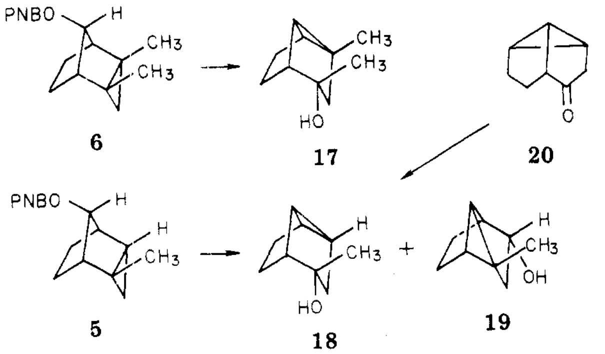
9-pentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]nonyl system,[8] which is commonly acknowledged to yield a nonclassical cation.[8,9]

Fortunately, product studies provided reasonably solid evidence for the symmetrical nature of the cation generated from the tricyclo[3.2.1.0^{2,4}]octyl system. The solvolysis of **6** gave, after ten half-lives, an 85% yield of **17** as the only observable product. A detailed lanthanide shift reagent study of **17**, in combination with NMR spectral comparisons with tricyclo[3.3.0.0^{2,8}]octan-*endo*-4-ol and **18**, left no doubt as to the endo nature of the substitution. This represents a case where the attacking nucleophile, water, added from the more hindered side of the molecule.[10] It has been argued that most tertiary cations are classical.[1] If this were true in the present case, the solvolysis product should have had the hydroxyl function in the exo position, not in the endo position.

The solvolysis of **5** gave, after ten half-lives, 82% of a 97:3 mixture of **18** and **19**. Again, NMR studies[11] left little doubt that the attacking nucleophile had added to the cationic intermediate from the endo (more hindered) side. In addition, an authentic sample of **18** was prepared by the addition of methylmagnesium iodide to **20**.[12] The formation of only endo products was inconsistent with the intermediacy of classical cationic species such as **11** and **12**. More significantly, the formation of substantial amounts of **19** would require that solvent capture by **12** compete effectively with solvent capture by **11**.[13]



Analogy can be made with the 1-methyl- and 2-methylbicyclo[2.2.1]hept-2-yl cations, where the tertiary cation is reported to be 5.5–7.5 kcal/mol more stable than the secondary ion.[14,15] It has been postulated that these ions are not mesomerically associated.[14,16] Extrapolation of these arguments to the pair of ions represented by **11** and **12** would require that **11** be the only ion present. The classical ion **11** would be expected to undergo nucleophilic attack from the exo side. Significantly, the product which would result from nucleophilic attack on **11** has the wrong stereochemistry. In addition, 3% of the product mixture was the secondary alcohol **19**, which also has endo stereochemistry. If **11** and **12** were equilibrating ions and we accepted the minimal value of 5.5 kcal/mol as the difference between these ions, greater than 99.95% of the product mixture should result from **11**.[17,18] This is inconsistent with the experimental data. In summary, the solvolysis of 2-methyl- and 2,4-dimethyltricyclo-[3.2.1.0^{2,4}]oct-8-yl *p*-nitrobenzoates provides products which are only consistent with the formation of a delocalized (trishomocyclopropenium) type ion.

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Paul G. Gassman,* Jonathan N. Chasman
William F. Reus, III[19]

Department of Chemistry, University of Minnesota
Minneapolis, Minnesota 55455

Merle A. Battiste,* John Haywood-Farmer

Department of Chemistry, University of Florida
Gainesville, Florida 32611

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(8) R. M. Coates and J. L. Kirkpatrick, *J. Am. Chem. Soc.*, **92**, 4883 (1970); R. M. Coates and E. R. Fritz, *ibid.*, **99**, 297 (1977).

(9) H. C. Brown and M. Ravindranathan, *J. Am. Chem. Soc.*, **99**, 299 (1977).

(10) It has been demonstrated that both hydride reduction[3] and the addition of organometallic reagents occur on the exo face of both tricyclo[3.3.0.0^{2,8}]octan-4-one and 2-methyltricyclo[3.3.0.0^{2,8}]octan-4-one.

(11) For instance, the structural assignment of **19** was based on a detailed comparison of its NMR spectrum with that of tricyclo[3.3.0.0^{2,8}]octan-*endo*-4-ol (**21**)[3] and by decoupling experiments at 270 MHz. In the NMR spectrum of **19**, a one-proton sextuplet at δ 4.28 corresponded to the hydrogen at C-4. This was coupled to the protons at C-3 (J = 8.9 Hz) and to the proton at C-5 (J = 6.4 Hz). These values are almost identical with those observed for the similar proton of **21**.[3]

(12) The ketone **20** was identical in all respects with that reported in the literature: R. G. Buckeridge, K. J. Fayne, and B. L. Johnson, *Aust. J. Chem.*, **28**, 1311 (1975).

(13) Control experiments established that **18** and **19** were not equilibrated under the reaction conditions.

(14) Reference 1, p 152; R. Haseltine, E. Huang, T. S. Sorensen, and N. Wong, *Can. J. Chem.*, **53**, 1876 (1975).

(15) A more typical value for secondary cation–tertiary cation energy differences would be the 14.5 ± 0.5 kcal/mol noted for the *sec*-butyl vs. *tert*-butyl cation: E. W. Bittner, E. M. Arnett, and M. Saunders, *J. Am. Chem. Soc.*, **98**, 3734 (1976).

(16) M. H. Rei and H. C. Brown, *J. Am. Chem. Soc.*, **88**, 5335 (1966); H. C. Brown, F. J. Chloupek, and M. H. Rei, *ibid.*, **86**, 1247 (1964); see also H. C. Brown, *Chem. Br.*, 199 (1966). See also H. C. Brown, M. Ravindranathan, C. G. Rao, F. J. Chloupek, and M. H. Rei, *J. Org. Chem.*, **43**, 3667 (1978).

(17) This prediction of percentages assumes diffusion-controlled collapse of the cations with solvent, or nonselective collapse with solvent. It should be noted that the 2-methylbicyclo[2.2.1]hept-2-yl cationic system gives only tertiary products.[16] The same reasoning which has been used to support the presence of a classical structure for this cation can be used to argue against the presence of **11** in the solvolysis of **5**.

(18) A similar capture of solvent by both secondary and tertiary centers has been observed by Coates and Fritz[8] for the methylated 9-pentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]nonyl system. This product mixture was deemed to represent what might be expected from a nonclassical carbonium ion.[8,9]

(19) Lando Undergraduate Fellow, Summer 1975.

α-Palladated Thioamides. σ or π Complexes?

Summary: α-Palladated thioamides (**3**) have been prepared by the addition reaction of soft carbonucleophiles to α,β-unsaturated thioamides in the presence of an equimolar amount of Pd(II). The structures of these yellow crystalline solids have been characterized by spectroscopic studies (^{1}H NMR, ^{13}C NMR, and IR) and chemical degradations (hydrogenation, carbonylation, base-induced cyclization to give dihydrofuran derivatives **8**, etc.).

Sir: Recently it has been shown that α,β-unsaturated thioamides serve as excellent Michael acceptors for a variety of organolithium and -magnesium compounds possessing hard anion character, such as alkyllithium, phenylmagnesium bromide, dimsyllithium,[1] and enolates of ketones, esters, and amides.[2] On the other hand, so-

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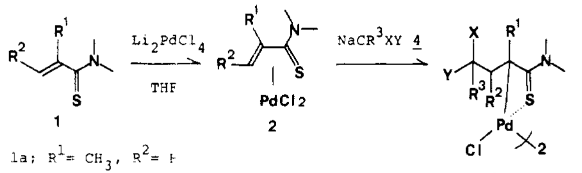
(1) Y. Tamaru, T. Harada, H. Iwamoto, and Z. Yoshida, *J. Am. Chem. Soc.*, **100**, 5221 (1978).

(2) Y. Tamaru, T. Harada, and Z. Yoshida, *J. Am. Chem. Soc.*, **101**, 1316 (1979).

dium diethyl malonate, with soft anion character, was either unreactive [with *N*,*N*-dimethylthiomethacrylamide (**1a**)] or gave many intractable products[3] [with *N*,*N*-dimethylthiocrotonamide (**1b**)]. During the attempts to overcome this undesirable feature with soft nucleophiles, we have found that palladium(II) salt nicely assists the soft carbonucleophiles to undergo the addition reaction, giving rise to α-palladated thioamides **3**.[4] Here we wish to describe the isolation of the first "possible" thia-π-allylpalladium complexes **3** and some of their properties and reactivities.

Into an orange suspension of **2**,[5,6] prepared from *N*,*N*-dimethylthiomethacrylamide (**1a**, 1.22 mol) and lithium tetrachloropalladate (1.0 mmol) in 13 mL of anhydrous THF, was added a THF solution of sodium diethyl malonate (1.54 mmol) via a syringe at ambient temperature and the reaction mixture was stirred for 20 h under argon. The solvent was evaporated and the residual solid was washed with CH_2Cl_2. The CH_2Cl_2 extracts were washed with aqueous NH_4Cl and dried over Na_2SO_4 and then evaporated to give a yellow solid **3b**[6] in quantitative yield:[7] mp 180 °C (dec, from EtOH); NMR ($CDCl_3$) δ 1.30 (t, *J* = 7 Hz, 6 H), 1.37 (s, 3 H), 1.60 (dd, *J* = 14 and 10 Hz, 1 H), 2.35 (dd, *J* = 14 and 3 Hz, 1 H), 3.23 (s, 6 H), 4.23 (quint, *J* = 7 Hz, 4 H), and 5.30 (dd, *J* = 10 and 3 Hz, 1 H); IR (KBr disk) 1755 (s), 1735 (s), 1580 (s), 1270 (s), and 1160 (s) cm^{-1}. Similarly **1a** was allowed to react with typical soft carbonucleophiles (**4a** and **4c–e**) to give **3a** and **3c–e** (eq 1). The reaction of **1b** with sodium dimethyl malonate provided a 1:1 diastereoisomeric mixture (**3f**) in 31% yield, one of which was isolated by the repeated recrystallization from EtOH:[8] mp 185 °C dec; NMR ($CDCl_3$–CD_2Cl_2 1:1) δ 1.37 (d, *J* = 7 Hz, 3 H), 2.0 (m, 1 H), 2.52 (d, *J* = 4 Hz, CHPd, 1 H), 3.20, 3.34, 3.66, 3.68 (s, 12 H), and 3.83 (d, *J* = 9 Hz, 1 H).



(1)

1a; $R^1 = CH_3$, $R^2 = H$

1b; $R^1 = H$, $R^2 = CH_3$

3

3a; $R^1 = CH_3$, $R^2 = R^3 = H$, $X = Y = CO_2CH_3$ 88%

3b; $R^1 = CH_3$, $R^2 = R^3 = H$, $X = Y = CO_2C_2H_5$ 100%

3c; $R^1 = CH_3$, $R^2 = R^3 = H$, $X = CO_2C_2H_5$, $Y = COCH_3$ 12%

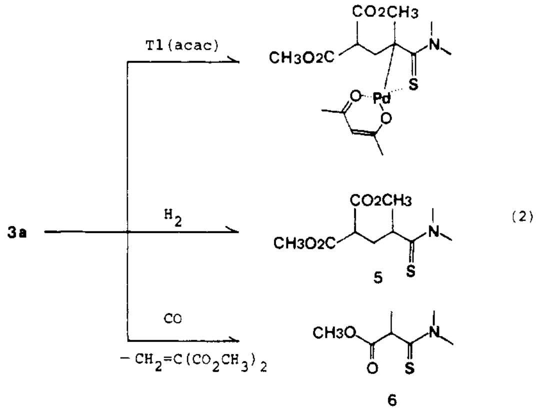
3d; $R^1 = CH_3$, $R^2 = R^3 = H$, $X = Y = COCH_3$ 36%

3e; $R^1 = CH_3$, $R^2 = H$, $R^3 = CH_3$, $X = Y = CO_2CH_3$ 56%

3f; $R^1 = H$, $R^2 = CH_3$, $R^3 = H$, $X = Y = CO_2CH_3$ 36%

It seems worthwhile to compare the thus obtained complexes **3** with oxa-π-allylpalladium complexes. Oxa-π-allylpalladium complexes[9,10] isolated so far are limited only to those either without hydrogen α to Pd–C carbon[11] or with hydrogen whose elimination as hydridopalladium is sterically prohibited.[12] Despite the presence of hydrogen(s) α to the Pd–C carbon, **3** is thermally stable and stable to air and moisture, withstanding shelf storage without noticeable decomposition. This remarkable stability of **3**, compared with oxa-π-allylpalladium complexes, may be ascribed to its strong coordination to palladium through sulfur.[13] Interestingly, these complexes seem to possess Pd–C σ-bond character, as observed in the NMR spectra (19.0 ppm for C–Pd and 212.9 ppm for C=S in the ^{13}C NMR spectrum of **3b**[14] and 2.52 ppm for CHPd in the ^1H NMR spectrum of **3f**).[15,16]

Monomeric pyridine, acetylacetonato, and triphenylphosphine complexes of **3a** could be readily prepared by allowing **3a** to react with 3–4 equiv of pyridine (room temperature, in EtOAc, 0.5 h, 50% yield, recrystallized from EtOH) and 1 equiv of Tl(acac) (room temperature in CH_3CN, 1 day, 52%, recrystallized from EtOH).



(2)

6

In order to shed more light on the structure of **3**, **3a** was degradated to organic compounds: hydrogenation of **3a**

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(3) Sodium diethyl malonate did not react with **1a** (in THF, ambient temperature) and both materials were recovered completely. With **1b**, sodium dimethyl malonate gave many intractable products (at least seven spots except for the starting spot on a silica gel plate, 8:1 benzene–ethyl acetate) and sodium ethyl acetoacetate reacted very slowly to give the 1,4-addition product, *N*,*N*-dimethyl-3-methyl-4-carbethoxy-5-oxothiohexanamide (76% yield based on 25% conversion, in THF at ambient temperature for 43 h). Recently we have found that the reactions of dimethyl malonate and ethyl acetoacetate with **1b** yield the expected 1,4-addition products in 50 and 51% yields, respectively, when 3 equiv of each of these carbonucleophiles was reacted with **1b** in the presence of 0.2 equiv of KO-*t*-Bu in refluxing THF for 23 h. Neither diethyl malonate nor ethyl acetoacetate was unreactive with **1a** even under the above-mentioned conditions.

(4) For the reaction of soft nucleophiles with allylic sulfides (with structural similarity to **1**) in the presence of lithium chloropalladate to form the five-membered palladocycles, see R. A. Holton and R. A. Kjonaas, *J. Am. Chem. Soc.*, **99**, 4177 (1977); see also Y. Takahashi, A. Tokuda, S. Sakai, and Y. Ishii, *J. Organomet. Chem.*, **35**, 415 (1972).

(5) Complex **2** was isolated in quantitative yield by the reaction of **1a** with 1 equiv of $(PhCN)_2PdCl_2$ in THF: mp 185 °C (dec, from CH_2Cl_2); IR (KBr disk) 1620 cm^{-1} (vs).

(6) All new compounds gave satisfactory elemental analyses.

(7) Yields refer to isolated, spectrally and chromatographically homogeneous material; reported yields are not based on recovered starting material.

(8) Another diastereomer decomposed during recrystallization.

(9) For a current comprehensive review on π-allylpalladium complexes, see B. M. Trost, *Tetrahedron*, **33**, 2615 (1977).

(10) Oxa-π-allylpalladium complexes as synthetic intermediates: (a) E. Yoshisato and S. Tsutsumi, *Chem. Commun.*, 33 (1968); (b) H. Alper and E. C. H. Keung, *J. Org. Chem.*, **37**, 2566 (1972); (c) V. B. Bierling, K. Kirschke, and H. Oberender, *J. Prakt. Chem.*, **314**, 170 (1972); (d) S. Wolff and W. C. Agosta, *Synthesis*, 240 (1976); (e) Y. Ito, T. Hirao, and T. Saegusa, *J. Org. Chem.*, **43**, 1011 (1978); (f) Y. Ito, H. Aoyama, T. Hirao, A. Mochizuki, and T. Saegusa, *J. Am. Chem. Soc.*, **101**, 494 (1979).

(11) (a) M. A. Bennett and R. Watt, *Chem. Commun.*, 95 (1971); (b) N. Yoshimura, S.-I. Murahashi, and I. Moritani, *J. Organomet. Chem.*, **52**, C58 (1973); (c) E. A. Jeffery and A. Meisters, *ibid.*, **82**, 315 (1974).

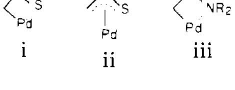
(12) Recently the oxa-π-allylpalladium complex of 2-norbornanone has been isolated: Y. Ito, T. Hirao, and T. Saegusa, private communication.

(13) R. A. Holton and R. G. Davis, *J. Am. Chem. Soc.*, **99**, 4175 (1977).

(14) ^{13}C NMR of **3b** (ppm in $CDCl_3$, Me_4Si as an internal standard) 212.9 (C=S), 170.4, 170.0 (CO), 61.7, 61.4 (CO_2CH_2), 38.9 (NCH_3), 51.8 ($CHCO_2CH_3$), 37.3 (CH_2CPd), 26.5 (CH_3CPd), 19.0 (CPd), and 14.2 (CH_3CH_2O).

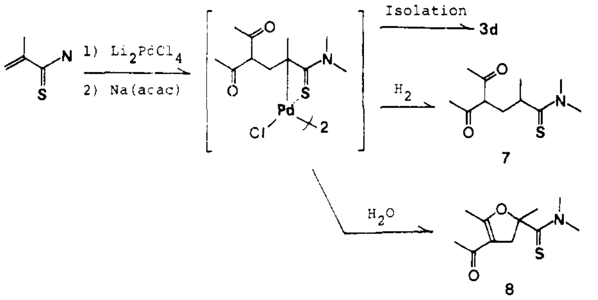
(15) X-ray study of the complex **3a** is under progress.

(16) Another possible structure for **3**, which possesses a four-membered ring through nitrogen as depicted in iii, seems to be unlikely on the bases of IR spectra: although ν_{CN} absorption in iii was expected to appear at lower wavenumber than (or similar wavenumber to) that of **5** (1510 cm^{-1}, neat film), **3a** showed the ν_{CN} absorption at higher wavenumber (1580 cm^{-1}, both KBr disk and CH_2Cl_2 solution), as might be expected as the structure of i (or ii); cf. 1620 cm^{-1} for **2** ($R^1 = CH_3$, $R^2 = H$, KBr disk).



i ii iii

in CH_2Cl_2 at ambient H_2 pressure provided the expected product, *N*,*N*-dimethyl-4,4-bis(carbomethoxy)-2-methylthiobutylamide (**5**), in 82% yield: bp 160 °C (6 mmHg) (Kugelrohr); NMR ($CDCl_3$) 1.18 (d, J = 7 Hz, 3 H), 2.75–1.8 (m, 2 H), 3.0–3.7 (m, 2 H), 3.33, 3.47 (s, 6 H), and 3.70 (s, 6 H); IR (neat film) 1740 (vs) and 1510 (s) cm^{-1}. Carbonylation (CO, 30 atm, in CH_3OH–pyridine, 80 °C for 8 h) gave *N*,*N*-dimethyl-2-carbomethoxythiopropionamide **6**[17] in quantitative yield, probably via an elimination of dimethyl methylenemalonate after a normal carbonylation as shown in eq 2.



(3)

Direct hydrogenation of the reaction mixture of **3d** gave *N*,*N*-dimethyl-4,4-diacetyl-2-methylthiobutylamide (**7**) in 55% yield (eq 3), whereas when 2 mL of H_2O was added to the reaction mixture, cyclization took place to give dihydrofuran derivative **8** in 48% yield: bp 170 °C (5 mmHg) (Kugelrohr); NMR ($CDCl_3$) δ 1.70 (s, 3 H), 2.10 (s, 3 H), 2.18 (t, J = 1.5 Hz, 3 H), 2.93 (dq, J = 16 and 1.5 Hz, 1 H), 3.46, 3.56 (br s, 6 H), and 4.20 (dq, J = 16 and 1.5 Hz, 1 H); IR (neat film) 1670 (s), 1620 (br s), 1510 (s), 1390 (br s), 1250 (s), 1140 (s), 1050 (m), 1030 (m), 935 (s), and 790 (s); mass (*m*/*e*, relative intensity) 227 (P^+, 21) and 184 (100). Similar treatment of the reaction mixture of **3c** gave **8** (with carbethoxy group in place of acetyl group) in 56% yield. The latter reaction,[18] which apparently involves a displacement of palladium by an enolate oxygen, could be realized by treatment of the isolated **3c** or **3d** with KO-*t*-Bu THF.

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Yoshinao Tamaru, Masahiro Kagotani
Zen-ichi Yoshida*

Department of Synthetic Chemistry
Kyoto University, Yoshida, Kyoto 606, Japan

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(17) **6**: NMR ($CDCl_3$) δ 1.46 (d, J = 7 Hz, 3 H), 3.36, 3.44, 3.68 (s, 9 H), and 3.95 (q, J = 7 Hz, 1 H); IR (neat film) 1740 (s), 1530 (s), 1270 (s), and 1215 (s); mass (*m*/*e*, relative intensity) 175 (P^+, 100), 143 (41), 116 (74), 115 (52), and 88 (74).

(18) The similar reaction to give dihydrofuran derivatives has been reported, where an intermediate like **3d** is postulated: (a) S. Uemura and K. Ichikawa, *Bull. Chem. Soc. Jpn.*, **40**, 1016 (1967); (b) S.-I. Murahashi, M. Yamamura, and N. Mita, *J. Org. Chem.*, **42**, 2870 (1977).