Table IV. Comparison of Mean Bond Distances (Å) and Angles (deg) in Compounds Containing Al_2N_2 Four-Membered Rings

compd	Al–N	Al···Al	Al–N–Al	ref
$[(CH_3)_2AlN(CH_3)_2]_2$	1.958 (7)	2.809 (4)	91.7 (2)	*a*
$[\{(CH_3)_2AlN(CH_3)\}_2\text{-}\{(CH_3)AlN(CH_3)\}_6]$	1.910 (6)	2.683 (3)	88.4 (3)	*b*
cis-$[Al(CH_3)_2NHC(CH_3)_2]_2$	1.945 (5)	2.800	91.85 (2)	*c*
trans-$[Al(CH_3)_2NHC(CH_3)_2]_2$	1.959 (5)	2.789	90.8 (2)	*c*
$[Al(CH_3)]_2[C_{10}H_{20}N_4][Al(CH_3)_3]_2$	1.936 (4)	2.735 (2)	89.9 (2)	this study

[a] Reference 34. [b] Reference 35. [c] Reference 36.

bond distances and angles between the title compound and these Al_2N_2 condensation products is given in Table IV. It is important, however, to note the inherent difference between the title compound and the condensation products reported by Smith. The condensation products containing the Al_2N_2 fragments are the result of the reaction of AlR_3 with simpler amine units at high temperatures. The title compound is novel in that the macrocycle is essentially left unchanged. The Al_2N_2 ring, in fact, results from an intramolecular condensation specific to the interior cavity of the macrocycle.

The facile cleavage of Al–C and N–H bonds coupled with the novel structure of the title compound will serve as a benchmark in our studies as we explore the potential of nitrogen-based macrocycles in facilitating liquid clathrate behavior based on transition metals.

Acknowledgment. We are grateful to the National Science Foundation for support of this work to G.H.R. (RII-8520554).

Registry No. $[Al(CH_3]_2[C_{10}H_{20}N_4][Al(CH_3)_3]$, 107799-50-8; 1,4,8,11-tetraazacyclotetradecane, 295-37-4; trimethylaluminum, 75-24-1.

Supplementary Material Available: Tables of bond distances and angles, final fractional coordinates, and thermal parameters (8 pages); a listing of observed and calculated structure factors (9 pages). Ordering information is given on any current masthead page.

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(36) Amirkhalili, S.; Hitchcock, P. B.; Jenkins, A. D.; Nyathi, J. Z.; Smith, J. D. *J. Chem. Soc., Dalton Trans.* **1981**, 377.

Is Thermal Stability of σ-Alkyl Transition-Metal Complexes Compatible with the Presence of Conformationally Free β-Hydrogens and Absence of Stabilizing Ligands? The Isolation of Novel and Unexpectedly Stable Four-Membered Cyclic (σ-Alkyl)palladium Complexes[1]

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A novel type of four-membered cyclic (σ-alkyl)palladium complexes has been isolated. These (2-aminoalkyl-*C,N*)palladium(II) complexes (or 2-azapalladacyclobutanes) are thermally semistable, although they lack the support of stabilizing ligands. Conformationally free β-hydrogens do not imply increased lability, and an X-ray structure of such a complex, chloro[2-(dimethylamino)-1-methylpropyl-*C,N*](dimethylamine)palladium(II) (4), has been obtained. The unexpected order of stability of the complexes provides new prospects on how to stabilize σ-alkyl transition-metal species.

Introduction

The thermal lability of σ-alkyl transition-metal complexes constitutes a persistent problem not only for organometallic chemists but also for synthetic chemists utilizing the expanding set of convenient and highly specific tools offered by modern organometallic chemistry.

One synthetically useful reaction, which illustrates this situation, is the transition-metal-catalyzed cross-coupling between organic halides and alkyl main-group-metal compounds outlined in a general form in eq 1.

$$\mathrm{RX} + \mathrm{R'{-}m} \xrightarrow[\mathrm{L}]{\mathrm{M}} \mathrm{R{-}R'} + \mathrm{mX} \qquad (1)$$

R= aryl, vinyl, allyl
R'= aryl, alkyl, vinyl, allyl
X= Br, I
m= MgBr, Li, Zn, B, Al, Zr, Hg, Sn
M= Ni, Pd, Rh

From an origin of restricted scope (nickel-catalyzed coupling of aryl Grignard reagents with aryl or vinyl halides[2]) this reaction now, with the proper combination of reactants, appears as general as in eq 1.[3,4] However,

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[†] Department of Inorganic Chemistry.

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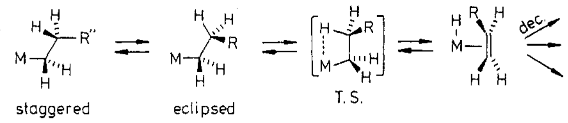
(1) In part presented at the XIIth International Conference on Organometallic Chemistry in Vienna, September 1985.

(2) (a) Tamao, K.; Sumitani, K.; Kumada, M. *J. Am. Chem. Soc.* **1972**, *94*, 4374. (b) Couriu, R. I. P.; Masse, J. P. *J. Chem. Soc., Chem. Commun.* **1972**, 144.

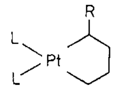
(3) (a) Negishi, E. *Acc. Chem. Res.* **1982**, *15*, 340. (b) Negishi, E.; Luo, F. T. *J. Org. Chem.* **1983**, *48*, 1560 and references therein. (c) Hayashi, T.; Konishi, M.; Kobori, Y.; Kumada, M.; Higuchi, T.; Hirotsu, K. *J. Am. Chem. Soc.* **1984**, *106*, 158 and references therein. (d) Beletskaya, I. P. *J. Organomet. Chem.* **1983**, *250*, 551. (e) Davies, S. G. In *Organotransition Metal Chemistry: Applications to Organic Synthesis*; Pergamon Press: Oxford, 1982; p 218. (f) Laroch, R. C.; Narayanan, K.; Hershberger, S. S. *J. Org. Chem.* **1983**, *48*, 4377. (g) Goliaszewski, A.; Schwartz, J. *J. Am. Chem. Soc.* **1984**, *106*, 5028. (h) Tsuji, J. *Organic Synthesis with Palladium Compounds*; Springer-Verlag: Berlin, 1980. (i) Sheffy, F. K.; Godschalx, J. P.; Stille, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 4833 and references therein. (j) Russel, C. E.; Hegedus, L. S. *Ibid.* **1983**, *105*, 943.

Scheme I

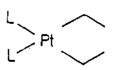


one remaining important restriction is that ordinary alkyl halides do not work, a serious inconvenience ascribed to the low thermal stability of the intermediate β-hydrogen-containing σ-alkyl transition-metal complexes formed in the catalytic cycle.[5] In fact, this type of substrate limitation is the rule for many potentially, extremely useful transition-metal-catalyzed synthetic procedures.[6] σ-Alkyl transition-metal complexes owe their thermal lability to several decomposition routes.[7] The major downhill pathway is considered to be β-hydride elimination (outlined in Scheme I).[8] In order to avoid decomposition when preparing alkyl transition-metal complexes, three ways are clearly discernible: (a) the alkyl groups lack β-hydrogens, (b) the complex is supported by stabilizing ligands (phosphines, arsines, cyclopentadienyl, olefins), and, (c) the alkyl group is a part of an energetically favored five- or six-membered metallacycle, where the β-hydrogens are conformationally locked and thus cannot adopt the cisoid conformation needed in the transition state (cf. Scheme I).

This last concept has been pedagogically illustrated by Whitesides in an important study of the β-elimination in the platinum case, where cyclic complexes, such as **1**, have superior stability compared to the acyclic complexes **2**.[9]



1 a R=H
b R=CH$_3$



2

However the question why **1b** with conformationally free β-hydrogens on the methyl group remained about as stable as **1a** was left unanswered. Thorough studies on thermolysis of bis(σ-alkyl)palladium and -platinum complexes have been performed;[10] the reactivity patterns show significant differences between palladium and platinum.

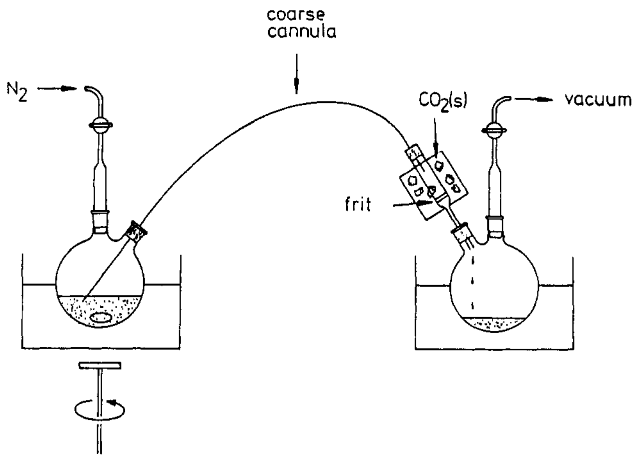
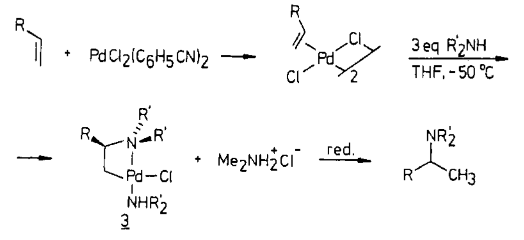


Figure 1.

We now want to present a new class of (σ-alkyl)palladium complexes, which show unexpectedly high thermal stability (vide infra). Small structural changes result in large changes in stability. The synthesized complexes are neutral or cationic. An X-ray structure of a representative complex is also presented.

Results

Recently we presented a mechanistic study in the palladium-assisted nucleophilic addition to double bonds (eq 2).[11] By low-temperature NMR, we could monitor how

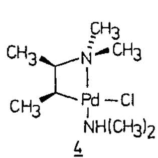


(2)

different intermediates in equilibria resulted in the formation of the four-membered cyclic structure **3**, and we also briefly described the isolation of two (σ-alkyl)palladium complexes **3** (**a**, R = Et, R′ = Me; **b**, R = H, R′ = Et) at reduced temperature.[11a]

Complexes **3** could be handled in crystalline form for short periods of time at room temperature. This relative thermal stability was unexpected, as these complexes lack stabilizing ligands, and, although the complexes are cyclic, the alkyl groups are not within a five-membered but rather in a less favorable four-membered, cyclic structure. At the time it seemed reasonable to ascribe the stability to the conformationally locked β-hydrogens.

Similarly from propene, we have now been able to isolate **3c** (R = CH$_3$), which could (as complexes **3a** and **3b**) be stored at −20 °C for shorter periods. More surprising, however, was the high stability of complex **4** from *trans*-2-butene.



4

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[4] The synthetic value of this reaction is further increased as bidentate, chiral ligands can induce optically active coupling products in high ee from racemic starting reagents. (a) Hayashi, T.; Konichi, M.; Fukushima, M.; Mise, T.; Kagotani, M.; Tajika, M.; Kumada, M. *J. Am. Chem. Soc.* **1982**, *104*, 180. (b) Hayashi, T. *Chem. Scr.* **1985**, *25*, 61 and references therein.

[5] An exception to this is reported as α-bromobutyrolactone can undergo palladium-catalyzed coupling with allyl- and acetonyltin compounds. Simpson, J. H.; Stille, J. K. *J. Org. Chem.* **1985**, *50*, 1759.

[6] Good examples may be found in: Collman, J. P.; Hegedus, L. S. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1980; pp 570, 576, 577, 584, and 597.

[7] As interesting examples of different decompositions, see: (a) Hacksell, U.; Daves, G. D. *Organometallics* **1983**, *2*, 772 and references therein. (b) Hacksell, U.; Kalinoski, H.; Barofsky, D. F.; Daves, G. D. *Acta Chem. Scand., Ser. B* **1985**, *39*, 469 and references therein.

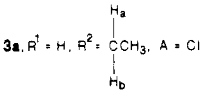
[8] See ref 6; pp 73 and 536.

[9] McDermott, J. X.; White, J. F.; Whitesides, G. M. *J. Am. Chem. Soc.*, **1976**, *98*, 6521.

[10] (a) Gillie, A.; Stille, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 4933. (b) Loar, M.; Stille, J. K. *Ibid.* **1981**, *103*, 4174. (c) Moravskiy, A., Stille, J. K. *Ibid.* **1981**, *103*, 4182. (d) Yamamoto, A.; Yamamoto, T.; Komiya, S.; Ozawa, F. *Pure Appl. Chem.* **1984**, *56*, 1621. (e) Komiya, S.; Morimoto, Y.; Yamamoto, A.; Yamamoto, T. *Organometallics* **1982**, *1*, 1528. (f) Ozawa, F.; Ito, T.; Nakamura, Y.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1868. (g) For a comparison with photolysis of diethylbis(tertiary phosphine)palladium(II) see: Ozawa, F.; Yamamoto, A.; Ikariya, T.; Grubbs, R. H. *Organometallics* **1982**, *1*, 1481. (h) McCarthy, T. J.; Nuzzo, R. G.; Whitesides, G. M. *J. Am. Chem. Soc.* **1981**, *103*, 1676. (i) McCarthy, T. J.; Nuzzo, R. G.; Whitesides, G. M. *Ibid.* **1981**, *103*, 3396.

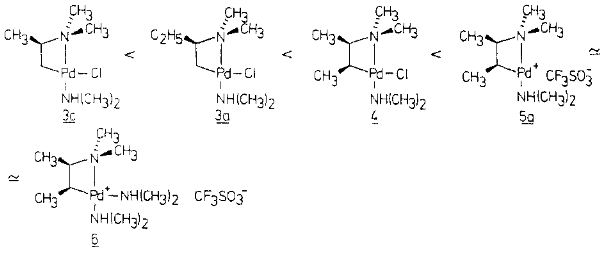
[11] (a) Hegedus, L. S.; Akermark, B.; Zetterberg, K.; Olsson, L. F. *J. Am. Chem. Soc.* **1984**, *106*, 7122. (b) Akermark, B.; Zetterberg, K. *Ibid.* **1984**, *106*, 5560.

Table I. NMR Data of Complexes 3, 4, and 5[a]

	R^1	H_α	R^2	H_β	CH_3-N
3c, R^1 = H, R^2 = CH_3, A = Cl	0.09 (1 H, dd, J_{trans} = 9.33, J_{gem} = 6.44)	0.80 (1 H, dd, J_{cis} = 8.06, J_{gem} = 6.44)	1.00 (3 H, d, J = 6.80)	4.06 (1 H, m)	2.45–2.87
 **3a**, R^1 = H, R^2 = $\overset{H_a}{\underset{H_b}{C}}CH_3$, A = Cl	0.11 (1 H, dd, J_{trans} = 9.90, J_{gem} = 6.30)	0.89 (1 H, dd, J_{cis} = 8.05, J_{gem} = 6.30)	CH_3, 0.81 (3 H, t,[b] J = 7.37), H_a, 1.54 ($J_{H_a-H_\beta}$ = 4.87, J_{gem} = 12.8), H_b, 1.29 ($J_{H_b-H_\beta} \approx 10.0$)	3.72 (1 H, dd app t,[b] J_{cis} = 8.08, J_H = 4.87, $J_{H_\beta-H_b} \approx J_{trans} \approx 10.0$)	2.48–2.68
4, R^1 = CH_3, R^2 = CH_3, A = Cl	0.77 (3 H, d, J = 7.28)	1.31 (1 H, dq, J_{cis} = 8.70)	1.03 (3 H, d, J = 7.17)	4.202 (1 H, dq)	2.55–2.68
5b, R^1 = H, R^2 = CH_3, A = $CF_3SO_3^-$	0.50 (1 H, dd, J_{trans} = 9.36, $J_{gem} \approx 6.4$)	1.21 (1 H, br app t, $J_{cis} \approx 7.5$)	1.06 (3 H, d, J = 6.79)	4.11 (1 H, m)	2.4–2.6
5a, R^1 = CH_3, R^2 = CH_3, A = $CF_3SO_3^-$	0.67 (3 H, d, J = 7.23)	1.55 (1 H, dq, J_{cis} = 8.65)	1.04 (3 H, d, J = 7.18)	4.11 (1 H, dq)	2.5–2.6
6, R^1 = CH_3, R^2 = CH_3, A = $NH(CH_3)_2$ or $CF_3SO_3^-$	0.71 (3 H, d, J = 7.29)	1.39 (1 H, br m)	1.037 (3 H, d, J = 7.13)	4.17 (1 H, m)	2.5–2.6

[a] Coupling constants in Hz; δ relative Me_4Si signal; solvent is $CDCl_3$. [b] Enhanced resolution was obtained via Gaussian multiplication of the FID.

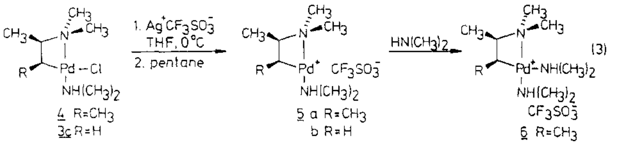
Scheme II. Stability Order for Some (σ-Alkyl)palladium Compounds



Conformationally free β-hydrogens in the vicinity of the coordination vacancy of palladium were supposed to render this complex thermally labile.[12] As a matter of fact, this is the most stable complex in our series of neutral (σ-alkyl)palladium complexes. It can be kept in crystalline form for at least an hour at 25 °C without noticeable decomposition and can be stored for months at −20 °C. It gave a satisfactory elementary analysis, and we succeeded in obtaining an X-ray structure (vide infra) under moderate cooling (~−10 °C). In solution, however, it decomposes markedly within 15 min at 25 °C.

The isolation procedure is quite simple and involves the use of a low-cost setup depicted in Figure 1. We think this setup in most cases can replace the classical but somewhat cumbersome Schlenk apparatus. In contrast to the basic Schlenk method, this procedure also enables the isolation of thermally semilabile compounds.

In our procedure precipitated $(CH_3)_2NH_2^+Cl^-$ was filtered in the cold. Crystallization of the product (soluble in THF at −50 °C) was brought about by the addition of pentane, and a second cold filtration afforded the product typically in the 80% region. Cationic complexes **5** and **6** can be conveniently synthesized at 0 °C according to eq 3.



These complexes behave similarly to the corresponding neutral complexes, but **5a** possesses a higher degree of thermal stability in solution compared to that of **4**. The thermal stability order is summarized as shown in Scheme II.

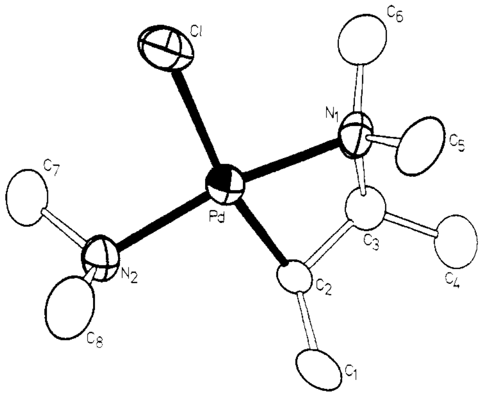


Figure 2. An ORTEP drawing of complex **4**. Hydrogen atoms are omitted.

Table II. Intramolecular Bond Lengths (Å; Non-Hydrogen Atoms) for Complex

Pd–Cl	2.469 (2)	C_1–C_2	1.503 (11)	N_1–C_5	1.473 (10)
Pd–N_1	2.060 (5)	C_2–C_3	1.524 (9)	N_1–C_6	1.466 (10)
Pd–N_2	2.081 (5)	C_3–C_4	1.503 (11)	N_2–C_7	1.461 (11)
Pd–C_2	2.023 (6)	C_3–N_1	1.520 (9)	N_2–C_8	1.481 (11)

^1H NMR data of these complexes form a characteristic consistent pattern (see Table I).

Protons attached to the β-carbon in the four-membered palladacycle appear at low field (δ 3.6–4.2), while protons attached to the α-carbon and trans to a β-hydrogen in the ring are observed at high field (δ 0.1–0.5). The trans coupling constants are typically larger (9–10 Hz) than the cis coupling constants (7.5–8.7 Hz). Similar patterns are seen in the case of the corresponding four-membered cyclic platinum complexes.[13]

The Structure of Complex 4. X-ray structures of (σ-alkyl)palladium compounds are numerous, but usually these complexes fulfill at least one of three requirements:[7b,14,15] i, stabilization from π-accepting ligands like

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(12) (a) For an attractive Pd–H–C–L interaction (2.52 Å), see: Natile, G.; Gasparrini, F.; Galli, B.; Manatti-Lanfaldi, A. M.; Tiripicchio, A. *Inorg. Chem. Acta* **1980**, *44*, L29. (b) For a similar Pd–H interaction (2.46 Å), see: Hosokawa, T.; Ohta, T.; Murahashi, S.; Kido, M. *J. Organomet. Chem.* **1982**, *228*, C55.

(13) (a) De Renzi, A.; Panunzi, A.; Vitagliano, A. *Gazz. Chim. Ital.* **1978**, *108*, 45. (b) De Renzi, A.; De Blasio, B.; Morelli, G.; Vitagliano, A. *Inorg. Chim. Acta* **1982**, *63*, 233. (c) Green, M.; Sarkan, J. K. K.; Al-Najjar, I. M. *Organometallics* **1984**, *3*, 520. (d) Sarkan, J. K. K.; Green, M.; Al-Najjar, I. M. *J. Chem. Soc., Dalton Trans.* **1984**, 771. (e) Green, M.; Sarkan, J. K. K.; Al-Najjar, I. M. *Ibid.* **1981**, 1565. (f) Al-Najjar, I. M.; Green, M.; Kerrison, S. J. S.; Sadler, P. J. *J. Chem. Soc., Chem. Commun.* **1979**, 311.

Table III. Selected Bond Angles (deg) for Complex[a]

C_2–Pd–N_1	70.77 (23)	C_1–C_2–Pd	113.85 (49)	C_3–N_1–Pd	90.82 (36)
C_2–Pd–N_2	96.44 (25)	C_1–C_2–C_3	118.07 (60)	C_3–N_1–C_5	112.82 (56)
C_2–Pd–Cl	168.24 (19)	Pd–C_2–C_3	92.15 (41)	C_3–N_1–C_6	114.44 (54)
N_1–Pd–N_2	167.12 (22)	C_2–C_3–$C_4$1	119.25 (67)	C_7–N_2–Pd	112.55 (48)
N_1–Pd–Cl	98.48 (15)	C_2–C_3–N_1	101.95 (52)	C_7–N_2–C_8	110.44 (63)
N_2–Pd–Cl	94.39 (17)	C_4–C_3–N_1	114.94 (64)	C_8–N_2–Pd	112.48 (49)

[a] The angles of the palladacycle are underlined.

Table IV. Intramolecular Distances (Å) between Selected Hydrogen Atoms and Palladium[a]

Pd–H_{1A}	3.15 (7)	Pd–H_2	2.33 (6)
Pd–H_{1B}	3.78 (8)	Pd–H_3	2.90 (5)
Pd–H_{1C}	3.07 (7)		

[a] H_{1A}, H_{1B}, and H_{1C} are conformationally free β-hydrogens in solution. H_3 is locked.

Table V. Final Fractional Atomic Positional Parameters

atom	*x*	*y*	*z*
Pd	0.22974 (5)	0.01714 (3)	0.88722 (4)
Cl	0.1267 (2)	0.8423 (1)	0.7788 (2)
N1	0.2763 (5)	0.9653 (4)	0.0862 (4)
N2	0.2034 (5)	0.1022 (4)	0.7049 (5)
C1	0.1979 (7)	0.2337 (5)	0.0164 (7)
C2	0.3034 (6)	0.1479 (5)	0.0098 (6)
C3	0.3562 (6)	0.0719 (5)	0.1318 (6)
C4	0.3545 (8)	0.1127 (7)	0.2703 (7)
C5	0.3607 (8)	0.8640 (6)	0.1191 (7)
C6	0.1545 (7)	0.9531 (6)	0.1353 (7)
C7	0.0604 (7)	0.1229 (6)	0.6367 (7)
C8	0.2717 (8)	0.0464 (6)	0.6122 (7)
H1A	0.110 (6)	0.196 (5)	0.050 (5)
H1B	0.731 (6)	0.215 (5)	0.583 (6)
H1C	0.160 (6)	0.261 (5)	0.937 (5)
H2	0.371 (5)	0.164 (4)	0.981 (5)
H3	0.445 (4)	0.058 (4)	0.134 (4)
H4A	0.376 (5)	0.060 (4)	0.334 (5)
H4B	0.263 (7)	0.125 (7)	0.261 (7)
H4C	0.412 (6)	0.164 (5)	0.295 (6)
H5A	0.556 (5)	0.119 (5)	0.909 (5)
H5B	0.697 (5)	0.197 (5)	0.921 (5)
H5C	0.606 (7)	0.142 (5)	0.791 (6)
H6A	0.899 (5)	0.107 (4)	0.921 (5)
H6B	0.826 (6)	0.054 (5)	0.766 (6)
H6C	0.093 (5)	0.026 (4)	0.118 (5)
H7A	0.044 (7)	0.156 (6)	0.549 (7)
H7B	0.036 (8)	0.177 (6)	0.702 (8)
H7C	0.030 (8)	0.036 (6)	0.633 (7)
H8A	0.770 (6)	0.031 (5)	0.414 (6)
H8B	0.373 (7)	0.032 (5)	0.651 (6)
H8C	0.254 (7)	0.089 (6)	0.532 (7)
H9N	0.240 (6)	0.155 (5)	0.723 (6)

phosphines, arsines, etc.; ii, stabilization from chelation, where the σ-alkyl group is part of a favorable five-membered or larger palladacycle; iii, stabilization due to absence of β-hydrogens. Thus an X-ray structure of **4**, which is void of the above stabilizing factors, may be of interest. Complex **4** survived long enough in a moderately cool nitrogen stream (around −10 °C) to yield an X-ray structure as depicted in Figure 2.

All the hydrogens could be located at reasonable positions (the fractional atomic positional parameters are found in Table V in the Experimental Section). Bond distances for non-hydrogen atoms are given in Table II and selected bond angles in Table III.

The palladium–carbon bond length (2.021 Å) is in quite good agreement with observed values from phosphine-stabilized four-membered alkylpalladacycles.[14a–c] The value (70.9°) of the C_2–Pd–N-angle may at first seem small but is well within the range of other four-membered alkylpalladacycles,[14a–c] as well as similar platinacycles.[13b,16,17] It has been proposed that four-membered metallacycles are just moderately strained species compared to the favored five-membered metallacycles.[18]

None of the β-hydrogens are close to the palladium atom. The β-hydrogen on C_3 is the closest (2.90 Å), while all the β-hydrogens at C_1 are more than 3 Å away (as seen from Table IV).

Discussion

The observed order of stability of Scheme II is, in some significant respects, unexpected. For example one would at first anticipate that the charged, three-coordinate complex **5a** to be more prone to undergo β-elimination than the neutral, four-coordinate complex **4** as β-elimination of **5a** would restore a more favorable (or at least more common) four-coordinate situation. It may be further argued that in solution, **5a** is coordinating a solvent molecule and thus is not as reactive as anticipated from the sheer three-coordinate formula. However, this coordination must be weak. Furthermore, as **5a** is precipitated from a THF solution, at least an equilibrating fraction of **5a** in solution must exist without coordinating solvent.

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(14) For some representative X-ray structures of (σ-alkyl)palladium complexes see: (a) Kemmit, R. D. W.; McKenna, P.; Russel, D. R.; Sherry, L. J. S. *J. Chem. Soc., Dalton Trans.* **1985**, 239. (b) Oliver, J. D.; Mullica, D. F.; Milligan, W. O. *Inorg. Chem.* **1982**, *21*, 3284. (c) Kai, Y.; Yasuoka, N.; Kasai, N. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 737. (d) Parra-Hake, M.; Rettig, M. F.; Wing, R. M.; Woolcock, J. C. *Organometallics* **1982**, *1*, 1478. (e) Newkome, G. R.; Puckett, W. E.; Gupta, V. K.; Fronczek, F. R. *Ibid.* **1983**, *2*, 1247. (f) Newkome, G. R.; Kawato, T.; Kohli, D. K.; Puckett, W. E.; Olivier, B. D.; Chiari, G.; Fronczek, F. R.; Deutsch, W. A. *J. Am. Chem. Soc.* **1981**, *103*, 3423. (g) Claverini, R.; De Renzi, A.; Ganis, P.; Panunzi, A.; Pedone, C. *J. Organomet. Chem.* **1973**, *51*, C30. (h) Dehand, J.; Mauro, A.; Ossor, H.; Pfeffer, M.; Santos, R. H. DeA.; Lechet, J. R. *Ibid.* **1983**, *250*, 537. (i) Rheingold, A. L.; Fultz, W. C. *Organometallics* **1984**, *3*, 1414. (j) Errington, R. J.; McDonald, W. S.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1982**, 1829. (k) Constable, A. G.; McDonald, W. S.; Sawkins, L. C.; Shaw, B. L. *Ibid.* **1980**, 1992. (l) Andrews, M. A.; Chang, T. C.; Cheng, C. F.; Emge, T. J.; Kelly, K. P.; Koetzle, T. F. *J. Am. Chem. Soc.* **1984**, *106*, 5913.

(15) An even vaster variety of stable (σ-alkyl)palladium complexes, which have not undergone an X-ray analysis, have been isolated during the years. Still they appear to fulfill at least one of the requirements mentioned. See, for example: (a) Chatt, J.; Vallarino, L. M.; Venanzi, L. M. *J. Chem. Soc.* **1959**, 3413. In this reference the first reported (σ-alkyl)palladium complexes are to appear. (b) Andrews, M. A.; Chang, T. C.; Cheng, C. F.; Kapustay, L. V.; Kelly, K. P.; Zweifel, M. J. *Organometallics* **1984**, *3*, 1479. (c) Stille, J. K.; Morgan, R. A. *J. Am. Chem. Soc.* **1966**, *88*, 5135. (d) Cope, A. C.; Kliegman, J. M.; Friedrich, E. C. *J. Am. Chem. Soc.* **1967**, *89*, 287. (e) Weinberg, E. L.; Hunter, B. K.; Baird, M. C. *J. Organomet. Chem.* **1982**, *240*, 95. (f) Bottomley, A. R. H.; Crocker, C.; Shaw, B. L. *Ibid.* **1983**, *250*, 617. (g) Diversi, P.; Ingrosso, G.; Lucherini, A.; Murtas, S. *J. Chem. Soc., Dalton Trans.* **1980**, 1633. (h) Diversi, P.; Fasce, D.; Santini, R. *J. Organomet. Chem.* **1984**, *269*, 285. (i) McCrindle, R.; McAlees, A. J. *J. Chem. Soc., Dalton Trans.* **1983**, 127. (j) McCrindle, R.; Alyea, E. C.; Ferguson, G.; Dias, S. A.; McAlees, A. J. *Ibid.* **1980**, 137. This reference presents an unusual seven-membered palladacycle. (k) McCrindle, R.; Ferguson, G.; Khan, M. A.; McAlees, A. J. *Ibid.* **1981**, 986. (l) McCrindle, R.; McAlees, A. J. *J. Organomet. Chem.* **1983**, *244*, 97. (m) Ozawa, F.; Sugimoto, T.; Yuasa, Y.; Santra, M.; Yamamoto, T.; Yamamoto, A. *Organometallics* **1984**, *3*, 683. (n) Nakazawa, H.; Ozawa, F.; Yamamoto, A. *Ibid.* **1983**, *2*, 241. (o) Anderson, G. K. *Ibid.* **1983**, *2*, 665.

(16) Ibers, J. A.; DiCosimo, R.; Whitesides, G. M. *Organometallics* **1982**, *1*, 13.

(17) For a four-membered (σ-alkyl)platinum(IV) cycle with a C–Pt–C angle of 70.2° see: Burton, J. T.; Puddephatt, R. J.; Jones, N. L.; Ibers, J. A. *Organometallics* **1983**, *2*, 1487.

(18) The ring strain differens for platinacycles is estimated to ~5 kcal/mol. Moore, S. S.; DiCosimo, R.; Sowinski, A. F.; Whitesides, G. M. *J. Am. Chem. Soc.* **1981**, 103, 948.

In the platinum case, β-elimination for bis(phosphine) dialkyl complexes takes place after dissociation of a phosphine to a three-coordinate species.[10d,e,h,i] Whether *trans*-chloroethylbis(triethylphosphine)platinum(II) β-eliminates before or after ligand dissociation is not clear.[19] The corresponding dialkylpalladium complexes β-eliminate mainly via a nondissociative path, while reductive elimination is favored (against intuition?) by dissociation.[10d,f] Therefore we cannot safely predict in the palladium case whether the propensity for a three-coordinate species like **5a** to β-eliminate is stronger or at least not comparable to a four-coordinate complex like 4, but an anticipated higher reactivity for **5a** would seem reasonable. What factor is causing a reactivity order reversed from that expected? We suggest that the *geometrical rigidity* of the four-membered ring is the main stabilizing factor but is not necessarily a hindrance against β-hydrogens to adopt cisoid conformation toward the metal. Instead this geometrical rigidity acts as a hindrance against orbital reorganization at the metal; the reorganization is needed to initiate decomposition. The more rigid a system is, the more will geometrical changes increase the total energy of the system.

Thus as long as the rigid four-membered palladacycle is maintained, decomposition is prevented. Complex **5a** will therefore be more thermally stable than 4 because a cationic palladium atom holds the ring nitrogen more firmly than the neutral palladium of 4.

This concept will explain why complex **4**, containing conformationally free β-hydrogens, is more stable than complexes **3a–c** (without "free" β-hydrogens). A ring opening of **4** will cause an increased steric repulsion between the two cis methyl groups, and these therefore act to preserve the metallacycle.

Similar reasoning may offer an explanation why Whitesides' platinum complexes **1a** and **1b** are of comparable stability.

From our X-ray data, it is clear that our structure does not show any extraordinary or significantly different features compared to those of, e.g., phosphine-supported (σ-alkyl)palladium complexes. It may thus be asked whether the "stabilizing effect" of such π-accepting—as well as polydentate—ligands is a result (at least in part) of ligand-induced geometrical rigidity.

Conclusions

This study presents (a) the first isolated (σ-alkyl)palladium complexes where a four-membered cyclic array constitutes the sole stabilizing factor, (b) an X-ray structure of such a complex (**4**), containing conformationally free β-hydrogens and lacking the support of stabilizing ligands, (c) a stability order of the σ-alkyl complexes that indicates the importance of *geometrical rigidity* around the metal preventing orbital reorganization as an important stabilizing factor, and (d) evidence that the introduction of conformationally free β-hydrogens will not necessarily render a transition-metal complex thermally less stable.

Experimental Section

The NMR spectra were recorded at 200 MHz on a Bruker Model WP 200 spectrometer equipped with a Bruker B-VT-1000 temperature-control unit. Tetrahydrofuran (THF) was distilled from potassium/benzophenone under nitrogen. *trans*-2-Butene (99%) was purchased from Fluka in tin lecture bottles and used without further purification. Elementary analyses were performed by Mikro-Kemi AB, S-750 19 Uppsala, Sweden.

Preparation of Chloro[2-(dimethylamino)propyl-*C*,*N*]-(dimethylamine)palladium(II) (3c).[20] Dichlorobis(benzonitrile)palladium(II) (1.536 g, 4.0 mmol) was dissolved in 50 mL of THF after degassing under nitrogen. At −15 °C propene (2 × 100 mL gas) was injected from a syringe.

The brown solution was cooled to −55 °C. Injection of dimethylamine (5 × 100 mL gas) from a syringe gave a whitish suspension, which was stirred for 1 h at reduced temperature. Cold filtration according to Figure 1 separated 298 mg of dimethylammonium chloride (theoretical 326 mg). Dropwise addition of 100 mL of pentane to the cold filtrate and stirring of the cream white precipitate for 40 min preceded a second cold filtration affording 0.897 g of **3c** (82%). The crystalline material could be handled (e.g. for weighing) for short periods of time at 25 °C. While the material was stored in the freezer, the color turned gradually darker. Anal. Calcd for $C_7H_{19}N_2ClPd$: C, 30.80; H, 7.01; N, 10.26. Found: C, 30.2; H, 6.9; N, 10.3.

Chloro[2-(dimethylamino)butyl-*C*,*N*](dimethylamine)-palladium(II) (3a).[20] Dichlorobis(benzonitrile)palladium(II) (384 mg, 1.0 mmol), degassed under nitrogen, was dissolved in 9 mL of THF, and the temperature was decreased to −20 °C, whereafter 1-butene (200 mL of gas) was added from a balloon. The brown solution was cooled to −60 °C and dimethylamine (125 mL gas) was injected slowly from a syringe. After the mixture was stirred for 0.5 h, dimethylammonium chloride was filtered in the cold, the filtrate treated with 30 mL of pentane at −70 °C, and after a second cold filtration **3a** was afforded as 229 mg of cream white crystals (80%), slightly more stable than **3c**.

Chloro[2-(dimethylamino)-1-methylpropyl-*C*,*N*](dimethylamine)palladium(II) (4).[20] This complex was prepared (85%) similarly to **3c** except that *trans*-2-butene was used instead of 1-butene. Anal. Calcd for $C_8H_{21}N_2ClPd$: C, 33.49; H, 7.37; N, 9.76. Found: C, 33.4; H, 7.3; N, 9.7.

[2-(Dimethylamino)-1-methylpropyl-*C*,*N*](dimethylamine)palladium(II) Trifluoromethanesulfonate (5a).[20] Complex 4 (115.2 mg, 0.40 mmol) was flushed in N_2 and dissolved in 10 mL of THF at 0 °C. Silver trifluoromethanesulfonate (102.8 mg, 0.40 mmol), dissolved in 2 mL of THF, was slowly added, and the precipitated silver chloride was removed after stirring for 0.5 h via filtration. The volume of the clear, light yellow filtrate was concentrated at 0 °C on a rotovap to around 2 mL. After dropwise addition of 2 mL of pentane slight precipitation appeared. The crystallization was improved by storage in the freezer overnight, and further addition of 5 mL of pentane afforded 155 mg of whitish, rather large crystals of **5a** (97%).

[2-(Dimethylamino)propyl-*C*,*N*](dimethylamine)palladium(II) Trifluoromethanesulfonate (5b).[20] This compound was prepared similarly to **5a**, but in half the scale. The complex was obtained as 77 mg of a light yellow oil (crude yield 99%).

[2-(Dimethylamino)-1-methylpropyl-*C*,*N*]bis(dimethylamine)palladium(II) Trifluoromethanesulfonate (6).[20] Complex 4 (43.2 mg, 0.15 mmol) was flushed with N_2 and dissolved in 5 mL of THF at 0 °C. Silver trifluoromethanesulfonate (39.5 mg, 0.15 mmol) dissolved in 1 mL of THF was slowly added, and the mixture was stirred for half an hour at 0 °C before filtration. After addition of dimethylamine (4 mL of gas) the volume was decreased at 0 °C until slight precipitation appeared. Addition of 4 mL of pentane and storage in the freezer overnight afforded, after filtration, 66 mg of white crystals of **6** (99%).

X-ray Diffraction Data of Complex 4. Intensity data were collected at of about −10 °C in a Syntex P2₁ automatic four-circle diffractometer, equipped with a low-temperature device, with Mo Kα radiation (λ = 0.7107 Å); ω-scanning was used with scan speeds variable from 0.49 up to 29.5° min^{-1}. Complex 4 was dissolved at 0 °C in a small volume of methylene chloride. Ether was added dropwise, and cooling overnight in the freezer afforded suitable crystals. The crystal used had the dimensions 0.3 × 0.2 × 0.2 mm. Precession and Weissenberg photographs were used to determine

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(19) Brainard, R. L. H.; Whitesides, G. M. *Organometallics* **1985**, *4*, 1550.

(20) Alternatively these complexes could be described as 2-azapalladacyclobutanes. The following names are not systematic: **3c**, 1-chloro-1-(dimethylamine)-2,2,3-trimethyl-2-azapalladacyclobutane; **3a**, 1-chloro-1-(dimethylamine)-2,2-dimethyl-3-ethyl-2-azapalladacyclobutane; **4**, 1-chloro-1-(dimethylamine)-2,2-dimethyl-(*Z*)-3,4-dimethyl-2-azapalladacyclobutane; **5a**, 1-(dimethylamine)-2,2-dimethyl-(*Z*)-3,4-dimethyl-2-azapalladoniacyclobutane trifluoromethanesulfonate; **5b**, 1-(dimethylamine)-2,2,3-trimethyl-2-azapalladoniacyclobutane trifluoromethanesulfonate; **6**, 1,1-bis(dimethylamine)-2,2-dimethyl-(*Z*)-3,4-dimethyl-2-azapalladoniacyclobutane trifluoromethanesulfonate.

symmetry and initial values for the unit-cell dimensions. The lattice constants were refined by centering 25 selected reflections on the diffractometer. A monoclinic unit cell was found with a = 10.1949 (14) Å, b = 11.9786 (25) Å, c = 10.2306 (19) Å, β = 105.409 (13)°, and V = 1204.5 Å^3. The calculated density was 1.58 g cm^{-3} for $Z = 4$. The density determined by displacement in decane was 1.56 g cm^{-3}. Systematically absent reflections were $0k0$ for $k = 2n + 1$ and $h0l$ for $h + l = 2n + 1$ consistent with space group $P2_1/n$. (The setting differs from that used in ref 24.) Out of 2754 independent reflections, 2000 had intensities larger than $1.96\sigma(I)$ and were considered observed. The intensities were corrected for Lorentz and polarization effects and converted to scaled $|F_o|$ values. After every 100th reflection five check reflections were measured. After about 1200 reflections ($2\theta \leq 40°$) the intensities had decreased about 10% which probably reflects a slow decomposition of the crystal.

The absorption coefficient μ(Mo Kα) is 16.9 cm^{-1}. Semiempirical absorption corrections were applied by using values for the variation in intensity of selected reflections when rotated around the diffraction vector.[21] The Syntex XTL program system[22] and the thermal ellipsoid plot program,[23] ORTEP-II, were used for the calculations.

The scattering factors used for all non-hydrogen atoms were calculated from analytical expressions for the neutral atoms.[24] For the hydrogen atoms the spherical form factors proposed by Stewart et al. were used.[25] Anomalous dispersion corrections were included for palladium, chlorine, and nitrogen.[24]

Structure Determination and Refinement. The positions of the palladium atoms were found from the three-dimensional Patterson map and were used as the starting point for a full-matrix least-squares refinement. The function minimized was $\sum w||F_o| - |F_c||^2$ including reflections with $F_o > 3.92\sigma(F_o)$ with the weighting factor $w^{-1} = \sigma^2(F_o) + (0.09F_o)^2$. The chlorine, nitrogen, and carbon atoms were found from a subsequent Fourier difference synthesis. Full-matrix least-squares refinements with all atoms isotropic gave R = 0.089. From a difference map likely positions for 17 of the 21 hydrogen atoms could be found. When these were included in the least-squares refinement with isotropic temperature factors, together with the non-hydrogen atoms with anisotropic temperature coefficients, the R value became 0.056. Refinement with the additional four hydrogen atoms inserted gave R = 0.049. In the final refinement cycle the shifts in positional and thermal parameters for the non-hydrogen atoms were less than 10% of the corresponding standard deviations; for some of the hydrogen atoms the corresponding figure was higher but always less than 15%. In a final difference map the highest remaining peak was 0.77 e Å^{-3}.

In a separate refinement cycle only reflections for $2\theta \leqslant 40°$ were used; in this range the intensities of the check reflections kept almost constant (within 10%). The positional and thermal parameters came out within the same values, within the standard deviations, as those in the treatment of the full data set. The R value in this case became 0.034, and the highest remaining peak in the difference map was 0.36 e Å^{-3}.

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Registry No. **3a**, 92314-30-2; **3c**, 107513-97-3; **4**, 91409-21-1; **5a**, 107495-32-9; **5b**, 107495-34-1; **6**, 107513-99-5; $PdCl_2(C_6H_5CN)_2$, 14220-64-5; $CH_2{=}CHCH_3$, 115-07-1; Me_2NH, 124-40-3; $CH_2{=}C\text{-}HCH_2CH_3$, 106-98-9; *trans*-$CH_3CH{=}CHCH_3$, 624-64-6.

Supplementary Material Available: Tables of fractional coordinates and isotropic thermal parameters, isotropic thermal parameters, and the hydrogen atoms, and anisotropic thermal parameters for **4** (3 pages); a listing of observed and calculated structure factors for **4** (63 pages). Ordering information is given on any current masthead page.

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