Table I. Typical High-Resolution ^{207}Pb Nmr Data[a]

Compound	Solvent (molar concn)	Line width, Hz	Chemical shift,[b] ppm	T_1, sec
$Pb(CH_3)_4$	Toulene (3.7)	2	0	0.6
$Pb(C_2H_5)_4$	Neat	6	70.6	1.2
$Pb_2(C_6H_5)_6$	Carbon disulfide 87% (0.2) benzene 17%	4	−73.2	
$Pb(CH_3)_3OCOCH_3$	Acetic acid (0.8)	6	408.1	
$Pb(C_2H_5)_3OCOCH_3$	Acetic acid (2.0)	8	412.0	
$Pb(n\text{-}C_3H_7)_3OCOCH_3$	Acetic acid (1.0)	12	428.8	
$Pb(n\text{-}C_4H_9)_3OCOCH_3$	Acetic acid (2.0)	12	424.0	
$Pb(i\text{-}C_4H_9)_3OCOCH_3$	Acetic acid (2.0)	9 (320°) 5 (270°)	432.0	0.08 (270°)
$Pb(C_6H_5)_3C_2H_5$	Carbon tetrachloride (0.5)	11	−114.5	
$Pb(OCOCH_3)_2$	Water (1.1)	100	−1337.0	
$Pb(OCOCH_3)_2$	Acetic acid (2.1)	100	−1519.0	
$Pb(NO_3)_2$	Water (1.0)	12	−2961.2	1.1

[a] Results obtained at 304 ± 4°K, unless otherwise indicated. [b] Chemical shifts given with respect to 3.7 *M* $Pb(CH_3)_4$; higher values correspond to lower shielding.

nuclei, $I = 1/2$),[1-9] mainly by wide-line or INDOR methods, there are no previous reports of the application of modern, high-resolution, on-line pulse Fourier transform approaches to this nuclide.

Spectra were obtained in natural abundance at 18.83 MHz, using a Bruker HFX-90 spectrometer and Digilab FTS/NMR-3 data system and 400-S pulser. Details of the spectrometer configuration that permits observation of the nmr spectra of ^{207}Pb and many other nuclides will be presented elsewhere.

Table I summarizes some of the chemical shifts that have been determined by this technique. The data show that even rather minor structural variations give rise to large chemical shifts, which shows the great structural selectivity that ^{207}Pb offers for chemical studies. Considered together with the very large structural sensitivity of ^{207}Pb chemical shifts from the earlier wide-line and INDOR work on ^{207}Pb,[1-7] these data demonstrate the promise of ^{207}Pb chemical shift measurements for studies of structure and dynamics in lead compounds and for analytical applications. In addition, very large effects of solvent and temperature variation (about 0.5 ppm decrease in shielding per degree increase in temperature for 2 *M* triisobutyllead acetate in acetic acid) on the ^{207}Pb chemical shifts of the acetates have been observed in this work, implying that significant changes in species identity and/or environment accompany such variations. Systematic studies of these phenomena should elucidate the detailed nature of structural alterations and the dynamics and thermodynamics of complexation equilibria in these and other systems.

Spin–lattice relaxation times have been determined by a $180°\text{–}\tau\text{–}90°$ method for some of the samples indicated in Table I. These T_1 values range typically from about 0.1 to 2 sec. These values are remarkably short, in view of the generally larger T_1's for ^{13}C and ^{29}Si, especially the latter, in analogous compounds.[10,11] With no possibility of quadrupole relaxation mechanisms, this implies substantial contributions to spin–lattice relaxation from mechanisms such as chemical exchange, chemical shift anisotropy, and spin rotation. It should be emphasized that the T_1 values reported here are properties of *typical samples*, not scrupulously purified materials. Hence, they are representative of the parameters one encounters in optimizing experimental procedures, but are not necessarily characteristic of the intrinsic properties of the indicated species.

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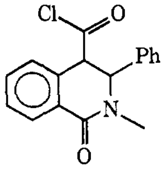
Alkylation of Acid Halides by Alkylrhodium(I) Complexes

Sir:

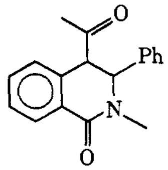
As part of our studies directed toward transition metal catalyzed functionalization of olefins, we have examined the reactions of alkylrhodium(I) complexes with acid halides to produce ketones. The general reaction as well as the proposed mechanism for the transformation are detailed in Scheme I. The results, collected in Table I, demonstrate the range of unsymmetrical ketones available by this method.

Organolithium reagents and organomagnesium halides are equally useful for the production of the necessary alkylrhodium(I) complexes. These complexes react smoothly with alkoyl, benzoyl, and cinnamoyl chlorides, as well as those of greater complexity, to produce unsymmetrical ketones in high yield. Furthermore, the alkylrhodium(I) complexes do *not* react with

Table I. Reaction of Alkylrhodium(I) Complexes with Carboxylic Acid Chlorides (Scheme I)



A



B

Acid chloride	RM	Product[a]	Yield, %[b]
$CH_3(CH_2)_{10}COCl$	CH_3Li	$CH_3(CH_2)_{10}COCH_3$	86
	CH_3MgI	$CH_3(CH_2)_{10}COCH_3$	58
	n-C_4H_9Li	$CH_3(CH_2)_{10}CO(CH_2)_3CH_3$	80
	C_6H_5Li	$CH_3(CH_2)_{10}COC_6H_5$	96
	C_6H_5MgBr	$CH_3(CH_2)_{10}COC_6H_5$	85
trans-$C_6H_5CH:CHCOCl$	CH_3Li	*trans*-$C_6H_5CH:CHCOCH_3$	68
	n-C_4H_9Li	*trans*-$C_6H_5CH:CHCO(CH_2)_3CH_3$	68
	C_6H_5Li	*trans*-$C_6H_5CH:CHCOC_6H_5$	85
	C_6H_5MgBr		58
C_6H_5COCl[c]	CH_3Li	$C_6H_5COCH_3$	82
	n-C_4H_9Li	$C_6H_5CO(CH_2)_3CH_3$	74
	C_6H_5Li	$C_6H_5COC_6H_5$	94
CH_3COCl	C_6H_5Li	$CH_3COC_6H_5$	65
A	CH_3Li	B	55

[a] Identified by infrared, nmr, mass spectra, and comparison with authentic material. [b] Yield of isolated product purified by distillation or silica gel column chromatography. [c] Excess (10%) alkylrhodium(I) complex must be used to ensure complete conversion with this substrate.

Scheme I

$$\begin{tikzcd}
\underset{\mathbf{1}}{Rh^{I}Cl(CO)L_2} + RM \arrow[r, "THF", "-78^\circ"'] & MCl + \underset{\mathbf{2}}{[Rh^{I}R(CO)L_2]} \arrow[d, "R'\overset{O}{\overset{\|}{C}}-Cl\ \ add"', "-78^\circ\ THF\ ox"] \\
\underset{\mathbf{1}}{Rh^{I}Cl(CO)L_2} + R-\overset{O}{\overset{\|}{C}}-R' & \underset{\mathbf{3}}{[Rh^{III}R(Cl)(R'CO)(CO)L_2]} \arrow[l, "red", "elim"']
\end{tikzcd}$$

$L = Ph_3P$; $M = Li$ or MgX

aldehydes, esters, or nitriles, as evidenced by the quantitative recovery of benzaldehyde, ethyl benzoate, and benzonitrile, added concurrently with the acid chloride and carried through the normal reaction and isolation procedures. Thus, this procedure allows the ready conversion of acid chlorides to ketones in high yield under very mild conditions (−78°, THF), in the presence of other highly reactive functional groups.[1] An additional benefit is that the starting halogenorhodium(I) complex is regenerated in *reusable* form in the last step, obviating the need for continual resynthesis, and resulting in *no net consumption* of the rhodium complex.

A typical procedure is illustrated by the reaction of cinnamoyl chloride with bis(triphenylphosphine)carbonylphenylrhodium(I).[2] Phenyllithium (6.41 ml of 0.78 *M* solution in ether, 5.0 mmol) was added to a stirred suspension of $Rh^{I}Cl(CO)L_2$ (3.45 g, 5.0 mmol) in 75 ml of THF at −78° over 1 hr. After an additional 0.5 hr at this temperature cinnamoyl chloride (0.83 g, 5.0 mmol) in 5 ml of THF was added dropwise to the stirred yellow homogeneous solution. The resulting mixture was allowed to warm to 25° and was stirred at this temperature for 18 hr.[3] During this time, large amounts of yellow solid ($Rh^{I}Cl(CO)L_2$) precipitated. Petroleum ether (200 ml) was added to precipitate the remaining $Rh^{I}Cl(CO)L_2$ and the LiCl, and the mixture was filtered under vacuum. The solid was washed with 50 ml of 5:1 petroleum ether–ether, and the combined filtrates were evaporated to dryness. The resulting crude product was purified by silica gel column chromatography, eluting with 4:1 hexane–ether, to produce 0.88 g (85% yield) of 1,3-diphenyl-2-propen-1-one, mp 58°, with consistent ir, nmr, and mass spectral properties.

The $Rh^{I}Cl(CO)L_2$ was separated from LiCl by dissolution in a minimum amount of chloroform, followed by precipitation with excess methanol. After filtration and drying, the complex was suitable for reuse in this reaction sequence.[4]

Although the alkylrhodium(I) and alkylacylrhodium(III) complexes proposed as intermediates in this reaction have not yet been isolated, there is ample precedent for their existence and their role in this reaction sequence. The reaction of organolithium or Grignard reagents and halogenorhodium(I) complexes to produce alkylrhodium(I) complexes (**1** → **2**) is well established.[5] The iridium analog of **2**, synthesized by

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(1) Dialkylcadmium compounds convert acid halides to ketones, but the reaction is not of general application; see P. A. Shirley, *Org. React.*, 8, 28 (1958). Dialkyl cuprate reagents also effect this conversion, but are not compatible with aldehydes; see G. Posner, C. E. Whitten, and P. E. McFarland, *J. Amer. Chem. Soc.*, **94**, 5106 (1972). Iron tetracarbonyl dianion reagents appear to be of general utility for the synthesis of ketones from acid halides; see J. P. Collman, S. R. Winter, and D. R. Clark, *ibid.*, **94**, 1788 (1972).

(2) The reactions were run under an atmosphere of argon with complete exclusion of air. The THF was freshly distilled from $LiAlH_4$ under nitrogen. The acid halides were freshly distilled. The methyllithium (in ether) and butyllithium (in hexane) were purchased from Alfa Chemical Co. The phenyllithium and phenylmagnesium bromide (both in ether) were prepared by standard methods.

(3) With the more reactive *n*-butyl- and methylrhodium(I) complexes, the reaction ensued at −78°, and the mixture was never allowed to warm above −20°.

(4) All residues suspected to contain Rh were saved. When sufficient quantities accumulated, they were converted to $Rh^{I}Cl(CO)L_2$ by simply heating them in an ethanol solution containing excess LiCl, Ph_3P, and formaldehyde (37%, aqueous).

(5) W. Keim, *J. Organometal. Chem.*, **14**, 179 (1968); **19**, 161 (1969); M. Michman and M. Balog, *ibid.*, **31**, 395 (1971).

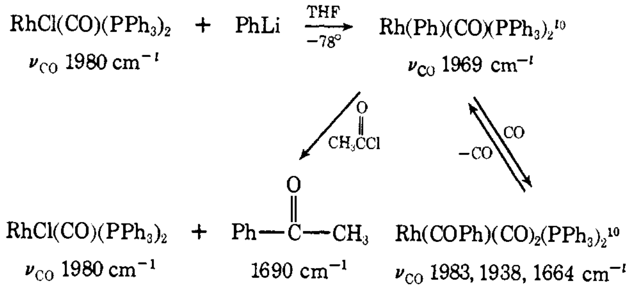
this method, has recently been isolated and characterized.[6] The oxidative addition of acid chlorides to coordinatively unsaturated metal(I) complexes to produce acylmetal(III) complexes (**2** → **3**) is also well known.[7] The enhanced reactivity toward oxidative addition of acid halides displayed by **2** (hours at −78°) compared with **1** (inert)[8] is likely a result of the increase of electron density at the central metal caused by replacement of halogen with alkyl.[9] The reductive elimination step (**3** → **1** + ketone) (reverse of oxidative addition) is likewise a well-known reaction.[7,9]

In an attempt to characterize some of the intermediates proposed in Scheme I, the reaction mixture was periodically examined by infrared spectroscopy (AgBr sealed cells) as the reaction ensued. Bis(triphenylphosphine)carbonylchlororhodium(I) (ν_{CO} (THF) 1980 cm^{-1}) was treated with methyllithium at −78°. After 1 hr, all the starting complex had dissolved producing $Rh(CH_3)(CO)(PPh_3)_2$. The infrared spectrum showed a shift of the CO absorption to 1962 cm^{-1}, as expected ($CH_3 > Cl$ in electron-donating abilities). Benzoyl chloride was added. The resulting solution had absorptions at 1980 (ν_{CO} $RhCl(CO)(PPh_3)_2$), 1962 (ν_{CO} $Rh(CH_3)(CO)(PPh_3)_2$), 1794 and 1734 (ν_{CO} PhC(=O)-Cl), and 1690 cm^{-1} (ν_{CO} $PhC(=O)CH_3$). There were *no* absorptions in the 2100–2000-cm^{-1} region, indicating the absence of any rhodium(III) carbonyl species, and none in the 1650-cm^{-1} region, indicating the absence of acylrhodium species. Thus, the Rh^{III}(alkyl)(acyl) complex **3** must be very unstable, and immediately collapse to ketone and $RhCl(CO)(PPh_3)_2$. As the reaction progressed, the band at 1962 cm^{-1} decreased and the band at 1980 cm^{-1} increased, as $Rh(CH_3)(CO)(PPh_3)_2$ was converted to $RhCl(CO)(PPh_3)_2$.

A portion of the $Rh(CH_3)(CO)(PPh_3)_2$ solution was stirred for 1 hr under an atmosphere of CO. The color of the solution went from red to pale yellow and developed bands at 1983 and 1955 cm^{-1} (RhCO) as well as a band at 1679 cm^{-1} ($RhC(=O)CH_3$). The complex is likely to be $Rh(COCH_3)(CO)_2(PPh_3)_2$ resulting from carbonylation and insertion of CO by $Rh(CH_3)(CO)(PPh_3)_2$. This complex readily lost CO.

A similar series of reactions was carried out using phenyllithium and acetyl chloride at −78° in THF. The infrared spectral results are summarized in Scheme II. Again no Rh^{III}(acyl)(alkyl) complex could be detected.

Scheme II



We have also initiated investigations directed toward producing alkylrhodium(I) complexes from hydridorhodium(I) complexes and unsaturated carbon compounds.[10,11] An initial result is reported in eq 1.[12] The full details of these studies, as well as further

$$Rh(H)(CO)L_3 + PhC{\equiv}CPh + CH_3COCl \xrightarrow[25°\ 40\%]{THF} PhCH{=}C(Ph)COCH_3 + Rh(Cl)(CO)L_2 \quad (1)$$

reactions of alkylrhodium(I) complexes with reactive organic substrates, will be forthcoming.

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[9] J. P. Collman, *Accounts Chem. Res.*, **1**, 137 (1968); J. P. Collman and W. R. Roper, *Advan. Organometal. Chem.*, **7**, 53 (1968).

[10] G. Yagupsky, C. K. Brown, and G. Wilkinson, *J. Chem. Soc. A*, 1392 (1970), report infrared data on the following complexes: $Rh(Ph)(CO)(PPh_3)_2$, ν_{CO} 1978 cm^{-1} in cyclohexane; $Rh(COPh)(CO)_2(PPh_3)_2$, ν_{CO} 1985, 1955, 1630 cm^{-1} in benzene. These complexes were *not* isolated.

[11] B. L. Booth and A. P. Lloyd, *J. Organometal. Chem.*, **35**, 195 (1972).

[12] After submission of this paper, J. Schwartz, D. W. Hart, and J. L. Holden, *J. Amer. Chem. Soc.*, **94**, 9269 (1972), published the results of a very careful study of oxidative addition–reductive elimination reactions between vinylrhodium(I) complexes and methyl iodide, in which all intermediates were isolated and characterized.

New Metalloboranes. $[Mn(CO)_3(B_9H_{13})]^-$ and $Mn(CO)_3[B_9H_{12}(OC_4H_8)]$

Sir:

In studying the chemistry of the $B_9H_{14}^-$ anion we have found that reaction with $Mn(CO)_5Br$ in refluxing tetrahydrofuran (THF) produces several metalloboranes. To date we have isolated salts of the metalloborane anion $[Mn(CO)_3(B_9H_{13})]^-$ (I) and the neutral $Mn(CO)_3[B_9H_{12}(THF)]$ (II).

The tetramethylammonium salt of I, obtained in about 40% yield, is an air-stable reddish orange crystalline material exhibiting 1:1 electrolyte behavior in acetonitrile. *Anal.* Calcd for $[(CH_3)_4N][Mn(CO)_3(B_9H_{13})]$: C, 25.97; H, 7.79; N, 4.33; B, 30.08; Mn, 16.99. Found: C, 23.21; H, 7.93; N, 4.37; B, 30.65; Mn, 17.18; mp 200° (dec). The neutral II is also an air-stable reddish orange crystalline material that will sublime in high vacuum at 50–70°, mp 189° (dec). High-resolution mass spectral data confirmed the composition: calcd for $^{55}Mn(^{12}C^{16}O)_3(^{11}B_9{}^1H_{12}\cdot{}^{16}O^{12}C_4{}^1H_8)$, 322.1580; found, 322.1604. The electronic spectra of I and II were virtually identical, consisting of two broad, well defined peaks at 4570 and 3080 Å.

The infrared spectrum of I contains BH stretching frequencies at 2630 (m), 2560 (s), and 2480 (s) cm^{-1} and CO stretching frequencies at 2060 (s), 2005 (vs), and 2025 (vs) cm^{-1}. The infrared spectrum of II is somewhat different, having BH stretching frequencies at 2610 (s), 2580 (s), and 2520 (s) cm^{-1} and CO stretching frequencies at 2055 (vs), 1950 (vs sh), and 1930 (vs) cm^{-1}.