

(equivalent to $\sim 15 \text{ \AA}$ at full coverage) can be used for electrochemistry. In this situation the electrochemical reactions must be taking place in an environment dominated by the polymer.

To demonstrate that adsorbed layers can be synthetically elaborated, this polypeptide surface was treated with a 1% solution of 3,5-dinitrobenzoyl chloride in acetonitrile, containing 0.5% lutidine. After 1 h at 45 °C the electrode was removed and washed thoroughly by soaking in acetonitrile, methanol, water, and dimethyl sulfoxide. Analysis by x-ray photoelectron spectroscopy (XPS) showed a new N (1s) peak due to the nitro group. Since neither XPS or AES showed a C1 (2p) band after this amidation procedure even though the polylysine surface had a weak band for chlorine before amidation, this indicates a successful reaction. Cyclic voltammetry in Me_2SO produced two reduction peaks on the first scan at $E_p = -0.79$ and -1.23 V. The corresponding anodic peaks were absent. The integrated current corresponds to 1.63×10^{-9} mol/cm² assuming a $2e^-$ reduction. The background current was negligible, but the true n value is, of course, unknown. The peak potentials are consistent with a surface bound 3,5-dinitrobenzamide, but it was expected that the process will be reversible as above. Even when the negative going scan was held to -0.9 V avoiding the second wave, no reversibility was seen at sweep rates up to 5.0 V/s. Thus, when attached to the surface, the dinitrobenzoyl anion radical moiety is quite unstable. It has been found previously that, when this species is attached to metal oxides via silylation, reversibility is seen.¹¹ After a few scans, however, the electroactive surface functionality is also destroyed in this case.

Platinum sheet/polyester electrodes prepared identically with those examined spectroscopically were also used for electrochemistry. We emphasize here the stability and, therefore, the utility of these electrodes for preparative electrochemistry. Steady-state i - E curves were recorded for mM ferrocene in 50% aqueous ethanol, for 0.07 M ferrocene in ethanol, for oxidation of phenyl acetic acid in 3:7 pyridine-methanol, and for hydrogen evolution in 50% ethanol. Using electrodes coated from 0.03% solution, these curves showed that filming decreased the current density at any potential by about 10% compared with plain platinum. After recording the ferrocene curve (10-min oxidation) and after Kolbe electrolysis of phenyl acetic acid at 100 mA/cm² for 30 min, the coated electrodes were rinsed, dried, and reanalyzed by XPS, AES, and CV. These data indicated that the adsorbed polymer was still present. The Kolbe oxidation is an exceptionally rigorous test of film conductance and stability since it shows that high current densities are supported with little added overpotential and that the film is not destroyed under conditions where the electrode is held at a very anodic potential and gas is evolved. We note again that the electrodes are prepared by dipping and there is no polymer added to the electrolysis solution.

There are many points to be fully explored and future publications will demonstrate that a wide variety of metals and polymers give similar results, that interesting electrochemical phenomena are observed and that surface spectroscopy gives some detailed and very useful information about the ultrathin polymer layers.

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References and Notes

- B. F. Watkins, J. R. Behling, E. Kariv, and L. L. Miller, *J. Am. Chem. Soc.*, **97**, 3549 (1975).
- B. E. Firth, L. L. Miller, M. Mitani, T. Rogers, R. Murray, and J. Lennox, *J. Am. Chem. Soc.*, **98**, 8271 (1976).
- J. C. Lennox and R. W. Murray, *J. Am. Chem. Soc.*, **78**, 395 (1977); C. M. Elliot and R. W. Murray, *Anal. Chem.*, **48**, 1247 (1976).
- M. T. Henne, G. P. Royer, J. F. Evans, and T. Kuwana, *J. Electroanal. Chem.*, **80**, 409 (1977).
- M. Fujihira, A. Tamura, and T. Osa, *Chem. Lett.*, 361 (1977).
- P. R. Moses, L. Wier, and R. W. Murray, *Anal. Chem.*, **47**, 1882 (1975).
- P. R. Moses and R. W. Murray, *J. Am. Chem. Soc.*, **98**, 7435 (1976).
- N. R. Armstrong, A. W. C. Lin, M. Fujihira, and T. Kuwana, *Anal. Chem.*, **48**, 741 (1976).
- B. E. Firth and L. L. Miller, *J. Am. Chem. Soc.*, **98**, 8272 (1976).
- M. Fujihira, T. Matsue, and T. Osa, *Chem. Lett.*, 875 (1976).
- J. R. Lenhard and R. W. Murray, *J. Electroanal. Chem.*, **78**, 195 (1977).
- R. J. Burt, G. J. Leigh, and C. J. Pickett, *J. Chem. Soc., Chem. Commun.*, 940 (1976).
- D. F. Untereker et al., *J. Electroanal. Chem.*, **81**, 309 (1977).
- R. F. Lane and A. T. Hubbard, *J. Phys. Chem.*, **77**, 1401, 1411 (1973); **81**, 734 (1977).
- A. P. Brown, C. Koval, and F. C. Anson, *J. Electroanal. Chem.*, **72**, 379 (1977).
- Yu. S. Lipatov and L. M. Sergeeva, "Adsorption of Polymers", Wiley, New York, N.Y., 1974.
- Compound **1** was obtained from Polysciences, Inc., Cat. No. 4301, Lot No. 303-125; **2** was supplied by Professor W. Miller.
- T. A. Carlson, "Photoelectron and Auger Spectroscopy", Plenum Press, New York, N.Y., 1975; D. M. Hercules and J. C. Carver, *Anal. Chem.*, **46**, 133R (1974), and references cited therein.
- This is based upon elemental carbon as an experimental analogue and is widely accepted.²⁰ We note, however, that very much longer escape depths would be calculated using data obtained from oriented fatty acid monolayers.²¹
- C. J. Powell, *Surf. Sci.*, **44**, 29 (1974).
- B. L. Henke, *J. Phys. (Paris) C*, **4**, 115 (1971).

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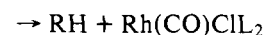
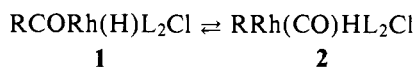
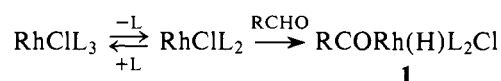
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Isolation of a Stable Acylrhodium(III) Hydride Intermediate Formed during Aldehyde Decarbonylation. Hydroacylation

Sir:

The decarbonylation of aldehydes by $\text{RhCl}(\text{PPh}_3)_3$ has been established as a useful synthetic reaction, appearing in numerous total syntheses of natural products, and is the key step in a method for the stereospecific introduction of angular methyl groups.¹ The mechanism

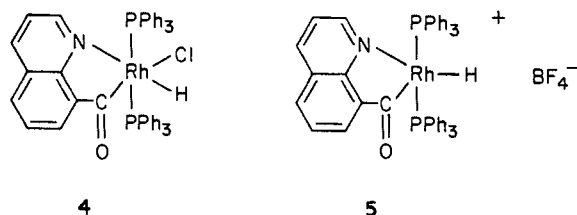


proposed for decarbonylation involves oxidative addition of the aldehyde C-H bond to form a coordinatively unsaturated complex, an acylrhodium(III) hydride (**1**), as an intermediate. This intermediate can then undergo an acyl-alkyl rearrangement, and subsequent hydrogen transfer to the alkyl group forms *trans*- $\text{Rh}(\text{CO})\text{Cl}(\text{PPh}_3)_2$ and hydrocarbon.² The principal support for this proposal comes from studies on the decarbonylation of acid chlorides by $\text{RhCl}(\text{PPh}_3)_3$, in which intermediates analogous to **1** and **2** can be isolated.³ However, prior to this work, no intermediates have been isolated from $\text{RhCl}(\text{PPh}_3)_3$ -promoted aldehyde decarbonylation reactions.⁴

The cleavage of a carbon-hydrogen bond, as in the formation of **1**, occurs often in organometallic reactions. In some cases (e.g., PtCl_2 catalyzed hydrogen-deuterium exchange)⁵ carbon-metal bonded species are transient intermediates, while, in others, where a coordinating group is available to form a five-membered chelate (the cyclometalation reaction),⁶ ex-

ceptionally stable complexes containing a carbon-metal σ bond can be isolated. We expected that an aldehyde containing a coordinating group could form an isolable complex corresponding to **1** since the extra ligand would give a coordinatively saturated, 18-electron complex, retarding acyl to alkyl rearrangement. Chelation would also disfavor reductive elimination to return the starting aldehyde.⁷

A readily available aldehyde able to form a chelate is 8-quinolinecarboxaldehyde (**3**).⁸ Addition of **3** to a saturated solution of $\text{RhCl}(\text{PPh}_3)_3$ in CH_2Cl_2 gave a yellow precipitate after 10 min. One recrystallization from CH_2Cl_2 -ether gave the acylrhodium(III) hydride **4** in 95% yield.⁹ The low value



of the Rh-Cl stretching frequency (230 cm^{-1}) implies that the chlorine is trans to the acyl group,¹⁰ leading to the stereochemistry shown. The acyl hydride **4** is the first stable intermediate to be isolated from a $\text{RhCl}(\text{PPh}_3)_3$ promoted aldehyde decarbonylation reaction and provides support for the mechanism given above. Differential thermal analysis of **4** showed it to be stable up to its melting point of $175\text{--}176\text{ }^\circ\text{C}$. Heating **4** in benzene at reflux for several hours caused no decomposition. Only after 4 h in xylene at reflux was reductive elimination completed, giving quantitative yields of quinoline and *trans*- $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$. Addition of excess triphenylphosphine slowed this decomposition.

Treatment of **4** with AgBF_4 in toluene- CH_2Cl_2 at $0\text{ }^\circ\text{C}$ gave rise to the coordinatively unsaturated **5** (as the CH_2Cl_2 solvate), isolated in quantitative yield as hygroscopic yellow needles after one recrystallization from CH_2Cl_2 -ether.¹¹ This salt is stable indefinitely at room temperature, even though a vacant (solvent occupied) site is available in **5** to facilitate the acyl to alkyl rearrangement.¹² Decarbonylation at room temperature does not occur, presumably because the intermediate alkyl would be part of a strained, four-membered-ring chelate. As with **4** decarbonylation occurs at elevated temperatures.

Earlier work has suggested acylrhodium(III) hydrides react with olefins, in effect adding an aldehyde C-H bond across an olefin to form a ketone.¹³ For example, the reaction of 4-pentenal with $\text{RhCl}(\text{PPh}_3)_3$ gave cyclopentanone. This process, by analogy to the hydroformylation reaction, has been termed hydroacylation.¹⁴ With the isolation of **5** we can confirm the suggestion that acylrhodium(III) hydrides are reagents for the hydroacylation of terminal olefins. Treatment of a THF suspension of **5** with excess 1-octene and 8-quinolinecarboxaldehyde at $50\text{ }^\circ\text{C}$ gave, after 30 min, a 55% yield (based on **5**) of 8-quinolinyl *n*-octyl ketone. Reaction with the coordinatively saturated **4** gave no hydroacylation product under these conditions. None of the branched-chain ketone was detected. The unreacted hydrocarbon consisted of a mixture of octenes, in which the 3- and 4-octenes predominated. The nature of the rhodium species remaining is under investigation. No Rh-H bonds remain, as determined by IR spectroscopy.

Further work is in progress on the stabilization of other acylrhodium(III) hydrides and the development of systems for catalytic hydroacylation.

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References and Notes

- J. Tsuji and K. Ohno, *Synthesis*, **1**, 157 (1967); B. M. Trost and M. Preckel, *J. Am. Chem. Soc.*, **95**, 7862 (1973); P. D. Hobbs and P. D. Magnus, *J. Chem. Soc., Chem. Commun.*, 856 (1974); D. J. Dawson and R. E. Ireland, *Tetrahedron Lett.*, 1899 (1968).
- M. C. Baird, C. J. Nyman, and G. Wilkinson, *J. Chem. Soc. A*, 348 (1968); H. M. Walborsky and L. E. Allen, *J. Am. Chem. Soc.*, **92**, 5465 (1971); J. Tsuji in "Organic Synthesis via Metal Carbonyls", Vol. 2, I. Wender and P. Pino, Ed., Wiley, New York, N.Y., 1977, pp 595-654.
- J. K. Stille and M. T. Regan, *J. Am. Chem. Soc.*, **96**, 1508 (1974); J. K. Stille and R. W. Fries, *ibid.*, **96**, 1518 (1974); D. L. Egglestone, M. C. Baird, C. J. Lock, and G. Turner, *J. Chem. Soc., Dalton Trans.*, 1576 (1977).
- A. M. Abeysekera, R. Grigg, J. Trocha-Grimshaw, and V. Viswanatha, *J. Chem. Soc., Perkin Trans. 1*, 1395 (1977), recently reported the first acylrhodium(III) complexes isolated from the reaction of a rhodium(I) complex with aldehydes.
- C. Masters, *J. Chem. Soc., Chem. Commun.*, 1258 (1972); R. J. Hodges, D. E. Webster and P. B. Wells, *Chem. Commun.*, 462 (1971).
- M. I. Bruce, *Angew. Chem., Int. Ed. Engl.*, **16**, 73 (1977); G. W. Parshall, *Acc. Chem. Res.*, **8**, 113 (1975).
- We propose the term chelate trapping to describe this strategy of attaching a coordinating group to the organic substrate near the site at which reaction occurs to stabilize by chelation an otherwise labile transition metal complex.
- V. M. Rodionov and M. A. Berkengeim, *J. Gen. Chem. USSR*, **14**, 330 (1944); *Chem. Abstr.*, **39**, 4076 (1945).
- Anal. Calcd for $\text{C}_{46}\text{H}_{37}\text{ClINOP}_2\text{Rh}$: C, 67.37; H, 4.54; N, 1.71. Found: C, 67.03; H, 4.65; N, 1.65. IR (CH_2Cl_2): 2020, 1660 cm^{-1} . $^1\text{H NMR}$ (90 MHz) (CDCl_3): δ 8.85 (1 H, d, $J = 5\text{ Hz}$, α -H on quinoline ring), -11.93 (1 H, overlapping d of t, $J_{\text{P-H}} = 6$, $J_{\text{Rh-H}} = 15\text{ Hz}$).
- J. W. Dart, M. K. Lloyd, R. Mason, and J. A. McCleverty, *J. Chem. Soc., Dalton Trans.*, 2039 (1973).
- Anal. Calcd for $\text{C}_{47}\text{H}_{39}\text{BCl}_2\text{F}_4\text{NOP}_2\text{Rh}$: C, 59.02; H, 4.11; N, 1.46. Found: C, 59.08; H, 3.98; N, 1.33. IR (CH_2Cl_2): 2020, 1724, 1689, 1065 (cm^{-1}). $^1\text{H NMR}$ (90 MHz) (CD_2Cl_2): δ 8.94 (1 H, d, $J = 5\text{ Hz}$), 5.33 (2 H, s), -10.70 (1 H, d of t, $J_{\text{P-H}} = 6$, $J_{\text{Rh-H}} = 20\text{ Hz}$). Of the two bands in the acyl region, the 1689- cm^{-1} one may be a quinoline band; however, see ref 4 for other instances of acyl groups in acylrhodium(III) complexes appearing as doublets.
- A. Wojcicki, *Adv. Organomet. Chem.*, **11**, 87-145 (1973).
- K. Sakai, J. Ide, O. Oda, and N. Nakamura, *Tetrahedron Lett.*, 1287 (1972); K. Sakai and O. Oda, *ibid.*, 4375 (1972); C. F. Lochow and R. G. Miller, *J. Am. Chem. Soc.*, **98**, 1281 (1976).
- P. Pino, F. Piacenti, and M. Bianchi in "Organic Synthesis via Metal Carbonyls", Vol. 2, I. Wender and P. Pino Ed., Wiley, New York, N.Y., 1977, pp 215-228; J. Schwartz and J. B. Cannon, *J. Am. Chem. Soc.*, **96**, 4721 (1974).

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A Priori Calculations on Isotopic Exchange Equilibria

Sir:

According to molecular orbital theory, the lowest lying acceptor orbital of a methyl group is CH antibonding.¹ It follows, therefore, that transfer of electron density into the group will lead to a weakening of its CH linkages. A like result derives from resonance arguments, $\text{H}_3\text{C-X}^- \leftrightarrow \text{H}_2\text{C(H}^-)=\text{X} \leftrightarrow \text{etc.}$, and has been aptly termed "negative hyperconjugation".² The observation of significant β -deuterium isotope effects for the gas phase ion-molecule equilibria (1-3 in Table I) has recently been cited as evidence for such an effect.³ We now present theoretical results based on ab initio molecular orbital calculations which further support such an interpretation.

Equilibrium geometries and quadratic force constants, molecular parameters which, within the Born-Oppenheimer approximation, are invariant to isotopic substitution, have been evaluated with the split-valence-shell 4-31G basis representation^{4,5} for the species in reactions 1 and 2.⁶ Theoretical equilibrium constants (K_{theory}) for equilibria 1 and 2 have been calculated,⁷ and are presented in Table I, along with the corresponding experimental quantities (K_{expt}). Also tabulated are the contributions made by the C-H bond stretching motions alone (K_{stretch}) to the total calculated equilibrium constants, obtained by the perturbation theory method of Singh and Wolfsberg.⁸ (In this approach, the zeroth-order vibrational problem corresponds to uncoupled bond stretches and bond