Generation of $[C_5(CH_3)_5Ru(NO)(CH_3)(H_2O)]^+[BAr'_4]^-$ (Ar' = 3,5-$C_6H_3(CF_3)_2$) and Its Reaction with Methyl Acrylate To Produce Chelate Complexes of the Type $C_5(CH_3)_5Ru(NO)(CH(R)CH_2COOCH_3)^+$ (R = H, CH_3)

Elisabeth Hauptman and Maurice Brookhart*

Department of Chemistry, The University of North Carolina, Chapel Hill, North Carolina 27599-3290

Paul J. Fagan and Joseph C. Calabrese

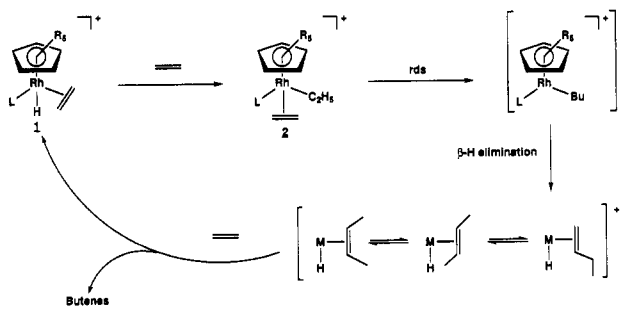
Central Research and Development Department, E. I. du Pont de Nemours & Co., Inc., Experimental Station, P.O. Box 80328, Wilmington, Delaware 19880-0328

Received November 3, 1993®

Protonation of $C_5(CH_3)_5Ru(NO)(CH_3)_2$, **8**, with $[(3,5\text{-}(CF_3)_2C_6H_3)_4B]^-[H(OEt_2)_2]^+$ in the presence of water generates the complex $C_5(CH_3)_5Ru(NO)(CH_3)(H_2O)^+$, **9**, which upon treatment with methyl acrylate yields a transient η^2-acrylate complex $C_5(CH_3)_5Ru(NO)(CH_2CHCO_2CH_3)\text{-}CH_3^+$, **10**, observed by ^1H NMR spectroscopy. Migratory insertion in **10** gives the chelate complex $C_5(CH_3)_5Ru(NO)(CH(CH_3)COOCH_3)^+$, **12**, which has been fully characterized by conventional spectroscopic methods (^1H and ^{13}C NMR spectroscopy) and by a single-crystal X-ray analysis ($C_{47}H_{36}BF_{24}NO_3Ru$, monoclinic, $P2_1$, a = 12.124(2) Å, b = 17.376(4) Å, c = 13.355(2) Å, β = 116.31(1)°, V = 2522.0 Å^3, and Z = 2). Treatment of **12** with excess methyl acrylate results in conversion to the unsubstituted chelate $C_5(CH_3)_5Ru(NO)(CH_2CH_2COOCH_3)^+$, **5**.

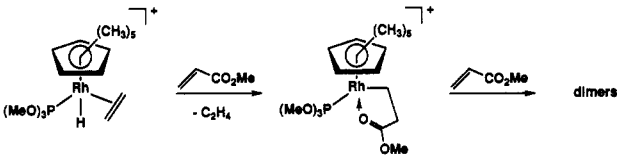
Introduction

Complexes of the type $C_5R_5Rh(L)(C_2H_4)H^+$ (R = H, CH_3; L = $P(OMe)_3$, PMe_3), **1**, are catalysts for the dimerization of ethylene.[1] The catalytic cycle is shown below; complex **2** is the catalyst resting state, and β-migratory insertion of **2** is turnover-limiting.



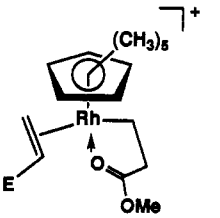
In formation of **2** from **1**, a vacant coordination site is generated by hydride migration to the bound ethylene ligand followed by trapping by external ethylene.

In an effort to extend this chemistry to functionalized olefins, catalytic dimerization of methyl acrylate was attempted with $C_5Me_5(P(OMe)_3)Rh(C_2H_4)H^+$, the most efficient complex in this series for ethylene dimerization.[2a] While tail-to-tail dimerization did occur, it was extremely slow. The catalyst resting state was identified as **3**. We proposed that the exceedingly slow rate of dimerization (relative to ethylene dimerization) resulted from a high barrier to dechelation of the ester carbonyl oxygen, a necessary step for η^2-complexation of external acrylate.



3

A solution to this problem was found by replacement of the $P(OMe)_3$ ligand with the labile ethylene ligand. The substitution resulted in a highly efficient catalytic system for acrylate dimerization. The resting state was identified as **4**. In this system η^2-acrylate coordination can be achieved *without* ester carbonyl dechelation, and β-migratory insertion can occur directly from **4**. A full account of the details of this catalytic cycle has appeared.[2b]



4

In the search for other catalysts for acrylate dimerization,[3,4] the above work suggested that systems capable of forming chelate structures such as those present in **3** and **4** together with the ability to generate an open coordination site may be good candidates. An analog of **3** which has the

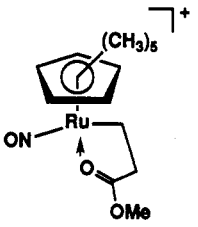
• Abstract published in *Advance ACS Abstracts*, January 1, 1994.

(1) (a) Brookhart, M.; Lincoln, D. M. *J. Am. Chem. Soc.* **1988**, *110*, 8719. (b) Brookhart, M.; Hauptman, E.; Lincoln, D. M. *J. Am. Chem. Soc.* **1992**, *114*, 10394.

(2) (a) Brookhart, M.; Sabo-Etienne, S. *J. Am. Chem. Soc.* **1991**, *113*, 2777. (b) Brookhart, M.; Hauptman, E. *J. Am. Chem. Soc.* **1992**, *114*, 4437.

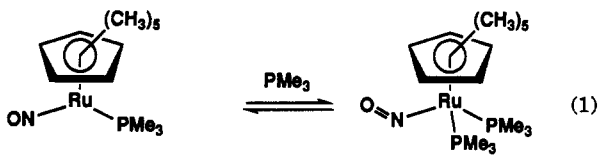
0276-7333/94/2313-0774$04.50/0

capability of generating a vacant coordination site is the nitrosyl complex **5**. The linear nitrosyl ligand (three-



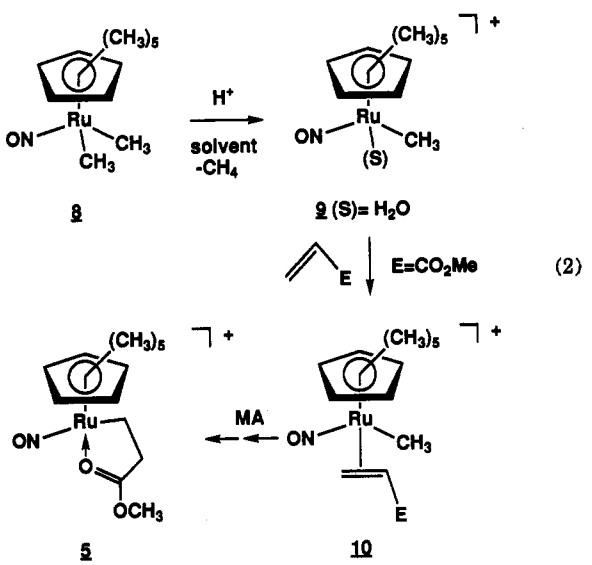
5

electron donor) potentially may bend and become a one-electron donor ligand thereby opening a vacant coordination site for η^2-complexation of external acrylate. Supporting the plausibility of this scheme, Bergman has observed the equilibrium shown in eq 1, which involves interconversion of a linear ruthenium nitrosyl complex **6** with the corresponding bent nitrosyl complex **7** via PMe_3 addition to the linear NO complex.[5]



6 **7** (1)

An attractive entry into chelate complexes such as **5** involves protonolysis of $Cp^*(NO)Ru(CH_3)_2$, **8**, ($Cp^* = C_5(CH_3)_5$) followed by trapping with acrylate and migratory insertion as shown in eq 2. In this paper we report the



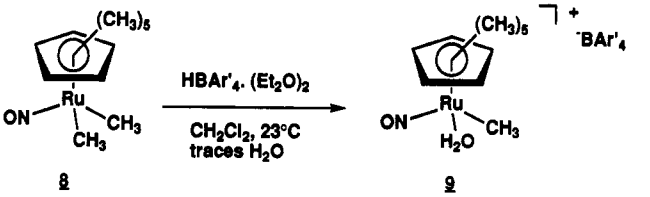
8 **9** (S)= H_2O (2)

5 **10**

generation of **9** (S = H_2O) and its reactivity toward methyl acrylate, including the β-migratory insertion reaction of **10**.

Results and Discussion

Generation of $[C_5Me_5Ru(NO)(H_2O)(Et_2O)_{1.5}(CH_3)]^+[BAr'_4]^-$, 9. Protonation of $Cp^*Ru(NO)(CH_3)_2$, **8**, with $[H(OEt_2)_2]^+[BAr'_4]^-$ ($Ar' = 3,5\text{-}C_6H_3(CF_3)_2$) in CH_2Cl_2 at ambient temperature led to the formation of $[Cp^*Ru(H_2O)(CH_3)(NO)]^+[BAr'_4]^-$.[6] Recrystallization from diethyl ether/hexane gave red crystals of **9** (83%) as a diethyl ether solvate (1.5 equiv/ruthenium). Traces of water present resulted in the formation of the aqua complex **9** rather than the ether complex. Complex **9** was fully



8 **9**

characterized by conventional spectroscopic methods (^1H and ^{13}C NMR spectroscopy) and combustion analysis. The presence of a linear NO ligand is indicated by an intense IR absorption at 1793 cm^{-1}. Holding **9** under high vacuum (23 °C) for prolonged periods causes decomposition presumably by loss of Et_2O or H_2O. Additional support for the structure shown above was obtained by treating **9** with trimethylphosphine leading to **11**, isolated as dark orange crystals (see eq 3).[7]

9 **11** (3)

Reaction of 9 with Methyl Acrylate (MA). Treatment of **9** (0.009 mmol in 0.6 mL of CD_2Cl_2) with excess methyl acrylate at 25 °C leads to NMR observation of three ruthenium complexes, **10**, **12**, and **5**, in a ca. 1:1:2 ratio after 10 min. After 30 min, complex **10** can no longer be detected; a ca. 2:3 ratio of **12**:**5** remains. On a time scale of hours, complex **12** reacts to give **5**. After 15 h, only complex **5** is detected. The only organic byproduct observed by both GC–mass spectrometry and NMR spectroscopy is methyl crotonate, $CH(CH_3)CHCO_2CH_3$ (see the Experimental Section for details). As shown in Chart 1, complex **10** is assigned as the η^2-acrylate complex, **12** as the methyl-substituted chelate complex, and **5** as the unsubstituted chelate complex.[8] Support for each structural assignment will be offered below.

The first insertion product, complex **12**, could be isolated as an analytically pure crystalline compound by treatment of **9** with 5 equiv of methyl acrylate in dilute CH_2Cl_2 solution and isolation of the product after a short reaction time (ca. 5–10 min). The presence of a methyl-substituted

(3) For reports of other Rh-based acrylate dimerization catalysts, see: (a) Alderson, T. U.S. Patent 3013066, 1961. (b) Alderson, T.; Jenner, E. L.; Lindsey, R. V. *J. Am. Chem. Soc.* **1965**, *87*, 5638. (c) Nugent, W. A.; McKinney, R. J. *J. Mol. Catal.* **1985**, *29*, 65. (d) Singleton, D. M. U.S. Patent 4638084, 1987. For reports of Ru-based acrylate dimerization catalysts, see: (e) McKinney, R. J. U.S. Patent 4 485 256, 1986. (f) McKinney, R. J.; Colton, M. C. *Organometallics* **1986**, *5*, 1080. (g) McKinney, R. J. *Organometallics* **1986**, *5*, 1752. (h) Ren, C. Y.; Cheng, W. C.; Chan, W. C.; Yeung, C. H.; Lau, C. P. *J. Mol. Catal.* **1990**, *59*, L1.

(4) For references to Pd- and Ni-based acrylate dimerization catalysts, see footnote 4 of ref 2a.

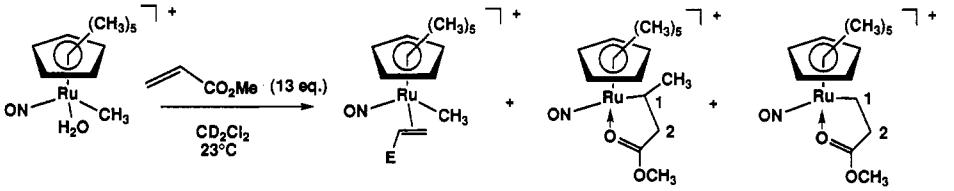
(5) Chang, J.; Bergman, R. G. *J. Am. Chem. Soc.* **1987**, *109*, 4298.

(6) Protonation of complex **8** has been reported previously. (a) By Bergman[5] using HCl. Evolution of methane was observed, and $Cp^*Ru(NO)CH_3Cl$ was obtained. (b) By Hubbard using HOTf. Evolution of methane was observed, and $Cp^*Ru(NO)(CH_3)OTf$ was obtained: Hubbard, J. L.; Burns, R. M.; Zoch, C. R. *Abstracts of Papers*, 204th National Meeting of the American Chemical Society, Washington, DC; American Chemical Society: Washington, DC, 1992; INOR 423.

(7) While protonation of $Cp^*Ru(NO)(CH_3)_2$ resulted in a stable aqua complex, protonation of the diethyl analog, $Cp^*Ru(NO)(Et)_2$, afforded visible decomposition products along with a metal hydride species (broad resonance at ca. −4.8 ppm at −90 °C) which could not be purified or characterized.

(8) Insertion of methyl acrylate in a Ru–H bond was described by Hiraki to yield an analogous neutral chelate complex $(PPh_3)_2RuCl(CH_2CH_2COOCH_3)$; see: Hiraki, K.; Ochi, N.; Sasada, Y.; Hayashida, H.; Fuchita, Y.; Yamanaka, S. *J. Chem. Soc., Dalton Trans.* **1985**, 873.

Chart 1



	9	10	12	5
10 min.		1	1	2
30 min.		0	2	3
15 hrs		0	0	only complex observed

chelate was confirmed by a typical ^{1}H NMR pattern for the proton α to the methyl group (2.54 ppm, ddq, J = 5, 7, and 11 Hz) and a methyl doublet (1.59 ppm, J = 7 Hz). The ^{1}H NMR data do not indicate whether the methyl substituent is on C_1 or C_2; however, assigned ^{13}C NMR shifts and coupling patterns for C_1 (41.4 ppm, d, J_{C-H} = 128 Hz) and C_2 (50.2 ppm, dd, J_{C-H} = 128, 134 Hz) are in strong support of structure **12**.

Unambiguous proof of the structure of **12** was provided by X-ray crystallographic analysis. Single crystals of **12** were grown from a saturated solution of diethyl ether/hexane at −20 °C. An ORTEP diagram and labeling scheme for complex **12** are given in Figure 1. Crystallographic data, collection parameters, and refinement parameters are listed in Table 1; selected interatomic distances and angles are summarized in Tables 2 and 3, respectively. Fractional coordinates and isotropic thermal parameters are listed in Table 4.

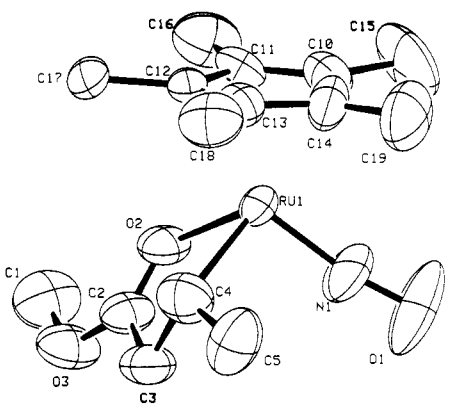


Figure 1. ORTEP drawing of [Cp*Ru(CH(CH$_3$)COOCH$_3$)(NO)]$^+$, **12**. Thermal ellipsoids are drawn at the 50% probability level. The counterion $[(CF_3)_2C_6H_3]_4B^-$ and the hydrogen atoms have been omitted.

For ruthenium, the coordination sphere is similar to that observed in the related complexes Cp*Ru(NO)(CH$_2$Cl)$_2$, **13**,[9] and CpRu(NO)[P(C$_6$H$_5$)$_3$]Cl$^+$, **14**.[10] Angles involving the Cp* (centroid) are as follows: Cp*(centroid)–Ru1–N1 = 124.2°, Cp*(centroid)–Ru1–O2 = 118.8°, Cp*(centroid)–Ru1–C4 = 123.4°. The Cp*(centroid)–Ru distance is 1.880 Å, which is ca. 0.06 Å longer than typically observed in the cations Cp*Ru(η^6-arene)$^+$,[11] but shorter than observed in the neutral complex **13** (1.93 Å). The

Table 1. Crystallographic Data, Collection Parameters, and Refinement Parameters for

$C_5(CH_3)_5Ru(NO)CH(CH_3)CH_2COOCH_3^+$, 12

molec formula	$RuF_{24}O_3NC_{47}BH_{36}$
fw	1230.72
cryst dimens, mm	0.30 × 0.20 × 0.41
space group	$P2_1$
cell params	
a, Å	12.124(2)
b, Å	17.376(4)
c, Å	13.355(2)
β, deg	116.31(1)
V, Å^3	2522.0
Z	2
D_c, g/cm^3	1.620
F(000)	1228
temp (°C)	−90
radiation (wavelength, Å)	Mo Kα (0.7107)
monochromator	graphite
linear abs coeff, cm^{-1}	4.30
scan mode	ω
2θ limits, deg	$4.1 \le 2\theta \le 58.0$
octants collcd	$+h,+k,\pm l$
total no. of unique reflns	6920
data with $I \ge 3.0\sigma(I)$	3809
R	0.059
R_w	0.053
GOF	1.70
no. of params	693
max Δ/σ	0.1
largest resd density, e/Å^3	0.74

Ru1–N1 distance of 1.734(10) Å for **12** is ca. 0.04 Å shorter than that observed in **14** (1.775(5) Å) but in the range observed for other ruthenium nitrosyl complexes.[12] As in **13** and **14**, the nitrosyl ligand of **12** is slightly bent, with Ru1–N1–O1 = 169(1)° (cf. Ru–N–O in **13**, 174.9(9)°; in **14**, 172.2(5)°).[9,10] The atoms Ru1, O2, C2, C3, O3, and C1 are coplanar to within 0.008 Å. This is similar to the complex Cp*Ir(CH$_2$CH$_2$COOCH$_3$)(η^2-CH$_2$CHCO$_2$CH$_3$)$^+$, **15**, in which the analogous portion of the molecule is coplanar to within 0.049 Å.[2b] Puckering of the metallacycle ring is observed, with the plane defined by Ru1, C4, and C3 forming an angle of 144.6° with the Ru1, O2, C2, C3, O3, and C1 plane (C4 is displaced toward the Cp* ligand by 0.61 Å from the latter plane). This puckering is larger than observed in **15** (159.7°), where the methylene attached to iridium is displaced only 0.32 Å from the corresponding plane.[2b] The Ru–O2 distance of 2.146(8) Å is in the range observed in other complexes containing a five-membered-

(9) Hubbard, J. L.; Morneau, A.; Burns, R. M.; Nadeau, O. W. *J. Am. Chem. Soc.* **1991**, *113*, 9180.
(10) Conroy-Lewis, F. M.; Redhouse, A. D.; Simpson, S. J. *J. Organomet. Chem.* **1990**, *399*, 307.
(11) Fagan, P. J.; Ward, M. D.; Calabrese, J. C. *J. Am. Chem. Soc.* **1989**, *111*, 1698.
(12) Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. *J. Chem. Soc., Dalton Trans.* **1989**, S1–S83.
(13) (a) Raghavan, N. V.; Davis, R. E. *J. Cryst. Mol. Struct.* **1975**, *5*, 163. (b) Romero, A.; Vegas, A.; Dixneuf, P. H. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 215. (c) Komiya, S.; Ito, T.; Cowie, M.; Yamamoto, A.; Ibers, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 3874. (d) Crook, J. R.; Chamberlain, B.; Mawby, R. J.; Körber, F. C. F.; Reid, A. J.; Reynolds, C. D. *J. Chem. Soc., Dalton Trans.* **1992**, 843.

Table 2. Interatomic Distances (Å) for $[Cp^*Ru(NO)(CH(CH_3)CH_2C(O)OCH_3)]^+$, 12[a]

Ru(1)–O(2)	2.146(8)	O(2)–C(2)	1.204(12)	C(11)–C(12)	1.410(15)
Ru(1)–N(1)	1.734(10)	O(3)–C(1)	1.415(15)	C(11)–C(16)	1.518(17)
Ru(1)–C(4)	2.095(10)	O(3)–C(2)	1.321(12)	C(12)–C(13)	1.409(17)
Ru(1)–C(10)	2.283(11)	C(2)–C(3)	1.497(15)	C(12)–C(17)	1.531(14)
Ru(1)–C(11)	2.222(11)	C(3)–C(4)	1.564(16)	C(13)–C(14)	1.435(15)
Ru(1)–C(12)	2.202(10)	C(4)–C(5)	1.476(20)	C(13)–C(18)	1.497(14)
Ru(1)–C(13)	2.243(9)	C(10)–C(11)	1.400(16)	C(14)–C(19)	1.485(18)
Ru(1)–C(14)	2.226(12)	C(10)–C(14)	1.460(16)		
O(1)–N(1)	1.182(13)	C(10)–C(15)	1.480(16)		

[a] Numbers in parentheses are the estimated standard deviations.

Table 3. Selected Bond Angles (deg) for $[Cp^*Ru(NO)(CH(CH_3)CH_2C(O)OCH_3)]^+$, 12[a]

C(1)–O(3)–C(2)	118(1)	Ru(1)–C(14)–C(19)	127(1)
Ru(1)–N(1)–O(1)	169(1)	C4–Ru(1)–C11	135.8(5)
Ru(1)–C(4)–C(3)	107.4(7)	C4–Ru(1)–C12	100.6(5)
Ru(1)–C(4)–C(5)	114(1)	C4–Ru(1)–C13	91.8(4)
Ru(1)–C(10)–C(11)	69.6(7)	C4–Ru(1)–C14	118.4(5)
Ru(1)–C(10)–C(14)	69.0(6)	C10–Ru(1)–C11	36.2(4)
Ru(1)–C(10)–C(15)	126(1)	C10–Ru(1)–C12	61.6(4)
Ru(1)–C(11)–C(10)	74.3(7)	C10–Ru(1)–C13	62.4(4)
O(2)–C(2)–O(3)	123(1)	C10–Ru(1)–C14	37.8(4)
O(2)–C(2)–C(3)	121(1)	C11–Ru(1)–C12	37.2(4)
O(3)–C(2)–C(3)	116(1)	C11–Ru(1)–C13	61.9(4)
C(2)–C(3)–C(4)	106.9(9)	C11–Ru(1)–C14	61.8(4)
C(3)–C(4)–C(5)	113(1)	C12–Ru(1)–C13	36.9(4)
C(11)–C(10)–C(14)	106(1)	C12–Ru(1)–C14	62.0(3)
C(11)–C(10)–C(15)	130(1)	C13–Ru(1)–C14	37.4(4)
C(14)–C(10)–C(15)	124(1)	C(11)–C(12)–C(13)	109(1)
C(10)–C(11)–C(12)	110(1)	C(11)–C(12)–C(17)	126(1)
C(10)–C(11)–C(16)	126(1)	C(13)–C(12)–C(17)	125(1)
C(12)–C(11)–C(16)	124(1)	C(12)–C(13)–C(14)	107(1)
O2–Ru(1)–N1	106.0(5)	C(12)–C(13)–C(18)	127(1)
O2–Ru(1)–C4	78.0(5)	C(14)–C(13)–C(18)	126(1)
O2–Ru(1)–C10	119.4(4)	C(10)–C(14)–C(13)	108(1)
O2–Ru(1)–C11	89.9(3)	C(10)–C(14)–C(19)	126(1)
O2–Ru(1)–C12	93.2(3)	C(13)–C(14)–C(19)	125(1)
O2–Ru(1)–C13	126.7(4)	C(22)–C(21)–C(26)	115.8(7)
O2–Ru(1)–C14	151.4(4)	Ru(1)–O(2)–C(2)	115.0(7)
N1–Ru(1)–C4	95.8(6)	Ru(1)–C(11)–C(12)	70.6(6)
N1–Ru(1)–C10	97.2(5)	Ru(1)–C(11)–C(16)	123.8(8)
N1–Ru(1)–C11	128.3(5)	Ru(1)–C(12)–C(11)	72.2(6)
N1–Ru(1)–C12	157.0(5)	Ru(1)–C(12)–C(13)	73.1(6)
N1–Ru(1)–C13	127.2(6)	Ru(1)–C(12)–C(17)	123.9(7)
N1–Ru(1)–C14	95.9(5)	Ru(1)–C(13)–C(12)	69.9(6)
C4–Ru(1)–C10	153.9(4)	Ru(1)–C(13)–C(14)	70.6(6)
Ru(1)–C(14)–C(10)	73.2(7)	Ru(1)–C(13)–C(18)	127.4(7)
Ru(1)–C(14)–C(13)	71.9(6)		

[a] Numbers in parentheses are the estimated standard deviations.

ring ruthenium metallacycle which has coordination of a ketone or ester functionality (e.g., Ru–O = 2.144(3) Å,[13a] 2.09(1) Å,[13b] 2.246(7) Å,[13c] 2.13(1) Å).[13d]

Complex **5** could be prepared analytically pure by reaction of **9** with a large excess of methyl acrylate (100 molar equiv) and allowing the reaction to proceed to completion (36 h). Key spectroscopic features include the observation of four nonequivalent methylene protons (δ 3.50, 3.28, 2.99, and 1.82) and two characteristic ^{13}C resonances for C_1 and C_2 at 21 and 42 ppm, respectively.

Complex **10** is a short-lived intermediate whose presence at 25 °C can only be detected by a signal at 1.85 ppm for the $C_5(CH_3)_5$ ring in the ^1H NMR spectrum. The presumed structure for the intermediate is the one just prior to C–C coupling, namely, $Cp^*Ru(NO)(\eta^2\text{-}CH_2CHCO_2CH_3)CH_3^+$, **10**. To verify this assumption, a low-temperature ^1H NMR study was carried out. At −78 °C, methyl acrylate (5 equiv) was added to complex **9**. Upon warming briefly to −5 °C, a new species with a resonance for the $C_5(CH_3)_5$ ring at 1.85 ppm is formed along with minor amounts of **12** and **5**, which result from migratory insertion of the methyl group. However, at this temperature, all the resonances (except that for Cp*) corresponding to the new complex are broadened. Upon cooling to −80 °C, all signals sharpen to a very characteristic pattern for an η^2-acrylate complex: 2.79 ppm (dd, J_{cis} = 8.6 Hz, J_{gem} = 2.2 Hz), 3.77 (dd, J_{trans} = 13.6 Hz, J_{cis} = 8.6 Hz), 3.86 (dd, J_{trans} = 13.6 Hz, J_{gem} = 2.2 Hz). The methyl signal appears at 1.71 ppm. It is unclear whether the broadening at higher temperatures is due to coordinated acrylate exchanging with free acrylate, or a rapid equilibrium with a minor isomer (for example, by acrylate rotation). Upon warming to ca. −10 °C, methyl migration occurs and both the methyl-substituted complex **12** and the unsubstituted complex **5** are formed.

A plausible mechanism for the formation of **12** and **5** is shown in Scheme 1. Methyl migration to C_β of the η^2-acrylate generates the unsaturated Ru–alkyl complex **16**; β-H elimination then yields the η^2-crotonate complex **17**. Two modes of reaction are available to **17**. Path A involves displacement of methyl crotonate by methyl acrylate to yield **18**, which upon migratory insertion and chelation of the ester carbonyl group yields complex **5**. Path B involves rotation of the crotonate ligand, migration of H to C_β of **17b**, and chelation of the ester carbonyl oxygen to yield **12**. Path A must account for the early and rapid formation of **5** since independent treatment of **12** with methyl acrylate results in a very slow conversion to **5** (only 50% conversion to **5** is observed when **12** is left standing at 23 °C in the presence of methyl acrylate for 30 h). We assume that this conversion occurs via **17b** (and/or **17a**) and that the slow rate of displacement of methyl crotonate from **12** is accounted for by the relatively high barrier for dechelation of the ester carbonyl oxygen from **12** to provide a 16-electron intermediate which can undergo β-H elimination. The reaction sequence proposed in Scheme 1 is also consistent with the best experimental procedure found for preparing **12** and **5**. As described above, **12** is isolated as the major product when **9** is treated with only a small excess of methyl acrylate in dilute solution and reaction times are short (little **5** is formed as methyl acrylate concentration is low and path B predominates; short reaction times do not allow significant conversion of **12** to **5**). High concentrations of methyl acrylate and long reaction times lead only to **5** as any **12** which is formed has sufficient time to convert to **5**.

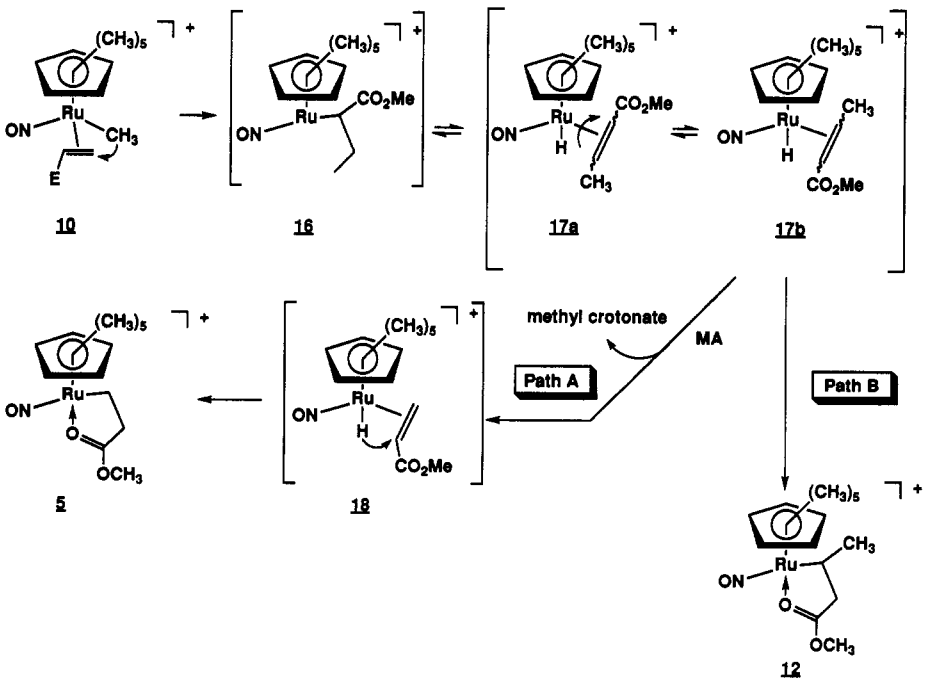
It is interesting to note that the methyl migration must occur to C_β, the unsubstituted carbon of the η^2-acrylate in **10** to yield the methyl-substituted complex **12**. We observed the same high regioselectivity for alkyl migration in our rhodium-based catalytic system for the dimerization of acrylates in which only linear dimers (C_β–C_β or tail-to-tail coupling) were produced.[2] Similarly, treatment of cationic palladium complexes of the type $(L\frown L)Pd(S)(COCH_3)^+$ (L = 1,2-bis(diphenylphosphino)ethane, S = CH_3CN,[14a] or L = 1,10-phenanthroline, S = Et_2O[14b]) with

Table 4. Fractional Coordinates (×10000) and Isotropic Thermal Parameters for $[Cp^*Ru(NO)(CH(CH_3)CH_2C(O)OCH_3)]^+[BAr'_4]^-$, 12 (Ar' = 3,5-$(CF_3)_2C_6H_3$)[a]

atom	x	x	z	B_{iso}	atom	x	x	z	B_{iso}
Ru(1)	2148.7(7)	6184.2(6)	8295.6(6)	3.6(1)′	C(15)	1078(15)	5646(12)	10126(12)	10.3(8)′
F(21)	7679(6)	3272(4)	3807(6)	6.4(3)′	C(16)	1104(12)	7453(9)	9524(12)	6.9(6)′
F(22)	8728(5)	4314(4)	4136(6)	5.6(3)′	C(17)	212(9)	7581(7)	6917(11)	5.7(5)′
F(23)	8221(5)	3860(4)	5341(5)	6.1(2)′	C(18)	−396(11)	5894(7)	5881(10)	6.4(5)′
F(24)	5601(17)	6767(7)	2686(13)	19.3(10)′	C(19)	230(13)	4712(8)	7873(14)	8.2(7)′
F(25)	5950(17)	6243(11)	1601(19)	24.2(14)′	C(21)	4524(7)	4543(4)	3506(6)	2.2(2)′
F(26)	4204(8)	6383(6)	1402(8)	11.8(4)′	C(22)	5647(7)	4150(4)	3910(6)	2.3(2)′
F(31)	2642(7)	649(4)	3156(7)	6.8(3)′	C(23)	6630(7)	4428(5)	3755(7)	2.8(3)′
F(32)	4520(7)	962(4)	3894(8)	9.1(4)′	C(24)	6564(9)	5096(6)	3204(9)	3.8(3)′
F(33)	3412(9)	1275(5)	4656(6)	9.3(4)′	C(25)	5427(9)	5480(5)	2740(8)	3.2(3)′
F(34)	1851(20)	3228(6)	−407(7)	21.6(11)′	C(26)	4449(7)	5211(5)	2908(7)	3.0(3)′
F(35)	2749(10)	2224(7)	−237(7)	10.8(5)′	C(27)	7801(9)	3953(6)	4254(10)	4.1(4)′
F(36)	1105(10)	2174(9)	−449(6)	13.1(5)′	C(28)	5279(10)	6199(10)	2095(12)	6.7(5)′
F(41)	−1709(6)	4324(5)	1653(7)	9.7(4)′	C(31)	3055(6)	3343(4)	3025(7)	2.0(2)′
F(42)	−1235(7)	4554(7)	404(7)	10.4(4)′	C(32)	3285(7)	2630(5)	3562(6)	2.6(3)′
F(43)	−2023(7)	5396(4)	974(10)	13.2(5)′	C(33)	3091(8)	1935(5)	3007(8)	3.0(3)′
F(44)	1395(13)	7376(5)	2926(8)	13.7(6)′	C(34)	2671(7)	1929(5)	1861(8)	3.1(3)′
F(45)	918(8)	7079(5)	4150(10)	11.5(5)′	C(35)	2425(8)	2631(5)	1288(7)	3.1(3)′
F(46)	2732(6)	7005(4)	4448(7)	8.4(3)′	C(36)	2636(8)	3316(5)	1859(7)	2.7(3)′
F(51)	2113(6)	3104(5)	7480(5)	8.1(3)′	C(37)	3417(10)	1221(8)	3653(8)	4.5(4)′
F(52)	1683(7)	2440(4)	6058(6)	7.1(3)′	C(38)	2079(14)	2646(10)	35(9)	8.1(6)′
F(53)	861(6)	3532(5)	5900(7)	7.9(3)′	C(41)	2180(7)	4779(5)	3202(6)	2.2(2)′
F(54)	7152(6)	4055(6)	7718(6)	7.8(3)′	C(42)	975(7)	4589(5)	2447(6)	2.3(3)′
F(55)	6300(7)	4772(6)	8365(7)	10.2(4)′	C(43)	21(7)	5117(5)	2125(7)	2.5(3)′
F(56)	6442(6)	3635(6)	8814(5)	10.4(3)′	C(44)	203(8)	5843(5)	2514(7)	3.0(3)′
O(1)	3652(12)	4873(7)	9462(11)	12.9(6)′	C(45)	1410(8)	6059(5)	3289(7)	3.1(3)′
O(2)	3249(6)	7210(5)	8712(7)	4.7(3)′	C(46)	2359(7)	5524(5)	3605(6)	2.3(3)′
O(3)	4634(6)	7875(5)	8417(7)	5.9(3)′	C(47)	−1231(8)	4863(6)	1299(9)	4.1(3)′
N(1)	3145(11)	5440(7)	8996(10)	7.2(5)′	C(48)	1641(11)	6881(7)	3691(10)	5.2(4)′
C(1)	4639(11)	8454(8)	9163(12)	7.3(6)′	C(51)	3698(7)	4025(4)	5000(6)	2.2(2)′
C(2)	3895(9)	7280(7)	8246(9)	4.4(4)′	C(52)	4825(6)	4125(4)	5924(6)	2.1(2)′
C(3)	3910(10)	6686(7)	7440(10)	5.1(4)′	C(53)	5024(7)	3922(5)	6975(7)	2.9(3)′
C(4)	2650(9)	6253(10)	6986(8)	5.6(4)′	C(54)	4080(8)	3596(5)	7192(6)	2.9(3)′
C(5)	2668(14)	5500(8)	6480(12)	7.5(6)′	C(55)	2946(8)	3511(5)	6281(7)	2.7(3)′
C(10)	789(10)	5998(7)	9029(9)	4.8(4)′	C(56)	2741(7)	3722(4)	5219(6)	2.5(3)′
C(11)	793(10)	6771(7)	8735(10)	4.2(4)′	C(57)	6243(10)	4054(8)	7964(8)	5.1(4)′
C(12)	406(9)	6830(7)	7574(9)	3.6(4)′	C(58)	1893(9)	3157(7)	6451(8)	4.2(4)′
C(13)	147(8)	6089(8)	7098(8)	4.3(4)′	B(1)	3368(8)	4190(5)	3673(7)	2.2(3)′
C(14)	431(11)	5557(7)	8001(11)	5.0(5)′					

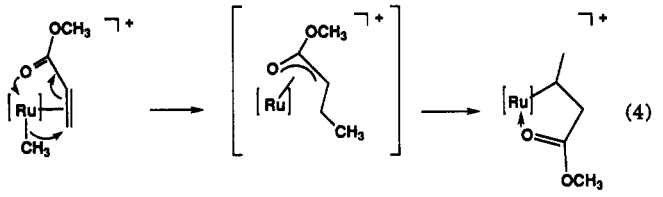
[a] Numbers in parentheses are the estimated standard deviations.

Scheme 1



methyl acrylate (MA) resulted in displacement of the labile ligand (S) by MA, formation of an η^2-acrylate intermediate $(L\frown L)Pd(\eta^2\text{-}CH_2CHCO_2CH_3)(COCH_3)^+$, and selective migration of the acyl group to C_β of coordinated MA to yield $(L\frown L)Pd(CH(CO_2CH_3)CHCOCH_3)^+$.

The origin of the high regioselectivity for R migration (R = alkyl or acyl)[15] to C_β is not clear. A plausible explanation involves steric effects where alkyl migration occurs preferentially to the least substituted carbon of the double bond.[14c] The polarity of the double bond induced by the ester substituent may also encourage migration to the more electrophilic C_β. However, for methyl acrylate, in addition to these factors, one can invoke a concerted mechanism in which the ester carbonyl oxygen of the acrylate assists the alkyl migration through the formation of an oxallyl intermediate. The latter mechanism, which is depicted in eq 4, does not involve a high-energy 16-electron intermediate and is consistent with the regioselectivity observed. Furthermore, we noticed that



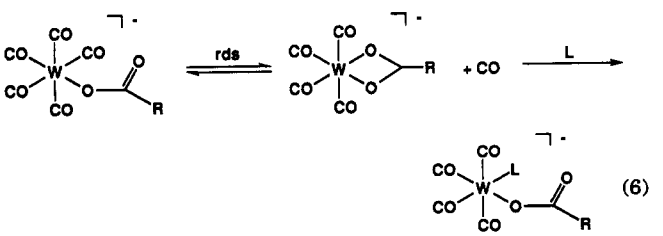
(4)

alkyl migration in $Cp^*Rh(\eta^2\text{-}CH_2CHCO_2CH_3)(CH_2CH_2COOCH_3)^+$, in addition to being regioselective, was substantially faster ($\Delta G^\ddagger$ = 19 kcal/mol) than the ethyl migration in the ethylene dimerization catalyst $Cp^*RhP(OCH_3)_3(C_2H_5)(C_2H_4)^+$ ($\Delta G^\ddagger$ = 22 kcal/mol).

The proposal of participation of a "neighboring" carbonyl group is well-known for metal acetates.[16] For example, Bassetti[16b] proposed a mechanism for migratory insertion in Rh(III) methyl carbonyl acetate complexes based on this scheme (eq 5). The rate of migratory insertion

$$Cp^*Rh(CO)(CH_3)(\eta^1\text{-}OCOCH_3) \rightleftharpoons Cp^*Rh(COCH_3)(\eta^2\text{-}O_2CCH_3) \xrightarrow{L} Cp^*Rh(COCH_3)(L)(\eta^1\text{-}OCOCH_3) \quad (5)$$

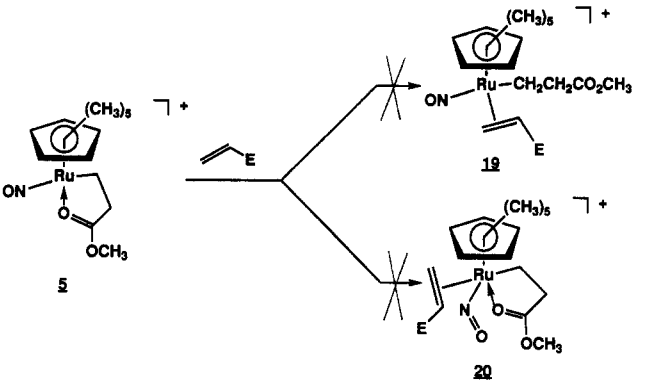
was shown to exhibit saturation kinetics with the rate being independent of the incoming nucleophile (L) at high concentrations. This supports a mechanism in which the carbonyl oxygen of the acetate group acts as a nucleophile by attacking at the rhodium center and thus promoting the methyl migration. Similarly, Darensbourg[16c] proposed a mechanism for dissociation of a *cis*-carbonyl group from anionic tungsten carbonyl carboxylates in which the synchronous dissociation of CO and chelation of the distal oxygen atom of the monodentate carboxylate results in stabilization of the transition state for *cis*-CO loss and significant rate acceleration relative to model systems (eq 6). Recently, Cooper[17] has invoked a mechanism involving



(6)

an η^2-acyl intermediate in the accelerated CO dissociation from $(CO)_5WC(O)C_6H_5^-$.

The mechanism described in Scheme 1 possesses all the features required for catalytic acrylate dimerization (e.g., alkyl migration, β-H elimination, and olefin exchange). But despite the fact that the alkyl migration (see, for example, the conversion of **10** to **16**) is expected to be facile, all our attempts to dimerize methyl acrylate using **5** as a catalyst precursor failed even at elevated temperatures (55 °C). This observation clearly indicates that in this cationic electrophilic ruthenium system the chelate interaction in **5** is strong; the carbonyl oxygen cannot be displayed by free acrylate to provide complexes of the type **19** which should result in dimer formation. Furthermore, complex **20**, in which a bent nitrosyl ligand provides a vacant site for coordination of external acrylate, also appears inaccessible. Despite the lack of catalytic



activity of the system described above, the surprisingly clean chemistry observed lends additional insight into the electronic and steric factors which may be required for the operation of an active catalytic system.

Experimental Section

All procedures were carried out in a glovebox equipped with a constant nitrogen flush or in Schlenk-type glassware interfaced to a high-vacuum (10^{-4}–10^{-5} Torr) line. Solvents were dried and distilled under dinitrogen before use by employing the following drying agents: Na/benzophenone for diethyl ether and hexane; CaH_2 for methylene chloride. ^1H and ^{13}C NMR spectra were recorded on either 250-, 300-, or 400-MHz spectrometers. Gas chromatography (GC) analyses were conducted on a Hewlett-Packard 5750 using flame ionization detection and a 30-m capillary fused silica column with DB-5 as the active phase. Gas chromatography followed by mass spectrometry analyses was performed by the UNC-Mass Spectrometry Facility using a VG 70-250 SEQ tandem-hybrid MS/MS system operated in the MS1 (first mass spectrometer only) mode, with data acquisition utilizing a 70-250J data system (DEC-Micro-PDP-11 computer). The following preparations were based on standard literature procedures: $[H(OEt_2)_2]^+[BAr'_4]^-$ (Ar' = 3,5-$C_6H_3(CF_3)_2$),[18] $Cp^*Ru(NO)(CH_3)_2$,[19] and $Cp^*Ru(NO)(Et)_2$.[19] Elemental analyses were performed by Oneida Research Services, Inc.

Synthesis of $[Cp^*Ru(NO)(CH_3)(H_2O)(Et_2O)_{1.5}]^+[BAr'_4]^-$, 9 (Ar' = 3,5-$(CF_3)_2C_6H_3$). A 50-mL round-bottomed flask was charged with 300 mg (1.01 mmol) of $Cp^*Ru(NO)(CH_3)_2$, **8**, and 1.09 g (1.08 mmol) of $HBAr'_4(Et_2O)_2$ (the acid is very hygroscopic

(14) (a) Ozawa, F.; Hayashi, T.; Koide, H.; Yamamoto, A. *J. Chem. Soc., Chem. Commun.* **1991**, 1469. (b) Brookhart, M.; Rix, F. C.; Barborak, J. C. Unpublished results. (c) Dekker, G. P. C. M.; Elsevier, C. J.; Vrieze, K.; van Leeuwen, P. W. N. M.; Roobeek, C. F. *J. Organomet. Chem.* **1992**, *430*, 357.

(15) The results of acyl and alkyl migration suggest that hydride migration in **18** may occur kinetically to C_β, but this is rapidly followed by β-H elimination and hydride readdition to C_α to give the thermodynamically favored five-membered-ring chelate **5**.

(16) (a) Maitlis, P. M.; Bailey, P. M.; Isobe, K. *J. Chem. Soc., Dalton Trans.* **1981**, 2003. (b) Bassetti, M.; Monti, D.; Maitlis, P.; Ellis, P.; Sunley, G. J. *Organometallics* **1991**, *10*, 4015. (c) Darensbourg, D. J.; Joyce, J. A.; Bischoff, C. J.; Reibenspies, J. H. *Inorg. Chem.* **1991**, *30*, 1137. (d) Hawthorne, M. F.; Kang, H. C. *Organometallics* **1990**, *9*, 2327.

(17) Cooper, J. N.; Lee, I. *J. Am. Chem. Soc.* **1993**, *115*, 4389.

(18) Brookhart, M.; Grant, B.; Volpe, A. F., Jr. *Organometallics* **1992**, *11*, 3920.

(19) Chang, J.; Seidler, M. D.; Bergman, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 3258.

and always contains traces of water). The solids were dissolved in 30 mL of methylene chloride at ambient temperature and stirred for 5 min. The solvent was then removed under reduced pressure to give a red powder. Recrystallization from Et_2O/hexane resulted in the isolation of **9** as red crystals (1.14 g, 88%). IR (Nujol): ν(NO) = 1793 cm^{-1}. Anal. Found (calcd): C, 46.20 (45.94); H, 3.72 (3.63); N, 0.94 (1.10). ^{1}H NMR (300 MHz, CD_2Cl_2, 23 °C): δ 7.72 (Ar′, 8H), 7.56 (Ar′, 4H), 4.70 (s, 2H, H_2O), 3.49 (q, 6H, ^3J = 7 Hz, $(CH_3CH_2)_2O$), 1.76 (s, 15H, $C_5(CH_3)_5$), 1.19 (t, 9H, ^3J = 7 Hz, $(CH_3CH_2)_2O$). ^{13}C NMR (75 MHz, CD_2Cl_2, 23 °C): δ 162.1 (q, J_{C-B} = 50 Hz, $C_{1'}$), 135.2 (d, J_{C-H} = 160 Hz, $C_{2'}$), 129.3 (q, $^2J_{C-F}$ = 32 Hz, $C_{3'}$), 125.0 (q, J_{C-F} = 272 Hz, CF_3), 117.9 (d, J_{C-H} = 164 Hz, $C_{4'}$), 109.0 (s, $C_5(CH_3)_5$), 66.4 (t, J_{C-H} = 142 Hz, $O(CH_2CH_3)_2$), 15.2 (q, J_{C-H} = 126 Hz, $O(CH_2CH_3)_2$), 9.6 (q, J_{C-H} = 129 Hz, $C_5(CH_3)_5$), 7.2 (q, J_{C-H} = 137 Hz, $RuCH_3$).

Synthesis of $[C_5(CH_3)_5Ru(NO)PMe_3CH_3]^+[BAr'_4]^-$, 11 (Ar′ = 3,5-$(CF_3)_2C_6H_3$). Trimethylphosphine (100 μL, 0.97 mmol) was added at ambient temperature to $Cp^*Ru(NO)(CH_3)(H_2O)^+(Et_2O)_{1.5}$ (127 mg, 0.10 mmol) in 10 mL of methylene chloride. The initially dark orange solution turned lighter immediately. After the mixture was stirred at room temperature for 1 h, the solvent and the excess trimethylphosphine were removed under vacuo. Complex **11** was recrystallized from diethyl ether/hexane at −30 °C and isolated as orange crystals (69 mg, 57%). IR (Nujol): ν(NO) = 1786 cm^{-1}. Anal. Found (calcd): C, 45.28 (45.26); H, 3.15 (3.22); N, 1.04 (1.15). ^{1}H NMR (300 MHz, CD_2Cl_2, 23 °C): δ 7.72 (8H, Ar′), 7.57 (4H, Ar′), 1.89 (d, 15H, J_{P-H} = 1.7 Hz, $C_5(CH_3)_5$), 1.57 (d, 9H, J_{P-H} = 11 Hz, $P(CH_3)_3$), 0.88 (d, 3H, J_{P-H} = 6 Hz, $RuCH_3$). ^{13}C NMR (75 MHz, CD_2Cl_2, 23 °C): δ 162.1 (q, J_{C-B} = 50 Hz, $C_{1'}$), 135.2 (d, J_{C-H} = 163 Hz, $C_{2'}$), 129.2 (q, $^2J_{C-F}$ = 35 Hz, $C_{3'}$), 125.0 (q, J_{C-F} = 273 Hz, CF_3), 117.9 (d, J_{C-H} = 164 Hz, $C_{4'}$), 107.6 (s, $C_5(CH_3)_5$), 15.2 (dq, J_{C-P} = 35 Hz, J_{C-H} = 135 Hz, $P(CH_3)_3$), 10.0 (q, J_{C-H} = 129 Hz, $C_5(CH_3)_5$), −2.3 (dq, J_{C-P} = 10 Hz, J_{C-H} = 137 Hz, $RuCH_3$).

Synthesis of $[Cp^*\overline{Ru(NO)(CH(CH_3)CH_2C(O)OCH_3)}]^+[BAr'_4]^-$, 12 (Ar′ = 3,5-$(CF_3)_2C_6H_3$). Methyl acrylate (60 μL, 0.67 mmol) was added at ambient temperature to $Cp^*Ru(CH_3)(NO)(H_2O)^+(Et_2O)_{1.5}$ (163 mg, 0.13 mmol) in 10 mL of methylene chloride. The initially dark orange solution turned lighter immediately. After stirring for ca. 5–10 min, the solvent and the excess methyl acrylate were removed under reduced pressure. The oily residue was washed twice with 5 mL of hexane. Complex **12** was recrystallized from diethyl ether/hexane at −20 °C and isolated as orange crystals (116 mg, 74%). IR (CD_2Cl_2): ν(NO) = 1785 cm^{-1}, ν(CO) = 1597 cm^{-1}. Anal. Found (calcd): C, 45.65 (45.87); H, 2.70 (2.95); N, 1.03 (1.14). ^{1}H NMR (300 MHz, CD_2Cl_2, 23 °C): δ 7.72 (Ar′, 8H), 7.57 (Ar′, 4H), 3.95 (s, 3H, CO_2CH_3), 3.59 (dd, $J_{H_1-H_2}$ = 19 Hz, $J_{H_1-H_3}$ = 5 Hz, H_1), 3.21 (dd, $J_{H_2-H_1}$ = 19 Hz, $J_{H_2-H_3}$ = 11 Hz, H_2), 2.54 (ddq, $J_{H_3-H_1}$ = 5 Hz, $J_{H_3-H_2}$ = 11 Hz, J = 7 Hz, H_3), 1.77 (s, 15H, $C_5(CH_3)_5$), 1.59 (d, 3H, J = 7 Hz, CH_3). ^{13}C NMR (75 MHz, CD_2Cl_2, 23 °C): δ 192.9 (s, C_3), 162.3 (q, J_{C-B} = 50 Hz, $C_{1'}$), 135.3 (d, J_{C-H} = 160 Hz, $C_{2'}$), 129.4 (q, $^2J_{C-F}$ = 31 Hz, $C_{3'}$), 125.1 (q, J_{C-F} = 272 Hz, CF_3), 118.0 (d, J_{C-H} = 164 Hz, $C_{4'}$), 109.7 (s, $C_5(CH_3)_5$), 57.2 (q, J_{C-H} = 151 Hz, OCH_3), 50.2 (dd, J_{C-H} = 128 Hz, J_{C-H} = 134 Hz, C_2), 41.4 (d, J_{C-H} = 128 Hz, other couplings < 10 Hz, C_1), 27.7 (q, J_{C-H} = 127 Hz, CH_3), 9.3 (q, J_{C-H} = 130 Hz, $C_5(CH_3)_5$).

X-ray Structural Analysis of $[Cp^*\overline{Ru(NO)(CH(CH_3)CH_2C(O)OCH_3)}]^+[BAr'_4]^-$, 12. A single red crystal of **12** (parallelepiped, ca. 0.30 × 0.20 × 0.41 mm) was grown from ether/hexane at −20 °C. The crystal is monoclinic ($P2_1$, No. 4) with the following cell dimensions determined from 25 reflections (μ(Mo) = 4.30 cm^{-1}): a = 12.124(2) Å, b = 17.376(4) Å, c = 13.355(2) Å, β = 116.31(1)°; V = 2522.0 Å^3, Z = 2; FW = 1230.72 ($C_{47}H_{36}BF_{24}NRu$); density (calcd) = 1.620 g/cm^3.

Data were collected at −90 °C on a Syntex R3 diffractometer with a graphite monochromator using Mo Kα radiation (λ = 0.7107 Å). A total of 7124 data were collected ($4.1° \le 2\theta \le 58.0°$; maximum h,k,l = 16,23,18; data octants +++, ++−; ω scan method, typical half-height peak width = 0.41° in ω; scan width = 1.60° in ω, scan speed = 3.90–11.70° min^{-1}); two standards were collected 78 times, and a correction for a 3% decrease in intensity was applied to the data; 4.1% variation in azimuthal scan; no absorption correction was applied to the data. There were 3809 unique reflections with $I \ge 3.0\sigma(I)$.

The structure was solved by automated Patterson analysis (PHASE). The asymmetric unit consists of one ion pair in a general position. Hydrogen atoms were idealized with C–H = 0.95 Å. The structure was refined by full-matrix least squares on F (H atoms fixed, all others anisotropic) with scattering factors from ref 20 including anamolous terms for Ru (biweight $\propto [\sigma^2(I) + 0.0009I^2]^{-1/2}$ (excluded 1)). There were 693 parameters, and the data to parameter ratio was 5.49; final R = 0.059 (R_w = 0.053). Error of fit = 1.70 with a maximum Δ/σ = 0.10 (several CF_3 groups show high thermal motion, and the difference between enantiomorphic models was insignificant). Largest residual density = 0.74 electron/Å^3 near Ru1.

Synthesis of $[Cp^*\overline{Ru(NO)(CH_2CH_2C(O)OCH_3)}]^+[BAr'_4]^-$, 5 (Ar′ = 3,5-$(CF_3)_2C_6H_3$). Methyl acrylate (1.5 mL, 16.7 mmol) was added at ambient temperature to $Cp^*Ru(CH_3)(NO)(H_2O)^+(Et_2O)_{1.5}$ (199 mg, 0.16 mmol) in 12 mL of methylene chloride. The initially dark orange solution turned lighter immediately. After stirring at room temperature for 36 h, the solvent and the excess methyl acrylate were removed under reduced pressure. The oily residue was dissolved in diethyl ether and filtered through a plug of Celite. The ether volume was then reduced and hexane added. The solution was then cooled to −25 °C to yield 96 mg of complex **5** as orange crystals (51%). IR (Nujol): ν(NO) = 1798 cm^{-1}, ν(CO) = 1601 cm^{-1}. Anal. Found (calcd): C, 45.48 (45.41); H, 2.75 (2.82); N, 1.16 (1.15). ^{1}H NMR (300 MHz, CD_2Cl_2, 23 °C): δ 7.72 (Ar′, 8H), 7.56 (Ar′, 4H), 3.96 (s, 3H, CO_2CH_3), 3.50 (ddd, $J_{H_1-H_2}$ = 19 Hz, $J_{H_1-H_3}$ = 6.5 Hz, $J_{H_1-H_4}$ = 2.3 Hz, H_1), 3.28 (ddd, $J_{H_2-H_1}$ = 19 Hz, $J_{H_2-H_3}$ = 11 Hz, $J_{H_2-H_4}$ = 8 Hz, H_2), 2.99 (ddd, $J_{H_4-H_3}$ = 10 Hz, $J_{H_4-H_2}$ = 8 Hz, $J_{H_4-H_1}$ = 2.3 Hz, H_4), 1.82 (ddd, $J_{H_3-H_2}$ = 11 Hz, $J_{H_3-H_4}$ = 10 Hz, $J_{H_3-H_1}$ = 6.5 Hz, H_3), 1.79 (s, 15H, $C_5(CH_3)_5$). ^{13}C NMR (125 MHz, CD_2Cl_2, 23 °C): δ 194.2 (s, C_3), 161.9 (q, J_{C-B} = 50 Hz, $C_{1'}$), 135.2 (d, J_{C-H} = 160 Hz, $C_{2'}$), 129.3 (q, $^2J_{C-F}$ = 32 Hz, $C_{3'}$), 125.0 (q, J_{C-F} = 272 Hz, CF_3), 117.9 (d, J_{C-H} = 165 Hz, $C_{4'}$), 109.2 (s, $C_5(CH_3)_5$), 57.1 (q, J_{C-H} = 151 Hz, OCH_3), 41.5 (dd, J_{C-H} = 136 Hz, J_{C-H} = 132 Hz, C_2), 20.7 (dd, J_{C-H} = 137 Hz, J_{C-H} = 144 Hz, C_1), 9.3 (q, J_{C-H} = 129 Hz, $C_5(CH_3)_5$).

In Situ Observation of the Reaction of 12 with Methyl Acrylate To Yield 5. An NMR tube was charged with 12.4 mg (0.010 mmol) of **12** in 0.6 mL of CD_2Cl_2. Then 14 equiv of methyl acrylate was added and the conversion to **5** followed by ^{1}H NMR spectroscopy at 25 °C. After 9 h **5** represented ca. 20% of the ruthenium species, and after ca. 30 h it represented 50%. After 96 h 91% conversion to **5** had been achieved. By ^{1}H NMR spectroscopy only the *trans* isomer of methyl crotonate as evidenced by ^{1}H NMR resonances at 6.93 ppm (m, $CH(CH_3)CHCO_2CH_3$) and at 1.83 ppm (dd, $CH(CH_3)CHCO_2CH_3$) can be observed and fully identified. The *cis* isomer is a minor component, and most of its NMR signals are obscured by methyl acrylate; however, a doublet of doublets at ca. 2.1 ppm seems to correspond to the methyl signal of *cis*-methyl crotonate. At this point the contents of the NMR tube were passed through a plug of alumina and analyzed by GC–mass spectrometry; this revealed the presence of the *cis* (29%) and *trans* (71%) isomers of methyl crotonate. No methyl methacrylate is observed by ^{1}H NMR spectroscopy or GC–MS analyses.

Acknowledgment. This work was supported by the National Science Foundation (CHE-8705534) and by E. I. du Pont de Nemours & Co., Inc.

Supplementary Material Available: X-ray data for **12**, including tables of fractional coordinates and isotropic thermal parameters, anisotropic thermal parameters, interatomic distances, intramolecular angles, intramolecular nonbonding distances, and intermolecular distances (8 pages). Ordering information is given on any current masthead page.

OM930753C

(20) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. 4.