between Co and Mn is likely. A two-electron reduction concomitant or subsequent to the metal exchange is necessary to balance the charge. The reducing agent is assumed to be $Co(CO)_4^-$.

The cluster-building reaction to form **1** is highly dependent on the cation associated with $Co(CO)_4^-$. The reaction of $Mn(CO)_5(CBr_3)$ with $NaCo(CO)_4$ yields $Mn(CO)_5Br$ and $Co_4(CO)_{12}$, with no formation of **1**. When the cation is PPh_4^+ or Et_4N^+, **1** forms, but in very low yield. When $Mn(CO)_5(CCl_3)$ is used in place of $Mn(CO)_5(CBr_3)$, the reaction proceeds much more slowly, in about 3 h at room temperature. The reaction is also highly solvent dependent. When tetrahydrofuran is used in place of dichloromethane, no reaction takes place.

The ketenylidene complex **1** reacts rapidly with 1 equiv of HSO_3CF_3 at room temperature (eq 3). Proton attack

$$[PPN][MnCo_2(CO)_9(\mu_3\text{-}CCO)] + HSO_3CF_3 \rightarrow MnCO_2(CO)_{10}(\mu_3\text{-}CH) + PPNSO_3CF_3 \quad (3)$$

occurs at the capping carbon atom, to produce a methylidyne complex, $MnCo_2(CO)_{10}(\mu_3\text{-}CH)$ (**2**).[20] This mode of reactivity is typical for negatively charged ketenylidene complexes of the first-row transition metals.[15,21]

In summary, the trihalomethyl transition-metal complexes $Mn(CO)_5(CX_3)$ (X = Cl, Br) have been used successfully to form a mixed-metal cluster containing at a ketenylidene ligand in which the α-carbon atom is derived from the CX_3 moiety. Further cluster building reactions are under investigation.

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Supplementary Material Available: Listings of observed and calculated structure factors, positional and anisotropic thermal parameters, and bond distances and angles (106 pages). Ordering information is given on any current masthead page.

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(20) Anal. Calcd for $C_{11}HO_{10}MnCo_2$: C, 28.35; H, 0.21; Mn, 11.79; Co, 25.30. Found: C, 28.13; H, 0.49; Mn, 11.82; Co, 25.16. IR (hexane): 2061 (s), 2050 (vs), 2002 (w), 1978 (m), 1920 (w) cm^{-1}. ^1H NMR (CD_2Cl_2): δ 9.37. Mass spectrum: m/e 466 (parent peak), successive loss of 10 CO's.

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Ruthenium-Catalyzed Acrylate Dimerization†

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Summary: Treatment of $(\eta\text{-}C_6H_6)(MA)_2Ru^0$ (MA = $CH_2{=}CHCO_2CH_3$) with 2 equiv of sodium naphthalenide in tetrahydrofuran generates a homogeneous species which selectively catalyzes the dimerization of methyl acrylate (MA) to dimethyl hexenedioate.

The selective tail-to-tail dimerization of acrylates (eq 1) is attractive both as an alternative to the currently practiced cyclohexane oxidation in the synthesis of adipic acid (an important nylon intermediate) and as an intermediate in fine chemicals synthesis.[1]

$$2CH_2{=}CHCO_2CH_3 \xrightarrow[MA]{} CH_3O_2CCH{=}CHCH_2CH_2CO_2CH_3 \quad (1)$$
$$\text{DHD}$$

Previously Alderson, Jenner, and Lindsey[2] reported that $RuCl_3{\cdot}3H_2O$ catalyzes the dimerization of acrylates in the presence of methanol. Our continuing studies of this system[3] have shown that zerovalent ruthenium complexes such as $(\eta\text{-}C_6H_6)(CH_2{=}CHCO_2CH_3)_2Ru^0$ (**1**) or $(\eta^6\text{-}C_6H_6)(\eta^4\text{-}C_6H_8)Ru^0$ catalyze the same reaction in the absence of additives under milder conditions (140 °C vs. 210 °C) (see Table I).[4]

Table I. Catalyst Activity and Selectivity in Methyl Acrylate Dimerization

cat.	methyl acrylate convn,[a] %	selectivity, % dimer	selectivity, % linear:branched[b]
$RuCl_3{\cdot}3H_2O$[c]	<0.1		
$(C_6H_6)(MA)_2Ru^0$ (**1**)	12	50	9:1
1 + $2NaC_{10}H_8$[d]	47	77	49:1

[a] At 140 °C for 1 h; [Ru] = 0.010 M; [MA] = 5.4 M in *N*-methylpyrrolidone with decane as internal standard. [b] Linear = dimethyl hexenedioate; branched = head-to-tail dimer, dimethyl α-methylpentenedioate. [c] Methanol ~5% v/v. [d] $(C_6H_6)(MA)_2Ru^0$ treated with 2 equiv of sodium naphthalenide (THF).

Kinetic studies using **1** as catalyst precursor reveal that the rate of DHD formation obeys the rate law

$$d[DHD]/dt = k[Ru]^{0.5}[MA]$$

A simple model consistent with this rate law is given by eq 2–4. Equation 2 shows an equilibrium consisting of

$$Ru_x \rightleftharpoons Ru + Ru_{x-1} \quad (2)$$

$$Ru + MA \rightarrow Ru' + DHD \quad (3)$$

$$Ru' + MA \rightarrow Ru \quad (4)$$

fragmentation of a cluster containing at least two ruthenium nuclei. Equation 3, showing a second-order reaction between one of the ruthenium fragments and MA, is rate limiting. Equation 4 balances the system by adding the second acrylate in a fast step. The half-order dependence on the catalyst results when the equilibrium of eq 2 lies far to the left side.[5] Solvent polarity has a dramatic effect on the catalytic activity with higher activity being favored by very polar, weakly coordinating solvents such as *N*-methylpyrrolidone (NMP). This led us to postulate that the fragmentation is ionic in nature and, since we start with zerovalent ruthenium, suggests one of the fragments may be anionic.

(1) For example see: Nugent, W. A.; Hobbs, F. W., Jr. *J. Org. Chem.* **1983**, *48*, 5364.

(2) Alderson, T.; Jenner, E. L.; Lindsey, R. V. *J. Am. Chem. Soc.* **1965**, *87*, 5638. Alderson, T.U.S. Patent 3 013 066, 1961.

(3) McKinney, R. J.; Colton, M. C. *Organometallics* **1986**, *5*, 1080.

(4) McKinney, R. J. U.S. Patent 4 485 256, 1984.

(5) ^1H NMR studies reveal that coordinated benzene of **1** is irreversibly lost at 90 °C, apparently allowing a dimer or higher cluster to rapidly form.

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Table II. Solvent and Additive Effects on Methyl Acrylate Dimerization Catalyzed by 1 + $2NaC_{10}H_8$

reactn medium[a]	ca. 1 h			ca. 3 h		
	% convn MA	% yield DHD[b]	TO[c]	% convn MA	% yield DHD[b]	TO[c]
1. MA	8	85	37	28	82	125
2. MA/NMP (1:1)	17	74	66	71	54	208
3. MA/NMP/crown (1:1:0.005)[d]	13	93	64	60	63	205
4. MA/crown (1:0.005)[e]	16	84	75	46	80	198
5. MA/Carbowax (1:0.01)[f]	19	86	88	43	84	195

[a] $(C_6H_6)(MA)_2Ru^0$ (0.005 M) treated with 2 equiv of sodium naphthalenide ($NaC_{10}H_8$/THF), sealed under vacuum in glass, and heated to 140 °C. NMP = N-methylpyrrolidone. [b] 2 × mol of DHD/mol of MA converted. [c] Turnover number = mol of DHD produced/mol of Ru. [d] 18-Crown-6 (see ref 9), approximately 2 equiv/Ru. [e] 18-Crown-6 (see ref 9), approximately 4 equiv/Ru. [f] Carbowax 200 (linear long-chain alkyl polyether).

Treating a solution of the zerovalent complex 1 with very strong reducing agents, e.g., sodium naphthalenide or sodium amalgam, generates a new species of unknown structure[6] which is superior as a catalyst for linear dimerization of acrylate (see Table I). Maximum activity is achieved with 2 equiv of sodium per ruthenium. Excess sodium results in yield loss due to anionic oligomerization of acrylate.[7] Addition of protic acids after reduction inhibits activity, suggesting that ruthenium hydride is not a primary catalytic species. Though solvents are not necessary, highly polar solvents such as *N*-methylpyrrolidone (NMP) increase the activity of the catalyst (see entries 1 and 2 of Table II). These observations can be interpreted to suggest that the active catalytic species is an anionic ruthenium complex.[8]

Hexenedioate (DHD) formation is accompanied by some oligomerization of MA. However, kinetic studies show that the latter arises primarily from decay of the dimerization catalyst to a new catalytic species which promotes oligomerization. The rate of catalyst decay is inversely proportional to the MA concentration: i.e., high MA concentrations inhibit decay. At high MA concentrations and low conversions, little oligomerization occurs but at high conversions large yield losses are observed (see entry 2, Table II). The turnover numbers (TO) indicate that the yield loss is due to an increase in oligomerization rather than a significant decrease in selective dimerization. It is noteworthy that the rate of catalyst decay is also dependent on the nature of the reducing metal and appears to correlate with the size of the corresponding cation so that the rate of catalyst decay increases in the order Li (0.60) < Na (0.99) ≃ Ca (0.99) < K (1.35) ≃ Ba (1.35), where the number in parentheses is the cationic radius. Consistent with the involvement of a cation in the catalyst decay process, the addition of crown ethers, e.g., 18-crown-6,[9] to a sodium-treated system significantly retards catalyst decay and therefore increases selectivity at higher conversions. Indeed we have found that in the presence of catalytic amounts of polyethers such as 18-crown-6 or Carbowax 200, the catalyst performs better, even in the absence of solvent (Table II).

Registry No. MA, 96-33-3; DHD, 6108-58-3; $(\eta\text{-}C_6H_6)(MA)_2Ru(O)$, 103149-99-1; sodium naphthalenide, 3481-12-7.

(6) A cream-colored solid may be isolated by precipitation with excess hexane. This solid is unstable in solution and exhibits a complex ^1H NMR spectrum in THF-d_8 which is dependent upon the temperature at time of isolation (25 °C vs. −30 °C) and changes with time. Coordinated benzene is present but easily lost from the solid isolated at −30 °C but not present in the material isolated at 25 °C. These isolated powders are similar to nonisolated catalyst preparations in catalytic activity.

(7) In the absence of ruthenium, acrylate treated with sodium reducing agents results in nonselective oligomerization.

(8) An apparent reduction of 1 is further suggested by comparing the electrochemical potential of 1 treated with sodium naphthalenide (1.0 V) with that of untreated 1 (0.1 V) and sodium naphthalenide (2.7 V). Measurements were obtained in 0.4 M naphthalene in tetrahydrofuran with platinum electrodes in a small H cell separated by a glass frit. For comparison, other species exhibit the following potentials: Na/Hg, 2.0 V; Ca/Hg, 1.5 V; Mg/Hg, 1.2 V; Mn/Hg, 0.7 V; Zn/Hg, 0.6 V; Cu, 0.1 V.

(9) 18-Crown-6 refers to 1,4,7,10,13,16-hexaoxycyclooctadecane.

Control of Organopalladium Glycal Adduct Decomposition Reactions. Role of Conformational Restriction and β-Carbon Substituents

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Summary: The mode of decomposition of organopalladium adduct intermediates, formed in a palladium-mediated reaction of glycals which leads to *C*-glycosides, is sensitive to adduct conformation and the leaving group ability of substituents β to palladium. Pyranoid glycals conformationally restricted by benzylidene formation through glycal 4- and 6-hydroxyls react with (1,3-dimethyl-2,4(1*H*,3*H*)pyrimidinedion-5-yl)mercuric acetate in the presence of palladium(II) acetate to form an intermediate adduct with palladium and the $C_{3'}$-oxy substituent *trans* diaxially disposed. When the substituent at $C_{3'}$ is a good leaving group (e.g., acetate), anti palladium acetate elimination occurs; when the substituent is a poor leaving group (e.g., alkoxy), the adduct undergoes a conformational change to eclipse palladium and β-hydrogen substituents and syn β-hydride elimination occurs. Similarly, in furanoid glycals the mode of adduct decomposition is determined by the leaving group ability of the $C_{3'}$-oxy substituent; if it is alkoxy, only syn β-hydride elimination is observed; if the substituent is carboxy, only anti palladium carboxylate elimination is observed.

We have developed a palladium-mediated coupling reaction of furanoid[1] and pyranoid[2] glycals, leading to *C*-glycosides,[3] which is direct and efficient. The organometallic chemistry involved is complex, involving four discrete organometallic reactions.[1,2,4-6] In previous reports

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