homogeneous yellow solution and the formation of ethyl isobutyrate (0.53 mmol, 70%) in the solution was confirmed. The precipitate was crystallized from a mixture of tetrahydrofuran (THF) and diethyl ether as yellow prisms of **2b** which were washed several times with *n*-hexane and dried under vacuum. The yield and analytical data are shown in Table I. Thermolysis of complex **2b** (512 mg, 0.519 mmol) at 200° liberated 0.40 mmol of ethyl methacrylate and 0.055 mmol of ethyl isobutyrate. Total yield of the esters liberated on thermolysis was calculated as 88% on the basis of **2b**. The reaction of ethyl *cis*-β-deuteriomethacrylate with **1** was similarly carried out. Partial deuteration of the hydridic hydrogen atom in the reaction product was demonstrated by a decrease of relative intensity of ν(Ru-H) in its ir spectrum compared with the undeuterated analogue (Table II).

Reaction of 1 with Isopropyl Methacrylate. Isopropyl methacrylate (5.0 ml) was added to complex **1** (978 mg, 0.850 mmol) to give a homogeneous solution in a day at room temperature. In the solution isopropyl isobutyrate (0.878 mmol, 103%) was detected. A yellow precipitate was obtained by addition of *n*-hexane to the solution. This precipitate was crystallized as yellow needles of **2c** from THF–diethyl ether, washed with *n*-hexane, and dried under vacuum.

Reaction of 1 with *n*-Butyl Methacrylate. *n*-Butyl methacrylate (5.0 ml) was added to complex **1** (1600 mg, 1.39 mmol) to give a yellow precipitate in a day at room temperature. In the solution *n*-butyl isobutyrate (1.59 mmol, 114%) was detected. The precipitate was crystallized as yellow parallelepipeds of **2d** from *n*-hexane and dried under vacuum.

Reaction of $RuD_2(PPh_3\text{-}d_6)_4$ with Ethyl Methacrylate. Excess ethyl methacrylate reacted with $RuD_2(PPh_3\text{-}d_6)_4$ to give $\overline{\text{RuH(CH=C(CH}_3\text{)C(O}}\text{)OC}_2\text{H}_5)(\text{PPh}_3\text{-}d_6)_3$, **3**. The ir spectrum of the resulting hydrido-σ-alkenyl complex showed no decrease in the relative intensity of the ν(Ru-H) band and little change was observed in the ir band attributable to ortho-deuterated triphenylphosphine ligands.

Thermal decomposition of the resulting complex at 200° gave deuterated ethyl methacrylate. Methyl and vinyl protons were deuterated as revealed by NMR spectroscopy (Table III). The extent of deuteration is listed in Table IV.

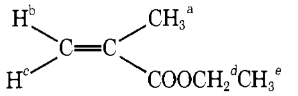
Reaction of 2a and 2b with Hydrogen. Under a hydrogen atmosphere heterogeneous benzene solutions of complexes **2a** and **2b** became homogeneous in a few hours at room temperature and after a

Table III. ^{1}H and ^{31}P {^{1}H} NMR Data for Hydrido-σ-Alkenyl Complexes[a]

		Complex, R[k] Et (**2**b)[b]	Complex, R[k] *i*-Pr (**2c**)[c]	Complex, R[k] *n*-Bu (**2d**)[c]
^{1}H NMR	Ru—H	−18.2 (t.d.)[d]	−18.0 (t.d.)[d]	−17.9 (t.d.)[d]
	$=CC\underline{H}_3$	1.94 (s)	1.32 (s)	1.30 (s)
	$=C\underline{H}$	—[e]	8.16 (q)[f]	8.16 (q)[f]
	R	$—CH_2C\underline{H}_3$ 1.32 (t)[g]	$—CH(C\underline{H}_3)_2$ 1.28 (d)[h]	1–2 (m)
		$—C\underline{H}_2CH_3$ 3.98 (q)[g]	$—C\underline{H}(CH_3)_2$ 4.76 (sep)[h]	3.68 (m)
^{31}P NMR	P_a	56.4 (d)[i]	51.6 (d)[j]	51.8 (d)[j]
	P_b	51.3 (t)[i]	48.4 (t)[j]	48.3 (t)[j]

[a] 100 MHz and 40.5 MHz for ^{1}H and ^{31}P NMR, respectively. Values in parts per million referred to Me_4Si and PPh_3, downfield positive, for ^{1}H and ^{31}P NMR spectra, respectively. ^{1}H NMR signals from PPh_3 which occur at 7.5–8.5 ppm are omitted. Multiplicity abbreviations: t.d., triplet of doublets; d, doublet; s, singlet; t, triplet; q, quartet; sep, septet; m, multiplet. [b] In CH_2Cl_2. [c] In toluene-d_8. [d] $|^2J(P_a\text{–}H)| = 28$ Hz; $|^2J(P_b\text{–}H)| = 12$ Hz. [e] The signal was not observable owing to the poor solubility of the complex. [f] $|^4J(H\text{–}H)| = 4$ Hz. [g] $|^3J(H\text{–}H)| = 7$ Hz. [h] $|^3J(H\text{–}H)| = 6$ Hz. [i] $|^2J(P_a\text{–}P_b)| = 24$ Hz. [j] $|^2J(P_a\text{–}P_b)| = 23$ Hz. [k] Designation of R is as indicated in Table I.

Table IV. Extent of Deuteration in Ethyl Methacrylate Released by Pyrolysis of Complex **3**



	Protons^a				
	a	b	c	d	e
No. of protons expected^b	3	1	1	2	3
No. of protons found^c	1.13	0.34	0.28	1.86	3.00
Degree of deuteration, %	62	66	72	7	0

^{a}Designation of each proton is as shown in structure above. ^{b}Number of protons expected when no deuteration is present. ^{c}Number of protons calculated from the ^{1}H NMR spectrum of the recovered ethyl methacrylate by assuming that the proton e is not deuterated.

Table V. Summary of Crystal Data and Intensity Collection

Compound	$RuH(CHC(CH_3)CO_2C_4H_9)(P(C_6H_5)_3)_3$
Formula weight	1030.15 amu
Formula	$C_{62}H_{59}O_2P_3Ru$
a	29.691 (8) Å
b	21.865 (5) Å
c	21.245 (6) Å
β	122.26 (1)°
V	11662.8 Å^3
Z	8
Density	1.173 g/cm^3 (calcd) 1.19 (1) g/cm^3 (exptl)
Space group	$C_{2h}{}^6$-$C2/c$
Crystal dimensions	0.40 × 0.56 × 0.18 mm
Crystal shape	Monoclinic prisms
Crystal volume	0.0416 mm^3
Temperature	22 °C
Radiation	Cu Kα_1 (λ 1.540562 Å)
Transmission factors	0.316–0.567
μ	32.99 cm^{-1}
Receiving aperture	6.0 × 6.0 mm; 30 cm from crystal
Takeoff angle	3.8°
Scan speed	2.0° in 2θ/min
Scan range	1.1° below Kα_1 to 1.1° above Kα_2 for $2\theta \leq 81.0°$; 1.2° and 1.2° for $2\theta > 81.0°$
Background counts	10 s for $2\theta \leq 70.0°$, 20 s for $2\theta \leq 86.0°$, 40 s for $2\theta > 86.0°$
2θ limits	3.0–100.0°
Final no. of variables	224
Unique data used $F_o{}^2 \geq 3\sigma(F_o{}^2)$	4801
Error in observation of unit weight	3.34 electrons

day white needles deposited. In the solutions hydrogenated products of these olefins were detected. The white needles were recrystallized from benzene and *n*-hexane mixed solvent. Anal. Calcd for $C_{54}H_{49}P_3Ru$: C, 72.7; H, 5.5. Found: C, 72.2; H, 6.2. An ir spectrum of these needles showed a ν(Ru–H) band[47,50] at 1940 cm^{-1}. By treating the needles with excess triphenylphosphine in benzene, $RuH_2(PPh_3)_4$ was formed with evolution of hydrogen at room temperature.

Reaction of 2b with dry HCl. Excess, dry hydrogen chloride (50 ml, STP) was introduced to complex **2b** (540 mg, 0.54 mmol) in diethyl ether by trap-to-trap distillation under vacuum. The color of the solution changed to orange and ethyl methacrylate (0.56 mmol, 103%) was detected in solution by gas chromatography. Hydrogen (11.2 ml, 0.50 mmol, 93%) was evolved as determined by mass spectroscopy.

Reaction of 2a with DCl. Excess, dry deuterium chloride (isotopic purity 95%) reacted with **2a** in benzene-d_6 to give methyl *cis*-β-deuteriomethacrylate; isotopic purity was calculated as 46% by comparing the peak area of the NMR spectrum of the recovered methyl *cis*-β-deuteriomethacrylate. Gaseous D_2, HD, and H_2 in a ratio of 60:34:6 were also evolved.

Reaction of 2a with Methyl Iodide. Excess methyl iodide (3.0 ml) reacted with **2a** (558 mg, 0.585 mmol) to give a brown heterogeneous solution in a day at room temperature. In the solution methyl angelate (0.007 mmol), methyl tiglate (0.081 mmol), methyl methacrylate (0.341 mmol), and small amounts of hydrogenated products of these olefins were detected by GLC–mass spectroscopy. Methane (0.554 mmol) was detected in the gas phase.

Reaction of 2b with Methyl Iodide. In a day at room temperature, excess methyl iodide (3.0 ml) reacted with **2b** (705 mg, 0.704 mmol) similarly to give methane (0.641 mmol), ethyl angelate (0.083 mmol), ethyl tiglate (0.188 mmol), ethyl methacrylate (0.265 mmol), and small amounts of their hydrogenated products.

Reaction of 3 with Methyl Iodide. Complex **3** (220 mg, 0.230 mmol) was allowed to react with 3 ml of methyl iodide in an analogous way as above. In this reaction, methane (0.233 mmol, 101% on the basis of the complex **3**) was evolved in which ca. 10% of CH_3D was detected by means of mass spectroscopy. In solution ethyl methacrylate (31%) and ethyl tiglate (36%) were detected by gas chromatography.

X-Ray Data Collection. Yellow prisms of the complex, $RuH(CHC(CH_3)CO_2C_4H_9)(PPh_3)_3$, suitable for x-ray diffraction studies were obtained from a THF–diethyl ether solution. The crystalline compound is stable in air for only a few hours but seems to be stable when stored under N_2. Therefore immediately upon removal from solution, crystals were mounted in N_2-filled capillaries.

Preliminary film data showed that the crystals belong to the monoclinic system, having extinctions (*hkl*, $h + k = 2n + 1$; *h0l*, $l = 2n + 1$) characteristic of the space groups $C_s{}^4$-Cc and $C_{2h}{}^6$-$C2/c$. The centrosymmetric space group was chosen and later verified by: (1) the successful refinement of the structure with acceptable positional parameters, thermal parameters, and agreement indices; (2) the location of all 45 phenyl hydrogen atoms in difference Fourier syntheses; (3) the statistical equivalence of 177 pairs of symmetry-related reflections. Accurate cell parameters were obtained by a least-squares procedure based on the angular setting for 18 hand-centered reflections from diverse regions of reciprocal space ($54.3° \geq 2\theta \geq 33.3°$), using a narrow x-ray source. See Table V for pertinent crystal information and details of data collection. The mosaicity of the crystal was found to be acceptable for the θ–2θ scan technique based on ω scans performed with an open counter.

Data were collected on a Picker FACS-I computer-controlled diffractometer equipped with a scintillation counter and a pulse height analyzer which was set to accept 90% of the Cu Kα peak. Background counts were measured at both ends of the scan range with both the counter and crystal stationary. The intensities of six standard reflections were measured every 100 reflections and all were found to decrease approximately uniformly and linearly by about 10% during the course of data collection. The observed intensities were modified to correct for this apparent crystal decomposition. The crystal darkened slightly during data collection.

The intensities of 6444 reflections with $2\theta \leq 100.0°$ were measured using nickel-filtered Cu X-radiation. Beyond this point very few reflections were observed. The data were processed in the usual way using a value of 0.05 for *p*.[51] Only those 4801 unique reflections with $F_o{}^2 \geq 3\sigma(F_o{}^2)$ were used in subsequent calculations. An absorption correction was applied to the data using Gaussian integration.[52] The *R* index for averaging 177 pairs of symmetry-related reflections was 1.9% after the absorption correction was applied.

Structure Refinement. The structure was solved using a sharpened, origin-removed Patterson synthesis to locate the ruthenium and three phosphorus atoms. Subsequent refinements in space group $C2/c$ and difference Fourier syntheses were used to locate all non-hydrogen atoms except the three terminal carbon atoms of the *n*-butyl group. This isotropic model refined to $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.096$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o{}^2]^{1/2} = 0.151$. During the refinements the quantity minimized was $\sum w(|F_o| - |F_c|)^2$, where $|F_o|$ and $|F_c|$ are the observed and calculated structure amplitudes and where the weight, *w*, is taken as $4F_o{}^2/\sigma^2(F_o{}^2)$. Atomic scattering factors for non-hydrogen atoms were taken from Cromer and Waber's tabulation whereas the hydrogen scattering factors were those of Stewart et al.[53] The anomalous dispersion terms for Ru and P were included in F_c. All phenyl groups were refined as rigid planar groups with C–C distances of 1.392 Å and with individual isotropic thermal parameters for each carbon atom. A difference Fourier map calculated at this time enabled us to locate all phenyl hydrogen atoms, atom H(1), and one of the missing carbon atoms (C(6)) of the *n*-butyl group. Refinement with all individual atoms undergoing anisotropic thermal motion, except C(5) and C(6) of the *n*-butyl group, gave agreement indices $R = 0.077$ and $R_w = 0.130$. Although the phenyl hydrogen atoms were located, they were included in subsequent calculations as a fixed

Table VI. Positional and Thermal Parameters for the Nongroup Atoms of $RuH(CHC(CH_3)COOC_4H_9)(PPh_3)_3$

ATOM	X[A]	Y	Z	B11 OR B, A^2 [B]	B22	B33	B12	B13	B23
RU	0.21212(3)	0.15685(3)	0.26638(4)	15.45(17)	12.95(20)	26.3(3)	-0.62(14)	11.38(18)	-0.23(18)
P(1)	0.20992(11)	0.04848(11)	0.26295(14)	16.8(5)	14.7(6)	28.1(10)	-0.2(5)	12.7(6)	0.0(6)
P(2)	0.29831(11)	0.17231(12)	0.29395(15)	17.0(5)	17.4(7)	31.1(10)	-1.7(5)	14.0(6)	-0.6(6)
P(3)	0.14298(11)	0.17471(11)	0.28423(15)	15.4(5)	14.3(6)	31.1(10)	-0.1(4)	12.0(6)	-1.0(6)
O(1)	0.1570(3)	0.1568(3)	0.1420(4)	22.2(16)	20.9(21)	27.3(26)	-1.8(14)	13.1(17)	-0.5(19)
O(2)	0.1091(4)	0.2189(4)	0.0446(5)	33.0(23)	30.2(25)	27.(3)	-2.8(19)	5.7(23)	7.5(24)
C(1)	0.2012(4)	0.2481(5)	0.2377(6)	17.7(22)	16.5(26)	36.(5)	-2.2(19)	14.7(28)	-0.6(27)
C(2)	0.1659(5)	0.2627(5)	0.1647(6)	19.5(24)	15.5(27)	42.(5)	-1.1(21)	16.(3)	2.(3)
C(3)	0.1512(5)	0.3273(5)	0.1314(7)	26.(3)	18.(3)	57.(6)	2.2(23)	16.(4)	17.(3)
C(4)	0.1431(5)	0.2101(5)	0.1170(7)	24.7(28)	21.(3)	37.(5)	2.1(24)	16.(3)	9.(3)
C(5)	0.0893(8)	0.1647(8)	-0.0020(8)	55.(6)	51.(6)	24.(5)	-14.(5)	-9.(4)	7.(5)
C(6)	0.0806(16)	0.1731(17)	-0.0875(22)	23.1(13)					
C(7)	0.022(3)	0.194(3)	-0.093(4)	37.(3)					
C(8)	0.012(8)	0.251(10)	-0.087(11)	39.(10)					
H(1)	0.215	0.285	0.275	5.0					
H(2)	0.114	0.133	0.021	11.9					
H(3)	0.056	0.153	-0.006	11.9					

[A] ESTIMATED STANDARD DEVIATIONS IN THE LEAST SIGNIFICANT FIGURE(S) ARE GIVEN IN PARENTHESES IN THIS AND ALL SUBSEQUENT TABLES. [B] THE FORM OF THE ANISOTROPIC THERMAL ELLIPSOID IS: $EXP(-(B11H^2+B22K^2+B33L^2+2B12HK+2B13HL+2B23KL))$. THE QUANTITIES GIVEN IN THE TABLE ARE THE THERMAL COEFFICIENTS X 10^4.

contribution, their positions being calculated from those of the phenyl carbon atoms using a C–H distance of 0.95 Å. Similarly the positions of H(1) (bonded to C(1)) and H(2) and H(3) (bonded to C(5)) were idealized assuming trigonal and tetrahedral coordinations about C(1) and C(5), respectively, and using a C–H distance of 0.95 Å. Each hydrogen atom was given a thermal parameter 1.0 Å^2 greater than the isotropically equivalent value of the carbon atom to which it is attached. An ensuing difference Fourier synthesis indicated possible positions for C(7) and C(8). These positions were chosen from a large region of electron density indicating a probable disorder of the positions of C(6), C(7), and C(8). The final least-squares analysis in which 224 parameters were varied resulted in agreement indices of R of 0.067 and R_w of 0.111 and an error in an observation of unit weight of 3.34 e$^-$.

A final difference Fourier synthesis of residual electron density revealed one peak (0.71 e Å^{-3}) located in the approximate position for the hydrido ligand. The highest residuals were in the vicinity of the n-butyl group (0.94–0.62 e Å^{-3}) and the phenyl rings (0.68–0.58 e Å^{-3}), as well as isolated from the molecule (0.70 e Å^{-3}). A typical phenyl carbon atom had a peak height of approximately 3.2 e Å^{-3} on earlier Fourier maps. Another difference synthesis using only data with $\lambda^{-1} \sin\theta \leq 0.35$ Å^{-1} caused the proposed hydrido peak to decrease in intensity (0.56 e Å^{-3}) but not to shift in position. Because of the relatively high agreement indices, which we ascribe to the partial disorder of the n-butyl chain, no attempt was made to refine the position of the hydrido ligand. A comparison of the observed and calculated structure amplitudes showed no need for an extinction correction. Of the 1451 unobserved reflections 15 had $|F_o^2 - F_c^2| > 4\sigma(F_o^2)$ and 10 had $|F_o^2 - F_c^2| > 5\sigma(F_o^2)$. There were no trends of the quantity $\sum w(|F_o| - |F_c|)^2$ as a function of $|F_o|$ or Miller indices. However, agreement was poorer at lower values of θ, as expected in view of the disorder of the n-butyl group.

The final positional and thermal parameters of atoms and groups appear in Tables VI, VII, and VIII. Root-mean-square amplitudes of vibration are given in Table IX.[54] A listing of the observed and calculated structure amplitudes for the data used in the refinements is available.[54]

Results and Discussion

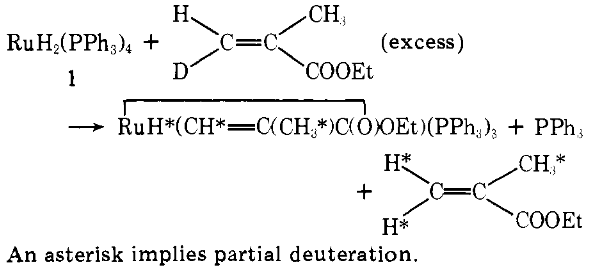
Preparation of Hydridopropenyl Complexes. We have reported previously that dihydridotetrakis(triphenylphosphine)ruthenium(II) (**1**) reacts with olefins such as ethylene and styrene to afford olefin-coordinated complexes, Ru(olefin)$(PPh_3)_3$, together with formation of the hydrogenated products of the olefins.[55] When a large excess of ethyl methacrylate was allowed to react with **1** at room temperature, a yellow complex with an apparent composition of Ru(ethyl methacrylate)$(PPh_3)_3$, precipitated out in a day with the concomitant formation of 1 mol equiv of ethyl isobutyrate, the hydrogenation product of ethyl methacrylate. Analyses of the complex by means of infrared and NMR spectra, elemental analyses, and chemical reactions, however, all suggest that this diamagnetic complex is hydrido(2-ethoxycarbonylpropenyl-C^1,O)tris(triphenylphosphine)ruthenium(II) (**2**). This formulation is confirmed by an x-ray diffraction study of the n-butoxy complex (vide infra). Isopropyl and n-butyl methacrylates react similarly with complex **1** to yield the corresponding hydrido-σ-propenyl complexes (**2c** and **2d**, respectively).

$$\underset{\mathbf{1}}{RuH_2(PPh_3)_4} + CH_2{=}C(CH_3)COOR \longrightarrow \underset{\mathbf{2}}{\overline{RuH(CH{=}C(CH_3)C(O)O}R)(PPh_3)_3} + (CH_3)_2CHCOOR + PPh_3 \quad (1)$$

R = Me (**2a**), Et (**2b**), i-Pr (**2c**), and n-Bu (**2d**)

The reaction of **1** with methyl methacrylate accompanied the polymerization reaction[56] and the reaction products are always contaminated with a small amount of poly(methyl methacrylate); hence the purification of complex **2a** and detection of the hydrogenated product were difficult. Results of elemental analyses and physical data of complexes **2a–d** are listed in Table I.

Reaction of ethyl cis-β-deuteriomethacrylate (isotopic purity 72%) with complex **1** gave **2**, in which the hydridic hydrogen atom was only partially deuterated.



(2)

An asterisk implies partial deuteration.

Table VII. Derived Parameters for the Rigid Group Atoms of $RuH(CHC(CH_3)COOC_4H_9)(PPh_3)_3$

ATOM	X	Y	Z	B, A^2	ATOM	X	Y	Z	B, A^2
C(11)	0.23808(27)	0.0148(3)	0.2110(3)	3.46(20)	C(54)	0.4253(3)	0.0322(4)	0.4504(5)	7.7(4)
C(12)	0.23719(28)	0.05131(24)	0.1567(4)	4.17(23)	C(55)	0.4223(3)	0.0881(4)	0.4792(3)	7.2(3)
C(13)	0.2591(3)	0.0298(3)	0.1170(4)	5.15(26)	C(56)	0.3855(3)	0.1318(3)	0.4324(4)	5.53(27)
C(14)	0.2818(3)	-0.0281(3)	0.1316(4)	5.50(27)	C(61)	0.3124(3)	0.1807(4)	0.2198(4)	4.20(22)
C(15)	0.2827(3)	-0.06466(26)	0.1859(4)	5.93(29)	C(62)	0.27057(25)	0.2001(4)	0.1505(4)	5.31(26)
C(16)	0.2608(3)	-0.04319(28)	0.2256(4)	4.75(24)	C(63)	0.2787(3)	0.2088(4)	0.0924(3)	7.1(3)
C(21)	0.24126(25)	0.00043(29)	0.3469(3)	3.59(20)	C(64)	0.3287(4)	0.1981(4)	0.1036(4)	7.2(3)
C(22)	0.28312(28)	0.02730(24)	0.4109(4)	4.34(23)	C(65)	0.37050(29)	0.1787(5)	0.1728(5)	8.5(4)
C(23)	0.31112(26)	-0.0064(3)	0.4765(31	5.81(28)	C(66)	0.36236(27)	0.1700(4)	0.2309(4)	6.6(3)
C(24)	0.2972(3)	-0.0669(3)	0.4781(31	6.2(3)	C(71)	0.15109(27)	0.23979(27)	0.3453(4)	3.72(21)
C(25)	0.2554(3)	-0.09375(24)	0.4140(4)	5.82(28)	C(72)	0.20009(23)	0.2691(3)	0.3870(4)	4.23(22)
C(26)	0.22738(251	-0.0601(3)	0.3484(3)	4.50(23)	C(73)	0.20665(23)	0.3166(3)	0.4348(4)	5.11(25)
C(31)	0.14135(20)	0.0162(3)	0.2070(3)	3.54(20)	C(74)	0.1642(3)	0.3348(3)	0.4409(4)	5.73(28)
C(32)	0.11651(25)	0.0151(3)	0.1299(3)	4.24(22)	C(75)	0.11520(26)	0.3055(4)	0.3991(5)	6.1(31
C(331	0.06502(26)	-0.0079(3)	0.08578(25)	4.90(25)	C(76)	0.10864(21)	0.2580(3)	0.3513(4)	5.17(26)
C(34)	0.03837(20)	-0.0297(4)	0.1187(4)	5.62(27)	C(81)	0.12706(26)	0.11789(28)	0.3333(3)	3.64(20)
C(35)	0.06321(26)	-0.0287(3)	0.1958(4)	5.19(26)	C(82)	0.17025(19)	0.0906(3)	0.3955(4)	3.98(22)
C(36)	0.11469(25)	-0.0057(3)	0.23993(25)	3.93(21)	C(83)	0.16178(251	0.0487(3)	0.4374(3)	5.19(26)
C(41)	0.32442(28)	0.24695(24)	0.3432(3)	3.47(20)	C(841	0.1101(31	0.0341(3)	0.4172(4)	5.69(27)
C(42)	0.32328(28)	0.25760(27)	0.4069(4)	3.84(21)	C(85)	0.06693(21)	0.0613(3)	0.3550(4)	5.40(26)
C(43)	0.3403(3)	0.3136(3)	0.4435(3)	4.69(241	C(86)	0.07540(22)	0.1032(3)	0.3130(3)	4.65(24)
C(44)	0.3585(3)	0.35887(251	0.4164(4)	5.68(28)	C(91)	0.07832(24)	0.1922(3)	0.1982(3)	3,78(21)
C(45)	0.3596(3)	0.34823(28)	0.3527(4)	5.90(28)	C(92)	0.0484(3)	0.14469(24)	0.1504(4)	4.66(24)
C(46)	0.3426(3)	0.2923(3)	0.3161(3)	4.88(25)	C(93)	0.00283(29)	0.1575(3)	0.0816(4)	6.3(3)
C(51)	0.35164(27)	0.1196(3)	0.3569(4)	3.82(211	C(94)	-0.01283(27)	0.2179(4)	0,0604(3)	6.4(3)
C(52)	0.3546(3)	0.0637(4)	0.3281(3)	5.57(27)	C(95)	0.0171(3)	0,26542(26)	0.1082(4)	6.3(31
C(53)	0.3915(4)	0.01997(29)	0.3749(5)	7.3(3)	C(96)	0.0627(3)	0.25257(27)	0.1771(4)	5.05(26)

RIGID GROUP PARAMETERS

GROUP	X_C [A]	Y_C	Z_C	DELTA [B]	EPSILON	ETA
RING1	0.25995(18)	-0.00668(22)	0.17131(25)	-2.862(5)	-2.673(4)	-1.861(5)
RING2	0.26925(19)	-0.03322(22)	0.41248(26)	2.509(4)	2.956(4)	2.374(51
RING3	0,08986(18)	-0.00679(20)	0.16286(251	-1,200(4)	-3.054(4)	1.401(4)
RING4	0.34146(181	0.30291(21)	0.37982(25)	-0,569(13)	1.953(4)	1.787(13)
RING5	0.38847(21)	0.07591(25)	0.4036(3)	-0.479(7)	-2.342(5)	0.437(7)
RING6	0.32053(24)	0.18938(24)	0.1617(3)	-1.849(61	-3,036(5)	-1.744(5)
RING7	0.15765(20)	0.28729(211	0.39307(26)	1.676(4)	-2.851(4)	0.753(5)
RING8	0.11859(191	0.07598(21)	0.37523(25)	1.456(4)	3.039(4)	2.307(41
RING9	0.03275(20)	0.20505(24)	0.12934(28)	-0.151(4)	-3.000(5)	-2.574(5)

[A] X_C, Y_C, AND Z_C ARE THE FRACTIONAL COORDINATES OF THE ORIGIN OF THE RIGID GROUP. [B] THE RIGID GROUP ORIENTATION ANGLES DELTA, EPSILON, AND ETA(RADIANS) HAVE BEEN DEFINED PREVIOUSLY(S.J. LA PLACA AND J.A. IBERS, ACTA CRYSTALLOGR., 18, 511(1965).

In this reaction the ethyl *cis*-β-deuteriomethacrylate used in excess was converted into ethyl methacrylate which contained ca. 14% of deuterium at vinylic positions and the α-methyl group as revealed by the ^1H NMR spectrum of the recovered methacrylate. Thus scrambling of the propenyl protons of the ethyl methacrylate took place in the reaction (vide infra). The triphenylphosphine ligand was not deuterated in this reaction.

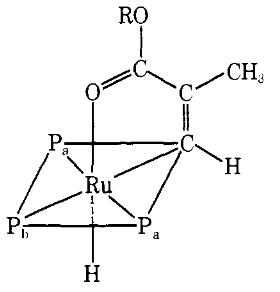
$RuD_2(PPh_3\text{-}d_6)_4$,[47,48] in which 87% of the hydridic hydrogen atoms and ortho-hydrogen atoms of the triphenylphosphine ligand were deuterated, reacted with ethyl methacrylate similarly to give the hydrido-σ-alkenyl complex, $RuH(CH{=}C(CH_3)C(O)OEt)(PPh_3\text{-}d_6)$, **3**, in which the hydridic hydrogen atom was not deuterated.

Complex **2** was also obtained by reaction of the ethylene complex, $Ru(C_2H_4)(PPh_3)_3$,[55] with ethyl methacrylate with no production of ethyl isobutyrate. Therefore, the reaction of **1** with alkyl methacrylate may actually involve the oxidative addition of alkyl methacrylate to a zero-valent ruthenium complex which has been produced by insertion of the alkyl methacrylate into a Ru-H bond, followed by reductive elimination of the hydrido-alkyl type complex. The most straightforward explanation for the oxidative addition of alkyl methacrylate to the Ru(0) complex is the splitting of the C-H bond at the vinylic group. Another less straightforward pathway involves C-H bond splitting at the α-methyl group of the methacrylate forming a π-allyl-hydrido type complex which then rearranges to the 2-alkoxycarbonylpropenyl complex by hydrogen transfer. We favor the mechanism involving the splitting of the C-H bond at the vinylic group since a similar reaction has been observed in the reaction of a methyl-copper complex with vinyl acetate which has no α-methyl group.[57] However, the H-D scrambling reaction involving the α-methyl group of the alkyl methacrylate suggests that the π-allylic intermediate may intervene in the scrambling process (vide infra).

Infrared Spectra. Ru-H and carboxyl stretching frequencies of complex **2** are summarized in Table II. The complete disappearance of the band at 2080 cm^{-1} assigned to ν(Ru-H) of the starting dihydrido complex **1**[46,47] and the appearance of a new ν(Ru-H) band at 1960-1980 cm^{-1} suggest formation of a new type of hydrido complex. In the ir spectrum of **3**, which was prepared from $RuD_2(PPh_3\text{-}d_6)$, no ν(Ru-D) band was observed and the ν(Ru-H) band was observed at the same frequency as that of **2b**. The out-of-plane phenyl C-H and C-D deformation bands in the ir spectrum of **3** were essentially the same as those in the spectrum of $RuD_2(PPh_3\text{-}d_6)_4$. These results clearly indicate that the hydridic hydrogen atom in **2** or **3** comes neither from the original hydridic hydrogen atoms in **1** nor from ortho-hydrogen atoms in the triphenylphosphine ligands, but most probably from the hydrogen atom adjacent to the double bond in the methacrylate.

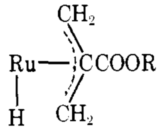
The ester carboxyl stretching frequency which occurs at 1720–1730 cm^{-1} in the starting alkyl methacrylate exhibits a 140 cm^{-1} shift to lower frequency on complex formation. This may be explained if there is ring formation involving the coordination of the C=O moiety through the oxygen atom to the ruthenium atom. In such a ring the carboxyl double bond order will decrease. A shift of ν(C=O) towards lower frequency has been reported for the complex formed between methyl methacrylate and zinc chloride.[58] More recently, van Baar et al. reported that the ν(N=N) vibration in $IrHCl(C_6H_4N{=}NPh)(PPh_3)_2$, where coordination of nitrogen to form a chelate ring is also considered,[35] is much lower than that of the free ligand vibration.

NMR Spectra. Owing to the poor solubility of complex **2a**, NMR studies were carried out on complexes **2b**, **2c**, and **2d**. As is shown in Table III, proton-decoupled ^{31}P NMR spectra of the complexes indicate the presence of two kinds of the triphenylphosphine ligands, P_a and P_b. The doublet at the lower field is assignable to two triphenylphosphine ligands in the mutually trans positions (P_a) and a triplet at a higher field to the triphenylphosphine trans to the vinylic entity (P_b). ^1H NMR spectra show the resonance of a hydridic hydrogen nucleus at ca. −18 ppm as a triplet of doublets indicating the different coupling constants between $J(H\text{-}P_a)$ (28 Hz) and $J(H\text{-}P_b)$ (12 Hz). The signal of the vinylic proton appears at a very low field (8.2 ppm) with a coupling to three phosphorus atoms. Disagreement of this low δ value with the reported value of 4.86 ppm for the corresponding vinylic proton in chloro(2-methyl-3-(dimethylamino)propenyl)(triphenylphosphine)platinum(II)[33] and of 1.58 ppm in the metalated 2-(methylazo)propene complex of iridium[35] suggests that the chemical shift of the proton on a carbon atom attached directly to the metal is very sensitive to the electronic environment of the metal. The ^1H NMR spectra of complex **2d** observed in the presence of an equimolar amount of *n*-butyl methacrylate in $C_6D_5CD_3$ at room temperature and at 90 °C can be accounted for as a simple mixture of each component, indicating that no exchange between the vinylic entity and the free methacrylate takes place in this system. The ^1H NMR spectrum of **2c** in pyridine shows some broadening of the α-methyl proton signal at 100 °C. This may be related to formation of the hydrido-π-allylic intermediate (vide infra). An attempt to observe the coalescence of the methyl resonance with the vinyl resonance failed owing to decomposition of the complex at higher temperatures.



2

Thermolysis. Pyrolysis of complexes **2** in the solid state at 200 °C liberates over 0.8 equiv of methacrylic esters together with small amounts of their hydrogenation products and benzene, which must arise from decomposition of the triphenylphosphine ligands. Thermolysis of **3**, the ortho-deuterated analogue of **2**, at 200 °C liberates ethyl methacrylate in which ca. 70% of the vinylic and α-methyl protons are deuterated (Table IV) as analyzed by its ^1H NMR spectrum. Thus there is exchange of the vinylic and α-methyl protons of ethyl methacrylate with the ortho-deuterium atoms of the triphenylphosphine ligands. The extent of this exchange was calculated to be 68%. The scrambling, including the α-methyl protons, suggests that a hydrido-π-allylic species such as



is involved in the thermolysis with participation of ortho metalation of the triphenylphosphine ligands.

Scrambling of the vinylic and α-methyl protons, but without participation of the ortho-phenyl protons, was also observed in the reaction of *cis*-β-deuteriomethacrylate with **1** (vide supra). A similar hydrido-π-allylic intermediate may also be involved in the reaction.

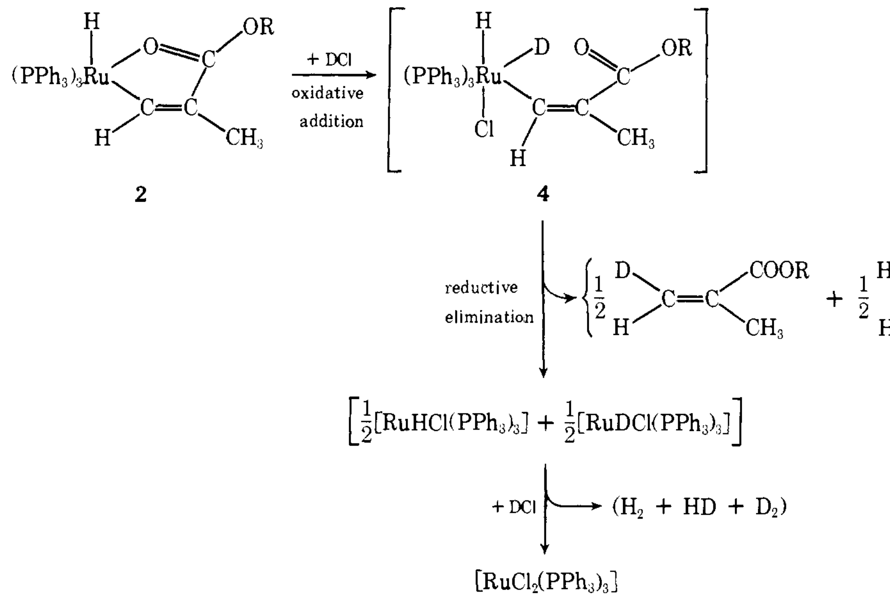
The presence of a similar equilibrium between a propylene complex and a hydridoallyl complex has been reported by Bonneman.[59]

Reaction of 2 with H_2. Complex **2** reacted with hydrogen in benzene at room temperature to afford alkyl isobutyrate and the known tetrahydridotris(triphenylphosphine)ruthenium.[47,50] This feature of the reaction is similar to those observed in the reactions of hydrogen with olefin coordinated complexes, $Ru(olefin)(PPh_3)_3$.[60]

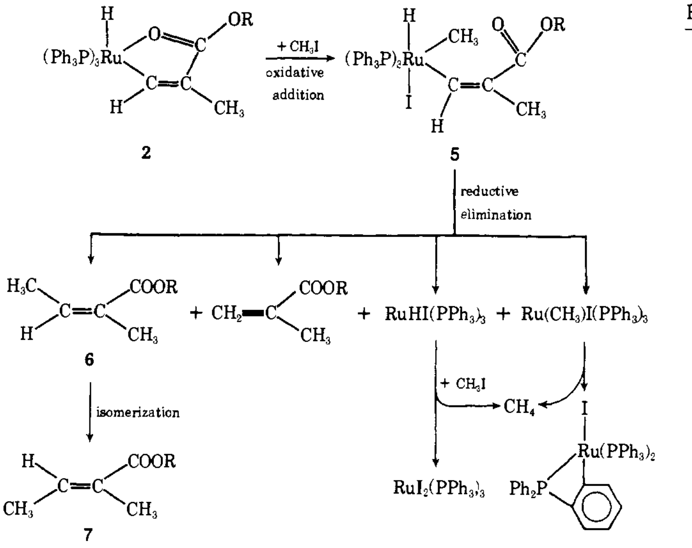
Reaction of 2 with gaseous HCl and DCl. Complex **2b** was allowed to react with excess HCl gas in diethyl ether at room temperature releasing equimolar amounts of ethyl methacrylate and gaseous hydrogen. Dry DCl with an isotopic purity of 95% reacted with **2a** in benzene-d_6 at room temperature to afford 1 mol equiv of a 1:1 mixture of methyl methacrylate and methyl *cis*-β-deuteriomethacrylate and 1 mol equiv of hydrogen gas containing H_2, HD, and D_2 in a ratio of 6:34:60. The result suggests that the vinylic entity in **2** is bonded to ruthenium at the cis position with respect to the ester group and that the reaction proceeds as shown in Scheme I. DCl probably adds oxidatively to **2** to give an unstable intermediate **4** containing both hydrido and deuterido ligands. Reductive elimination of **4** would then produce the *cis*-β-deuteriomethacrylate and the undeuterated methacrylate leaving a 1:1 mixture of $RuHCl(PPh_3)_3$ and $RuDCl(PPh_3)_3$, which on further reaction with DCl would liberate the mixture of H_2, HD, and D_2. Calculated ratio of H_2:HD:D_2 from DCl of the 95% isotopic purity is 8:41:51 which is in approximate agreement with the experimental value.

Reaction of 2 and 3 with Methyl Iodide. Complex **2b** reacts with an excess amount of methyl iodide at room temperature to liberate 1 mol equiv of methane and a mixture of ethyl methacrylate (38% on the basis of complex **2b** used), ethyl angelate **6** (12%), ethyl tiglate **7** (27%), and a small amount of ethyl isobutyrate as confirmed by GLC–mass spectroscopic analysis. Complex **2a** reacts similarly with methyl iodide to yield analogous methyl esters (methyl methacrylate, 58%; methyl angelate, 1%; and methyl tiglate, 14%). On raising the reaction temperature the ratio of methyl tiglate to methyl angelate increases indicating that the isomerization of methyl angelate, initially produced by methylation, to methyl tiglate takes place in the course of the reaction. Methyl angelate has an inherent tendency to isomerize spontaneously to methyl tiglate at elevated temperatures. Possible pathways of this reaction are summarized in Scheme II. Methyl iodide oxidatively adds to **2** to give an unstable hydridomethyl intermediate

Scheme I



Scheme II



5 which on reductive elimination is converted into a mixture of hydridoiodo- and methyliodo-complexes liberating methyl angelate **6** and ethyl methacrylate. The hydridoiodo complex would react further with a mole of methyl iodide to release methane. Another portion of methane may be produced from a methyliodo intermediate via ortho-proton participation. In fact, ca. 10% of CH_3D was detected in the evolved methane when complex **3**, $RuH(CH{=}C(CH_3)C(O)OEt)(PPh_3\text{-}d_6)_3$, was allowed to react with methyl iodide at room temperature. The somewhat low CH_3D content may be an indication that an H-D exchange involving the ortho metalation of **5** may intervene prior to the reductive elimination, but we did not examine the deuterium contents in the liberated esters.

Description and Discussion of Structure. The complex, $RuH(CHC(CH_3)CO_2C_4H_9)(PPh_3)_3$, consists of discrete monomeric units as is shown in the stereoscopic packing view in Figure 1. There are no unusual intermolecular contacts (see Table X). A three-dimensional representation of the molecule, showing the numbering scheme used, is presented in Figure 2. Figure 3 shows the inner coordination sphere including the entire *n*-butyl methacrylate ligand. Some relevant bond distances and angles are shown.

Table X. Selected Distances (Å) in $RuH(CHC(CH_3)CO_2C_4H_9)(PPh_3)_3$

	Bond Distances		
Ru–P(1)	2.370 (3)	C(6)–C(7)	1.75 (7)
Ru–P(2)	2.327 (3)	C(7)–C(8)	1.3 (2)
Ru–P(3)	2.311 (3)		
Ru–C(1)	2.061 (10)	P(1)–C(11)	1.856 (10)
Ru–O(1)	2.246 (7)	P(1)–C(21)	1.838 (6)
C(1)–C(2)	1.368 (15)	P(1)–C(31)	1.864 (6)
C(2)–C(3)	1.535 (15)	P(2)–C(41)	1.858 (6)
C(2)–C(4)	1.442 (15)	P(2)–C(51)	1.842 (7)
C(4)–O(1)	1.254 (12)	P(2)–C(61)	1.841 (11)
C(4)–O(2)	1.327 (13)	P(3)–C(71)	1.852 (8)
O(2)–C(5)	1.454 (18)	P(3)–C(81)	1.838 (9)
C(5)–C(6)	1.70 (4)	P(3)–C(91)	1.851 (5)
			1.849 (11)[a]
	Nonbonded Distances		
Ru–H(1)[b]	2.81	C(26)–H(16)	2.52
Ru–H(12)	3.07	C(42)–H(56)	2.43
O(1)–H(12)	2.36	C(42)–H(72)	2.56
O(1)–H(62)	2.59	C(61)–H(46)	2.50
C(4)–H(62)	2.52	H(42)–H(72)	2.19
C(11)–H(52)	2.52	H(42)–H(56)	2.28

[a] The estimated standard deviation is the larger of an individual standard deviation or the standard deviation of a single observation as calculated from the mean. [b] H(1) is attached to C(1).

The ruthenium atom is six-coordinate, with a distorted octahedral environment. Three of the coordination sites are occupied by the phosphines in a meridional arrangement and two are occupied by the bidentate *n*-butyl methacrylate ligand, coordinated to ruthenium via the vinylic carbon atom and carboxyl oxygen atom. The hydrido ligand completes the coordination about ruthenium. Two phosphines are mutually trans while the third is trans to the vinylic carbon atom. The hydrido ligand is trans to the oxygen atom.

The coordination geometry in this complex is remarkably similar to that in two closely related complexes, $RuH(O_2CMe)(PPh_3)_3$, an effective hydrogenation catalyst,[61] and $RuH(O_2CH)(PPh_3)_3$.[62] In these complexes the *n*-butyl methacrylate ligand is replaced by the bidentate acetate and formate ligands, respectively. The similarities in the geometries are especially evident in the metric parameters of the triphenylphosphine ligands. For the methacrylate, acetate, and formate complexes, respectively, the trans P-Ru-P angles are 152.5 (1)°, 154.9 (1)°, and 151.5 (6)°. The cis P-Ru-P angles

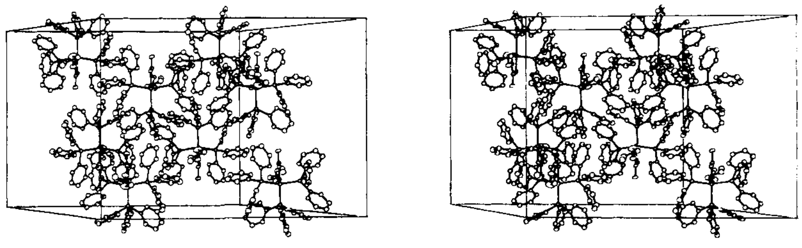


Figure 1. A stereo drawing of a unit cell of $RuH(CHC(CH_3)CO_2C_4H_9)(PPh_3)_3$. The *x* axis is horizontal to the left, the *y* axis runs from top to bottom, and the *z* axis comes out of the paper towards the reader. Vibrational ellipsoids are drawn at the 20% level except for the terminal three atoms of the *n*-butyl group which are drawn arbitrarily small here and subsequently for clarity.

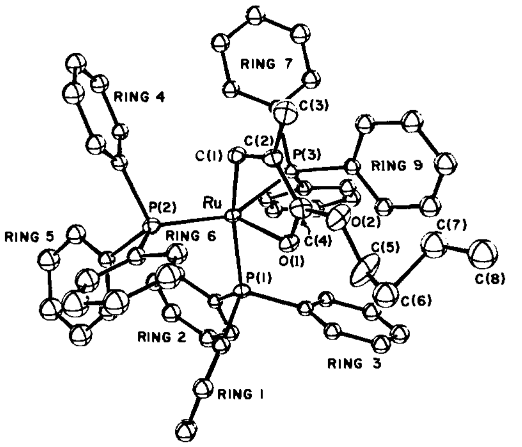


Figure 2. A molecule of $RuH(CHC(CH_3)CO_2C_4H_9)(PPh_3)_3$ showing the numbering scheme used. Hydrogen atoms are omitted for clarity of the drawing. Vibrational ellipsoids are shown at the 20% level, except C(6), C(7), and C(8).

for these same complexes are: 99.62 (10)°, 99.30 (9)°; 98.6 (1)°, 99.7 (2)°; and 98.2 (4)°, 101.4 (4)°. These angles reflect both the repulsive interactions between the bulky phosphine ligands with all cis P-Ru-P angles greater than the ideal 90°, and the reduced steric requirement of the hydrido ligand, with the phosphines bent towards this coordination site. Only P(1) in the present complex does not seem to be bent towards the hydrido site, as shown by the relatively small O(1)-Ru-P(1) angle of 88.4 (2)°. This seems to result from close contacts between ring 1 and ring 5 which prevents P(1) from moving closer to the hydrido ligand. The shortest such contact is C(11)-H(52) at 2.52 Å. The close approach of P(1) and O(1) is facilitated by the staggering of rings 1 and 3 with respect to O(1) as shown by the O(1)-Ru-P(1)-C(11) and O(1)-Ru-P(1)-C(31) torsion angles about the Ru-P(1) bond (see Table XI). This is also clearly shown in Figure 2.

Although the angular parameters, and thus the spacial arrangements of the phosphine ligands, are similar in the above complexes there are notable differences in the Ru-P distances. In the methacrylate complex the mutually trans Ru-P distances (2.327 (3) and 2.311 (3) Å) are significantly shorter than the unique cis Ru-P distance of 2.370 (3) Å. This is the opposite to what is observed in the acetate and formate complexes where the cis Ru-P distances are shorter by ca. 0.127 and 0.083 Å, respectively. It has been suggested[62] that in the formate complex the shorter Ru-P distance results from the lower trans influence of oxygen compared with phosphorus. However, Skapski and Stephens[61] believe that the observed difference is too great to result merely from this difference in trans influence and suggest instead that if the acetate (or formate) ligand be viewed as occupying one coordination site, then the complex can be considered as quasi-five-coordinate. Hence the unique phosphine would occupy the apical position of a square pyramid with no trans competition for electrons, resulting in a short Ru-P distance. The coordination in the methacrylate complex is more nearly octahedral (the O(1)-Ru-C(1) angle is 75.6 (4)° compared with 57.6 (4)° and 55.0 (13)° in the acetate and formate complexes) so the trans ligand is more nearly opposed to the phosphine. By this criterion one would therefore expect a slightly longer cis Ru-P distance than in the quasi-five-coordinate complexes. However, clearly the largest effect is the strong trans influence of the vinyl carbon atom. Cetinkaya et al.[63] have compared the trans influence of several ligands in octahedral Rh(III) systems, based on Rh-Cl distances trans to the ligand in question and have established the order: σ-alkyl > σ-phenyl > *tert*-carbene[64] > *s*-carbene > *tert*-phosphine > *tert*-phosphite > *tert*-arsine ∼ π-olefin > chlorine ∼ amine ∼ pyridine > ROH. Ru-C(1) can be classified as a secondary carbene linkage[66] since the bonding within the chelate is delocalized (this is discussed later) with the result that C(1)-C(2) is less than a formal double bond. Atom C(1) therefore exerts the expected large trans influence with Ru-P(1) being 0.043 Å longer than Ru-P(2) and 0.059 Å longer than Ru-P(3). In this respect it is unusual that in $RuH(C_{10}H_7)(Me_2PCH_2CH_2PMe_2)_2$[20] and $Ru_2(Me_2PCH_2CH_2PMe_2)_4$[21] the Ru-P distances trans to the coordinated

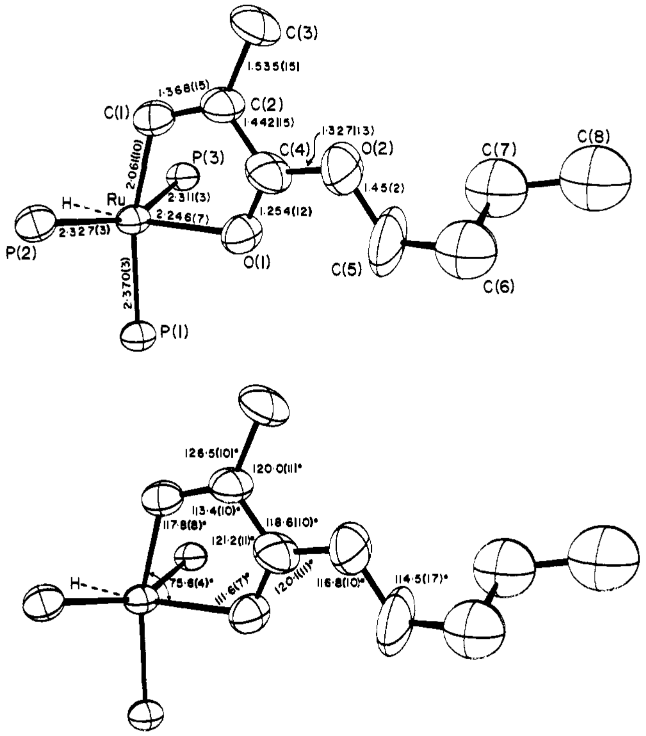


Figure 3. The inner coordination sphere of the molecule, including the entire *n*-butyl methacrylate ligand. Some relevant bond lengths and angles are shown. Vibrational ellipsoids are shown at the 50% level, except C(6), C(7), and C(8).

Table XI. Selected Angles (deg) in $RuH(CHC(CH_3)CO_2C_4H_9)(PPh_3)_3$

P(2)–Ru–P(3)	152.50 (10)		
P(1)–Ru–P(2)	99.62 (10)	C(6)–C(7)–C(8)	121 (12)
P(1)–Ru–P(3)	99.30 (9)	Ru–P(1)–C(11)	113.7 (3)
P(1)–Ru–C(1)	164.0 (3)	Ru–P(1)–C(21)	123.4 (2)
P(1)–Ru–O(1)	88.4 (2)	Ru–P(1)–C(31)	113.7 (2)
P(2)–Ru–C(1)	84.6 (3)	Ru–P(2)–C(41)	110.2 (3)
P(2)–Ru–O(1)	108.0 (2)	Ru–P(2)–C(51)	119.4 (3)
P(3)–Ru–C(1)	82.6 (3)	Ru–P(2)–C(61)	121.3 (2)
P(3)–Ru–O(1)	92.3 (2)	Ru–P(3)–C(71)	116.7 (3)
C(1)–Ru–O(1)	75.6 (4)	Ru–P(3)–C(81)	119.9 (3)
Ru–C(1)–C(2)	117.8 (8)	Ru–P(3)–C(91)	114.6 (3)
C(1)–C(2)–C(4)	113.4 (10)	C(11)–P(1)–C(21)	101.2 (3)
C(1)–C(2)–C(3)	126.5 (10)	C(11)–P(1)–C(31)	99.0 (3)
C(3)–C(2)–C(4)	120.0 (11)	C(21)–P(1)–C(31)	102.5 (3)
C(2)–C(4)–O(1)	121.2 (11)	C(41)–P(2)–C(51)	101.8 (3)
C(2)–C(4)–O(2)	118.6 (10)	C(41)–P(2)–C(61)	100.7 (4)
O(1)–C(4)–O(2)	120.1 (11)	C(51)–P(2)–C(61)	100.3 (4)
C(4)–O(1)–Ru	111.6 (7)	C(71)–P(3)–C(81)	95.7 (4)
C(4)–O(2)–C(5)	116.8 (10)	C(71)–P(3)–C(91)	102.2 (3)
O(2)–C(5)–C(6)	114.5 (17)	C(81)–P(3)–C(91)	104.7 (3)
C(5)–C(6)–C(7)	71 (3)		
	Torsion Angles		
Ru–P(1)–C(11)–C(12)	−25.1 (5)	Ru–P(3)–C(71)–C(72)	−10.2 (7)
Ru–P(1)–C(21)–C(22)	−24.4 (8)	Ru–P(3)–C(81)–C(82)	41.1 (6)
Ru–P(1)–C(31)–C(32)	79.6 (6)	Ru–P(3)–C(91)–C(92)	77.5 (8)
Ru–P(2)–C(41)–C(42)	53.8 (5)	O(1)–Ru–P(1)–C(11)	63.2 (3)
Ru–P(2)–C(51)–C(52)	78.5 (8)	O(1)–Ru–P(1)–C(31)	−48.9 (4)
Ru–P(2)–C(61)–C(62)	24.2 (7)		

carbon atoms (2.301 (3) and 2.26 (1) Å, respectively) are not longer than the mutually trans Ru–P distances (2.303 (3), 2.280 (3); and 2.32 (1), 2.28 (1) Å, respectively). Even viewing Ru–C(1) as a simple vinyl linkage, rather than as a carbene linkage, the large trans influence is again expected. In two other σ-vinyl complexes, *trans*-$PtCl(CH{=}CH_2)(PEt_2Ph)_2$[67] and $PtCl(o\text{-}Ph_2PC_6H_4C{=}CHC_6H_4PPh_2\text{-}o)$,[68] the Pt–Cl bonds trans to the vinyl carbon atoms (2.398 (4) and 2.377 (2) Å, respectively) are significantly larger than observed (2.294 (4) Å) in *trans*-$PtCl_2(P(CH_2CH_3)_3)_2$[69] where the chloro ligands are mutually trans.

The trans Ru–P distances in the methacrylate complex, at 2.327 (3) and 2.311 (3) Å, are also unusually short. For example in other complexes containing meridional phosphine ligands the trans Ru–P distances average 2.37 (2) Å.[61,62,70–72] The distances in the present complex are actually closer to Ru–P distances which are cis, as for example in *fac*-$[Ru_2Cl_3(PEt_2Ph)_6]^+$ (average 2.318 (7))[70] and $Ru(SC_5H_4N)_2(PPh_3)_2$,[73] at 2.319 (2) and 2.332 (2) Å.

Apart from the phenyl rings, the complex under study has approximate mirror symmetry. However, the twisting of the phenyl groups about the P–C bonds destroys the opportunity for such symmetry. The steric interaction between the bulky PPh_3 groups results in a wide range of torsion angles about the P–C bonds, as is shown in Table XI. Ring 9 is approximately parallel to the methacrylate chelate plane. However, its pseudo-mirror-related mate, ring 6, is approximately perpendicular to this plane, resulting in close contacts between ring 6 and the chelate (see Table X) and a corresponding increase in the P(2)–Ru–O(1) angle over the P(3)–Ru–O(1) angle (108.0 (2)° and 92.3 (2)°, respectively). The bulky triphenylphosphines are obviously of paramount importance in determining the overall geometry, as confirmed already by the similarities between the methacrylate, acetate, and formate complexes. The effect of the phosphines is further emphasized by the similarities of the P–Ru–P angles in these six-coordinate complexes to those in the five-coordinate complexes $RuHCl(PPh_3)_3$[72] and $RuCl_2(PPh_3)_3$.[71]

There are no unusual features in either the P–C distances, the Ru–P–C angles, or the C–P–C angles in the present structure.

The mode of coordination of the methacrylate ligand, which had been proposed on the basis of spectroscopic and chemical evidence, has been confirmed by the x-ray determination. Thus the ligand is bidentate and is coordinated via the vinyl carbon atom and the carboxyl oxygen atom. Although the location of most of the atoms in this ligand was straight forward, the terminal three atoms of the *n*-butyl group were located only approximately owing to a disorder of these atoms. Viewing the packing diagram it is not difficult to imagine why this group is disordered, since it fits into a large cavity created by the phenyl rings from adjacent molecules, and has no obvious orientational preference.

The Ru–C(1) bond, at 2.061 (10) Å, is approximately what one would expect for a Ru–C single bond (2.06 Å), based on the covalent radii of Ru[74] and C(sp^2).[75] It is also comparable with several σ-bonded Ru–C(sp^2) distances reported,[39,41,76–80] ranging from 2.01 (3) to 2.160 (10) Å. It has been suggested[39,78,79] that a Ru–C distance of this magnitude represents some degree of multiple bond character. Indeed this distance in the methacrylate complex is among the shortest of such distances observed. However, these distances are all longer than a Ru–C(isocyanide) distance[79] of 1.979 Å[81] and several Ru–C (carbonyl) distances ranging from 1.825 to 1.87 (6) Å.[39,41,77,79,82] Although carbonyls function as good π acceptors, isocyanide ligands are generally regarded[83,84] as poorer π acceptors. This suggests that in the present complex, based on the Ru–C(1) distance, C(1) is a poorer π-acceptor than the isocyanide ligand.

The oxygen atom in the methacrylate ligand seems to be only weakly coordinated to the ruthenium atom. The Ru–O(1) distance at 2.246 (7) Å is comparable with the Ru–O distances in the acetate[61] (2.198 (13) and 2.210 (10) Å) and the formate[62] (2.29 (4) and 2.23 (3) Å) complexes. Since these ligands are replaced readily in solution they may be regarded as weakly coordinated. In addition these Ru–O distances are significantly longer than the sum of the covalent radii (1.99 Å)[74,85] and are greater than several Ru–O distances reported[82,86,87] (ranging from 1.96 (2) to 2.103 (7) Å). The long Ru–O distance in the present complex probably results from the large trans influence of the hydrido ligand. A similar lengthening of the Ru–O bond trans to H was observed in the formate complex. However, in that quasi-five-coordinate complex the small bite of the chelate results in both Ru-O distances being long.

Within the planar ring of the methacrylate ligand the distances suggest delocalized bonding over the chelate framework with bond lengths generally being intermediate between single and double bond values. Thus C(1)—C(2), at 1.368 (15) Å, is slightly longer than one might expect for the C=C bond (1.33 Å). Similarly C(2)—C(4) is short (1.442 (15) Å) for a single-bonded C—C distance (1.46 Å) involving sp^2 hybridized carbon atoms. The value of C(2)—C(3) (1.535 (15) Å), exo to the ring, is as expected. In addition the C(4)—O(1) distance (1.254 (12) Å) is very long for a C=O double bond, in agreement with the low value found for $\nu_{C=O}$ A comparison with several other coordinated carboxyl groups verifies that C(4)—O(1) has a bond order less than 2. In $RuH(O_2CCH_3)(PPh_3)_3$,[61] $RuH(O_2CH)(PPh_3)_3$,[62] $Ru_2(O_2CC_3H_7)_4Cl$,[86] and $Ru_3O(O_2CCH_3)_6(PPh_3)_3$[87] in which the C—O bonds are generally considered to be intermediate between single and double bonds, the average C—O distances are 1.259 (18), 1.25 (6), 1.27 (3), and 1.26 (3) Å, respectively. Similarly in $Ru_2(CO)_6H(C_{10}H_9O)$ the coordinated C—O bond measures 1.259 (13) Å.[82] The C(4)—O(1) bond in the present complex is, however, considerably shorter than the coordinated C—O distance (1.318 (10) Å) in $Pt(PPh_3)_2(PhCON_2COPh)$[88] showing that it maintains a significant component of multiplicity. Carbonyl distances in which this group is not coordinated have been observed in the range 1.19 (2) to 1.223 (10) Å.[65,88,89]

Exo to the chelate ring, the C(4)-O(2) bond (1.327 (13) Å) in the ester linkage is shorter than might be expected but the O(2)-C(5) bond at 1.45 (2) Å is normal. Other distances within the *n*-butyl group are not reliable because of the disorder problem. The overall geometry of this group is, however, clear.

As mentioned previously the ^1H NMR signal from the vinylic proton is at very low field (8.2 ppm) compared with two other complexes with coordinated vinyl groups (4.86 and 1.58 ppm),[33,35] suggesting that the chemical shift of this proton is very sensitive to the electronic environment of the metal. Indeed in the present complex this proton (H(1)) is only 2.81 Å from the Ru atom. The coordination mode of the vinylic entity might also be important, since in the chelated form the possibility of delocalization leading to ring currents within the chelate which might deshield this proton must be considered. The closest approach of an ortho-hydrogen atom of the phenyl groups to the Ru atom is Ru-H(12) at 3.07 Å.

Conclusions

Detailed spectroscopic and chemical studies of a seemingly simple π-olefin complex, as judged from its composition alone, have revealed that a new hydrido-alkenyl type complex was formed by oxidative addition involving C-H cleavage of alkyl methacrylate to a zero-valent ruthenium complex. The x-ray crystallographic analysis of the *n*-butyl methacrylate complex confirms the molecular structure proposed on the basis of spectroscopic and chemical evidence. The behavior of this type of complex, as demonstrated by introduction of a methyl group into a β-position of the alkyl methacrylate, suggests a variety of synthetic applications.

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Supplementary Material Available: The tables of observed and calculated structure amplitudes, the idealized phenyl H positions (Table VIII), and root-mean-square amplitudes of vibration (Table IX) (38 pages). Ordering information is given on any current masthead page.

References and Notes

(1) (a) Tokyo Institute of Technology; (b) Northwestern University.
(2) A. D. Ketley, L. P. Fisher, A. J. Berlin, C. R. Morgan, E. H. Gorman, and T. R. Steadman, *Inorg. Chem.*, **6**, 657 (1967).
(3) K. Maruya, T. Mizoroki, and A. Ozaki, *Bull. Chem. Soc. Jpn.*, **46**, 993 (1973).
(4) J. M. Davidson and C. Triggs, *J. Chem. Soc. A*, 1324, 1331 (1968).
(5) Y. Fujiwara, I. Moritani, S. Danno, R. Asano, and S. Teranishi, *J. Am. Chem. Soc.*, **91**, 7166 (1969).
(6) R. F. Heck, *J. Am. Chem. Soc.*, **90**, 5535 (1968), and references therein.
(7) R. F. Heck, *J. Am. Chem. Soc.*, **91**, 6707 (1969).
(8) U. Klabunde and G. W. Parshall, *J. Am. Chem. Soc.*, **94**, 9081 (1972).
(9) E. K. Barefield, G. W. Parshall, and F. N. Tebbe, *J. Am. Chem. Soc.*, **92**, 5234 (1970).
(10) R. J. Hodges, D. E. Webster, and P. B. Wells, *J. Chem. Soc., Dalton Trans.*, 2577 (1972), and references therein.
(11) C. Masters, *J. Chem. Soc., Chem. Commun.*, 1258 (1972).
(12) N. F. Goldshleger, M. J. Tjabin, A. E. Shilov, and A. A. Shteinman, *Zh. Fiz. Khim.*, **43**, 2174 (1969); Abstract of the 5th International Conference on Organometallic Chemistry, Vol. 1, 1971, p 328.
(13) J. L. Garnett and R. S. Kenyon, *J. Chem. Soc., Chem. Commun.*, 1227 (1971).
(14) J. E. Bercaw, R. H. Marvich, L. G. Bell, and H. H. Brintzinger, *J. Am. Chem. Soc.*, **94**, 1219 (1972).
(15) J. E. Bercaw, *J. Am. Chem. Soc.*, **96**, 5087 (1974).
(16) L. P. Seiwell, *J. Am. Chem. Soc.*, **96**, 7134 (1974).
(17) E. L. Muetterties and F. J. Hirsekorn, *J. Am. Chem. Soc.*, **96**, 4063 (1974).
(18) J. Chatt and R. S. Coffey, *J. Chem. Soc. A*, 1963 (1969).
(19) J. Chatt and J. N. Davidson, *J. Chem. Soc.*, 843 (1965).
(20) U. A. Gregory, S. D. Ibekwe, B. T. Kilbourn, and D. R. Russel, *J. Chem. Soc. A*, 1118 (1971).
(21) F. A. Cotton, B. A. Frenz, and D. L. Hunter, *J. Chem. Soc., Chem. Commun.*, 755 (1974).
(22) W. Keim, *J. Organomet. Chem.*, **14**, 179 (1968); **19**, 161 (1969).
(23) G. W. Parshall, *Acc. Chem. Res.*, **3**, 139 (1970).
(24) R. A. Schunn, *Inorg. Chem.*, **9**, 2567 (1970).
(25) J. M. Duff, B. E. Mann, B. L. Shaw, and B. Turtle, *J. Chem. Soc., Dalton Trans.*, 139 (1974), and references therein.
(26) B. N. Cockburn, D. V. Howe, T. Keating, B. F. G. Johnson, and J. Lewis, *J. Chem. Soc., Dalton Trans.*, 404 (1973).
(27) N. Ahmad, E. W. Ainscough, T. A. James, and S. D. Robinson, *J. Chem. Soc., Dalton Trans.*, 1151 (1973).
(28) C. Masters, *J. Chem. Soc., Chem. Commun.*, 191 (1973).
(29) M. I. Bruce, B. L. Goodall, and F. G. A. Stone, *J. Chem. Soc., Chem. Commun.*, 558 (1973).
(30) A. C. Jarvis, R. D. W. Kemmitt, B. Y. Kimura, D. R. Russel, and P. A. Tucker, *J. Organomet. Chem.*, **66**, C53 (1974).
(31) M. A. Bennett, R. N. Johnson, and I. B. Tomkins, *J. Am. Chem. Soc.*, **96**, 61 (1974), and references therein.
(32) M. G. Clerici, S. DiGioacchino, F. Maspero, E. Perrotti, and A. Zanobi, *J. Organomet. Chem.*, **84**, 379 (1975).
(33) J. M. Kliegman and A. C. Cope, *J. Organomet. Chem.*, **16**, 309 (1969).
(34) R. J. Foot and B. T. Heaton, *J. Chem. Soc., Chem. Commun.*, 838 (1973).
(35) J. F. van Baar, K. Vrieze, and D. J. Stufkens, *J. Organomet. Chem.*, **85**, 249 (1975).
(36) S. Komiya and A. Yamamoto, *Chem. Lett.*, 475 (1975).
(37) C. Giannotti and M. L. H. Green, *J. Chem. Soc., Chem. Commun.*, 1114 (1972).
(38) K. Elmitt, M. L. H. Green, R. A. Forder, I. Jefferson, and K. Prout, *J. Chem. Soc., Chem. Commun.*, 747 (1974).
(39) A. Cox and P. Woodward, *J. Chem. Soc. A*, 3599 (1971).
(40) M. I. Bruce, M. A. Cairns, and M. Green, *J. Chem. Soc., Dalton Trans.*, 1293 (1972).
(41) M. Evans, M. Hursthouse, E. W. Randall, E. Rosenberg, L. Milone, and M. Valle, *J. Chem. Soc., Chem. Commun.*, 545 (1972).
(42) A. J. P. Domingos, B. F. G. Johnson, and J. Lewis, *J. Organomet. Chem.*, **36**, C43 (1972).
(43) A. J. Canty, A. J. P. Domingos, B. F. G. Johnson, and J. Lewis, *J. Chem. Soc., Dalton Trans.*, 2058 (1973).
(44) A. J. Deeming and M. Underhill, *J. Chem. Soc., Dalton Trans.*, 1415 (1974).
(45) J. B. Keister and J. R. Shapley, *J. Organomet. Chem.*, **85**, C29 (1975).
(46) J. J. Levison and S. D. Robinson, *J. Chem. Soc. A*, 2947 (1970).
(47) T. Ito, S. Kitazume, A. Yamamoto, and S. Ikeda, *J. Am. Chem. Soc.*, **92**, 3011 (1970).
(48) The abbreviation PPh_3-d_6 is used to mean the triphenylphosphine ligand where all six ortho-protons are deuterated. Other abbreviations used are: Ph, phenyl; Me, methyl; Et, ethyl; *i*-Pr, isopropyl; *n*-Bu, *n*-butyl.
(49) E. R. H. Jones, T. Y. Shen, and M. C. Whiting, *J. Chem. Soc.*, 230 (1950).
(50) W. H. Knoth, *J. Am. Chem. Soc.*, **90**, 7172 (1968).
(51) R. J. Doedens and J. A. Ibers, *Inorg. Chem.*, **6**, 204 (1967).
(52) The Northwestern absorption program, AGNOST, includes the Coppens–Leiserowitz–Rabinovich logic for Gaussian integration. In addition to various local programs for the CDC 6400 computer, modified versions of the following programs were employed: Zalkin's FORDAP Fourier summation program, Johnson's ORTEP thermal ellipsoid plotting program, and Busing and Levy's ORFFE error function program. Our full-matrix, least-squares program, NUCLS, in its nongroup form, closely resembles the Busing–Levy ORFLS program.
(53) D. T. Cromer and J. T. Waber, "International Tables for X-Ray Crystallography", Vol. IV, Kynoch Press, Birmingham, England, 1974, Table 2.2. For hydrogen atoms see R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965). For the values of $\Delta f'$ and $\Delta f''$ for Ru and P see D. T. Cromer and D. Liberman, *J. Chem. Phys.*, **53**, 1891 (1970).
(54) See paragraph at end of paper regarding supplementary material.
(55) S. Komiya, A. Yamamoto, and S. Ikeda, *J. Organomet. Chem.*, **42**, C65

(1972).
(56) S. Komiya, A. Yamamoto, and S. Ikeda, *Bull. Chem. Soc. Jpn.*, **48**, 101 (1975).
(57) A. Yamamoto, T. Yamamoto, T. Ito, S. Komiya, A. Miyashita, T. Ikariya, T. Saruyama, M. Kubota, and Y. Nakamura, 7th International Conference on Organometallic Chemistry, Abstracts, p 133, 1975, Venice, Italy.
(58) M. Imoto, T. Otsu, and Y. Harada, *Makromol. Chem.*, **65**, 180 (1963).
(59) H. Bonneman, *Angew Chem.*, **82**, 699 (1970).
(60) S. Komiya and A. Yamamoto, *Bull Chem. Soc. Jpn.*, in press.
(61) A. C. Skapski and F. A. Stephens, *J. Chem. Soc., Dalton Trans.*, 390 (1974).
(62) (a) A. I. Gusev, G. G. Aleksandrov, and Y. T. Struchkov, *Zh. Strukt. Khim.*, 14, 685 (1973); (b) *J. Struct. Chem.*, **14**, 633 (1973); (c) I. S. Kolomnikov, A. I. Gusev, G. G. Aleksandrov, T. S. Lobeeva, Y. T. Struchkov, and M. E. Vol'pin, *J. Organomet. Chem.*, **59**, 349 (1973).
(63) B. Cetinkaya, M. F. Lappert, G. M. McLaughlin, and K. Turner, *J. Chem. Soc., Dalton Trans.*, 1591 (1974).
(64) The *tert*-carbene was added to this series afterwards by M. Cowie et al.; see ref 65.
(65) (a) M. Cowie, J. A. Ibers, Y. Ishii, K. Itoh, I. Matsuda, and F. Ueda, *J. Am. Chem. Soc.*, **97**, 4748 (1975); (b) M. Cowie and J. A. Ibers, *Inorg. Chem.*, **15**, 552 (1976).
(66) D. J. Cardin, B. Cetinkaya, and M. F. Lappert, *Chem. Rev.*, **72**, 545 (1972).
(67) C. J. Cardin, D. J. Cardin, M. F. Lappert, and K. W. Muir, *J. Organomet. Chem.*, **60**, C70 (1973).
(68) G. B. Robertson and P. O. Whimp, *Inorg. Chem.*, **13**, 2082 (1974).
(69) G. G. Messmer and E. L. Amma, *Inorg. Chem.*, **5**, 1775 (1966).
(70) K. A. Raspin, *J. Chem. Soc. A*, 461 (1969).
(71) S. J. La Placa and J. A. Ibers, *Inorg. Chem.*, **4**, 778 (1965).
(72) A. C. Skapski and P. G. H. Troughton, *Chem. Commun.*, 1230 (1968).
(73) S. R. Fletcher and A. C. Skapski, *J. Chem. Soc., Dalton Trans.*, 635 (1972).
(74) J. P. Jesson and E. L. Muettertles, "Chemist's Guide Basic Chemical and Physical Data", Marcel Dekker, New York, N.Y., 1969, pp 2–3.
(75) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", 2d ed, Interscience, New York, N.Y., 1966, p 105.
(76) T. Blackmore, M. I. Bruce, and F. G. A. Stone, *Chem. Commun.*, 852 (1971).
(77) R. Belford, H. P. Taylor, and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 2425 (1972).
(78) R. J. Sundberg, R. F. Bryan, I. F. Taylor, Jr., and H. Taube, *J. Am. Chem. Soc.*, **96**, 381 (1974).
(79) D. F. Christian, G. R. Clark, and W. R. Roper, *J. Organomet. Chem.*, **81**, C7 (1974).
(80) M. I. Bruce, R. C. F. Gardner, B. L. Goodall, and F. G. A. Stone, *J. Chem. Soc., Chem. Commun.*, 185 (1974).
(81) No standard deviations are given in the paper.
(82) A. J. P. Domingos, B. F. G. Johnson, J. Lewis, and G. M. Sheldrick, *J. Chem. Soc., Chem. Commun.*, 912 (1973).
(83) A. C. Sarapu and R. F. Fenske, *Inorg. Chem.*, **11**, 3021 (1972).
(84) P. M. Treichel, *Adv. Organomet. Chem.*, **11**, 21 (1973).
(85) L. Pauling, "Nature of the Chemical Bond", 3rd ed, Cornell University Press, Ithaca, N.Y., 1960, p 224.
(86) M. J. Bennett, K. G. Caulton, and F. A. Cotton, *Inorg. Chem.*, **8**, 1 (1969).
(87) F. A. Cotton, J. G. Norman, A. Spencer, and G. Wilkinson, *Chem. Commun.*, 967 (1971).
(88) S. D. Ittel and J. A. Ibers, *Inorg. Chem.*, **12**, 2290 (1973).
(89) A. Bralbanti, A. Tiripicchio, A. M. Manotti Lanfredi, and M. Camellini, *Acta Crystallogr.*, **23**, 248 (1967).

Quenching of Triplet States by Inorganic Ions. Energy Transfer and Charge Transfer Mechanisms

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Abstract: The effect of inorganic anions on the triplet states of aromatic hydrocarbons and carbonyl compounds (M) in aqueous solution at room temperature was investigated using the fast-reaction techniques of flash and laser photolysis. The results have been interpreted on the basis of two major quenching mechanisms: energy transfer and charge transfer. Typical T–T energy transfer was demonstrated for NO_2^-. Its triplet energy was also determined and found to be $E_T = 53 \pm 2$ kcal/mol. The very fast quenching of triplet acetone by NCS^- may also involve energy transfer. In other cases, the quenching rate constant k_q was found to depend largely on the proximity of the CT level of the M–anion complex to the triplet level of M. The energies of such CT levels were calculated from the thermodynamic properties of the species involved. The dependence of k_q on $\Delta E_{CT} = E_{CT} - E_{M*}$ was examined when M* is either a singlet S_1 or a triplet T_1 excited state. For the systems examined, the analysis reveals that S_1 and T_1 states are quenched by inorganic ions via similar mechanisms, and in both cases k_q becomes diffusion-controlled when $\Delta E_{CT} \lesssim 0$. However, with the exception of SO_3^{2-}, no chemical reactions were found to result from the quenching reaction. Possible reasons for this behavior are discussed. In some of the systems where quenching was slow, minor reactions did take place and could be ascribed to redox interactions with radical ions (or their hydrolysis products) produced from the photoionization of the aromatic molecules, and not to a direct reaction of the ions with the triplet states. Evidence for such a photoionization was provided in a detailed study of naphthalene photolysis in water, and its mechanism is discussed.

I. Introduction

Quenching of excited singlet states by simple diamagnetic anions has been studied extensively through fluorescence measurements, and various mechanisms have been proposed.[2–6] Little is known, however, on the corresponding quenching of triplet states, and it was even concluded that diamagnetic ions hardly have any effect.[7] Some early indications, however, bear evidence to the opposite, e.g., a work[8] on the quenching of fluorescein type dyes with I^-. More recently this problem was studied for anthraquinone triplets by flash photolysis[9] and very efficient quenching by anions was reported involving, in some cases, net electron transfer reactions with the formation of inorganic radicals and the semiquinone. There is new evidence[10] that these results may be incorrect and that the transient species studied were not the triplets. Recently, the quenching of triplet pyrazine by inorganic anions has been investigated by laser photolysis.[11]

From their studies on triplet quenching by transition metal ions and their complexes, Linschitz et al.[12] reached the following conclusions: (a) diamagnetic ions can act as efficient quenchers; (b) there is no essential difference in mechanism between the quenching of excited singlets and triplets; (c) charge transfer states appear to play an important role. For the quenching and photoreduction of carbonyl triplets by amines this role is now reasonably well established,[13] but with simple anions as quenchers the picture is unclear even in the case of singlet quenching. In his recent works[5b,6] Watkins has presented serious arguments against the charge transfer mechanism although he still emphasizes the role of some kind of coupling with CT states. He also investigated the quenching of biphenyl, naphthalene, and anthracene triplets by I^-, NCS^-,