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 τ_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 τ 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 transcarbonylation, 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.[6] 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.[1-3] 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 ^{1}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_5H_{11}, R^2 = H), 3515-94-4; 4 (R' = *n*-C_7H_{15}, R^2 = H), 4359-57-3; 4 (R' = *n*-C_8H_{17}, R^2 = H), 5432-30-4; 4 (R' = *t*-C_4H_9, R^2 = H), 2568-29-8; 4 (R' = C_6H_5, R^2 = H), 936-51-6; 4 (R' = *n*-C_6H_{13}, R^2 = CH_3), 937-94-0; 6 (R^3 = *p*-$NO_2C_6H_4$, R^4 = H), 2403-53-4; 6 (R^3 = C_6F_5, R^4 = H), 19161-34-3; 6 (R^3 = *n*-C_5H_{11}, R^4 = CH_3), 4352-95-8; 6 (R^3, R^4 = C_2H_5), 4362-57-6; 6 (R^3 = C_6H_5, R^4 = CH_3), 3674-77-9; *n*-$C_5H_{11}CHO$, 66-25-1; *n*-$C_6H_{13}CHO$, 111-71-7; *n*-$C_7H_{15}CHO$, 124-13-0; *n*-$C_8H_{17}CHO$, 124-19-6; *i*-C_4H_9CHO, 590-86-3; *t*-C_4H_9CHO, 630-19-3; C_6H_5CHO, 100-52-7; *p*-$NO_2C_6H_4CHO$, 555-16-8; C_6F_5CHO, 653-37-2; *n*-$C_5H_{11}COCH_3$, 110-43-0; *n*-$C_6H_{13}COCH_3$, 111-13-7; $C_2H_5COC_2H_5$, 96-22-0; $PhCOCH_3$, 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

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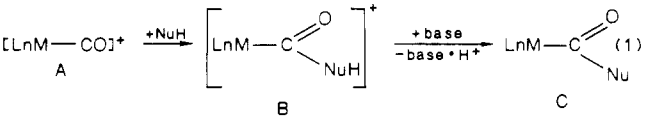
Summary: Reaction of *trans*-$[Pd(COPh)(CO)(PMe_3)_2]BF_4$ (**1**) with pyrrolidine affords a cationic benzoylpalladium complex with an O-protonated carbamoyl group, *trans*-$[Pd(COPh)\{C(OH)(N(CH_2)_3CH_2)\}(PMe_3)_2]BF_4$ (**2b**), which has been characterized by means of NMR spectroscopy. Complex **2b** reacts further with pyrrolidine to give benzoyl–carbamoyl complex *trans*-$Pd(COPh)(CON(CH_2)_3CH_2)(PMe_3)_2$ (**3**) together with the pyrrolidinium salt $CH_2(CH_2)_3NH_2BF_4$. 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*-$[Pd(COPh)\{C(OEt)N(CH_2)_4CH_2\}(PMe_3)_2]BF_4$ (**4**), which has been prepared by reaction of *trans*-$Pd(COPh)(CON(CH_2)_4CH_2)(PMe_3)_2$ with Et_3OBF_4.

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



NuH = amine, alcohol, or water

(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.

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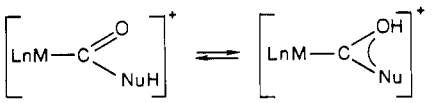
Nucleophilic attack of amines, alcohols, and water, respectively, on the CO ligand in A forms an adduct B which undergoes deprotonation with aid of a base to give carbamoyl, alkoxycarbonyl, and hydroxycarbonyl complexes C. Although it seems likely that B serves as a key intermediate in the reactions, no direct evidence for involvement of B has been reported so far despite extensive studies on preparation of carbamoyl, alkoxycarbonyl, and hydroxycarbonyl complexes by Angelici and others.[1] Furthermore, the intermediate B has an isomeric structure,

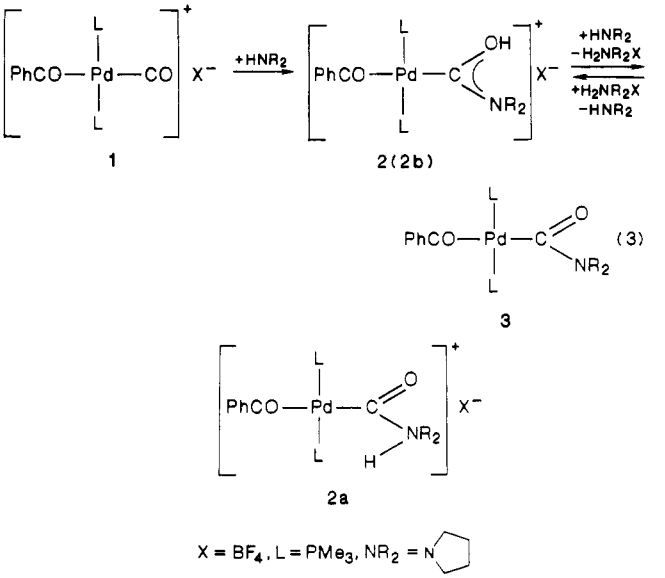


B D (2)

D formed by proton rearrangement in the C(O)NuH ligand in B (eq 2), but the possibility of participation of D in reaction 1 has not been considered.[3] We here report the first NMR observation of the intermediate in the reaction of a carbonyl complex with a secondary amine to give a carbamoyl complex.

Reaction of *trans*-$[Pd(COPh)(CO)(PMe_3)_2]BF_4$ (1; 0.1 M)[4] and pyrrolidine (2 equiv/Pd) in CD_2Cl_2 under atmospheric pressure of CO at −40 °C forms a cationic pyrrolidine adduct of the benzoylcarbonylpalladium complex (**2**) quantitatively. The formation of **2** is accompanied by consumption of 1 equiv of pyrrolidine as confirmed by NMR spectroscopy. The NMR data for **2** suggest that the complex has a structure of **2b** corresponding to D rather than of **2a** corresponding to B (vide infra).[6]

Addition of an excess amount of pyrrolidine to the reaction mixture containing **2** results in formation of benzoylcarbamoylpalladium complex **3** at the expense of **2**.[7] In the presence of 20 equiv of pyrrolidine/Pd, **2** and **3** have been observed in a 1:1 ratio in the $^{31}P\{^1H\}$ NMR spectrum. The relative ratio of **3** to **2** increases with an increase in the concentration of pyrrolidine in the system. Addition of $CH_2(CH_2)_3NH_2BF_4$ to a mixture of **2** and **3**, on the other hand, causes an increase in the amount of **2**. These results clearly indicate the occurrence of the deprotonation–protonation equilibrium between **2** and **3** in eq 3.[8]

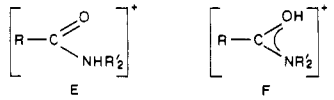


In the $^{31}P\{^1H\}$ NMR spectrum measured at −50 °C, **2** exhibits a singlet signal at −12.0 ppm, at a slightly higher field than that for **3** (−11.7 ppm).[5] In the $^{13}C\{^1H\}$ NMR spectrum of **2**, the signals of the carbonyl carbons in the benzoyl and the pyrrolidine-bound carbonyl group appear as two sets of triplets at δ 278.1 and 215.8, respectively, at fields close to but distinctly lower than those of the carbonyl carbons in the benzoyl and carbamoyl groups of **3**.[7] The P–Me carbons in **2** are observed as a virtual triplet, indicating the trans configuration of **2**. The four carbons in the pyrrolidino group in **2** appear as nonequivalent four singlets at δ 48.6, 44.3, 25.9, and 24.6, suggesting restricted rotation around the C–N bond. The observation is consistent with the structure **2b**, in which the C–N bond possesses double-bond character, but not with **2a** with a C–N single bond.

Since complex **2** is highly temperature sensitive and readily decomposes in solution in the absence of free CO, its isolation could not be accomplished. In order to obtain further information on the structure of **2**, we attempted to prepare the alkylated analogues of **2** by reactions of trans benzoyl–carbamoyl complexes with Et_3OBF_4. A complex afforded by treatment of **3** with Et_3OBF_4, probably *trans*-$[Pd(COPh)\{C(OEt)(N(CH_2)_3CH_2)\}(PMe_3)_2]BF_4$,

(2) Recent studies on carbonylation of isolated alkoxy- and hydroxy-transition-metal complexes suggested an alternative mechanism involving insertion of CO into transition-metal–alkoxy and transition-metal–hydroxy bonds for formation of alkoxycarbonyl and hydroxycarbonyl complexes. See: Bennett, M. A. *J. Mol. Catal.* **1987**, *41*, 1 and references cited therein. Bennett, M. A.; Robertson, G. B.; Rokicki, A.; Wickramasinghe, W. A. *J. Am. Chem. Soc.* **1988**, *110*, 7098. Bennett, M. A.; Rokicki, A. *Organometallics* **1985**, *4*, 180. Kim, Y.-J.; Osakada, K.; Sugita, K.; Yamamoto, T.; Yamamoto, A. *Ibid.* **1988**, *7*, 2182. Michelin, R. A.; Napoli, M.; Ros, R. *J. Organomet. Chem.* **1979**, *175*, 239. Bryndza, H. E. *Organometallics* **1985**, *4*, 1686. Bryndza, H. E.; Kretchmar, S. A.; Tulip, T. H. *J. Chem. Soc., Chem. Commun.* **1985**, 977. Rees, W. M.; Churchill, M. R.; Fettinger, J. C.; Atwood, J. D. *Organometallics* **1985**, *4*, 2179.

(3) The structures B and D in eq 2 can be compared with those of a protonated organic amide, E and F, respectively. The previous NMR



E F

studies on protonated amides have revealed that the O-protonated amide F is thermodynamically more stable than the N-protonated amide E, and both species are in rapid equilibrium on an NMR time scale: Fraenkel, G.; Franconi, C. *J. Am. Chem. Soc.* **1960**, *82*, 4478. Berger, A.; Loewenstein, A.; Meiboom, S. *Ibid.* **1959**, *81*, 62. The predominant contribution of F has been supported by the observation that reaction of amide with Et_3OBF_4 affords the O-ethylated amide $[RC(OEt)NR'_2]BF_4$ exclusively: Carey, F. A.; Sundberg, R. J. *Advanced Organic Chemistry. Part B: Reactions and Synthesis*; Plenum Press: New York, 1981; pp 208.

(4) Complex **1** was prepared by the reaction of *trans*-$[Pd(COPh)(acetone)(PMe_3)_2]BF_4$ with carbon monoxide and was characterized by means of IR and NMR spectroscopy. IR (KBr): ν(CO) 2138 and 1638 cm^{-1}. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −40 °C): δ 231.2 (br, PhCO), 180.2 (t, J_{P-C} = 18 Hz, CO), 14.8 (t, J = 16 Hz, PCH_3). ^1H NMR (CD_2Cl_2, −40 °C): δ 1.31 (t, J = 3.9 Hz, PCH_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −50 °C): −11.9 ppm (s).[5]

(5) The chemical shifts in $^{31}P\{^1H\}$ NMR spectra are relative to an external PPh_3 standard (downfield positive).

(6) NMR data of complex **2** are as follows. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −40 °C): δ 278.1 (br, PhCO), 215.8 (t, J_{P-C} = 15 Hz, C(OH)(NR_2)), 48.6 (s, NCH_2), 44.3 (s, $NC'H_2$), 25.9 (s, NCH_2CH_2), 24.6 (s, $NC'H_2C'H_2$), 15.2 (t, J = 16 Hz, PCH_3). ^1H NMR (CD_2CD_2, −40 °C): δ 8.0 (br, 1 H, COH), 3.8 (br, 2 H, NCH_2), 3.2 (br, 2 H, NCH'_2), 1.9 (br, 4 H, $NCH_2(CH_2)_2$), 1.11 (t, J = 3.5 Hz, 18 H, PCH_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −50 °C): −12.0 ppm (s).[5]

(7) Complex **3** has been isolated as red crystals (41%) and characterized by IR and NMR spectroscopy and elemental analysis. Anal. Calcd for $C_{18}H_{31}NO_2P_2Pd$: C, 46.8; H, 6.8; N, 3.0. Found: C, 46.7; H, 7.1; N, 3.1. IR (KBr): ν(CO) = 1561 and 1518 cm^{-1}. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 0 °C): δ 276.1 (t, J_{P-C} = 10 Hz, COPh), 211.9 (t, J_{P-C} = 14 Hz, $CONR_2$), 47.8 (s, NCH_2), 43.5 (s, $NC'H_2$), 25.8 (s, NCH_2CH_2), 24.8 (s, $NC'H_2C'H_2$), 15.8 (t, J = 15 Hz, PCH_3). ^1H NMR (CD_2Cl_2, room temperature): δ 3.8 (br, 2 H, NCH_2), 3.3 (br, 2 H, NCH'_2), 1.8 (br, 4 H, $NCH_2(CH_2)_2$), 1.14 (t, J = 3.5 Hz, PCH_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −50 °C): −11.7 ppm (s).[5] Preparation of a carbamoylpalladium complex *trans*-$Pd(COPh)(CONMe_2)(PMe_3)_2$ analogous to **3** has been reported previously: Ozawa, F.; Huang, L.; Yamamoto, A. *J. Organomet. Chem.* **1987**, *334*, C9.

(8) It has been also confirmed with NMR spectroscopy that treatment of the isolated complex **3** with $CH_2(CH_2)_3NH_2BF_4$ (1 equiv/3) in CD_2Cl_2 at −40 °C affords **2** in quantitative yield.

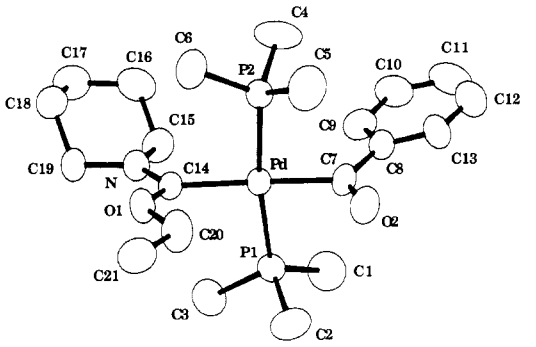
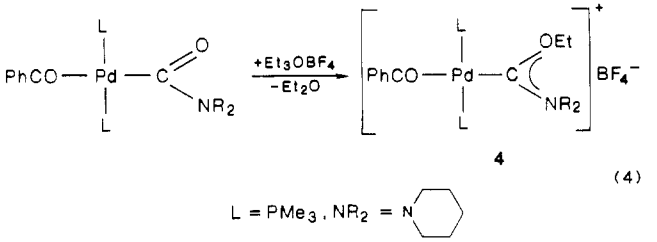


Figure 1. ORTEP drawing of complex 4 (4_{syn})[9] showing thermal ellipsoids drawn at 50% probability. The BF_4 anion is omitted for clarity. Selected bond lengths (Å) and angles (deg): Pd–C7 = 2.023 (7), Pd–C14 = 2.084 (6), Pd–P1 = 2.316 (2), Pd–P2 = 2.316 (2), O2–C7 = 1.201 (7), C7–C8 = 1.493 (9), O1–C14 = 1.329 (7), N–C14 = 1.298 (7), O2–C7–C8 = 119.5 (6), O2–C7–Pd = 118.3 (5), Pd–C7–C8 = 122.1 (4), N–C14–O1 = 111.8 (5), N–C14–Pd = 125.4 (4), O1–C14–Pd = 122.6 (4), C14–N–C15 = 120.9 (6), C14–N–C19 = 124.0 (5), C15–N–C19 = 115.0 (5).

has been found too unstable to be isolated. Reaction of benzoyl-carbamoyl complex with piperidino group *trans*-$Pd(COPh)(CON\overline{(CH_2)_4CH_2})(PMe_3)_2$ with Et_3OBF_4, on the other hand, gave a cationic benzoylpalladium complex with an O-ethylated carbamoyl group, *trans*-$[Pd(COPh)\{C(OEt)(\overline{N(CH_2)_4CH_2})\}(PMe_3)_2]BF_4$ (**4**), which is stable enough to allow its isolation.[9]

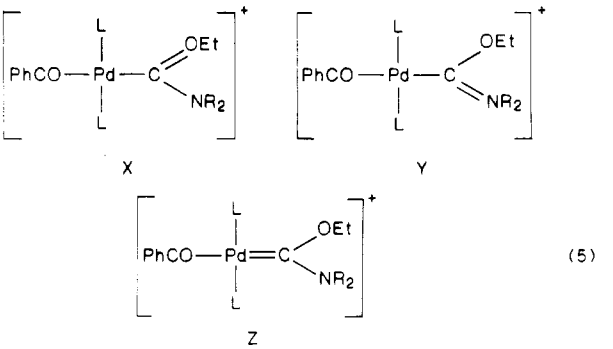


(4)

IR spectrum of **4** shows two strong absorption bands at 1606 and 1529 cm^{-1}. The latter absorption shifted to 1509 cm^{-1} in its ^{13}C-labeled complex *trans*-$[Pd(COPh)\{^{13}C(OEt)(\overline{N(CH_2)_4CH_2})\}(PMe_3)_2]BF_4$ (**4**-^{13}C), while the former absorption at 1606 cm^{-1} did not alter the frequency by introducing the ^{13}C label. Thus the absorption at 1606 cm^{-1} is assignable to the ν(CO) band of the benzoyl group and the other one at 1529 cm^{-1} to the ethylated carbamoyl group. The absorption frequency of 1509 cm^{-1} observed in the IR spectrum of **4**-^{13}C is in fair agreement with the calculated value for the asymmetric O–^{13}C–N stretching vibration (1507 cm^{-1}), but not with the values for pure $^{13}C{=}O$ and $^{13}C{=}N$ double bonds (1495 and 1497 cm^{-1}, respectively).[10] The fact indicates delocalization of the π electrons over the C–N and C–O bonds, consistent with the O-ethylated carbamoyl structure of **4** in eq 4.

The structural observation in the IR spectroscopy has been supported by the X-ray structure of **4**.[11] As seen from the ORTEP drawing in Figure 1, complex **4** has a slightly distorted square-planar structure with the benzoyl and O-ethylated carbamoyl groups in mutually trans positions. The distance between the benzoyl carbon (C7) and the palladium center is 2.023 Å which is somewhat shorter than the sum of the covalent radii of Pd(II) and sp^2 carbon (2.05 Å), indicating slight π-bonding character of the Pd–COPh bond. In contrast, the O-ethylated carbamoyl–palladium bond (Pd–C14) has a distance (2.084 Å) typical of a Pd–C single bond. The distance between carbon C14 and the nitrogen (1.298 Å) is significantly shorter than that for a typical C–N single bond. The carbon–oxygen in the O-ethylated carbamoyl group (C14–O1 = 1.329 Å) is longer than the C7–O2 bond in the benzoyl group (1.201 Å) but still shorter than a C–O single bond (ca. 1.5 Å). Similar structural feature has been observed for other palladium and platinum alkoxyaminocarbene complexes.[12]

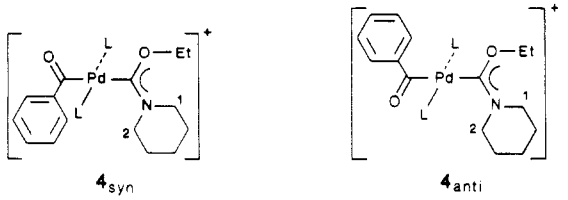
Complex **4** has the following three resonance structures X, Y, and Z. The X-ray structure suggests predominant



(5)

contributions of X and Y and a negligible contribution of Z with a Pd–C double bond. Thus, although complex **4** is considered formally as an ethoxyaminocarbene complex,

(9) Complex **4** has been isolated as yellow crystals (85%). The ^1H and $^{13}C\{^1H\}$ NMR spectroscopic data suggested the presence of two rotational isomers 4_{syn} and 4_{anti} in ca. 1:1 ratio. Details of the NMR assignments will be reported elsewhere. The analytical and spectroscopic data are



as follows. Anal. Calcd for $C_{21}H_{28}NO_2P_2BF_4Pd$: C, 42.6; H, 6.4; N, 2.4. Found: C, 42.4; H, 6.8; N, 2.3. IR (KBr): ν(CO) = 1606 and ν(OCN) = 1529 cm^{-1}. ^1H NMR (CD_2Cl_2, room temperature): δ 4.93 (q, J_{H-H} = 7 Hz, 1 H, OCH_2 in 4_{syn} or 4_{anti}), 4.66 (q, J_{H-H} = 7 Hz, 1 H, OCH_2 in 4_{syn} or 4_{anti}), 4.23 (br, 1 H, NC^2H_2 in 4_{syn} or 4_{anti}), 3.97 (br, 1 H, NC^2H_2 in 4_{syn} or 4_{anti}), 3.66 (br, 2 H, NC^1H_2 in 4_{syn} and 4_{anti}), 1.5–1.9 (br, 9 H, OCH_2CH_3 and $NCH_2CH_2CH_2CH_2$ in 4_{syn} and 4_{anti}), 1.21 (t, J = 3.7 Hz, 18 H, P*Me* in 4_{syn} and 4_{anti}). $^{13}C\{^1H\}$ NMR ($CDCl_3$, room temperature): δ 251.6 (t, *C*OPh), 223.9 (t, *C*(OEt)(NR_2)), 71.6 (s, OCH_2 in 4_{syn} or 4_{anti}), 71.2 (s, OCH_2 in 4_{syn} or 4_{anti}), 53.2 (s, NCH_2 in 4_{syn} and 4_{anti}), 45.2 (s, NCH_2 in 4_{syn} or 4_{anti}), 44.9 (s, NCH_2 in 4_{syn} or 4_{anti}), 26.9 (s, NCH_2CH_2 in 4_{syn} and 4_{anti}), 25.9 (s, NCH_2CH_2 in 4_{syn} or 4_{anti}), 25.7 (s, NCH_2CH_2 in 4_{syn} or 4_{anti}), 23.8 (s, $NCH_2CH_2CH_2$), 15.5 (s, OCH_2CH_3), 15.4 (t, PCH_3). The $^{31}P\{^1H\}$ NMR data are common to both isomers (CD_2Cl_2, room temperature): −17.0 ppm (s).[5]

(10) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*; Wiley-Interscience: New York, 1978; p 67.

(11) Yellow crystals of the syn isomer of complex **4** (4_{syn})[9] suitable for X-ray study were obtained by slow cooling of a CH_2Cl_2–Et_2O solution of **4**. Crystallographic data for $C_{21}H_{28}NO_2P_2PdBF_4$: space group $C2/c$,a = 28.449 (36) Å, b = 10.249 (8) Å, c = 19.952 (24) Å, β = 110.66 (9)°, V = 5443.5 Å^3, d_{calcd} = 1.449 g cm^{-3} for M = 591.70, Z = 8, μ(Mo Kα) = 8.31 cm^{-1}. Diffraction data were collected with a Rigaku AFC-5 diffractometer at room temperature using ω–2θ scan technique. All the data processing were performed on a FACOM A-70 using the R-CRYSTAN program. The Pd atom was positioned from a Patterson map, and all other nonhydrogen atoms were positioned by subsequent Fourier syntheses. Hydrogen atoms were not located. The difference maps suggested two types of orientation for the BF_4 anion approximately in same probability. The structure was refined by full-matrix least-squares with anisotropic thermal parameters for all non-hydrogen atoms. The final R = 0.059 and R_w = 0.054 for 4125 reflections [$F_o \geq 3\sigma(F_o)$] of 4823 unique reflections collected in the range of 3° < 2θ < 50°. Details of the structure determination are given in the supplementary material.

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the ethoxyaminocarbene group has little carbene character and it should be regarded as an O-ethylated carbamoyl group which is linked to the palladium center by a single bond.

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Supplementary Material Available: Atomic numbering scheme and tables of positional parameters, bond distances and angles, and anisotropic thermal parameters (4 pages); a listing of observed and calculated structure factors (20 pages). Ordering information is given on any current masthead page.

Thermolytic Rearrangement of *cis*-Bis(phosphine)bis[(trimethylsilyl)methyl]platinum(II) Complexes via β-Alkyl Transfer

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Summary: Bis[(trimethylsilyl)methyl]platinum(II) complexes *cis*-$Pt(CH_2SiMe_3)_2L_2$ (L = PEt_3, PPh_2Me, PPh_3) do *not* afford 1-metalla-3-silacyclobutanes via thermolytic γ-C-H migration but instead undergo a novel linkage isomerization, involving β-Si-CH_3 scission and transfer, to afford the unusual methylplatinum(II) products *cis*-$Pt(CH_3)(CH_2SiMe_2CH_2SiMe_3)L_2$. η^2-Silylene complexes are likely intermediates.

(Trimethylsilyl)methyl and neopentyl derivatives of transition metals were among the forefront of development in alkylmetal chemistry when it was realized that β-hydrogen migration was a major labilizing pathway.[1] More recently, a number of neopentylmetal complexes have been reported to undergo intramolecular aliphatic γ-C-H activation and transfer, generating 3,3-dimethylmetallacyclobutanes.[2] The mechanism has been explored in detail for platinum complexes. (Trimethylsilyl)methyl analogues often react similarly[2a,b,d,e,3] though, in general, less readily. It seems to be assumed widely that the mechanistic controls on the two systems are likely to be the same, irrespective of metal. Relatedly, several neophyl [CH_2CMe_2Ph] complexes rearrange by distal aromatic H migration to form 3,3-dimethylmetallaindans.[2e,4] Again, mechanisms are best understood for platinum derivatives[4c,d] and the corresponding reactions of sila-neophyl [CH_2SiMe_2Ph] species are slower.[5] Organo-f-block metal compounds—notably $Th(CH_2EMe_2R)_2(\eta^5\text{-}C_5Me_5)_2$ [E = C, Si; R = Me, Ph]—show similar reactivity trends.[6] Our interest in understanding the relative inertness of β-silaalkyl systems has prompted investigation of a range of bis[(trimethylsilyl)methyl]platinum(II) complexes.[7] The unexpected results of thermolytic rearrangement of several of these with monodentate tertiary phosphine ligands demonstrate that mechanistic analogies cannot be assumed, even for the same metal. In contrast to their neopentylplatinum analogues, they do *not* yield metallacycles. Thermolysis of toluene-d_8 solutions of the complexes $Pt(CH_2SiMe_3)_2L_2$ [1, L = PEt_3, PPh_2Me, PPh_3] results in quantitative rearrangement to novel methyl({[(trimethylsilyl)methyl]dimethylsilyl}methyl)platinum(II) complexes, *cis*-$Pt(CH_3)(CH_2SiMe_2CH_2SiMe_3)L_2$ (8), identified by their ^1H, ^{13}C, and ^{31}P NMR spectroscopic characteristics and by mass spectrometric and elemental analyses of the two isolable examples (where L = PEt_3, the pure product could not be recovered). The structure of the triphenylphosphine derivative has been confirmed by X-ray diffractometry.[8] Reaction of the trimethylphosphine complex requires more vigorous conditions, and though the predominant pathway is analogous, secondary and/or competitive reactions are apparent.

The asymmetric geometry of the products is most clearly evident from the $^{31}P\{^1H\}$ NMR data.[9] The $^{13}C\{^1H\}$ spectra allow unequivocal assignment of the structure.[10] Two distinct Pt-CH_n resonances are observed. Of these (from ADEPT measurements) the lower field resonance arises from a Pt-CH_2 grouping, while the higher field signal clearly corresponds to Pt-CH_3. Two Si-CH_3 environments are also evident, one displaying $^3J_{Pt-C}$ interaction (comparable to that in the parent complex 1) and a second, more intense, with no observable coupling. A further aliphatic carbon showing $^3J_{Pt-C}$ coupling is attributed to a Si-CH_2 group.

An important aspect of product analysis in this instance is the origin of the methyl group bound ultimately to platinum. Though rearrangement of the selectively deuterated complex *cis*-$Pt[CH_2Si(CD_3)_3]_2(PPh_2Me)_2$ is slower (vide infra), it generates an exactly analogous product whose $^{13}C\{^1H\}$ NMR spectrum reveals the presence *only* of Pt-CD_3 and Pt-CH_2-Si groups. Superficially, then, the

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(9) ^{31}P data for *cis*-$Pt(CH_3)(CH_2SiMe_2CH_2SiMe_3)L_2$ (in toluene-d_8; δ in ppm relative to external 60% H_3PO_4; *J* in Hz): L = PEt_3, $\delta(P_1) = 8.71$, $^1J(P_1\text{-Pt}) = 1976$, $\delta(P_2) = 6.84$, $^1J(P_2\text{-Pt}) = 1879$, $^2J(P_1\text{-}P_2) = 12$; L = PPh_2Me, $\delta(P_1) = 5.26$, $^1J(P_1\text{-Pt}) = 1943$, $\delta(P_2) = 5.26$, $^1J(P_2\text{-Pt}) = 1870$, $^2J(P_1\text{-}P_2) = 11$; L = PPh_3, $\delta(P_1) = 28.9$, $^1J(P_1\text{-Pt}) = 1955$, $\delta(P_2) = 26.0$, $^1J(P_2\text{-Pt}) = 1921$, $^2J(P_1\text{-}P_2) = 11$; L = PMe_3, $\delta(P) = -26.9$, $^1J(P_1\text{-Pt}) = 1952$, $\delta(P_2) = -25.8$, $^1J(P_2\text{-Pt}) = 1886$, $^2J(P_1\text{-}P_2) = 11$.

(10) Selected ^{13}C data for *cis*-$Pt(CH_3)(CH_2SiMe_2CH_2SiMe_3)L_2$ (in chloroform-*d*; δ(C) in ppm relative to external TMS; *J* in Hz). (a) L = PPh_2Me: Pt-CH_3, $\delta(C) = 4.81$, $^1J(C\text{-Pt}) = 596$, $^2J(C\text{-}P_{trans}) = 104$, $^2J(C\text{-}P_{cis}) = 13$; Pt-$CH_2$, $\delta(C) = 11.55$, $^1J(C\text{-Pt}) = 558$, $^2J(C\text{-}P_{trans}) = 85$, $^2J(C\text{-}P_{cis}) = 6$; Si$(CH_3)_3$, $\delta(C) = 1.74$; Si$(CH_3)_2$, $\delta(C) = 4.92$, $^3J(C\text{-Pt}) = 26$; Si-CH_2, $\delta(C) = 8.54$, $^3J(C\text{-Pt}) = 31$. (b) L = PPh_3: Pt-CH_3, $\delta(C) = 7.75$, $^1J(C\text{-Pt}) = 604$, $^2J(C\text{-}P_{trans}) = 97$, $^2J(C\text{-}P_{cis}) = 8$; Pt-$CH_2$, $\delta(C) = 14.05$, $^1J(C\text{-Pt}) = 645$, $^2J(C\text{-}P_{trans}) = 80$, $^2J(C\text{-}P_{cis}) = 5$; Si$(CH_3)_3$, $\delta(C) = 1.99$; Si$(CH_3)_2$, $\delta(C) = 6.28$, $^3J(C\text{-Pt}) = 20$, Si-CH_2, $\delta(C) = 8.80$, $^3J(C\text{-Pt}) = 27$.

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