Transition-Metal-Catalyzed C–C Bond Formation via C–H Activation. Intermolecular Hydroacylation: The Addition of Aldehydes to Alkenes

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Received September 25, 1987

Summary: The indenyl complex $[(\eta^5\text{-}C_9H_7)Rh(\eta^2\text{-}C_2H_4)_2]$ (**1**) is a catalyst for intermolecular hydroacylation, the addition of aldehydes to alkenes. Aldehyde decarbonylation is not a significant process with aromatic aldehydes and **1**. The model system PhCHO + C_2H_4 gives propiophenone cleanly with turnover rates of up to ca. 4 h^{-1} at 100 °C and 1000 psi charge of C_2H_4. Deuterium-labeling studies were conducted by in situ ^2H NMR spectroscopy under catalytic conditions using a specially designed high-pressure NMR tube. Other aldehydes and formates also add to ethylene using **1**.

There has been much recent effort to develop systems that will activate C–H bonds in organic substrates.[1] Many late-transition-metal complexes, particularly rhodium and iridium compounds, oxidatively add aldehyde C–H bonds in processes that lead to substrate decarbonylation.[2] The possibility of adding an aldehyde C–H bond across an alkene (hydroacylation) as a general route to ketones is an intriguing alternative. Although intramolecular hydroacylation has been studied in detail,[3a–g] the intermolecular reaction is not well-precedented.[4a–f] We report herein our discovery[5] that the indenyl complex $[(\eta^5\text{-}C_9H_7)Rh(\eta^2\text{-}C_2H_4)_2]$ (**1**)[6] is an active catalyst (or catalyst precursor) for the intermolecular addition of simple aldehydes to ethylene.

$$R\text{—}C(=O)\text{—}H + C_2H_4 \xrightarrow{1} R\text{—}C(=O)\text{—}C_2H_5 \quad (1)$$

Initial experiments conducted in glass reactors at 80 °C and 80 psi charge of C_2H_4 in C_6D_6 gave slow propiophenone production with **1** as catalyst and PhCHO as substrate (eq 1). No organic side products were observed by high-field FTNMR spectroscopy; however, some catalyst decomposition to bulk Rh was observed. Under increased C_2H_4 pressure (ca. 1000 psi at 25 °C), temperatures around 100 °C can be employed, allowing turnover rates of up to ca. 4 h^{-1} with no observable decomposition to metallic Rh.[7]

Importantly, aldehyde decarbonylation is not a significant side reaction at either ethylene pressure when aromatic aldehydes are used. Several runs, conducted under the above conditions, were monitored by in situ multinuclear FTNMR spectroscopy using a specially fabricated high-pressure sapphire NMR tube.[8] With use of $C_6H_5{}^{13}CHO$ (ca. 90% ^{13}C), only $C_6H_5{}^{13}CHO$ and $C_6H_5{}^{13}C(O)C_2H_5$ were observed by $^{13}C\{^1H\}$ NMR spectroscopy; no resonances due to $Rh^{13}CO$ or dissolved ^{13}CO were detected, consistent with the absence of any significant quantities of decarbonylation products.

In a series of experiments conducted in Hastelloy pressure reactors, several potential catalysts were examined for activity under the above conditions: **1**, $[(\eta^5\text{-}C_5H_5)Rh(\eta^2\text{-}C_2H_4)_2]$ (**2**), $[(acac)Rh(\eta^2\text{-}C_2H_4)_2]$ (**3**),[4d] and $[(PPh_3)_3RuCl_2]$ (**4**).[4c] Only **1** provided propiophenone in significant quantities; **3** and **4** were completely inactive and **2** produced only traces of propiophenone after extensive reaction periods. Other aromatic aldehydes (e.g. *p*-$CF_3C_6H_4CHO$, *p*-$CH_3C_6H_4CHO$) undergo clean hydro-

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‡ Du Pont Contribution No. 4169.

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(7) (a) Bulk Rh is not known to catalyze the reaction described. Reaction vessels that had become plated with Rh (from low-pressure runs) showed no catalytic activity when rinsed with C_6H_6, recharged with solvent, substrate, and C_2H_4, and heated to 100 °C. Results obtained at 1000 psi charge of C_2H_4 suggest that metallic Rh is not responsible for catalysis, and its formation at low C_2H_4 pressure represents catalyst deactivation. (b) For a typical reaction, a solution of **1** (0.36 mmol) and PhCHO (10 mmol, 1.0 mL) in C_6D_6 (2.0 mL) (or an aliquot thereof for *in situ* NMR studies) was placed in the pressure vessel that was then charged with C_2H_4 (1000 psi) and heated to 100 °C. *p*-Dioxane (2 mmol, 170 μL) was used as an internal integration standard for ^1H NMR spectroscopy.

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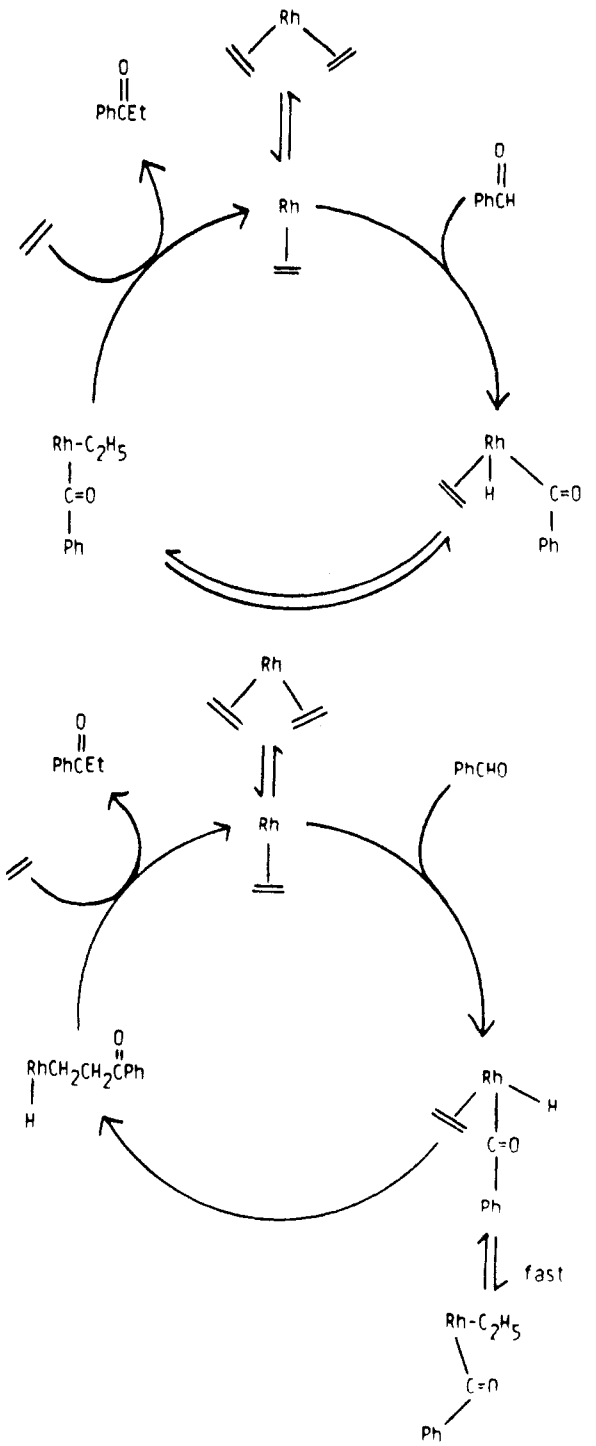

Figure 1. Two possible mechanisms (A, top; B, bottom) for the rhodium-catalyzed intermolecular hydroacylation reaction. The η-indenyl ligand is omitted for clarity.

acylation with ethylene using **1**. Methyl formate adds to ethylene yielding $CH_3O_2CCH_2CH_3$ as the only organic product although this reaction is quite slow with 2–3 turnovers observed in 24 h. Dry formaldehyde also reacts with ethylene in the presence of **1**. Proton and ^{13}C NMR and GC/MS studies (using $(H_2CO)_x$ and $(H_2{}^{13}CO)_x$) indicate that both CH_3CH_2CHO and $CH_3CH_2C(O)CH_2CH_3$ are formed in approximately equal yields within 3 h at 100 °C. Two factors limit the catalytic utility of the formaldehyde reaction: (1) the limited solubility of dry $(H_2CO)_x$ and (2) the deactivation of **1** via formation of [(indenyl)Rh(CO)] compounds as evidenced by ^1H and ^{13}C NMR and solution IR spectroscopy. Interestingly, 4-pentenal does not give cyclopentanone via intramolecular hydroacylation with **1** but rather undergoes rapid alkene isomerization[9] yielding 3-pentenal as the primary reaction product.

The reaction of aldehydes with Rh(I) centers usually proceeds via oxidative addition of the aldehyde C–H bond. Presumably, the hydroacylation reaction involves this C–H addition[2d,3a] followed by insertion of ethylene into the Rh–H bond[4f] and subsequent reductive elimination of the alkyl–acyl groups[4f] (mechanism A). An alternative, mechanism B, involving the C–H addition to Rh followed by ethylene insertion into the Rh–acyl bond[10] and subsequent reductive elimination of the alkyl–hydride groups is also possible.

The reaction of C_6D_5CDO with C_2H_4 in C_6H_6 using **1** as catalyst allowed us to examine certain aspects of the alkene insertion process. Analysis by ^1H, ^2H, and $^{13}C\{^1H\}$ NMR spectroscopy as well as GC/MS, using selected ion monitoring for accurate integrations of MS peak areas, showed that virtually all the propiophenone produced contained exactly one deuterium atom in the ethyl group, statistically scrambled between methyl and methylene sites (eq 2).

$$C_6D_5CDO + C_2H_4 \xrightarrow{1} \underset{3}{C_6D_5C(O)CH_2CH_2D} + \underset{2}{C_6D_5C(O)CHDCH_3} \quad (2)$$

In addition, recovered aldehyde showed little loss of deuterium (GC/MS), and in situ ^2H NMR spectroscopy showed no deuterium incorporation into unreacted ethylene. Therefore, insertion of ethylene into the Rh–D bond must take place rapidly and reversibly, and this equilibrium must be established significantly faster than either aldehyde reductive elimination or product formation. The results suggest that only one ethylene is bound to Rh during C–H(O) activation, consistent with the dissociative mechanisms shown in Figure 1. The labeling study alone does not allow us to distinguish between mechanisms A and B, as a rapid side equilibrium involving ethylene insertion into Rh–H(D) and β-H^-(-D^-) elimination in B would be consistent with our results. However, mechanism B would be expected to result in the formation of α,β-unsaturated ketones (e.g. $CH_2{=}CHC(O)Ph$) via β-hydride elimination from an Rh–$CH_2CH_2C(O)Ph$ species;[11] we do not observe such products.

Further studies aimed at elucidation of the scope and mechanism of the reaction are in progress.

Acknowledgment. We wish to thank B. C. West, M. P. Stepro, and G. F. Diffendall for skilled technical assistance and Prof. William D. Jones (Rochester) for helpful discussions. T.B.M. wishes to thank the Du Pont Co. for a generous donation of materials and supplies and Imperial Oil Ltd. for partial support of our ongoing efforts in this area at the University of Waterloo.

Registry No. **1**, 63428-46-6; **2**, 12211-95-9; **3**, 12082-47-2; **4**, 40237-23-8; C_2H_4, 74-85-1; PhCHO, 100-52-7; $PhC(O)CH_2CH_3$,

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(11) Note the similarity of this process with the recently reported reactions of $[(\eta^6\text{-}C_5R_5)Rh(\eta^2\text{-}C_2H_4)_2]$ (R = H, Me) with $HSiEt_3$ under photochemical conditions. The complexes $[(\eta^5\text{-}C_5R_5)Rh(\eta^2\text{-}C_2H_4)(H)(SiEt_3)]$ (R = H, Me) were observed with Et_4Si and, importantly, $Et_3SiC_2H_3$ as the organic products. The latter product must arise from ethylene insertion into the Rh–Si bond followed by β-H^- elimination. See: Haddleton, D. M.; Perutz, R. *J. Chem. Soc., Chem. Commun.* **1985**, 1372. Benz, P. O.; Ruiz, J.; Mann, B. E.; Spencer, C. M.; Maitlis, P. M. *Ibid.* **1985**, 1374. Belt, S. T.; Haddleton, D. M.; Perutz, R. N.; Smith, B. P. H.; Dixon, A. J. *Ibid.* **1987**, 1347.

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Synthesis and Molecular Structure of the Aluminum–Nitrogen Macrocyclic Cage $[Al(C_2H_5)]_2[C_{10}H_{20}N_4][Al(C_2H_5)Cl_2]_2$: Reaction of Disproportionation Products of the Diethylaluminum Chloride Dimer

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Received January 21, 1988

Summary: Reaction of diethylaluminum chloride with the macrocyclic tetradentate secondary amine 1,4,8,11-tetraazacyclotetradecane in chlorobenzene affords the crystalline complex $[Al(C_2H_5)]_2[C_{10}H_{20}N_4][Al(C_2H_5)Cl_2]_2$. The title compound crystallizes in the monoclinic space group $P2_1/n$ with unit cell parameters a = 11.871 (9) Å, b = 9.052 (7) Å, c = 14.299 (1) Å, β = 115.19 (4)°, and D_{calcd} = 1.31 g cm^{-3} for Z = 2. Least-squares refinement based on 1310 observed reflections with intensities $I \geq 3\sigma(I)$ in the range of 2.00° ≤ 2θ ≤ 50.0° converged at R = 0.0789 (R_w = 0.0949). The mean Al–N distance in the title compound is 1.956 (6) Å while the mean Al–Cl distance is 2.168 (3) Å.

Although the nitrogen-based macrocyclic ligand 1,4,8,11-tetraazacyclotetradecane[1] was reported decades prior to Pedersen's discovery of dibenzo-18-crown-6[2,3] the chemistry of aza macrocycles has not developed in parallel with that of their oxygen analogues. Nonetheless, the interaction of nitrogen-based macrocyclic ligands with transition-metal ions resulting in unusual or unique coordination complexes has been well-documented in the literature.[4-13]

The interaction of aluminum alkyls with macrocyclic ligands has proven to be a particularly fruitful area of organoaluminum chemistry. The reaction of crown ethers with aluminum alkyls has resulted in several $[AlR_3]_n$·CE (CE = crown ether) complexes.[14-16] The significance of these unusual organometallic products is due to the fact that they often serve as precursors to a class of nonstoichiometric organoaluminum inclusion compounds known as liquid clathrates.[17] An examination of the organoaluminum chemistry of nitrogen- and sulfur-based macrocycles represents an interesting extension of this work. We have reported a series of novel aluminum alkyl–nitrogen[18-21] and –sulfur[22,23] macrocyclic complexes. Herein, we report the synthesis[24] and structure of $[Al(C_2H_5)]_2[C_{10}H_{20}N_4][Al(C_2H_5)Cl_2]_2$ isolated from reaction of diethylaluminum chloride with 1,4,8,11-tetraazacyclotetradecane, $C_{10}H_{24}N_4$, in chlorobenzene. In addition to representing the first X-ray structural report of an alkylaluminum halide–macrocyclic amine complex, the title compound is interesting in that it may possibly result from reaction of disproportionation products of diethylaluminum chloride with the macrocycle.

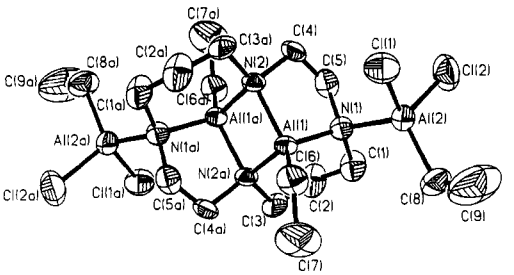

Figure 1. A view of the $[Al(C_2H_5)]_2[C_{10}H_{20}N_4][Al(C_2H_5)Cl_2]_2$ molecule showing the atom-labeling scheme. Thermal ellipsoids show 50% probability levels. Hydrogen atoms have been omitted.

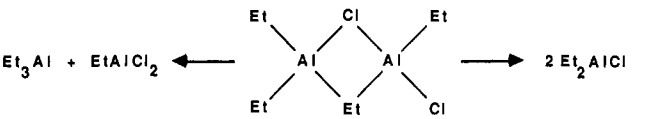

Figure 2. Organoaluminum products resulting from bridge cleavage of the proposed transient mixed alkyl–halo isomer of diethylaluminum chloride.

X-ray intensity data were collected on a Nicolet R3m/V diffractometer using an ω-scan technique with Mo Kα radiation (λ = 0.710 73 Å) at 26 °C. The title compound crystallizes in the monoclinic space group $P2_1/n$ with unit

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(24) Reaction of 1,4,8,11-tetraazacyclotetradecane (2.00 mmol) with diethylaluminum chloride (Aldrich Chemical Co.; purity > 97%) (8.00 mmol) in chlorobenzene (25 mL), under an atmosphere of nitrogen, affords the title compound after considerable heating (120 °C) and subsequent cooling. The system was frequently vented to relieve pressure. Upon cooling to room temperature, a multitude of colorless, rectangular, extremely air-sensitive, X-ray quality crystals deposited on the walls of the reaction vessel (in quantitative yield): mp 245 °C dec; ^{1}H NMR ($CDCl_3$) δ 0.164 (q, 4 H, $Al(CH_2CH_3)$), 0.740 (q, 4 H, $Al(CH_2CH_3)$, 1.192 (t, 6 H, $Al(CH_2CH_3)$), 1.444 (t, 6 H, $Al(CH_2CH_3)$). The resonance for the macrocycle consisted of a complex multiplet, δ 2.720–4.340 (m, 20 H).

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