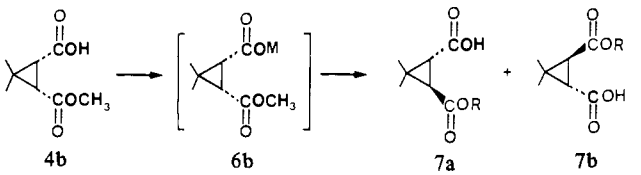
Scheme IV



4b 6b 7a 7b

		yield	7a	7b	ee[a]
entry a	4 equiv of *t*-BuOK/ C_6H_6, 70 °C, 1 h	44% (*R* = *t*-Bu)	73%	27%	46%
entry b	4 equiv of *t*-BuOK/ THF, 70 °C, 1 h	57% (*R* = *t*-Bu)	88%	12%	76%
entry c	4 equiv of KH/THF, 70 °C, 1 h	74% (*R* = Me)	87%	13%	74%
entry d	1 equiv of LiH/3 equiv of *t*-BuOK/THF, 70 °C, 1 h	76% (*R* = *t*-Bu)	98%	2%	96%

[a] ee = enantiomeric excess.

(1:1), 1.3 M solution, 70 °C, 15 h, and then careful acidification to pH 2 with 10% HCl, which produces the desired (1*R*,3*S*)-ester **4a** (R = *tert*-Butyl) (enantiomeric excess 99.6%) in 79% isolated yield.

The transformation of the cis-derivative **4b** (R = CH_3) to the trans-ester **7a** requires the selective epimerization at the ester group. We first tried on **4b** the reaction of *t*-BuOK (4 equiv., benzene or THF, 70 °C, 1 h) under conditions already successfully used by Julia[9] for the isomerization of the cis methyl chrysanthemate to its trans *tert*-butyl analogue. The combined yields of **7** (R = tBu) were modest (44% and 57%, respectively), but the optical purity of the compound was quite low (46% and 76% ee, respectively) (Scheme IV, entries a–b).

After several unsuccessful attempts (Scheme IV, entries a–c), we discovered that the potassium salt of the methyl hemicaronate **6b** (R = CH_3; M = K) quantitatively prepared on reaction of the corresponding acid **4b** (R = CH_3) with potassium hydride (1 equiv/THF) racemizes on heating at 70 °C for 1 h in the same solvent (after acidic hydrolysis, 96% recovery of **4**, **4b**/**4a** = 90:10). Such racemization probably occurs by an internal displacement of the methoxy group, which leads to the intermediate formation of the symmetrical anhydride **3**.

So that such side reaction could be avoided, a protecting group of the acid moiety was required. It must prevent the formation of the potassium salt **6b** (R = CH_3; M = K), must not acidify the hydrogen α to this carbonyl group, and must be cheap.

Lithium was found to be the best candidate since it satisfies the last two requirements and since the lithium salt **6b** (R = CH_3; M = Li) (from **4b** and LiH in THF) does not racemize on heating for 1 h (after acidic hydrolysis, 96% recovery of **4**, **4b**/**4a** = 97:3). Unfortunately, however, this salt does not isomerize to the trans derivative in the presence of an excess of LiH. Addition of some *tert*-butyl alcohol favors the last reaction; it does not, however allow the complete isomerization.

The desired transformation [**4b** (R = CH_3) to **7a** (R = *t*-Bu)] was finally stereoselectively achieved in 76% overall yield and 96% enantiomeric excess by the combination of the two observations just reported. Methyl hemicaronate **4b** was transformed to its lithium salt (1 equiv LiH/THF, 20 °C), potassium *tert*-butoxide (3 equiv, final concentration of **4b** = 0.2 M) was then added, and the solution was heated at 70°C for 1 h prior acidic hydrolysis (Scheme IV, entry d).

In the pyrethroid field only one synthetic strategy involving the separation of the two enantiomers and the recycling of the undesired one has been so far described.[10] Our method compares well with this industrial process since the separation of the enantiomers is accomplished at an early stage of the synthesis, no carbons are wasted, and the more economically valuable cis isomer is produced directly.

Registry No. 1 (R = H), 4638-92-0; **2** (R = H), 53179-78-5; **3**, 67911-21-1; **4a** (R = CH_3), 81873-49-6; (±)-**4** (R = CH_3), 81831-72-3; **4a** (R = CH_3) (+)-α-methylbenzylamine salt, 81938-54-7; **4a** (R = *t*-Bu), 81873-50-9; **4b** (R = CH_3), 81873-51-0; **4b** (R = CH_3) (−)-α-methylbenzylamine salt, 81938-55-8; **5a** (R = *t*-Bu), 81831-73-4; **6b** (M = K), 81938-56-9; **6b** (M = Li), 81938-57-0; **7a** (R = *t*-Bu), 81873-52-1; **7b** (R = CH_3), 27335-36-0; **7b** (R = *t*-Bu), 81873-53-2; **7b** (R = CH_3), 81938-58-1; **8a** (R = CH_3), 55701-02-5; **8a** (R = *t*-Bu), 56194-29-7; **2** (R = CH_3), 61775-87-9; **2** (R = *t*-Bu), 56194-58-2.

(9) S. Julia, M. Julia, and G. Linstrumelle, *Bull. Soc. Chim. Fr.*, 3499 (1966).

(10) (a) J. Martel, German Patent, 1, 935, 386; *Chem. Abstr.*, **72**, 100136d (1970); J. Martel, German Patent, 1, 935, 320; *Chem. Abstr.*, **72**, 121078b (1970). (b) J. Martel and J. Buendia, German Patent, 2, 010182; *Chem. Abstr.*, **73**, 109363c (1970).

Synthesis and Rapid Hydrolysis of a 12-Membered Macrocyclic Peptide Thiolactone

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A macrocyclic thiolactone is common to the metastable binding sites of three serum proteins, the protease inhibitor α_2-macroglobulin[1,2] and the complement components C3[3] and C4.[4] The thiolactone ring is assembled from a five-residue linear segment (**1**, Scheme I) common to polypeptide precursors of each of these proteins. In principle, the thiolactone could exist as either a 12-membered ring (**2**) or a 15-membered ring (**3**). These macrocyclic structures would result from formation of a thiolester linkage between the thiol group of the cysteine residue and the side-chain carboxyl group of the first or second glutamic acid residue, respectively. The data[1-4] are consistent with each of these proteins having partial structure **3** but not **2**.

Recently we described[5] the synthesis of several hexapeptides containing the 15-membered thiolactone ring present in structure **3**. This paper reports the synthesis, characterization, and rapid hydrolysis of hexapeptide **9** (Scheme II), which contains the novel 12-membered thiolactone ring of structure **2**. The 1-thia-5,8-diazacyclododecane ring contains two amide bonds, one thiolester bond, and two chiral centers (3*R*, 9*S*; Cys and Glu in the L configuration).

Macrocyclic peptide thiolactone **9** was assembled from glycine and four L-amino acids by the following strategy. The tripeptide acid **4** was obtained by mixed anhydride coupling[6] of Boc–Cys (4-CH_3Bzl) with Gly–OCH_3 (87% yield), acidolysis[7] of the *tert*-butyloxycarbonyl (Boc) group, mixed anhydride coupling[6] of CH_3CO–Gly to the resulting Cys(4-CH_3Bzl)–Gly–OCH_3 (82% yield), and saponification[8] of the methyl ester (72% yield). The tripeptide amine **5** was prepared by coupling[9] of Boc–Gln 4-

(1) Sottrup-Jensen, L.; Petersen, T. E.; Magnusson, S. *FEBS Lett.* **1980**, *121*, 275–279.
(2) Howard, J. B. *Proc. Natl. Acad. Sci. U.S.A.* **1981**, *78*, 2235–2239.
(3) Tack, B. F.; Harrison, R. A.; Janatova, J.; Thomas, M. L.; Prahl, J. W. *Proc. Natl. Acad. Sci. U.S.A.* **1980**, *77*, 5764–5768.
(4) Harrison, R. A.; Thomas, M. L.; Tack, B. F. *Proc. Natl. Acad. Sci. U.S.A.* **1981**, *78* 7388–7392.
(5) Khan, S. A.; Erickson, B. W. *J. Am. Chem. Soc.* **1981**, *103*, 7374–7376.
(6) The mixed anhydride was formed by reaction of the N-acylpeptide acid with *N*-methylmorpholine and isobutyl chloroformate in THF for 5 min at −15 °C. After addition of the amino component, the mixture was stirred for 0.5 h at −15 °C and for 2–20 h at 25 °C.
(7) Treatment with 1:1 (v/v) trifluoroacetic acid/dichloromethane for 0.5 h at 25 °C gave quantitative cleavage of the Boc group.
(8) The methyl ester was hydrolyzed by treatment with 0.1 M NaOH (1.1 equiv) in 9:1 (v/v) methanol/water for 3 h at 25 °C.
(9) Coupling[10] was carried out in DMF in the presence of 1-hydroxybenzotriazole (HOBt; 1.0 equiv) for 0.5 h at 25 °C.
(10) König, W.; Geiger, R. *Chem. Ber.* **1973**, *106*, 3626–3635.

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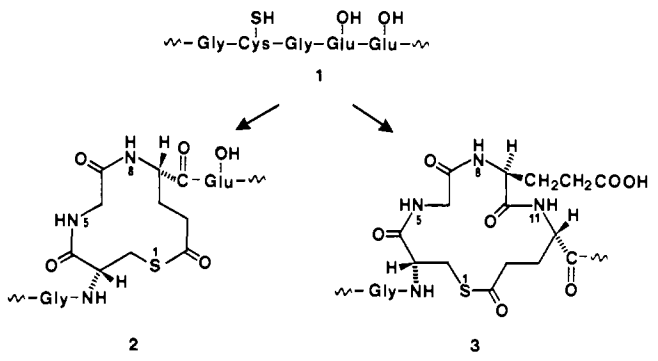
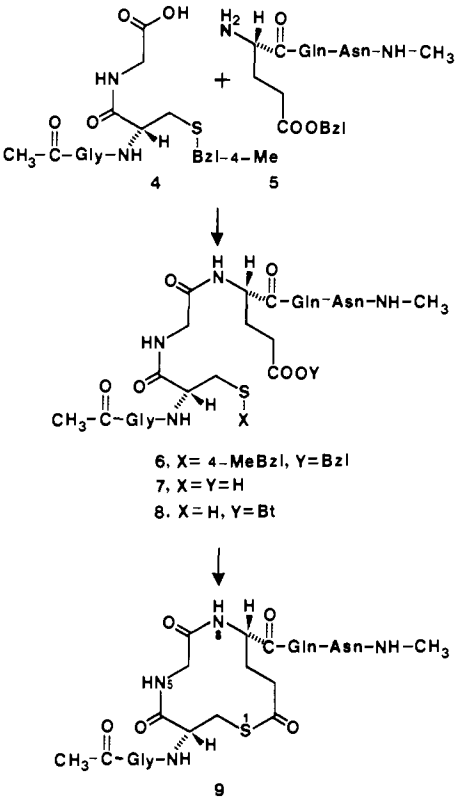
Scheme I



Scheme II



nitrophenyl ester with Asn–NH–CH_3 (83% yield), acidolysis[7] of the Boc group, mixed anhydride coupling[6] of Boc–Glu(OBzl) to the resulting Gln–Asn–NH–CH_3 (90% yield), and cleavage[7] of the Boc group.

Mixed anhydride coupling[6] of tripeptides **4** and **5** furnished the linear hexapeptide **6** in 77% yield. The *O*-benzyl and *S*-4-methylbenzyl[11] protecting groups were removed by treatment with liquid HF,[12] and the resulting mercapto acid **7** was cyclized[13] by way of the 1-benzotriazolo ester **8**. The extent of cyclization was at least 70% as measured by the increase in 412-nm absorbance due to the reaction of 5,5′-dithiobis(2-nitrobenzoic acid) (Ellman's reagent) with free thiol groups liberated upon hydrolysis of the thiolactone at pH 7.3. After two steps of reverse-phase chromatography, the 12-membered thiolactone **9** was isolated in 10-mg quantities and 38% overall yield from **7**. Both mercapto acid **7** and thiolactone **9** were homogeneous by thin-layer chromatography and reverse-phase liquid chromatography and gave acceptable elemental and amino acid analyses, mass spectral molecular weights, and 300-MHz proton magnetic resonance spectra.[14,15]

Hydrolysis of thiolactone **9** in phosphate-buffered saline (10 mM Na phosphate, 150 mM NaCl) at pH 7.3 and 37 °C was followed by monitoring the appearance of free thiol groups by using Ellman's reagent. The linear mercapto acid **7** was the sole product observed by reverse-phase liquid chromatography monitored at 220 nm. The initial first-order rate constant (k_1) for hydrolysis of thiolactone **9** was 1.8×10^{-2} s^{-1}, and the half-life ($t_{1/2}$) was 39 s. Hydrolysis of **9** proceeded 30 000 times faster than hydrolysis of *N*,*S*-diacetyl-L-cysteine methylamide[17] ($k_1 = 6.0 \times 10^{-7}$ s^{-1}, $t_{1/2}$ = 320 h), an acyclic thiolester that represents $^2/_3$ of the thiolactone ring. Hydrolysis of the 12-membered thiolactone **9** proceeded 7300 times faster than hydrolysis[18] of a 6-membered thiolactone (2-thianone: $k_1 = 2.5 \times 10^{-6}$ s^{-1}, $t_{1/2}$ = 78 h, pH 7.3, 30 °C) and about 900 times faster than direct hydrolysis[19] of a 15-membered thiolactone with partial structure **3** (compound **1f** of ref 5: k_1 = ca. 2.0×10^{-5} s^{-1}, $t_{1/2}$ = ca. 9.6 h, pH 7.3, 37 °C). Indeed, **9** undergoes hydrolysis as fast as ethyl trifluorothioacetate[20] ($CF_3COSCH_2CH_3$: $k_1 = 1.0 \times 10^{-2}$ s^{-1}, $t_{1/2}$ = 66 s, pH 7.3, 30 °C), which is the most readily hydrolyzed thiolester previously reported except for cases involving intramolecular or enzymatic catalysis. This enhanced rate for hydrolysis of **9** may be due to ring strain.

These results (1) provide the second example of formation[5] of a thiolactone by intramolecular coupling of a thiol with a 1-benzotriazolo ester, (2) constitute the first chemical synthesis of the 1-thia-5,8-diazacyclododecane ring system, and (3) demonstrate that the 12-membered thiolactone **9** is very labile under physiologic conditions.

Acknowledgment. We thank Professors Brian T. Chait and Frank H. Field for the mass spectra and Professor David Cowburn

(11) Erickson, B. W.; Merrifield, R. B. *Isr. J. Chem.* **1974**, *12*, 79–85.

(12) The *S*-(4-methylbenzyl)peptide benzyl ester was deprotected by treatment with 9:1 (v/v) liquid HF/anisole for 15 min at 0 °C.

(13) Mercapto acid **7** (0.20 mmol) in N_2-flushed DMF (9 mL) was treated with HOBt (0.80 mmol) and *N*,*N*′-dicyclohexylcarbodiimide (0.20 mmol) for 1 h at 0 °C and for 20 h at 25 °C. The mixture was added to N_2-flushed THF (250 mL) with stirring at 40 °C. Triethylamine (2 mmol) was added, and stirring was continued for 7 h. The organic solvents were removed by rotary evaporation. The solid obtained on addition of ether was purified by isocratic liquid chromatography on octadecyl-silica (μBondapak C_{18}, Waters Associates) by using water containing 0.05% trifluoroacetic acid and 1% acetonitrile. Thiolactone **9** was relatively stable to hydrolysis in aqueous solutions below pH 4.

(14) Thin-layer systems: A, 4:1:1 (v/v/v) 1-butanol/acetic acid/water; B, 23:10:3 (v/v/v) ethanol/acetic acid/water; C, 3:1:1:1 (v/v/v/v) 1-butanol/ethyl acetate/acetic acid/water. Reverse-phase chromatography conditions: 30-cm μBondapak C_{18} column was eluted isocratically with 0.05% trifluoroacetic acid and 1% acetonitrile in water; $k' = (t_{compd}/t_{solv}) - 1$, where t = retention time. Molecular ions were observed as $(M + Na)^+$ in the positive ion portion of the ^{252}Cf fission fragment-induced mass spectrum.[16] Molar ratios for Cys were not corrected for losses due to oxidation during acid hydrolysis (6 N HCl, 110 °C, 24 h). (a) Tripeptide **4**: R_f (A) 0.71, (C) 0.57. (b) Tripeptide **5**: R_f (A) 0.62, (C) 0.33. (c) Mercapto acid **7**: R_f (A) 0.16, (B) 0.14, (C) 0.13; $k' = 3.12$; *m/e* ($C_{24}H_{39}N_9O_{11}SNa$) calcd 684.24, found 684.24; $Asp_{1.02}Glu_{1.99}Gly_{2.00}Cys_{0.42}$; anal. ($C_{24}H_{39}N_9O_{11}S{\cdot}0.5H_2O$) C, H, N. (d) Thiolactone **9**: R_f (A) 0.67, (B) 0.41, (C) 0.32; $k' = 3.61$; *m/e* ($C_{24}H_{37}N_9O_{10}SNa$) calcd 666.23, found 666.28; $Asp_{1.07}Glu_{2.01}Gly_{2.00}Cys_{0.32}$; anal. ($C_{24}H_{37}N_9O_{10}S$) C, H.

(15) 300-MHz ^1H NMR (CF_3CO_2D): (a) mercapto acid **7** δ 2.1–2.6 (4 H, m, Glu β and Gln β), 2.40 (3 H, s, CH_3CO), 2.42 (1 H, s, SH), 2.74 (2 H, t 7, Glu γ), 2.78 (2 H, t 5, Gln γ), 3.02 (3 H, s, CH_3N), 3.04 (1 H, d 14, d 6, Cys β1), 3.15 (1 H, d 14, d 6, Cys β2), 3.15–3.25 (2 H, m, Asn β), 4.28 1 H, d 17, Gly α1), 4.38 (2 H, s, Gly α), 4.39 (1 H, d 17, Gly α2), 4.82 (1 H, d 7, d 5, Gln α), 4.85 (1 H, d 8, d 5, Glu α), 4.98 (1 H, t 6, Cys α), 5.20 (1 H, t 6, Asn α); (b) thiolactone **9** δ 2.2–2.5 (4 H, m, Glu β and Gln β), 2.39 (3 H, s, CH_3CO), 2.76 (2 H, t 6, Gln γ), 2.9–3.1 (2 H, m, Glu γ), 3.01 (3 H, s, CH_3N), 3.1–3.3 (2 H, m, Asn β), 3.1 (1 H, m, Cys β1), 3.7–3.9 (1 H, m, Cys β2), 4.11 (2 H, s, Gly α), 4.36 (2 H, s, Gly α), 4.72–4.92 (3 H, m, Cys α, Glu α, and Gln α), 5.21 (1 H, t 5, Asn α). Decoupling at δ 5.2 reduced the multiplet at δ 3.16 to an AB quartet, J = 16.5 Hz, ν = 3.10 and 3.22 ppm; decoupling at δ 3.2 reduced the triplet at δ 5.21 to a singlet.

(16) Chait, B. T.; Agosta, W. C.; Field, F. H. *Int. J. Mass Spectrom. Ion Phys.* **1981**, *39*, 339–366.

(17) CH_3CO–Cys($COCH_3$)–NH–CH_3 was prepared by mixed anhydride coupling[6] of *N*,*N*′-di-Boc-L-cystine with methylamine (88% yield), reduction[5] of the disulfide bond with tri-1-butylphosphine, acidolysis[7] of the Boc group, and acetylation of the resulting Cys–NH–CH_3 with acetic anhydride and 4-(dimethylamino)pyridine. It was homogeneous by thin-layer chromatography[14] (R_f (A) 0.68) and reverse-phase liquid chromatography[14] ($k' = 8.0$ in 0.05% acetic acid) and gave the expected elemental analysis ($C_8H_{14}N_2O_3S$: C, H, N) and protonated molecular ion by isobutane chemical ionization mass spectrometry ($(M + 1)^+$: calcd 219.07, found 219.05).

(18) Bruice T. C.; Bruno, J. J. *J. Am. Chem. Soc.* **1962**, *84*, 2128–2132.

(19) Khan, S. A.; Sekulski, J. M.; Erickson, B. W., unpublished results.

(20) Fedor, L. R.; Bruice, T. C. *J. Am. Chem. Soc.* **1964**, *86*, 5697–5698.

for the NMR spectra. This work was supported by Grant AI 18362 from the National Institute of Allergy and Infectious Diseases. The National Science Foundation (PCM 79-12083) and the Dreyfus Foundation supported the 7 T Nicolet NMR spectrometer, and the National Institutes of Health (RR 00862) supported the Mass Spectrometric Biotechnology Research Resource.

Registry No. 4, 82136-16-1; **5**, 82136-17-2; **6**, 82136-18-3; **7**, 82136-19-4; **8**, 82136-20-7; **9**, 82136-21-8; BOC-Cys(4-MeC$_6$H$_4$CH$_2$)-OH, 61925-77-7; H-Gly-OMe, 616-34-2; MeCO-Gly-OH, 543-24-8; Cys(4-CH$_3$Bzl)-Gly-OCH$_3$, 82136-22-9; BOC-Gln-OC$_6$H$_4$NO$_2$$^{-4}$, 15387-45-8; Asn-NH-CH$_3$, 82136-23-0; Gln-Asn-NH-CH$_3$, 82136-24-1; Boc-Glu-(OBzl), 13574-13-5.

Homo- and Heterodinuclear Platinum and Palladium Complexes with a Single Unsupported Monoatomic Bridging Group. Crystal Structure of the 2,6-Bis[(dimethylamino)methyl]phenylpalladium(II) Derivative [(Pd{C$_6$H$_3$(CH$_2$NMe$_2$)$_2$-*o*,*o*'})$_2$(μ-Cl)]BF$_4$

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There are few dinuclear complexes of the nickel triad metals in which the metals are only bridged by a single atom. It was only recently, for example, that [Ph(PEt$_3$)$_2$Pt(μ-H)Pt(PEt$_3$)$_2$H]$^+$, containing a single hydride bridge between two Pt(II) centers, was structurally characterized.[1]

We now report the first examples of homo- and heterodinuclear Pd(II) and Pt(II) complexes possessing a single unsupported chloro, bromo, or iodo bridge. The successful synthesis of these complexes (see Scheme I) involves the use of the terdentate anionic ligand {*o*,*o*'-(Me$_2$NCH$_2$)$_2$C$_6$H$_3$} (N-C-N) which, as a result of its special attachment, produces square-planar [M(N-C-N)(H$_2$O)]$^+$ (M = Pd, Pt) species with a loosely bound H$_2$O molecule in a site trans to a σ M-C bond. Displacement of this good leaving group (H$_2$O) by a terminal halide of a neutral [M'(N-C-N)X] complex then leads to formation of the new dinuclear species [(N-C-N)M'(μ-X)M(N-C-N)]$^+$, **1**. This Lewis acid–base pairing reaction[2] carried out at room temperature in CH$_2$Cl$_2$ affords these air-stable products in virtually quantitative yield upon evaporation of the solvent.[3] The proposal for **1** of a dinuclear ionic formulation was based on IR,[4] NMR (vide infra), and analytical data and is in accord with the observation that the complexes are readily soluble in polar solvents (e.g., CH$_2$Cl$_2$).

To firmly establish the presence of only a single halo atom bridge, we have completed a single-crystal X-ray structure determination on one representative member, **1a** (M = M' = Pd, X = Cl).[5]

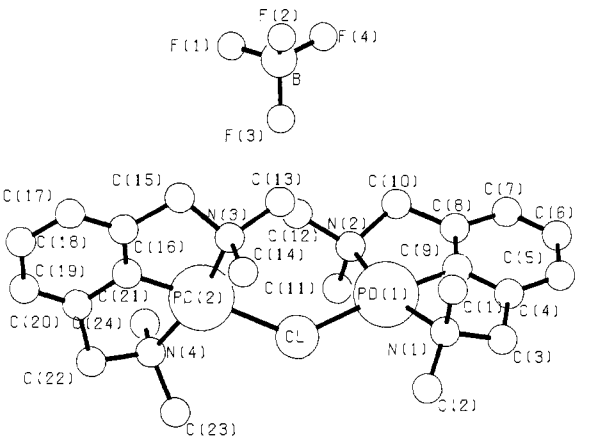
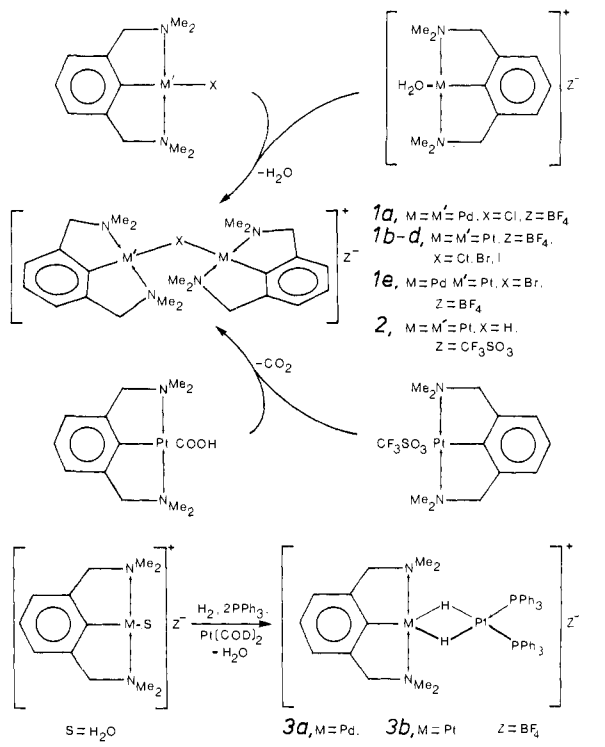


Figure 1. PLUTO drawing along with the adopted numbering scheme. Important distances (Å) are Pd(1)–Cl(1) = 2.463 (1), Pd(1)–N(1) = 2.105 (3), Pd(1)–N(2) = 2.100 (4), Pd(1)–C(9) = 1.929 (4), Pd(2)–Cl(1) = 2.458 (1), Pd(2)–N(3) = 2.094 (3), Pd(2)–N(4) = 2.104 (3), and Pd(2)–C(21) = 1.909 (4). Some relevant angles (°) are Cl(1)–Pd(1)–N(1) = 97.0 (1), Cl(1)–Pd(1)–N(2) = 100.3 (1), Cl(1)–Pd(1)–C(9) = 174.5 (1), N(1)–Pd(1)–N(2) = 162.6 (1), Cl(1)–Pd(2)–N(3) = 97.9 (1), Cl(1)–Pd(2)–N(4) = 97.6 (1), Cl(1)–Pd(2)–C(21) = 174.3 (1), and N(3)–Pd(2)–N(4) = 164.3 (1).

Scheme I



The cation (see Figure 1) as anticipated consists of two *trans-N,N',C*-[Pd[C$_6$H$_3$(CH$_2$NMe$_2$)$_2$]] units sharing a single bridging chlorine atom. Both Pd(II) centers have a slightly distorted square-planar coordination sphere (e.g., N(1)–Pd(1)–

(1) Bracher, G.; Grove, D. M.; Venanzi, L. M.; Bachechi, F.; Mura, P.; Zambonelli, L. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 778–779; *Angew. Chem.* **1978**, *90*, 826–827.

(2) For background information see: "Hard and Soft Acids and Bases"; Pearson, R. G., Ed.; Dowden, Hutchinson and Ross: Stroudsburg, PA, 1973.

(3) Although a dinuclear species is not isolated when [Ni(N-C-N)X] is included in this reaction scheme, the resultant formation of [Ni(N-C-N)H$_2$O]$^+$ strongly suggests the presence of such a Ni(II)-containing complex as the reactive intermediate.

(4) ν_{BF} 1080 cm^{-1}, no identifiable ν_{MX} or $\nu_{M'X}$.

(5) Pale yellow X-ray analysis crystals of **1a**, C$_{24}$H$_{38}$ClN$_4$Pd$_2$·BF$_4$, were monoclinic space group $P2_1/c$ with a = 11.163 (1) Å, b = 21.347 (2) Å, c = 12.246 (4) Å, β = 91.48 (2)°, Z = 4, d_{calcd} = 1.634 g/cm^3. The intensity data were measured on a Nonius-Enraf CAD4 diffractometer (Zr-filtered Mo Kα radiation) with θ–2θ scans. A total of 6691 unique reflections were measured for θ < 27.5° of which 5077 were considered observed [I < 2.5σ(I)]. The structure was solved by standard Patterson and Fourier techniques and refined by blocked full-matrix least-squares methods. In the final refinement hydrogen atoms were refined in a riding mode with a rotation parameter for the rigid methyl groups. There is some disorder in the BF$_4$ anion and the ligand on Pd(2) (two equivalent, mirror plane related puckering possibilities), both of which have the same occupation parameters (84:16). Final refinement converged at R_F = 0.042 and R_{wF} = 0.048. Figure 1 and the data apply to the 84% molecule.

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