

## Unusual rate acceleration in the presence of aldehydes of distannoxane-catalyzed acetalization of ketones and deactivated aldehydes: a new mode of carbonyl activation

Junzo. Otera, Toshiyuki. Mizutani, and Hitosi. Nozaki

*Organometallics*, 1989, 8 (8), 2063-2065 • DOI: 10.1021/om00110a039 • Publication Date (Web): 01 May 2002

Downloaded from <http://pubs.acs.org> on April 29, 2009

### More About This Article

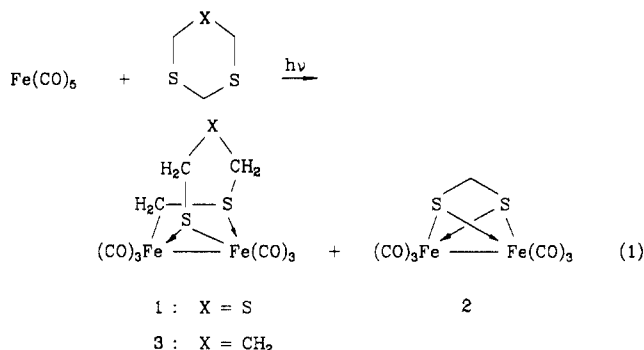
---

The permalink <http://dx.doi.org/10.1021/om00110a039> provides access to:

- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

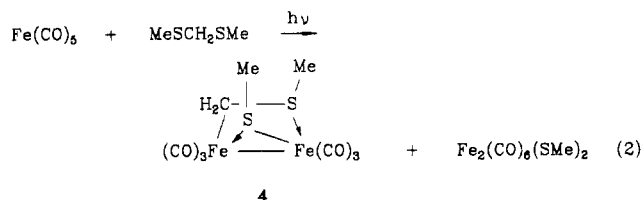


ACS Publications  
High quality. High impact.



compound compared to the Hieber-type structures  $\text{Fe}_2(\text{CO})_6(\mu\text{-SR})_2$ <sup>14</sup> is the lengthening of the Fe-Fe bond by ca. 0.35 to 2.609 (3) Å.<sup>4</sup>

Compounds structurally similar to 1, viz., 3 and 4, formed when  $\text{Fe}(\text{CO})_5$  reacted with 1,3-dithiane (eq 1) and the linear dithioacetal  $\text{MeSCH}_2\text{SMe}$  (eq 2), respectively. The phenyl analogue  $\text{PhSCH}_2\text{SPh}$ , however, reacted by eliminating  $\text{CH}_2$  (or  $\text{CH}_2\text{SPh}$  from two ligand molecules) and gave only the known compound  $\text{Fe}_2(\text{CO})_6(\mu\text{-SPh})_2$ .<sup>15</sup>



In addition, 1,3,5-trithiane, but not 1,3-dithiane, also underwent scission of two  $\text{CH}_2\text{-S}$  bonds, to split out  $\text{SCH}_2\text{S}$ , which coordinated and formed the known compound 2 (eq 1). The structure of 2 was assigned by comparison of its IR and mass spectra with published data.<sup>4</sup>

The <sup>1</sup>H NMR spectrum of complex 1 reflects its asymmetry in that the signals for two of the  $\text{CH}_2$  groups are split into two pairs of doublets (at 1.42, 2.23, 3.36, and 4.25 ppm), indicating that each proton is in a different chemical environment. The pair of doublets at 1.42 and 2.23 ppm is attributed to the methylene group attached to a metal. One  $\text{CH}_2$  group appears as a broad singlet at 3.22 ppm and, from a HETCOR diagram, was assigned to the hydrogen atoms on C9 (Figure 1). The <sup>13</sup>C{<sup>1</sup>H} NMR spectrum shows resonances at 18.8, 31.3, and 44.2 ppm, and from the <sup>1</sup>H-coupled spectrum these are assigned to C7, C8, and C9, respectively. The carbon bonded to the metal was assumed to have the highest upfield shift. The CO resonances are at 207.1, 210.4, and 214.9 ppm.

It is difficult to account for the large differences in the chemical shifts of the protons. From a three-dimensional model of 1 it was seen that one of the protons on C7 might be subject to an anomeric effect because of its proximity to a C=O group, but the H atoms on C8, which also appear

as a doublet of doublets, are too far from the C=O ligands for such an effect to be operative.

The <sup>1</sup>H NMR spectrum of complex 3 consists of a series of multiplets in the range 1.1-2.5 ppm, which includes doublets for the Fe- $\text{CH}_2$  protons at 1.15 and 2.00 ppm and a pair of multiplets at ca. 3.5 ppm. The <sup>13</sup>C{<sup>1</sup>H} NMR spectrum shows signals at 16.0, 26.6, 29.3, and 37.4 ppm for the four carbon atoms of the ligand. Resonances for the carbonyl carbons were not observed.

A proton-coupled <sup>13</sup>C NMR spectrum of the open chain compound 4 shows a triplet at 10.8 ppm for the Fe- $\text{CH}_2$  carbon, which confirmed our assignment of the highest field signal in the <sup>13</sup>C NMR spectrum of 1. The bridging SMe group gives rise to a simple quartet at 21.6 ppm, whereas for the methyl carbon,  $\delta$  32.4 ppm (as well as for the  $\text{CH}_2$ ) in the  $\text{CH}_2\text{SCH}_3$  group, the signals are split due to coupling through the S atom. Signals for the carbonyl carbons are at 208.6 and 209.5 ppm.

The proton NMR spectrum of 4 contains doublets at 1.07 and 1.59 ppm, assigned to the protons of Fe- $\text{CH}_2$ , and singlets at 2.00 and 2.45 ppm for the SMe groups. A HETCOR diagram indicated that the signal at 2.00 ppm belongs to the bridging SMe and the one at 2.45 ppm to the  $\text{CH}_2\text{SMe}$  group.

There is only one isomer of complex 4 in solution, and the chemical shift of the bridging SMe is downfield compared to that of the equatorial Me in  $\text{Fe}_2(\text{CO})_6(\text{SMe})_2$  (2.13 ppm).<sup>16</sup> From our data it is not possible to tell whether the configuration of the  $\text{SCH}_3$  groups is equatorial or axial.

The scission reactions of dithioacetals by which compounds 1-4 formed have not been noted before, and in compounds 1, 3, and 4 a unique  $\text{CH}_2\text{-SR}$  bridging ligand appears for the first time. Studies on the ring opening of other heterocycles, products obtained from other metal carbonyls, and the reactivity of the products are in progress.

**Acknowledgment.** We thank Dr. P. H. van Rooyen for his assistance with the refinement of the crystal structure.

**Registry No.** 1, 121097-06-1; 2, 69878-86-0; 3, 121097-07-2; 4, 121097-08-3;  $\text{Fe}(\text{CO})_5$ , 13463-40-6;  $\text{MeSCH}_2\text{SMe}$ , 1618-26-4; 1,3,5-trithiane, 291-21-4; 1,3-dithiane, 505-23-7.

**Supplementary Material Available:** Atomic coordinates (Table I), anisotropic temperature factors (Table II), calculated hydrogen atom coordinates (Table III), bond lengths and valence angles (Table IV), and crystal data (Table V) (9 pages); a listing of structure factors (12 pages). Ordering information is given on any current masthead page.

(16) King, R. B. *J. Am. Chem. Soc.* 1962, 84, 2460.

### Unusual Rate Acceleration in the Presence of Aldehydes of Distannoxane-Catalyzed Acetalization of Ketones and Deactivated Aldehydes: A New Mode of Carbonyl Activation

Junzo Otera,\* Toshiyuki Mizutani, and Hltosi Nozaki

Department of Applied Chemistry  
Okayama University of Science  
Ridai-cho, Okayama 700, Japan

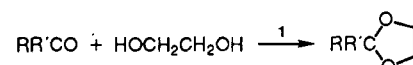
Received March 3, 1989

**Summary:** A distannoxane, 1-hydroxy-3-isothiocyanato-tetrabutylidistannoxane, catalyzes the acetalization of ketones and less reactive aldehydes in an unprecedented manner. This catalysis is discussed in terms of novel transcobonylation.

(13) Crystal data for  $\text{C}_9\text{H}_8\text{O}_6\text{S}_3\text{Fe}_2$ : monoclinic, space group  $P2_1$ ,  $a = 14.174$  (1) Å,  $b = 12.293$  (1) Å,  $c = 8.240$  (1) Å,  $\beta = 90.71$  (1)°,  $V = 1435.6$  (4) Å<sup>3</sup>,  $\rho(\text{calcd}) = 1.93$  g·cm<sup>-3</sup> for  $M_r$ , 418.0,  $Z = 4$ ,  $\mu = 23.55$  cm<sup>-1</sup> for Mo  $K\alpha$ .  $R = 0.078$ ;  $R_w = 0.060$ . An Enraf-Nonius CAD4F diffractometer with graphite-monochromated radiation was used for the experimental work. Three standard reflections were measured every hour (no appreciable decay of intensities was observed). The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods and refined by blocked-matrix least-squares methods using the SHELX76 (Sheldrick, G. M. *Program for Crystal Structure Determination*; University of Cambridge: Cambridge, 1976) range of crystallographic programs. Weights equal to  $1/\sigma^2(F)$  were used in the refinement. No significant difference in geometry was observed between the two molecules in the asymmetric unit. Bond lengths quoted refer to one molecule.

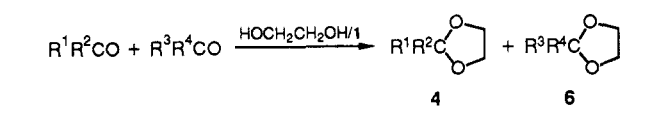
(14) Hieber, W.; Spacu, P. Z. *Anorg. Chem.* 1937, 233, 353.

(15) Characterized by MS, mp, and comparison with an authentic sample on thin-layer chromatographic plates with various eluants.

**Table I. Distannoxane-Catalyzed Acetalization of Carbonyl Compounds<sup>a</sup>**


R	R'	reactn time, min	yield, <sup>b</sup> %	$\tau_0$ , <sup>c</sup> min
<i>n</i> -C <sub>5</sub> H <sub>11</sub>	H	30	100	5.1
<i>n</i> -C <sub>6</sub> H <sub>13</sub>	H	110	97	20.0
<i>n</i> -C <sub>7</sub> H <sub>15</sub>	H	100	98	19.1
<i>n</i> -C <sub>8</sub> H <sub>17</sub>	H	190	96	35.6
<i>i</i> -C <sub>4</sub> H <sub>9</sub>	H	15	97	3.5
<i>t</i> -C <sub>4</sub> H <sub>9</sub>	H	80	92	21.5
C <sub>6</sub> H <sub>5</sub>	H	120	100	17.7
<i>p</i> -NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	H	3360	65	2685
C <sub>6</sub> F <sub>5</sub>	H	8640	39	15753 <sup>d</sup>
<i>n</i> -C <sub>5</sub> H <sub>11</sub>	CH <sub>3</sub>	381	86	142
<i>n</i> -C <sub>6</sub> H <sub>13</sub>	CH <sub>3</sub>	660	100	209
C <sub>2</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>5</sub>	180	84	109
C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>	1440	72	890

<sup>a</sup> Reaction conditions: RR'CO:HOCH<sub>2</sub>CH<sub>2</sub>OH:1 = 1:10:0.005; benzene; reflux. <sup>b</sup> Determined on the basis of GLC analyses. <sup>c</sup> Time for 50% yield. Deviation within  $\pm 10\%$ . <sup>d</sup> Obtained by extrapolation of the time-conversion curve.

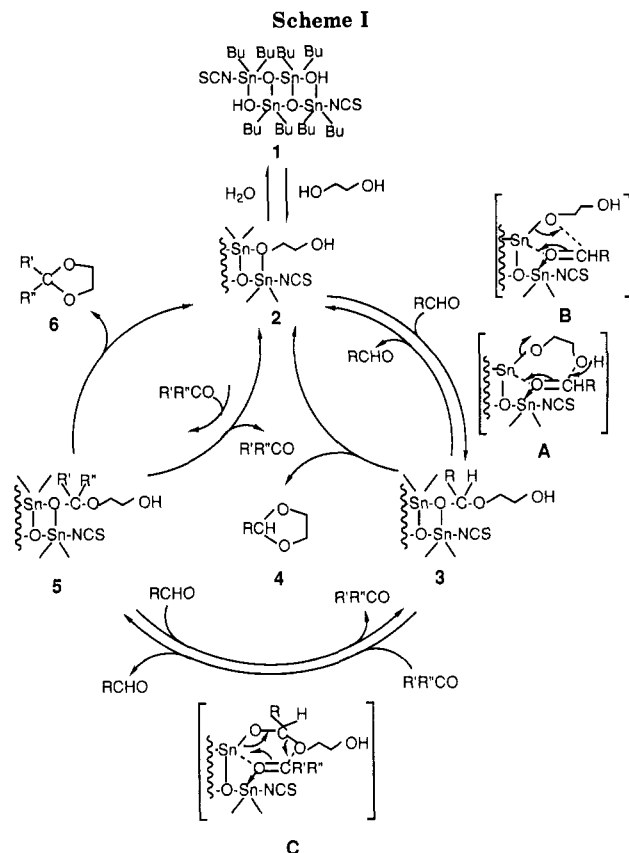
**Table II. Crossover Acetalization of Carbonyl Compounds<sup>a</sup>**

entry	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	R <sup>4</sup>	$\tau_4$ ( $\tau_4/\tau_{04}$ ) <sup>b</sup>	$\tau_6$ ( $\tau_6/\tau_{06}$ ) <sup>b</sup>
1	<i>n</i> -C <sub>5</sub> H <sub>11</sub>	H	<i>n</i> -C <sub>6</sub> H <sub>13</sub>	CH <sub>3</sub>	10.3 (0.5)	36.9 (5.7)
2	<i>n</i> -C <sub>5</sub> H <sub>11</sub>	H	<i>n</i> -C <sub>6</sub> H <sub>13</sub>	CH <sub>3</sub> <sup>c</sup>	8.6 (0.6)	56.0 (3.7)
3	<i>n</i> -C <sub>5</sub> H <sub>11</sub>	H	<i>n</i> -C <sub>6</sub> H <sub>13</sub>	CH <sub>3</sub> <sup>d</sup>	7.8 (0.7)	60.3 (3.5)
4	<i>n</i> -C <sub>5</sub> H <sub>11</sub>	H	<i>n</i> -C <sub>6</sub> H <sub>13</sub>	CH <sub>3</sub> <sup>e</sup>	6.9 (0.7)	34.9 (6.0)
5	<i>n</i> -C <sub>7</sub> H <sub>15</sub>	H	<i>n</i> -C <sub>6</sub> H <sub>13</sub>	CH <sub>3</sub>	24.0 (0.8)	38.8 (5.4)
6	<i>n</i> -C <sub>8</sub> H <sub>17</sub>	H	<i>n</i> -C <sub>6</sub> H <sub>13</sub>	CH <sub>3</sub>	35.1 (1.0)	38.9 (5.4)
7	<i>t</i> -C <sub>4</sub> H <sub>9</sub>	H	<i>n</i> -C <sub>6</sub> H <sub>13</sub>	CH <sub>3</sub>	28.9 (0.7)	44.7 (4.7)
8	<i>n</i> -C <sub>6</sub> H <sub>17</sub>	H	<i>n</i> -C <sub>5</sub> H <sub>11</sub>	CH <sub>3</sub>	45.2 (0.8)	42.3 (3.4)
9	<i>n</i> -C <sub>6</sub> H <sub>13</sub>	H	C <sub>2</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>5</sub>	17.4 (1.1)	18.3 (6.0)
10	C <sub>6</sub> H <sub>5</sub>	H	<i>n</i> -C <sub>6</sub> H <sub>13</sub>	CH <sub>3</sub>	18.5 (0.95)	143.8 (1.5)
11	<i>n</i> -C <sub>5</sub> H <sub>11</sub>	H	C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>	23.3 (0.2)	50.8 (18)
12	<i>n</i> -C <sub>5</sub> H <sub>11</sub>	H	<i>n</i> -C <sub>8</sub> H <sub>17</sub>	H	4.3 (1.2)	19.9 (1.8)
13	<i>n</i> -C <sub>5</sub> H <sub>11</sub>	H	<i>p</i> -NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	H	113 (0.2)	251 (10.7)
14	<i>n</i> -C <sub>5</sub> H <sub>11</sub>	H	C <sub>6</sub> F <sub>5</sub>	H	22 (0.9)	111 (142)
15	<i>n</i> -C <sub>6</sub> H <sub>13</sub>	CH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>	187 (1.1)	764 (1.2)

<sup>a</sup> Reaction conditions: R<sup>1</sup>R<sup>2</sup>CO:R<sup>3</sup>R<sup>4</sup>CO:HOCH<sub>2</sub>CH<sub>2</sub>OH:1 = 1:1:10:0.005 unless otherwise noted; benzene; reflux. <sup>b</sup> The  $\tau_4$  or  $\tau_6$  values indicate the time for 50% yield of 4 or 6 in the crossover experiments while  $\tau_{04}$  or  $\tau_{06}$  values are given in Table I. <sup>c</sup> R<sup>1</sup>R<sup>2</sup>CO:R<sup>3</sup>R<sup>4</sup>CO = 0.5:1. <sup>d</sup> R<sup>1</sup>R<sup>2</sup>CO:R<sup>3</sup>R<sup>4</sup>CO = 0.3:1. <sup>e</sup> R<sup>1</sup>R<sup>2</sup>CO:R<sup>3</sup>R<sup>4</sup>CO = 2:1.

Previously we reported catalysis by 1,3-disubstituted tetraorganodistannoxanes of functional group transformations of carbonyl compounds: transesterification,<sup>1</sup> esterification,<sup>2</sup> and deacetalization.<sup>3</sup> As a consequence of further extensions, we have found that distannoxanes are effective catalysts of acetalization as well. However, the reaction rate of ketones and deactivated aldehydes increased in the presence of coexisting aldehyde. This unusual mode of carbonyl activation is the subject of the present communication.

Table I summarizes the results of our studies of acetalization of aldehydes and ketones catalyzed by 1-hydroxy-3-isothiocyanatotetrabutyl-distannoxane (1) (0.5 mol % based on the carbonyls) in benzene using a Dean-



Stark apparatus. The  $\tau_0$  values represent the time for 50% yield. The reaction rates of ketones are much slower than those of aldehydes except for *p*-nitro- and pentafluorobenzaldehyde. In Table II are compiled the  $\tau$  values in competition reactions together with the  $\tau/\tau_0$  values which are a measure of the degree of acceleration or retardation of the reaction rate in comparison with the control data. The reaction rates of ketones increase in the presence of an aldehyde. An equimolar quantity of an aliphatic aldehyde accelerates the reaction of aliphatic ketones by ca. 3–6 times (entries 1, 5–9), whereas benzaldehyde does so only by a factor of 1.5 (entry 10). The rate of reaction of acetophenone in the presence of hexanal is ca. 18 times faster than the control experiment (entry 11). It is the aldehyde itself, but not the resulting aldehyde acetal, that plays a key role for the rate enhancement since addition of the corresponding acetal in place of the aldehyde has no influence on the rate. Use of less than 1 equiv of aldehyde is also effective, but to a lesser extent (entries 2, 3). Greater improvement is not attained when 2 equiv of aldehyde are used as compared with the standard conditions (entry 4).

The reaction probably proceeds as shown in Scheme I.<sup>4</sup> The initial step is formation of the ( $\beta$ -hydroxyethoxy)-distannoxane 2, which then preferentially incorporates an aldehyde to provide 3. The presence of a  $\beta$ -hydroxy group is crucial since stoichiometric treatment of the corresponding ( $\beta$ -methoxyethoxy)distannoxane<sup>5</sup> with benzaldehyde (1:1 molar ratio) in refluxing benzene gives rise

(4) For a mechanistic investigation of the reaction between 1 and carbonyl compounds in the presence of alcohol, see: Otera, J.; Yano, T.; Okawara, R. *Organometallics* 1986, 5, 1167.

(5) An equimolar mixture of 1 and 2-methoxyethanol is heated azeotropically in benzene for 3 h. The 1-(2-methoxyethoxy)-3-isothiocyanatotetraorganodistannoxane thus formed is used in benzene solution for the next reaction without isolation. Facile formation of alkoxydistannoxanes from hydroxydistannoxanes and alcohols has been well established.<sup>4</sup>

(1) Otera, J.; Yano, T.; Kawabata, A.; Nozaki, H. *Tetrahedron Lett.* 1986, 27, 2383.

(2) Otera, J.; Yano, T.; Himeno, Y.; Nozaki, H. *Tetrahedron Lett.* 1986, 27, 4501.

(3) Otera, J.; Nozaki, H. *Tetrahedron Lett.* 1986, 27, 5743.

to no reaction at all after 20 h, in striking contrast to 2 which incorporates 99% of benzaldehyde under analogous conditions (*vide infra*). Therefore, we suggest that the reaction goes through the seven-membered intermediate A rather than the four-membered one B. In the absence of a ketone, the aldehyde adduct 3 is solely converted into the acetal 4. When a ketone is present, the exchange reaction leading to the ketone adducts 5 competes with the aldehyde acetal formation. This exchange reaction, which may proceed via the intermediate C, proceeds more rapidly than the direct addition of ketone to 2 (*vide infra*). The exchange process is supported by the following observations. (1) In contrast to the acceleration of ketone reactions, the reaction rates of the aldehyde partners are diminished. (2) The exchange occurs between aldehydes as well. When a 1:1 mixture of hexanal and nonanal is used, the reaction of the latter is accelerated, while the rate of the former with a smaller  $\tau_0$  value remains at the about level of the control reaction (entry 12). More dramatic are the reactions with *p*-nitro- and pentafluorobenzaldehyde that are virtually inert toward the distannoxane-catalyzed acetalization (see Table I). The reactions of these compounds are greatly accelerated on addition of octanal (1 equiv) whose  $\tau$  value is increased (entries 13, 14). Thus, the acetals of these less reactive aldehydes are accessible in 72% yield after 8 h for *p*-nitrobenzaldehyde and 84% yield after 5 h for pentafluorobenzaldehyde. No such acceleration takes place between ketones, a quite reasonable result in terms of the slow initial uptake of ketone by 2 (entry 15).

In the hope of obtaining further confirmation of this novel transcobonylation, the stoichiometric reaction of 2 with carbonyl compounds has been monitored by means of GLC analysis. The failure to isolate 2 in pure form led us to make use of an *in situ* formed compound. A benzene solution of 1 and ethylene glycol (1:1 molar ratio) is heated azeotropically for 3 h.<sup>6</sup> Benzaldehyde (1 equiv) is added to this solution, and then the mixture is heated under reflux. After 20 h, the GLC peak of benzaldehyde had almost disappeared, showing that at least 99% of the aldehyde has been consumed. Occurrence of 3 can be deduced from the fact that no acetal is detected. Addition of 2-octanone (1 equiv) to this reaction mixture at this stage induces the exchange reaction. After 20 h, 39% of the 2-octanone had disappeared while the benzaldehyde peak reappeared indicative of a 25% recovery on the basis of the initially employed amount. Note that the reaction of 2-octanone with 2 under similar conditions occurs more sluggishly (10% after 20 h). Apparently, the reaction of ketone with 3 proceeds more easily than that with 2.

In conclusion, a distannoxane has proved to activate less reactive carbonyl compounds in an unprecedented manner. In contrast to the biased equilibrium between 2 and 5 to the side of the former, the equilibrium between 3 and 5 is more balanced. The susceptibility of 5 to be converted into 6 also assists the shift from 3 to 5. Finally, also noteworthy from the synthetic point of view is that various functional groups remain intact in this acetalization since the reaction proceeds under almost neutral conditions.<sup>1-3</sup> The synthetic utility is the subjects of future work.

**Acknowledgment.** This work was partially supported by Grant-in-Aid from The Ministry of Education, Science, and Culture, Japan, and by CIBA-GEIGY Foundation for the Promotion of Science, Takarazuka, Japan.

(6) Evaporation of the benzene solvent leaves amorphous powders. Although the <sup>1</sup>H NMR spectrum suggests the formation of the desired compounds, purification has not yet been successful.

**Registry No.** 1, 95971-04-3; 4 (R' = *n*-C<sub>5</sub>H<sub>11</sub>, R<sup>2</sup> = H), 3515-94-4; 4 (R' = *n*-C<sub>7</sub>H<sub>15</sub>, R<sup>2</sup> = H), 4359-57-3; 4 (R' = *n*-C<sub>8</sub>H<sub>17</sub>, R<sup>2</sup> = H), 5432-30-4; 4 (R' = *t*-C<sub>4</sub>H<sub>9</sub>, R<sup>2</sup> = H), 2568-29-8; 4 (R' = C<sub>6</sub>H<sub>5</sub>, R<sup>2</sup> = H), 936-51-6; 4 (R' = *n*-C<sub>6</sub>H<sub>13</sub>, R<sup>2</sup> = CH<sub>3</sub>), 937-94-0; 6 (R<sup>3</sup> = *p*-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>, R<sup>4</sup> = H), 2403-53-4; 6 (R<sup>3</sup> = C<sub>6</sub>F<sub>5</sub>, R<sup>4</sup> = H), 19161-34-3; 6 (R<sup>3</sup> = *n*-C<sub>5</sub>H<sub>11</sub>, R<sup>4</sup> = CH<sub>3</sub>), 4352-95-8; 6 (R<sup>3</sup>, R<sup>4</sup> = C<sub>2</sub>H<sub>5</sub>), 4362-57-6; 6 (R<sup>3</sup> = C<sub>6</sub>H<sub>5</sub>, R<sup>4</sup> = CH<sub>3</sub>), 3674-77-9; *n*-C<sub>5</sub>H<sub>11</sub>CHO, 66-25-1; *n*-C<sub>6</sub>H<sub>13</sub>CHO, 111-71-7; *n*-C<sub>7</sub>H<sub>15</sub>CHO, 124-13-0; *n*-C<sub>8</sub>H<sub>17</sub>CHO, 124-19-6; *i*-C<sub>4</sub>H<sub>9</sub>CHO, 590-86-3; *t*-C<sub>4</sub>H<sub>9</sub>CHO, 630-19-3; C<sub>6</sub>H<sub>5</sub>CHO, 100-52-7; *p*-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CHO, 555-16-8; C<sub>6</sub>F<sub>5</sub>CHO, 653-37-2; *n*-C<sub>5</sub>H<sub>11</sub>COCH<sub>3</sub>, 110-43-0; *n*-C<sub>6</sub>H<sub>13</sub>COCH<sub>3</sub>, 111-13-7; C<sub>2</sub>H<sub>5</sub>COC<sub>2</sub>H<sub>5</sub>, 96-22-0; PhCOCH<sub>3</sub>, 98-86-2; 2-hexanyl-1,3-dioxolane, 1708-34-5; 2-(2-methylpropyl)-1,3-dioxolane, 6135-52-0; 1-(2-methoxyethoxy)-3-isothiocyanatotetraorganodistannoxane, 121471-39-4.

### Characterization of an Intermediate in the Reaction of a Cationic Carbonyl Complex with Secondary Amine To Give a Carbamoyl Complex

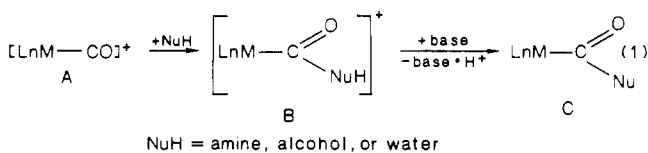
Li Huang, Fumiyuki Ozawa,\* Kohtaro Osakada, and Akio Yamamoto\*

Research Laboratory of Resources Utilization  
Tokyo Institute of Technology, 4259 Nagatsuta  
Midori-ku, Yokohama 227, Japan

Received March 13, 1989

**Summary:** Reaction of *trans*-[Pd(COPh)(CO)(PMe<sub>3</sub>)<sub>2</sub>]BF<sub>4</sub> (1) with pyrrolidine affords a cationic benzoylpalladium complex with an O-protonated carbamoyl group, *trans*-[Pd(COPh){C(OH)(N(CH<sub>2</sub>)<sub>3</sub>CH<sub>2</sub>)}(PMe<sub>3</sub>)<sub>2</sub>]BF<sub>4</sub> (2b), which has been characterized by means of NMR spectroscopy. Complex 2b reacts further with pyrrolidine to give benzoyl-carbamoyl complex *trans*-Pd(COPh)(CO-N(CH<sub>2</sub>)<sub>3</sub>CH<sub>2</sub>)(PMe<sub>3</sub>)<sub>2</sub> (3) together with the pyrrolidinium salt CH<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>NH<sub>2</sub>BF<sub>4</sub>. The conversion of 2b to 3 is a reversible process, and treatment of 3 with the pyrrolidinium salt regenerates 2b. The O-protonated carbamoyl structure of 2b is supported by X-ray structural analysis of its O-alkylated analogue *trans*-[Pd(COPh){C(OEt)-N(CH<sub>2</sub>)<sub>4</sub>CH<sub>2</sub>}(PMe<sub>3</sub>)<sub>2</sub>]BF<sub>4</sub> (4), which has been prepared by reaction of *trans*-Pd(COPh)(CON(CH<sub>2</sub>)<sub>4</sub>CH<sub>2</sub>)(PMe<sub>3</sub>)<sub>2</sub> with Et<sub>3</sub>OBF<sub>4</sub>.

Transition-metal carbonyl complexes are known to react with amines, alcohols, and water to give carbamoyl, alkoxycarbonyl, and hydroxycarbonyl complexes, respectively.<sup>1</sup> These complexes are postulated as key intermediates in various transition-metal-catalyzed carbonylation reactions. The following is a generally accepted reaction course.<sup>2</sup>



(1) (a) Angelici, R. *Acc. Chem. Res.* 1972, 5, 335 and references cited therein. (b) Angelici, R. J.; Blacik, L. *Inorg. Chem.* 1972, 11, 1754. (c) Green, C. R.; Angelici, R. J. *Ibid.* 1972, 11, 2095. (d) Byrd, J. F.; Halpern, J. *J. Am. Chem. Soc.* 1971, 93, 1634. (e) Beck, W.; Purucker, B. *J. Organomet. Chem.* 1976, 112, 361. (f) Ford, P. C.; Rokicki, A. *Adv. Organomet. Chem.* 1987, 28, 139 and references cited therein.