Rhodium-Catalyzed Reaction of *N*,*N*-Acetals with a Hydrosilane and Carbon Monoxide

Shin-ichi Ikeda, Naoto Chatani, and Shinji Murai*

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565, Japan

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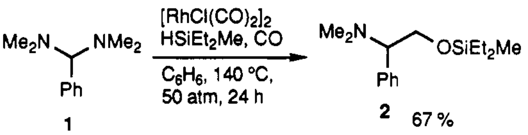
Summary: In the presence of $[RhCl(CO)_2]_2$, the reaction of *N*,*N*-acetals with a hydrosilane and carbon monoxide (140 °C, 50 atm of CO) resulted in incorporation of CO with cleavage of one of the carbon–nitrogen bonds in the substrate. The structure of the products was highly dependent on the structure of the *N*,*N*-acetals.

We wish to report new catalytic reactions which involve cleavage of a carbon–nitrogen bond with concomitant incorporation of carbon monoxide. Recently, we have reported that the reaction of enamines with $HSiEt_2Me$ and CO in the presence of $[RhCl(CO)_2]_2$ resulted in regioselective incorporation of CO into the olefinic carbon atom possessing an amino group to give α-(siloxymethylene)amines.[1] The reaction seemed to be applicable only to enamines, since other olefins such as 1-hexene, styrene, butyl vinyl ether, and phenyl vinyl sulfide did not undergo CO incorporation under the same reaction conditions using $[RhCl(CO)_2]_2$ as a catalyst. These results led us to examine the reactivity of a variety of nitrogen-containing compounds in the catalytic reaction system of $HSiR_3/CO/[RhCl(CO)_2]_2$. As a result, we have found new CO-incorporation reactions of *N*,*N*-acetals with $HSiEt_2Me$ and CO in the presence of $[RhCl(CO)_2]_2$. The type of products varied significantly according to the substitution patterns of the *N*,*N*-acetals.

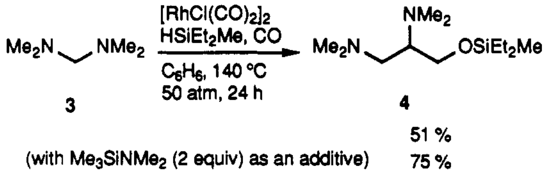
The reaction of *N*,*N*,*N'*,*N'*-tetramethylbenzylidenediamine (**1**; 1 equiv) with $HSiEt_2Me$ (3 equiv) and CO (50 atm, initial pressure at 25 °C) in the presence of $[RhCl(CO)_2]_2$ (2 mol %) in benzene at 140 °C for 24 h resulted in the incorporation of CO with the cleavage of a carbon–nitrogen bond in **1** to give diethyl[[2-(dimethylamino)-2-phenylethyl]oxy]methylsilane (**2**) in 67% yield (eq 1).[2,3]



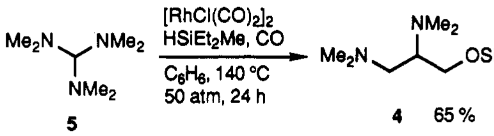
(1)

Thus, one of the dimethylamino groups in **1** was replaced by a (diethylmethylsiloxy)methyl group. In addition to **2**, benzyldimethylamine was obtained in 27% yield as a byproduct. In the presence of $Co_2(CO)_8$ or $RhCl(PPh_3)_3$, instead of $[RhCl(CO)_2]_2$, no reaction occurred.

Interestingly, the reaction of *N*,*N*,*N'*,*N'*-tetramethylmethylenediamine (**3**) with $HSiEt_2Me$ and CO gave the unexpected product **4** in 51% yield without forming a siloxymethylation product similar to **2** (eq 2). The product **4** was obtained by incorporation of two molecules of CO and, curiously, the transposition of one of the amino groups to an adjacent carbon atom arising from the first CO. Although the formation of **4** from **3** could not be adequately rationalized, the presumed byproduct $MeEt_2SiNMe_2$ seemed to have played an important role. Therefore, the same reaction was run in the presence of (trimethylsilyl)dimethylamine (2 equiv) and the yield of **4** was improved (75%).



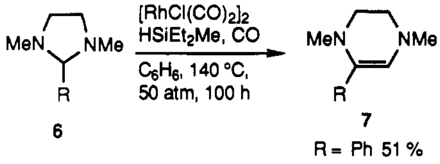
(2)



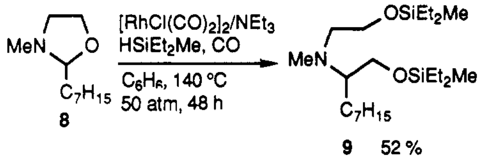
(3)

The reaction of triaminomethane **5** with $HSiEt_2Me$ and CO also gave **4** in 65% yield (eq 3). The first stage of the reaction would be reduction of **5** with $HSiEt_2Me$ to **3** and a silylamine, $MeEt_2SiNMe_2$. The subsequent reaction of **3** with $HSiEt_2Me$ and CO might have given **4**.

The peculiar transposition of an amino group prompted us to run the reaction of five-membered cyclic *N*,*N*-acetals **6**. The catalytic reaction of **6** (R = Ph) resulted in ring expansion with the incorporation of CO to give the cyclic enediamine **7** in 51% yield (eq 4). In contrast, the reaction of alkyl-substituted cyclic *N*,*N*-acetals (**6**; *R* = heptyl, *tert*-butyl) did not take place and the substrates were recovered. Interestingly, however, the corresponding *N*,*O*-acetal **8** underwent incorporation of CO and gave yet another type of product. The $[RhCl(CO)_2]_2$ (2 mol %)-catalyzed reaction of **8** (1 equiv) with $HSiEt_2Me$ (3 equiv) and CO (50 atm) gave the product **9** as the result of ring opening and siloxymethylation (eq 5). An *O*,*O*-acetal similar to **8** did not react at all.

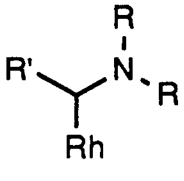


(4)



(5)

The present reaction stands for a rare example of catalytic carbon–nitrogen bond cleavage with incorporation of carbon monoxide.[4] It is likely that complexes **10**, in



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[1] Ikeda, S.; Chatani, N.; Kajikawa, Y.; Ohe, K.; Murai, S. *J. Org. Chem.* **1992**, *57*, 2.

[2] The reaction was run in a 50-mL stainless autoclave on a 2.5-mmol scale with **1** in 5 mL of benzene. Analysis of the reaction mixture by GC showed it to contain **2** in 67% GC yield. An analytical sample of **2** was obtained by Kugelrohr distillation (100 °C (oven)/2 Torr) followed by preparative GC (silicone OV-1). Toluene serves equally well as solvent.

[3] All new compounds were characterized by NMR, IR, and mass spectral data and by elemental analyses or high-resolution mass spectra (see the supplementary material).

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which rhodium is substituted at the position α to the nitrogen atom, are involved as common intermediates in the present catalytic reactions. An intermediate of type **10** may also be present in the Rh-catalyzed reaction of enamines with $HSiR_3$ and CO.[1] The interaction of a complex having a silicon–rhodium bond with *N,N*- or *N,O*-acetals would be responsible for the formation of **10**, while that of a complex having a hydrogen–rhodium bond with an olefinic moiety might be important in the case of enamines.[1]

Further study on the mechanism and substrate–product structure relationship of the new catalytic reactions is now in progress.

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Supplementary Material Available: Text giving typical experimental procedures and spectral and analytical data for the products obtained (3 pages). Ordering information is given on any current masthead page.

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(4) For reviews on carbonylation, see: (a) Falbe, J. *New Synthesis with Carbon Monoxide*; Springer-Verlag: New York, 1980. (b) Sneeden, R. P. A.; Villeurbanne, N. R. S. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Ed.; Pergamon Press: Oxford, U.K., 1982; Vol. 8. (c) Colquhoun, H. M.; Thompson, D. J.; Twigg, M. V. *Carbonylation: Direct Synthesis of Carbonyl Compounds*; Plenum Press: New York, 1991. For examples of the transition-metal-catalyzed carbonylation with cleavage of a carbon–nitrogen bond in strained molecules, see: (d) Alper, H.; Perera, C. P.; Ahmed, F. R. *J. Am. Chem. Soc.* **1981**, *103*, 1289. (e) Alper, H.; Mahatantila, C. P. *Organometallics* **1982**, *1*, 70. (f) Alper, H.; Urso, F.; Smith, D. J. H. *J. Am. Chem. Soc.* **1983**, *105*, 6737. (g) Roberto, D.; Alper, H. *Organometallics* **1984**, *3*, 1767. (h) Alper, H.; Hamel, N. *Tetrahedron Lett.* **1987**, *28*, 3237. (i) Calet, S.; Urso, F.; Alper, H. *J. Am. Chem. Soc.* **1989**, *111*, 931. (j) Roberto, D.; Alper, H. *J. Am. Chem. Soc.* **1989**, *111*, 7539. (k) Alper, H.; Delledonne, D.; Kameyama, M.; Roberto, D. *Organometallics* **1990**, *9*, 762. (l) Spears, G. W.; Nakanishi, K.; Ohfune, Y. *Synlett* **1991**, 91. For examples of the insertion of CO into a carbon–nitrogen bond of substrates other than strained heterocycles, see: (m) Merger, F.; Kummer, R.; Hutmacher, H. M. German Patent 3401503, 1985; *Chem. Abstr.* **1986**, *104*, 129650g. (n) Murahashi, S.-I.; Imada, Y.; Nishimura, K. *J. Chem. Soc., Chem. Commun.* **1988**, 1578.

Stable Bis(silyl)palladium Complexes: Synthesis, Structure, and Bis-Silylation of Acetylenes

Youlin Pan, Joel T. Mague, and Mark J. Fink*

Department of Chemistry, Tulane University, New Orleans, Louisiana 70118

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Summary: A class of unusually stable bis(silyl)palladium complexes is prepared by the reaction of a dinuclear Pd(I) hydride with either simple hydrosilanes or disilanes. The first structure of a palladium bis(silyl) compound and preliminary reaction chemistry with acetylenes are reported.

Silyl complexes of palladium have been implicated as important intermediates in a number of palladium-catalyzed transformations of organosilanes, including the hydrosilylation[1] and bis-silylation[2–4] of organic substrates. In contrast to analogous platinum complexes, palladium silyls are generally considered to be unstable. The few isolated complexes that have been reported to date possess special stabilization from either strongly electron-withdrawing silyl groups (e.g. $SiCl_3$)[5] or by inclusion of the silyl group in a chelate ring.[5,6] Since a fundamental knowledge of the reactivity of palladium silyl compounds is essential to understanding their role as catalytic intermediates, the preparation of simple silyl derivatives of palladium was sought. We now report the general synthesis of a new class of thermally stable (silyl)palladium complexes, the first crystal structure of a palladium–silicon compound, and some preliminary reaction chemistry with acetylenes.

Stable *cis*-bis(silyl)palladium complexes were prepared from the direct reaction of either hydrosilanes or 1,2-dihydrodisilanes with the novel dinuclear palladium hydride $[(dcpe)Pd]_2(\mu\text{-}H)_2$ (**1**; dcpe = 1,2-bis(dicyclohexylphosphino)ethane).[7,8] Reaction of **1** with the hydrosilanes **2a–c** as either neat liquids or toluene solutions, afforded the *cis*-bis(silyl) complexes **3a–c** in 50–70% yields (eq 1)[9].

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(7) A similar Pd(I) hydride has been recently reported: Fryzuk, M. D.; Lloyd, R. B.; Clentsmith, G. K. B.; Rettig, S. C. *J. Am. Chem. Soc.* **1991**, *113*, 4332–4334.

(8) Preparation of 1: A solution consisting of 62 mg (0.1 mmol) of (dcpe)Pd(oxalate) in 35 mL of CH_3CN was placed in a quartz Schlenk tube. While a constant flow of H_2 was maintained through the solution, the tube was irradiated at 350 nm in a Rayonet photochemical reactor for 45 min. Cooling of the photolysate to 0 °C resulted in the formation of an air-sensitive green precipitate. The precipitate was separated from the supernatant, washed in hexane, and dried in vacuo to yield 45 mg (85%) of 1. Characterization for 1: ^1H NMR (δ, THF-d_8) −2.28 (quintet, $^1J_{P\text{-}H}$ = 39.8 Hz), 1.2–2.0 (br m, dcpe); $^{31}P\{^1H\}$ NMR (δ, THF-d_8) 50.4 (s); IR (KBr, cm^{-1}) 1620 (s, Pd–H–Pd); MS (EI, 70 eV) m/z 1058 (M^+, 5%), 528 ($(dcpe)Pd^+$, 10%), 422 ($dcpe^+$, 20%), 340 ($Cy_2PCH_2CH_2Cy^+$, 100%). Anal. Calcd for $C_{52}H_{98}P_4Pd_2$: C, 58.92; H, 9.32. Found: C, 58.03; H, 9.13.

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