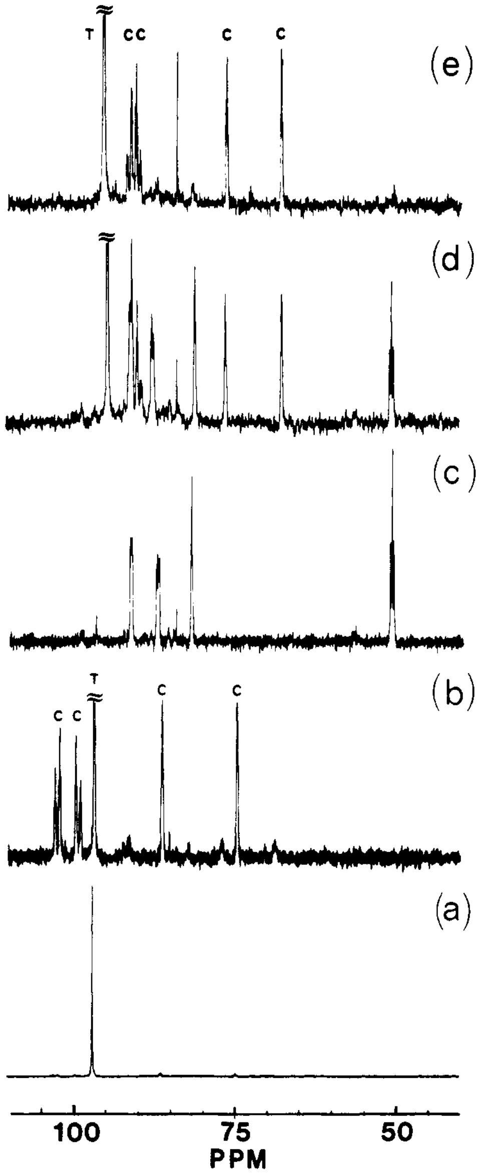

Figure 1. ^{31}P NMR spectra (162.0 MHz; proton decoupled). (a) *trans*-FeH(DEPE)$_2$Me (3) 228 K in toluene-d_8. (b) Mixture of *cis*- and *trans*-FeH(DEPE)$_2$Me obtained by warming the sample in Figure 1a to 240 K (toluene-d_8). Resonances of 3 labeled T, and resonances of 4 labeled C. (c) Spectrum of 5 (298 K· THF-d_8 solution). (d) Equilibrium mixture of 5, 6, and 7 (330 K; benzene). (e) Equilibrium mixture of 5, 6, and 7 (300 K; benzene). Resonances of 6 labeled C, and resonances of 7 labeled T.

termolecularly with a suitably "electron-rich" arene. The equilibrium, 1 $\rightleftarrows$ 5 is analogous to that proposed[16] to rationalise the reactions and infrared spectrum of Ru(DMPE)$_2$ [DMPE = 1,2-*bis*(diethylphosphino)ethane]. In the series of iron complexes described above, the close stability of **5**, **6**, and **7** balances the equilibrium so that all three complexes exist at comparable concentrations in the equilibrium mixture.

5 reacts intermolecularly with C–H bonds in naphthalene, toluene, and other organic compounds to yield alkyl and aryl iron hydrides in a manner similar to that reported[15] for the coordinatively unsaturated species Fe(DMPE)$_2$ generated from FeH(DMPE)$_2$Np [Np = 2-naphthyl].

Acknowledgment. We gratefully acknowledge financial support from the Australian Research Grants Scheme and the Australian Government for a Commonwealth Postgraduate Award (M.V.B.).

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A Catalytic Procedure for the Preparation of Carbonyl-Labeled Acyl Chlorides: More Mechanistic Insights into Decarbonylation Reactions Promoted by Rhodium(I) Complexes

J. A. Kampmeier,* S. Mahalingam, and Tong-Zhou Liu

Department of Chemistry, University of Rochester
Rochester, New York 14627

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Summary: The reaction of RhCl(CO)(PPh$_3$)$_2$ with aliphatic acid chlorides in the presence of free ^{13}CO in CDCl$_3$ or C$_6$D$_6$ at 110 °C leads to catalytic incorporation of ^{13}CO. In this manner, carbonyl-labeled acetyl, phenylacetyl, butanoyl, octanoyl, 2-methylpropanoyl, 2-phenylpropanoyl, cyclopentanecarboxylic acid, and cyclohexanecarboxylic acid chlorides were prepared. Decarbonylation products, alkyl chloride or olefin, are not formed in significant yields and are not intermediates in the labeling process. Reductive elimination of alkyl chloride and β-hydrogen elimination of olefin from the intermediate organometallic complexes are slower, therefore, than the equilibration processes and reductive elimination of acid chloride that lead to CO exchange.

In previous publications we provided evidence for an interlocking set of organometallic intermediates in the reaction of RhCl(CO)(PPh$_3$)$_2$ (1) with aromatic acid chlorides at temperatures of the order of 100 °C (Scheme I).[1] The net equilibration, ArCOCl + RhCl(CO)(PPh$_3$)$_2$ $\rightleftharpoons$ 2CO + RhCl$_2$(Ar)(PPh$_3$)$_2$, provides a catalytic route to carbonyl-labeled aromatic acid chlorides by exchange with added ^{13}CO or with other carbonyl-labeled acid chlorides.[2] The reactions of the organometallic intermediates that lead to exchange must be faster than the formation of aryl chlorides from these intermediates, since aryl chlorides are not formed under the conditions of the equilibration.[2] It seemed clear from literature reports that the rate of formation of alkyl chlorides or olefins (by β-hydrogen elimination) is greater than the rate of formation of aryl chlorides in these systems.[3] Therefore, it was not obvious

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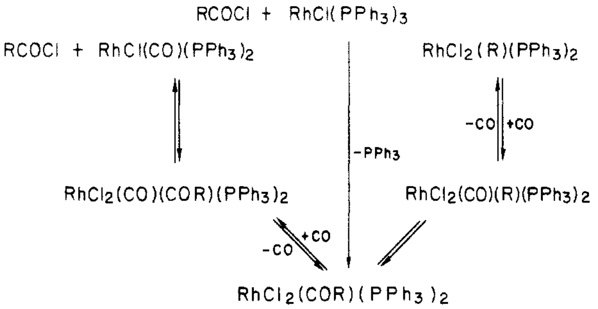
(1) Kampmeier, J. A.; Rodehorst, R. M.; Philip, J. B., Jr. *J. Am. Chem. Soc.* **1981**, *103*, 1847–1849.

(2) Kampmeier, J. A.; Mahalingam, S. *Organometallics* **1984**, *3*, 489–491. It is important to emphasize that the equilibration proceeds in both the presence and the absence of added ^{13}CO. Aryl chloride is not formed in either case.[1] Added ^{13}CO, therefore, simply serves to reveal the equilibration reactions.

Scheme I



R = aryl, vinyl, alkyl (primary and secondary), benzyl

that the equilibration reactions could compete with product formation in the aliphatic series. We now report[4] that the equilibration reactions of a variety of aliphatic acid chlorides are also faster than the formation of decarbonylation products. As a result, these acid chlorides can be conveniently labeled by reaction with 1 in the presence of ^{13}CO.

In a typical experiment, cyclohexanecarboxylic acid chloride (0.44 mmol) was charged to a reaction tube with 1 (0.032 mmol) in 1 mL of $CDCl_3$. The tube was degassed and ^{13}CO (99%) admitted to the void space (ca. 10 mL).[5] The tube was sealed, heated at 110 °C for 24 h, and opened, and the reaction mixture was analyzed by both ^{1}H and ^{13}C NMR. The ^{1}H spectrum corresponded to that of cyclohexanecarboxylic acid chloride contaminated by about 2% cyclohexene product and traces of unknown peaks; no absorption due to cyclohexyl chloride could be discerned. The methine region was more complicated than that of starting material; the pattern was analyzed as the original triplet of triplets ($^3J_{HH}$ = 12, 3.5 Hz) superimposed on the more complex pattern of $CH^{13}COCl$ molecules ($|^2J|$ = 7.0 Hz)[6]. The ^{13}C spectrum showed the methine carbon as a singlet at δ 55.1 ($^{13}CH^{12}COCl$) with a satellite doublet for the labeled compound ($^{13}CH^{13}COCl$, ^1J = 52.8 Hz).[7,8] Simple integration of the singlet to the doublet areas showed there to be 51% label (6.9 turnovers) in the carbonyl position. Finally, the carbonyl peak (δ 176.7) was many times more intense than any other peak in the spectrum, providing qualitative evidence of labeling.[9]

These standard procedures were used to study and demonstrate the labeling of acetyl and phenylacetyl chlorides (compounds without β-hydrogens) and butanoyl, 2-methylpropanoyl, and 2-phenylpropanoyl chlorides (compounds with β-hydrogens). The results are presented in Table I. With the exception of the two benzylic substrates (vide infra), the other acid chlorides were successfully labeled under our standard conditions with less than 8% formation of decarbonylation products.[10] The procedure failed with 2,2-dimethylpropanoyl chloride; there was no evidence of any reaction.[11] In a different set of experiments at a different $^{13}CO/RCOCl$ ratio,[2,4] cyclopentanecarboxylic acid chloride was labeled. The organic phase was isolated by bulb-to-bulb distillation at reduced pressure and hydrolyzed to give labeled cyclopentanecarboxylic acid in 43% isolated yield, ef = 20%.[12] In similar manner, acetyl, phenylacetyl, octanoyl, and cyclohexanecarboxylic acid chlorides were also converted to isolated labeled acids.[2,4]

Table I. Reactions of RCOCl with 1 in the Presence of ^{13}CO[a]

R	% $R^{13}COCl$[b] (turnovers)	$R^{13}COCl$ chem shift[c] ($^1J_{C-COCl}$; $\lvert ^2J_{H-C-COCl}\rvert$)	other products
CH_3	55 (7.8)	169.9 (55.6; 7.2)	6% CH_3Cl
cyclohexyl	51 (6.9)	176.8 (52.8; 7.0)	2% cyclohexene
$PhCH_2$	52	171.7 (52.1; 8.1)	81% $PhCH_2Cl$
$Ph(CH_3)CH$	53	175.1 (48.8; ...)[d]	65% $Ph(CH_3)CHCl$ 9% styrene
$Ph(CH_3)$-CH[e]	47		13% $Ph(CH_3)CHCl$
n-C_3H_7[f]	40 (12)	178.3 (51.3; ...)	1% i-C_3H_7COCl
i-C_3H_7	31 (4.2)	173.5 (55.8; ...)	3% n-C_3H_7COCl 2% propene
n-C_3H_7[g]	18 (2.9)		1% i-C_3H_7COCl
i-C_3H_7[h]	17 (0.9)		3% n-C_3H_7COCl 8% propene

[a] Standard reaction conditions: 0.5 mmol of RCOCl, 0.03 mmol of 1, 1 mL of $CDCl_3$, 0.2–0.5 mmol of ^{13}CO, sealed tube, 110 °C, 24 h; see the text. [b] % $R^{13}COCl$ = $[R^{13}COCl]/([R^{12}COCl] + [R^{13}COCl])$ turnovers = mmol of $R^{13}COCl$/mmol of 1. [c] High-field ^{1}H (300.15 MHz) and ^{13}C (75.48 MHz) NMR spectra were recorded on a Nicolet QE-300 FT NMR NMR spectrometer; chemical shifts are reported in units of δ (ppm downfield from tetramethylsilane) and were measured relative to residual ^{1}H resonances in the deuterated solvents, $CDCl_3$ (δ 7.27) or C_6D_6 (δ 7.37); coupling constants J in Hz. [d] $^3J_{H-C-C-COCl}$ = 6.7 Hz. [e] Doped with 1.2 equiv of $PhCH_2Cl$; experiment run in C_6D_6. [f] 62-h reaction time. [g] Doped with 2.2 equiv of $(CH_3)_2CHCl$. [h] Doped with 0.6 equiv of $CH_3CH_2CH_2Cl$.

One has the general impression that β-hydrogen elimination is an easy process. For example, when the acid chloride has β-hydrogens the major decarbonylation product is olefin rather than alkyl chloride.[3] There is also evidence that the stereochemistry and regiochemistry of alkylrhodium complexes can be scrambled by elimination and readdition of rhodium hydride.[13] Even though olefins are not formed in significant amounts under our reaction conditions, we considered the possibility of a fast pre-

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[3] For a recent review of this decarbonylation chemistry, see: Doughty, D. H.; Pignolet, L. H. In "Homogeneous Catalysis with Metal Phosphine Complexes"; Pignolet, L. H. Ed.; Plenum Press: New York, 1983; pp 343–375. See also: Baird, M. C. In "The Chemistry of Acid Derivatives"; Patai, S. Ed.; Wiley: New York, 1979; Supplement B, part 2, pp 825–857.

[4] Part of this work was reported earlier: Kampmeier, J. A.; Mahalingam, S. 187th National Meeting of the American Chemical Society, St. Louis, MO, April 1984; American Chemical Society: Washington, D. C., 1984; Abstract ORGN-41.

[5] The amount of ^{13}CO in the reaction tube was 0.2–0.5 mmol, depending on the pressure of ^{13}CO in the reservoir.

[6] ^2J = −6.7 Hz (carbonyl to α-proton) for cyclohexanecarboxylic acid. Marshall, J. L.; Seiwell, R. *Org. Magn. Reson.* **1976**, *8*, 419–425.

[7] ^1J = 55.7 Hz (carbonyl to α-carbon) for cyclohexanecarboxylic acid. Marshall, J. L.; Miller, D. E. *J. Am. Chem. Soc.* **1973**, *95*, 8305–8308.

[8] In addition, the γ methylene carbon at δ 25.1 also showed satellite doublet absorptions ($^{13}CH_2CH_2CH^{13}COCl$), ^3J = 3.8 Hz. For cyclohexanecarboxylic acid, ^2J = 0 (carbonyl to β-carbon) and ^3J = 4 Hz (carbonyl to γ-carbon), see ref 7.

[9] In some other experiments, the incorporation of the label was measured by quantitative integration of carbonyl absorption with respect to the natural abundance carbons in the ^{13}C NMR spectra in the presence of added $Cr(acac)_3$ (ca. 0.05 M), 10-s delay between observing pulses, decoupler on during acquisition; see: Schoolery, J. N. *Prog. NMR Spectrosc.* **1977**, *11*, 79–93.

[10] It is important to recognize that the yields of decarbonylation products in these experiments depend on the structure of the acid chloride but not on ^{13}CO pressure. For example, the first four experiments in Table I are all done at essentially the same ^{13}CO pressure; the experiments give comparable incorporation of ^{13}CO but different product distributions. The clear variable is the structure of RCOCl, not ^{13}CO pressure. In addition, the reaction of 2-methylpropanoyl chloride with 1 under our standard conditions, but without added ^{13}CO for 72 h, showed no evidence for product formation or rearrangement. Formation of propene (2%) or rearrangement to n-butanoyl chloride (3%) would have been detected by NMR.

[11] Labeling (4%) or decarbonylation (1%) would have been easily detected by NMR.

[12] The enrichment factor, ef, was obtained from mass spectrum of the isolated acid:[2] ef = $10^2\,(m^+ + 1)/[(m^+ + 1)\,m^+]$.

[13] (a) Stille, J. K.; Lau, K. S. Y.; Becker, Y.; Huang, F.; Baenziger, N. *J. Am. Chem. Soc.* **1977**, *99*, 5664–5672. (b) Dunham, N. A.; Baird, M. C. *J. Chem. Soc., Dalton Trans.* **1975**, 774–779.

equilibrium between (alkyl)Rh and (olefin)Rh complexes, followed by slow labeling. If so, butanoyl and 2-methylpropanoyl chlorides should equilibrate because they would both decarbonylate to the same intermediate (propene)Rh complex. In fact, both acid chlorides were labeled with >97% retention of initial structure. In another experiment, 2,2-dideuteriopropanoyl chloride (90% d_2) was prepared[14] and reacted at 110 °C in toluene for 24 h. Sodium propionate was isolated after bulb-to-bulb separation and hydrolysis of the organic phase. Sodium propionate was also prepared from the starting acid chloride before carbonyl labeling. A comparison of the carbonyl to methyl intensities in the ^{13}C NMR spectra before and after labeling clearly demonstrated the incorporation of ^{13}CO at the carbonyl position. The ^{2}H NMR spectra showed peaks at δ 2.9 (–CD$_2$–) in both samples, but no peak at δ 1.3 (–CHD$_2$) in either. Finally, the CH$_3$/CH$_2$ ratio in the ^{1}H NMR spectra before (14) and after (13) labeling showed little change. Thus, from both experiments, it is clear that the observed labeling is not preceded by fast, reversible β-hydrogen elimination.

The incorporation of ^{13}CO is not preceded by reversible reductive elimination of alkyl chlorides either. 2-Phenylpropanoyl chloride was doped with 1.2 equiv of benzyl chloride and subjected to the labeling conditions. At the end of the reaction, 2-phenylpropanoyl chloride was labeled but phenylacetyl chloride could not be detected.[15] In a pair of experiments, butanoyl and 2-methylpropanoyl chlorides were doped with the opposite alkyl chlorides and then subjected to the labeling conditions. Although the starting acid chlorides were labeled in each case, <3% of the opposite acid chlorides were formed; i.e., no more than were formed in the absence of added alkyl chlorides.

The reactions of benzylic substrates are particularly interesting because only they give significant yields of decarbonylation products under our labeling conditions. 2-Phenylpropanoyl chloride reacted to give labeled acid chloride (26%), styrene (9%), and 1-phenylethyl chloride (65%, 8.1 turnovers). The reaction with phenylacetyl chloride proceeded similarly to give labeled acid chloride (19%) and benzyl chloride (81%, 12 turnovers). Reactions of phenylacetyl chloride in CDCl$_3$ and in C$_6$D$_6$ were followed at 0.5-h intervals by ^{1}H NMR. In both solvents, the incorporation of ^{13}CO (corresponding to the satellite doublet to the –CH$_2$– singlet, $|{}^2J_{HCC}| = 8.1$ Hz) is substantially faster than the formation of benzyl chloride. There is an interesting solvent effect on the rate of product formation: after 3 h, labeling was >90% complete in both solvents while conversion to benzyl chloride was 26% in CDCl$_3$ and only 6% in C$_6$D$_6$.

In summary, **1** catalyzes the incorporation of ^{13}CO into a wide variety of acid chlorides. The reaction is useful and convenient for the preparation of carbonyl-labeled aromatic,[2] vinylic,[2] benzylic, and primary or secondary aliphatic acid chlorides. Although free CO is clearly involved in the labeling, the CO exchange does not proceed by decarbonylation–recarbonylation sequences involving aryl and alkyl chlorides or olefin (whether free or complexed). The incorporation of ^{13}CO, therefore, proceeds by equilibration of organometallic intermediates as described in Scheme I. The important mechanistic conclusion from this work is that the kinetically preferred paths for the organometallic intermediates in these reactions of aliphatic and benzylic acid chlorides are the equilibration processes and the reductive elimination to give acid chlorides and RhCl(CO)(PPh$_3$)$_2$ (**1**).[16] The system is best thought of as a set of organorhodium(III) intermediates in fairly ready equilibrium. The system can be entered by reactions of acid chlorides with either **1** or RhCl(PPh$_3$)$_3$ and departed by reductive elimination to give acid chloride and **1** or by decarbonylation reactions to give alkyl chloride or olefin. *The barriers to the formation of decarbonylation products vary with the structure of the acid chlorides but are clearly greater than the barriers to reductive elimination of acid chlorides in all cases we have studied.* We are continuing to study the detailed nature of the decarbonylation product forming steps in these systems.[17]

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work and to Grant #IN-18 from the American Cancer Society. We are grateful to Johnson Matthey, Inc., for a generous loan of RhCl$_3$·xH$_2$O. T.Z.L. is grateful to the University of Rochester for Sherman Clarke and E. H. Hooker Fellowships.

Registry No. 1, 13938-94-8; CH$_3$COCl, 75-36-5; c-C$_6$H$_{11}$COCl, 2719-27-9; PhCH$_2$COCl, 103-80-0; i-C$_3$H$_7$COCl, 79-30-1; PhCH$_2$Cl, 100-44-7; Ph(CH$_3$)CHCl, 672-65-1; ^{13}CO, 1641-69-6; Ph(CH$_3$)-CHCOCl, 22414-26-2; c-C$_5$H$_9$COCl, 4524-93-0; n-C$_3$H$_7$COCl, 141-75-3; CH$_3$^{13}COCl, 1520-57-6; c-C$_6$H$_{111}$^{13}CoCl, 100899-34-1; PhCH$_2$^{13}COCl, 63583-47-1; Ph(CH$_3$)CH^{13}COCl, 100899-35-2; c-C$_5$H$_9$^{13}Co$_2$H, 50530-15-9; n-C$_3$H$_7$^{13}COCl, 100899-36-3; i-C$_3$H$_7$-^{13}COCl, 71010-19-0.

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(14) Atkinson, J. G.; Crakvary, J. J.; Herbert, G. T.; Stuart, R. S. *J. Am. Chem. Soc.* **1968**, *90*, 498–499.

(15) Formation of 1% of phenylacetyl chloride would have been detected by ^{1}H NMR.

(16) These equilibrations proceed in both the presence and absence of added ^{13}CO. For example, PhCOCl and CH$_3$^{14}COCl exchange CO in the presence of **1**, without formation of CH$_3$Cl.[2] Stille observed chlorine isotope scrambling in reactions of RhCl(PPh$_3$)$_3$ with several acid chlorides;[13] this chlorine exchange is a direct consequence of the equilibrations summarized in Scheme I and provides further evidence of the equilibration reactions in the absence of added CO. The added ^{13}CO, therefore, simply serves to mark the equilibrations of the intermediates.

(17) Kampmeier, J. A.; Harris, S. H.; Rodehorst, R. M. *J. Am. Chem. Soc.* 1981, *103*, 1478–1485.

False Impressions from ^{27}Al NMR Spectroscopy

R. Benn,* A. Rufińska, E. Janssen, and H. Lehmkuhl
Max-Planck-Institut für Kohlenforschung
D-4330 Mülheim a.d. Ruhr, West Germany

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Summary: The $\delta(^{27}\mathrm{Al})$ values of dissolved organometallic compounds of the type $[\mathrm{Et_2\overline{AlOCH_2CR_2X}}]_2$ (R = H, X = OMe, **1**; R = H, X = NEt$_2$, **2**; CR$_2$X = 2-H$_4$C$_5$N, **3**) with five-coordinate Al atoms show no significant temperature dependence in the ranges from 310 down to 223, 253, and 243 K, respectively. Different observations for **3**[1] were caused by background signals, and thus conclusions from ^{27}Al NMR spectra invoking an equilibrium between complexes with four- and five-coordinate Al atoms in this temperature range are incorrect.

We have recently shown that there is a correlation between the coordination number of the aluminum atom and the ^{27}Al NMR chemical shift in organoaluminum compounds of the type (R$_2$AlY)$_n$ (Y = R, OR, NR$_2$, H, and halogen).[2] At 310 K the ^{27}Al NMR shifts of the com-

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