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 ^2H 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 ^1H 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_6D_6 were followed at 0.5-h intervals by ^1H 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_6D_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]

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Registry No. **1**, 13938-94-8; CH_3COCl, 75-36-5; c-$C_6H_{11}COCl$, 2719-27-9; $PhCH_2COCl$, 103-80-0; *i*-C_3H_7COCl, 79-30-1; $PhCH_2Cl$, 100-44-7; $Ph(CH_3)CHCl$, 672-65-1; ^{13}CO, 1641-69-6; $Ph(CH_3)CHCOCl$, 22414-26-2; c-C_5H_9COCl, 4524-93-0; *n*-C_3H_7COCl, 141-75-3; $CH_3{}^{13}COCl$, 1520-57-6; c-$C_6H_{111}{}^{13}CoCl$, 100899-34-1; $PhCH_2{}^{13}COCl$, 63583-47-1; $Ph(CH_3)CH^{13}COCl$, 100899-35-2; c-$C_5H_9{}^{13}Co_2H$, 50530-15-9; *n*-$C_3H_7{}^{13}COCl$, 100899-36-3; *i*-$C_3H_7{}^{13}COCl$, 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 ^1H 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_3Cl.[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

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Summary: The $\delta(^{27}Al)$ values of dissolved organometallic compounds of the type $[Et_2\overline{AlOCH_2CR_2X}]_2$ (R = H, X = OMe, **1**; R = H, X = NEt_2, **2**; CR_2X = 2-H_4C_5N, **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 $(R_2AlY)_n$ (Y = R, OR, NR_2, H, and halogen).[2] At 310 K the ^{27}Al NMR shifts of the com-

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(1) van Vliet, M. R. P.; Buysingh, P.; van Koten, G.; Vrieze, K.; Kojic-Prodic, B.; Spek, A. L. *Organometallics* **1985**, *4*, 1701.

0276-7333/86/2305-0825$01.50/0

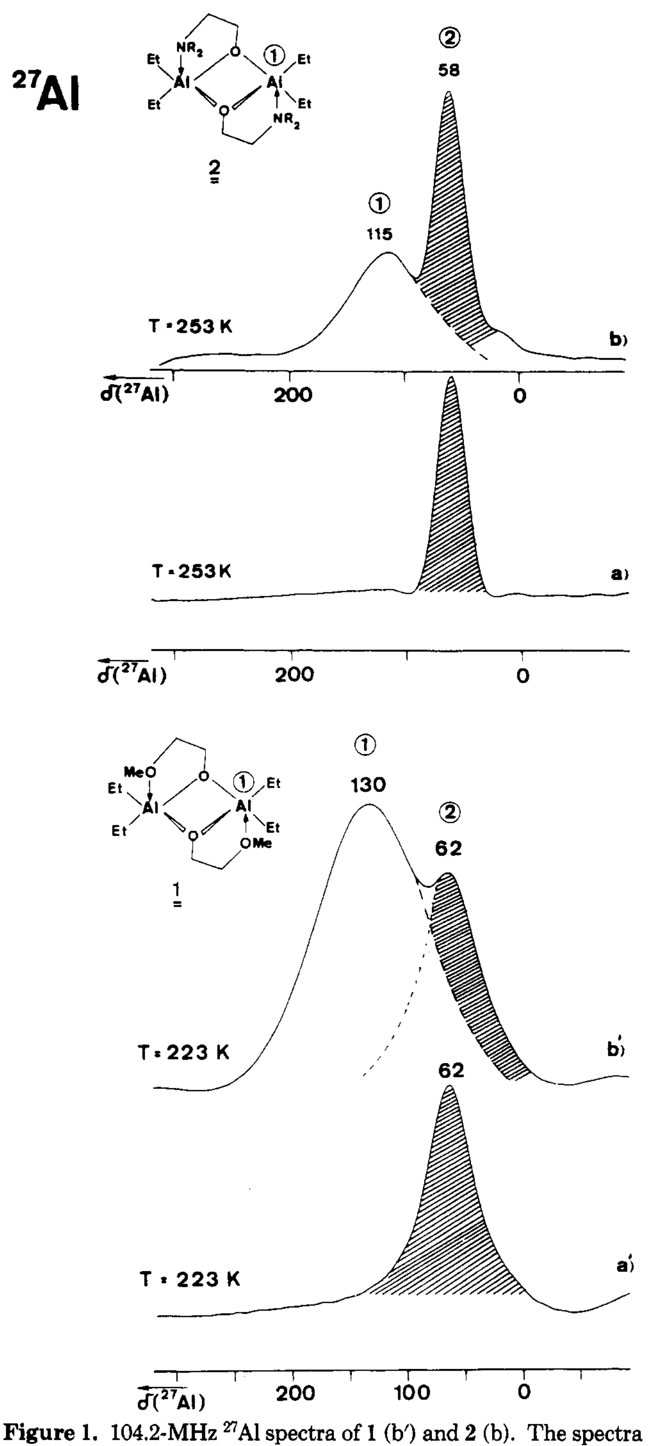

Figure 1. 104.2-MHz ^{27}Al spectra of 1 (b′) and 2 (b). The spectra a′ and a respectively were recorded under identical conditions to the spectra b′ and b except that the sample was an NMR tube containing only the solvent (toluene-d_8). Note the strength of the error signals (shaded) relative to the signals from of the sample. Different Lorentz (gauss) multiplication of the FIDs of spectra a′ and b′ on the one hand, and of spectra a and b, on the other, were performed.

pounds $[R_2\overline{AlO(CH_2)_2X}]_2$ (R = Me, Et; X = OMe, OEt, NEt_2) dissolved in toluene lie between δ(^{27}Al) ~112 and 126, and this was interpreted as arising from the pentacoordination of the aluminum atom.[2] This was confirmed by X-ray analysis of one of these compounds (R = Me, X = OMe). The 104-MHz low-temperature ^{27}Al NMR spectra of 1 and 2 are illustrated in Figure 1. However,

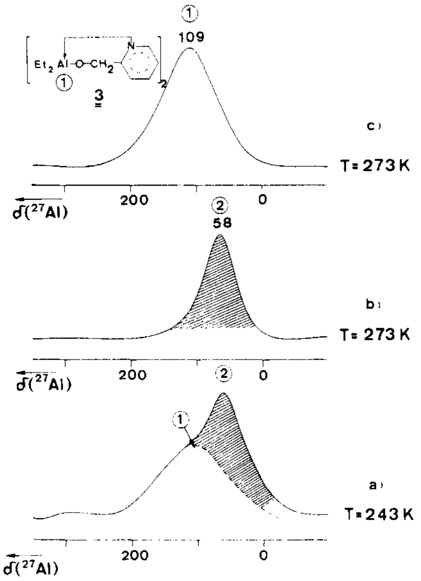

Figure 2. 104.2-MHz ^{27}Al spectra of 3 and the background signal (shaded) at various temperatures. Spectrum b: background signal only. The ^{27}Al spectra were recorded with a WH 400 spectrometer equipped with the standard 10-mm multinuclear probehead.

there are two ^{27}Al NMR signals in the spectra b and b′ of which only the unshaded lower field resonances at δ(^{27}Al) ~130 (cf. Figure 1b′) and at ~115 (cf. Figure 1b) stems from 1 and 2, respectively. This is easily proved by recording under identical conditions the ^{27}Al NMR spectrum of a sample tube which merely contains the solvent (spectra a and a′) in Figure 1. The shaded signals therefore must be regarded as extraneous. The temperature dependence of the ^{27}Al NMR shifts of 1 and 2 is insignificant in the temperature range from 310 K (1, δ ~121; 2, δ ~112) to 223 K (1, δ ~130) and to 253 K (2, δ ~115). In line with the higher concentration of 1, the extraneous signal interfers more in the ^{27}Al NMR spectrum of 2. Furthermore, the line width, $W_{1/2}$, of the ^{27}Al NMR signal of 1 and 2 increases with decreasing temperature as one would expect.[3]

Van Koten and co-workers[1] recently reported compounds of type $[R_{2-n}X_n\overline{AlOCH_2\text{-}2\text{-}H_4C_5N}]_2$ which are of similar structure. They also gave proof for the fivefold coordinated aluminum atom by X-ray analysis (R = i-Bu, n = 0). However, they reported a significant temperature dependence of the ^{27}Al NMR signal for, e.g., 3 (R = Et, n = 0) between 295 and 213 K and attributed these shifts to the existence of equilibria between fourfold (δ ~105) and fivefold (δ ~44) coordinated aluminum atoms in 3.

These findings contradict what we have found for threefold (δ ~260), fourfold (δ ~160), and fivefold (δ ~ 120) coordinated aluminum atoms in diorganoaluminum compounds.[2] Therefore, we have investigated compound 3 by ^{1}H, ^{13}C, and ^{27}Al NMR spectroscopy. We found for 3 an analogous behavior as for 1 and 2. The 104.2-MHz ^{27}Al spectra of 3 are presented in Figure 2 in traces a and c. The spectrum b stems from a sample containing only the solvent, and it was recorded under otherwise identical conditions as spectrum c. The shaded signal, which is not attributable to the sample, begins to hide the ^{27}Al NMR signal of 3 at temperatures below 243 K. Again, the ^{27}Al NMR signal of 3 lies around δ 109, and the shift is inde-

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(2) Benn, R.; Rufińska, A.; Lehmkuhl, H.; Janssen, E.; Krüger, C. *Angew. Chem.* **1983**, *95*, 808; *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 779.

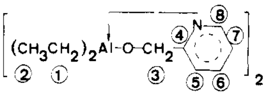
(3) For the quantitative relationship between $W_{1/2}$ and the temperature, cf., e.g., Harris, R. K. "Nuclear Magnetic Resonance Spectroscopy"; Pittman: London, 1983, or also the literature cited in ref 5 and 6 of this work.

Table I. ^{1}H, ^{13}C, and ^{27}Al NMR Signal Assignments of 3 at Various Temperatures

	position for numbering								
	1A	1B	2	3	4	5	6	7	8
					^{1}H[a]				
δ	0.57	0.46	1.52	4.85		5.97	6.64	6.33	8.17
multiplicity	dq	dq	q	s		d	dd	dd	d
J, Hz	13.6	13.6	8.0			7.9	7.9	7.4	5.4
	8.0	8.0					7.4	5.4	
					^{13}C[b]				
δ	2.21		11.16	63.00	159.11	119.76	137.60	122.38	144.91
multiplicity	t		q	t	s	d	d	d	d
^{1}J(C,H), Hz	115		124.0	142.5		166.0	164.0	167.0	181.5

^{27}Al	3[c,f]				background signal[d]	
T	310	300	273	243	273	243
δ	106	108	109	~110	58	62
$W_{1/2}$ Hz	5400	6200	10000	e	5800	6000

[a] C_7D_8; T = 213 K; 5 mm sample, ~1%. [b] C_7D_8; T = 273 K; 10 mm sample, ~8%. [c] C_7D_8; T, cf. Table I; 10 mm sample, ~8%. [d] Present also in spectra of samples containing no ^{27}Al nuclei. [e] $W_{1/2}$ not determined exactly. [f] Atom numbering:



3

pendent of the temperature between 310 and 243 K. Due to the reduced solubility of **3** and to the increasing line width ($W_{1/2}$ of **3** at 273 K is already about 10000 Hz) with decreasing temperature, its ^{27}Al NMR signal below 243 K is difficult to detect. The temperature dependence of $W_{1/2}$ of **3** is normal (cf. Table I) ($W_{1/2}$ increases with decreasing temperature. Note that according to ref 1 $W_{1/2}$ at 223 K should be smaller than that at 295 K!). In line with a fivefold coordinated Al atom in **3** the α-protons of the terminal ethyl groups are diastereotopic between 213 and 273 K. Revised assignments of the observed ^{27}Al and ^{1}H NMR spectra of **3** are also presented in Table I together with the ^{13}C NMR signal assignments as obtained from a two-dimensional ^{13}C, ^{1}H shift correlated spectrum.[4]

From our findings we conclude that there is no significant temperature dependence of the ^{27}Al NMR shifts of **1** between 310 and 223 K nor of **2** and **3** between 310 and 253 K and between 310 and 243 K, respectively, and these spectra provide no evidence for the existence of an equilibrium between four- and five-coordinated aluminum atoms. The ^{1}H NMR spectra of **3**, however, indicate that dissociation occurs to some minor extend at temperatures above 310 K (cf. also ref 1). Moreover, caution is necessary when NMR spectra of dilute samples of broad quadrupolar metal nuclei are recorded, since there are many causes for background signals.[5] Nevertheless, in spite of these difficulties, NMR spectroscopy of metal nuclei[5,6] is extremely useful for investigating many problems in organometallic chemistry.

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(4) The assignments of $^{2}J(H_A,H_B)$ and $\delta(H_6)$ and $\delta(H_7)$ in Table I differ from those given in ref 1. A comprehensive paper on the preparation and the NMR spectra of organoaluminium compounds is in preparation: Benn, R.; Janssen, E.; Lehmkuhl, H.; Rufińska, A., to be submitted for publication.

(5) Benn, R.; Rufińska, A. *Angew. Chem.* **1986**, *98*, 000.

(6) (a) Kidd, R. G. *Annu. Rep. NMR Spectrosc.* **1980**, *10A*, 1. (b) Dechter, J. J. *Prog. Inorg. Chem.* **1982**, *29*, 285. (c) Rehder, D. *Magn. Reson. Rev.* **1984**, *9*, 125.

Additions and Corrections

John H. Freudenberger and Richard R. Schrock*: Preparation of Di-*tert*-butoxytungsten(VI) Alkylidene Complexes by Protonation of Tri-*tert*-butoxytungsten(VI) Alkylidyne Complexes. **1985**, *4*, 1937.

The correct title is published above. The title was incorrectly published as "Preparation of Di-*tert*-butoxytungsten(VI) Alkylidene Complexes by Protonation of Tri-*tert*-butoxytungsten(VI) Alkylidene Complexes".