# Palladium(II) Complexes of 2,2,6,6-Tetramethylpiperidine *N*-Oxyl Radical

Masaaki OKUNAKA, Gen-etsu MATSUBAYASHI, and Toshio TANAKA

*Department of Applied Chemistry, Faculty of Engineering, Osaka University, Yamada-kami, Suita, Osaka 565*

(Received November 9, 1976)

2,2,6,6-Tetramethylpiperidine *N*-oxyl radical $(CH_3)_4C_5H_6NO\cdot$ (TMPNO·) reacts with palladium dichloride to give complexes of both anionic and cationic TMPNO; $[PdCl(TMPNO)]_2$ (I) and $[TMPNO^+]_2[Pd_2Cl_6]^{2-}$ (II). I further reacts with dimethylsulfonium phenacylide or triphenylphosphine (L) to afford a mononuclear complex of the PdCl(TMPNO)(L) type. II undergoes a facile reaction with acetone to yield bis(*N*-acetonyl-*N*-hydroxy-2,2,6,6-tetramethylpiperidinium)hexachlorodipalladate, $[(CH_3)_4C_5H_6\overset{+}{N}(OH)CH_2COCH_3]_2[Pd_2Cl_6]^{2-}$. Configurations of these complexes are described.

Di-*t*-butyl nitroxide radical (DTBNO·) reacts with palladium dichloride to give a diamagnetic dipalladium complex, $[PdCl(DTBNO)]_2$, involving the $DTBNO^-$ anion.[1] This is in contrast with other metal complexes of DTBNO·, in which the nitroxide coordinates to the metal as a neutral radical through the oxygen atom.[2-7] 2,2,6,6-Tetramethylpiperidine *N*-oxyl radical (TMPNO·) is also known to coordinate to several metal ions through the oxygen atom.[4-7] In addition, this radical reacts with tin(IV) halides to afford stable hexahalogenostannate(IV) complexes containing the $TMPNO^+$ cation.[8] Marked stabilities of the TMPNO· radical and its cation have been demonstrated by the electrochemical study.[9] Thus, no metal complex containing the $TMPNO^-$ anion has been isolated so far. This paper reports the isolation and configuration of some palladium(II) complexes of the $TMPNO^-$ anion as well as the $TMPNO^+$ cation; $[PdCl(TMPNO)]_2$, PdCl(TMPNO)(L) (L=dimethylsulfonium phenacylide, triphenylphosphine), and $[TMPNO^+]_2[Pd_2Cl_6]^{2-}$. It is also described that the latter compound easily reacts with acetone, giving bis(*N*-acetonyl-*N*-hydroxy-2,2,6,6-tetramethylpiperidinium) hexachlorodipalladate, $[(CH_3)_4C_5H_6\overset{+}{N}(OH)CH_2COCH_3]_2[Pd_2Cl_6]^{2-}$.

## Experimental

*Materials.* The TMPNO·radical,[8] $(CH_3)_4C_5H_6NO\cdot$, and dimethylsulfonium phenacylide,[10] $Me_2\overset{+}{S}\overset{-}{C}HCOPh$, were prepared as described in the literatures.

*Isolation of $[PdCl(TMPNO)]_2$ (I), $[TMPNO^+]_2[Pd_2Cl_6]^{2-}\cdot 2CH_3CN$ (II), and $[(CH_3)_4C_5H_6\overset{+}{N}(OH)CH_2COCH_3]_2[Pd_2Cl_6]^{2-}$ (III).* A suspension of $PdCl_2$ (1.77 g, 10.0 mmol) in a dichloromethane solution (2 ml) of TMPNO· (2.34 g, 15.0 mmol) was stirred for 72 h at room temperature, followed by evaporation to dryness under reduced pressure. The resulting product was washed with diethyl ether several times to remove the unreacted radical. The solid (3.01 g) thus obtained was dissolved in dichloromethane (100 ml) in order to separate a soluble product from an insoluble one (1.44 g). To the dichloromethane solution was added ethanol (20 ml). The mixture was evaporated to about one-fifth volume under reduced pressure to give reddish brown crystals (0.31 g), mp 160—162 °C, whose elemental analysis agreed well with the composition of PdCl(TMPNO)·0.1$PdCl_2$, although this compound has not been further studied. Further evaporation of the residual solution to about a half volume yielded dark red crystals of I (0.14 g, 0.23 mmol, 9% yield), mp 151—154 °C. Found: C, 36.28; H, 6.25; N, 4.77%; mol wt, 622. Calcd for $C_9H_{18}NOClPd$: C, 36.26; H, 6.09; N, 4.70%; mol wt, 298.

The insoluble product in dichloromethane was recrystallized from a mixture of acetonitrile and diethyl ether to give brown crystals of II (1.12 g, 1.36 mmol, 55% yield), mp 94—96 °C. Found: C, 32.06; H, 5.25; N, 6.71%. Calcd for $C_9H_{18}NOCl_3Pd\cdot CH_3CN$: C, 32.21; H, 5.16; N, 6.83%. II (1.00 g, 1.22 mmol) was dissolved in acetone (20 ml), followed by the addition of diethyl ether (10 ml) to develop dark red crystals of III (0.58 g, 0.68 mmol, 56% yield), mp 164—166 °C. Found: C, 33.56; H, 5.90; N, 3.31%. Calcd for $C_{12}H_{24}NO_2Cl_3Pd$: C, 33.74; H, 5.66; N, 3.28%.

*Isolation of PdCl(TMPNO)(L) (L=$Me_2\overset{+}{S}\overset{-}{C}HCOPh$ (IV) and $PPh_3$ (V)).* To a dichloromethane (5 ml) solution of I (0.15 g, 0.5 mmol) was added dimethylsulfonium phenacylide (0.09 g, 0.5 mmol) in dichloromethane (5 ml). The mixture was stirred for 10 min at room temperature, and evaporated to dryness under reduced pressure. The resulting product was recrystallized from benzene–petroleum ether to give orange crystals of IV (0.14 g, 0.29 mmol, 59% yield), mp>145 °C (dec). Found: C, 46.99; H, 6.14; N, 2.60%; mol wt, 466. Calcd for $C_{19}H_{30}NO_2SClPd$: C, 47.70; H, 6.32; N, 2.93%; mol wt, 478. Orange crystals of V were similarly prepared by the reaction of I with triphenylphosphine, and recrystallized from benzene–petroleum ether (65% yield), mp >150 °C (dec). Found: C, 58.18; H, 5.97; N, 2.36%; mol wt, 553. Calcd for $C_{27}H_{33}NOPClPd$: C, 57.87; H, 5.93; N, 2.50%; mol wt, 560.

*Physical measurements.* Infrared and $^1H$ NMR spectra were recorded as described previously.[8,11] Molecular weight determinations were carried out in dichlomethane using a vapor pressure osmometer. Electric conductivities were measured at 25 °C as described elsewhere.[12]

## Results and Discussion

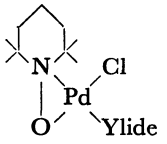
Molecular weight determinations indicate that both IV and V are essentially monomeric in dichloromethane. The infrared spectrum of I shows the $\nu$(Pd–Cl) band at 270 $cm^{-1}$, which is close to the $\nu$(Pd–Cl) frequency of the corresponding DTBNO complex (303 $cm^{-1}$),[11] while this band of IV is obscured by ylide vibrations. The $^1H$ NMR spectrum of IV shows only one methine signal (Table). In addition, no exchange is observed between the coordinating ylide and free ylide added into the solution of the complex. These results suggest the presence of only one species of IV in solution. In the infrared spectrum, the $\nu$(C=O) band of the ylide shifts to high frequency upon complexation (complexed ylide: 1605 $cm^{-1}$, free ylide: 1508 $cm^{-1}$), indicating, as

Table. Chemical shifts of the TMPNO complexes in chloroform-$d_1$ at 24 °C[a)]

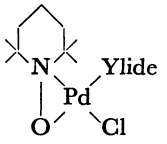
| Complex | $CH_3$ | $-CH_2-$ | Other protons |
|---|---|---|---|
| $[PdCl(TMPNO)]_2$ | 1.45(s), 2.33(s) | 1.60(m) | — |
| $PdCl(TMPNO)(PPh_3)$ | 1.38(s), 1.97(s) | 1.62(m), 1.77(m) | 7.41(m), 7.57(m)($PPh_3$) |
| $PdCl(TMPNO)(Me_2\overset{+}{S}\overset{-}{C}HCOPh)$ | 1.12(s), 1.25(s) 1.54(s), 1.93(s) | 1.61(m) | 2.87(s), 3.15(s)(SMe); 2.54(s) (CH); 7.42(m), 8.21(m) (Ph) |

a) s: singlet, m: multiplet.

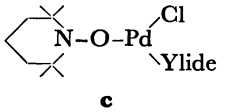
discussed previously,[13)] the coordination through the ylide-carbon atom. Thus, the coordinating ylide-carbon is an asymmetric center. This is also supported from the occurrence of two *S*-methyl proton signals with an identical intensity (Table), while free ylide exhibits only one *S*-methyl signal.




**a**

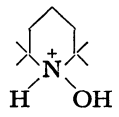



**b**




**c**

There are three possible configurations for IV, **a**—**c**, of which **a** and **b** are geometrical isomers. In spite of the presence of the chiral ylide-carbon, four methyl groups of TMPNO in the configuration **c** may be magnetically equivalent, because the inversion at the nitrogen atom would be very fast.[14)] On the other hand, both **a** and **b** involve a quadrivalent nitrogen atom, which predicts no inversion at the nitrogen. In fact, this kind of inversion is restricted in the *N*-hydroxyl-2,2,6,6-tetramethylpiperidinium cation (**d**), as confirmed by the $^1H$ NMR spectrum in dichloromethane at room temperature, which shows two separated methyl signals at $\delta$ 1.39 and 1.65 ppm.[15)] Thus, both configurations

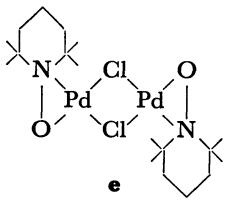



**d**

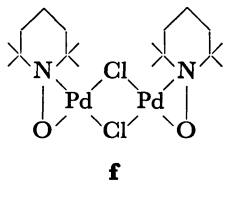
**a** and **b** predict the occurrence of the axial and equatorial methyl proton signals with an equal intensity. Furthermore, each signal should be split into two owing to the presence of the chiral ylide-carbon. This is compatible with the occurrence of two doublet signals due to the methyl protons (Table). Stereochemical considerations support the preference of **a** to **b**, since in **b** the piperidine ring is placed near to the bulky ylide.

The complex V involving no chiral atom exhibits two methyl proton signals with an equal intensity. This does not contradict with the assumption that the complex exists as only one species in solution and the inversion at the nitrogen atom of TMPNO is restricted. The bulkiness of triphenylphosphine suggests the configuration similar to **a**.

The conductivity measurement and molecular weight determination indicate that I is a non-electrolyte (0.02 $ohm^{-1}\,cm^2\,mol^{-1}$ at $1.51\times10^{-3}$ M) and dimeric in dichloromethane. By analogy with $[PdCl(DTBNO)]_2$,[1)] I is considered to adopt chloride-bridged configurations (**e**) and/or (**f**). This is compatible with the occurrence



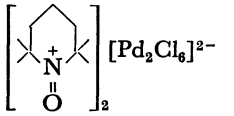

**e**



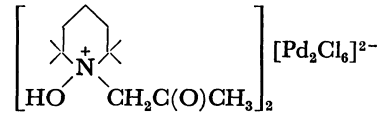

**f**

of the $\nu$(Pd–Cl) band at 270 $cm^{-1}$. The $^1H$ NMR spectrum shows two methyl signals with an identical intensity, suggesting the presence of either **e** or **f** with the restriction of inversion at the nitrogen atom.

Ionic structures of II and III are confirmed by conductivity measurements; $\Lambda_M$=256 and 121 $ohm^{-1}\,cm^2\,mol^{-1}$ ($1.35\times10^{-3}$ M in acetonitrile), respectively. Infrared spectra of both compounds show the $\nu$(Pd–Cl) bands at 343 (very strong) and 303 (medium) $cm^{-1}$, which are characteristic of the hexachlorodipalladate anion.[16)] In addition, II exhibits a strong band at 1605 $cm^{-1}$, which is assigned to $\nu(\overset{+}{N}{=}O)$.[8)] The $^1H$ NMR spectrum of II in liquid sulfur dioxide shows somewhat broad methyl and methylene signals at $\delta$ 1.88 and 2.72 ppm, respectively; there is no separation of the methyl signal. These observations are consistent with the ionic formulation having the piperidineoxoammonium cation (**g**). On the other hand, III exhibits the $\nu$(C=O) band at 1730 $cm^{-1}$, but no $\nu(\overset{+}{N}{=}O)$. The $^1H$ NMR spectrum shows again two methyl signals with an equal intensity, suggesting the presence of a quadrivalent nitrogen atom. These results and the following proton signals observed can well explain the formulation of **h**; $\delta$ 1.60 [singlet, 6 (relative intensity)] and 1.78 [s, 6] for the ring methyl; 1.96 [multiplet, 6] for the ring methylene; 2.36 [s, 3] for $CH_3$–C(O)–; 5.37 [s, 2] for $-CH_2$–C(O); 9.03 [broad, 1] for OH.




**g**




**h**

## References

1) W. Beck and K. Schmidtner, *Chem. Ber.*, **100**, 3363 (1967).

2) W. Beck, K. Schmidtner, and H. J. Keller, *Chem. Ber.*, **100**, 503 (1967).

3) R. A. Zelonka and M. C. Baird, *J. Am. Chem. Soc.*, **93**, 6066 (1971).

4) T. B. Eames and B. M. Hoffman, *J. Am. Chem. Soc.*, **93**, 3141 (1971).

5) Y. Y. Lim and R. S. Drago, *Inorg. Chem.*, **11**, 1334 (1972).

6) N. M. Karayannis, C. M. Paleos, C. M. Kikulski, L. L.

Pytlewski, H. Blum, and M. M. Labes, *Inorg. Chim. Acta*, **7**, 74 (1973).
7) A. H. Cohen and B. M. Hoffman, *Inorg. Chem.*, **13**, 1484 (1974).
8) Y. Takaya, G. Matsubayashi, and T. Tanaka, *Inorg. Chim. Acta*, **6**, 339 (1972).
9) M. Tsunaga, C. Iwakura, and H. Tamura, *Electrochim. Acta*, **18**, 241 (1973).
10) K. W. Ratts and A. N. Yao, *J. Org. Chem.*, **31**, 1185 (1966).
11) M. Okunaka, G. Matsubayashi, and T. Tanaka, *Bull. Chem. Soc. Jpn.*, **48**, 1826 (1975).
12) G. Matsubayashi, K. Wakatsuki, and T. Tanaka, *Org. Magn. Reson.*, **3**, 703 (1971).
13) H. Koezuka, G. Matsubayashi, and T. Tanaka, *Inorg. Chem.*, **15**, 417 (1976).
14) D. L. Griffith, B. L. Olson, and J. D. Roberts, *J. Am. Chem. Soc.*, **93**, 1648 (1971).
15) M. Okunaka, G. Matsubayashi, and T. Tanaka, unpublished.
16) D. M. Adams, P. J. Chandler, and R. G. Churchill, *J. Chem. Soc., A*, **1967**, 1272.