Preparations and Properties of Some Cationic Palladium(II) Complexes of the Di-*t*-butylnitroxide Radical

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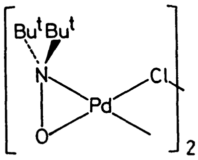
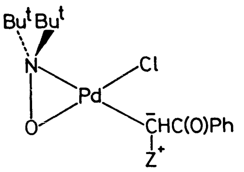
Cationic palladium(II) complexes of the di-*t*-butylnitroxide radical, $[Pd(Bu^t{}_2NO)(L\text{-}L)]X$ (L-L=2,2′-bipyridine, 1,10-phenanthroline, *N*-substituted 2-pyridylmethyleneamine and bis(triphenylphosphine); $X^-=ClO_4{}^-$ and/or $BPh_4{}^-$), were prepared. ^1H NMR spectra of the complexes indicate that the nitroxide forms a three-membered ring with the palladium atom. The *N*-methyl- and *N*-ethyl-2-pyridylmethyleneamine complexes exist as two geometrical isomers in solution, whose ratios are 1 : 1 and 1 : 0.2, respectively. In the *N*-butyl and *N*-*p*-tolyl analogs, however, only one of the isomers exists in solution. These results are interpreted in terms of steric repulsion between the *t*-butyl groups and *N*-substituents. The bipyridine complex reacts with dialkyl disulfides in the presence of catalytic amounts of bipyridine to give a sulfur-bridged dimeric complex, $[Pd(bipyridine)(SR)]_2(ClO_4)_2$(R=Me and Pr), and a free nitroxide radical.

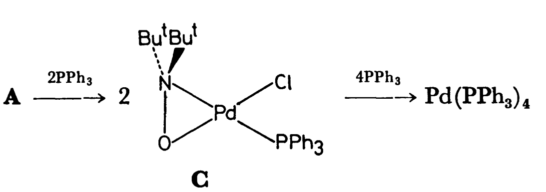
Nitroxide radicals ($R_2NO\cdot$) usually coodinate to metal ions through the oxygen atom as a neutral ligand.[1–7] However, di-*t*-butylnitroxide has been reported to react with palladium dichloride to form a chloride-bridged diamagnetic complex **A**, in which the nitroxide was assumed to coordinate to the palladium atom as an anionic ligand.[8] A recent ^1H NMR study by the present authors on the nitroxide-palladium(II) complexes **B** which involve prochiral phenacylides, $\overset{+}{Z}\overset{-}{C}HC(O)Ph$ ($Z=PPh_2Me$, PPh_3, $AsPh_3$, and SMe_2), has demonstrated that a three-membered ring exists in the complexes.[9] It was also found that **A** reacts with triphenylphosphine to give a mononuclear complex **C**, which undergoes a novel redox reaction of the nitroxide-palladium moiety by nucleophilic attack of excess triphenylphosphine yielding tetrakis-(triphenylphosphine)palladium(0).[10]



A



B



C

+ $PdCl_2(PPh_3)_2$ + $2Bu_2{}^tNO\cdot$

This reaction indicates a characteristic coordination property of the nitroxide toward palladium. However, few palladium complexes with nitroxides have so far been isolated. It is, therefore, of interest to extend the study of the nitroxide-palladium(II) complexes.

This paper reports the preparations and properties of cationic palladium(II) complexes having the chemical formula $[Pd(Bu^t{}_2NO)(L\text{-}L)]X$ (L-L=2,2′-bipyridine (bipy), 1,10-phenanthroline(phen), *N*-substituted 2-pyridylmethyleneamine(pyma-R) and bis(triphenylphosphine); $X^-=ClO_4{}^-$ and/or $BPh_4{}^-$), and the redox reactions using dialkyl disulfides as oxidizing reagents.

Experimental

Materials. The chloride-bridged dipalladium complex, $[PdCl(Bu^t{}_2NO)]_2$, and *N*-substituted 2-pyridylmethyleneamines, $2\text{-}C_5H_4N\text{-}CH{=}N\text{-}R$ (R=Me, Et, Bu, and *p*-tolyl), were prepared as described elsewhere.[8,11]

Preparation of $[Pd(Bu^t{}_2NO)(L\text{-}L)]X$ *(L-L=bipy, phen, pyma-R and bis(triphenylphosphine);* $X^-=ClO_4{}^-$ *and/or* $BPh_4{}^-$*).* Into a dichloromethane solution (10 ml) of $[PdCl(Bu^t{}_2NO)]_2$ (286 mg, 0.5 mmol) was poured an acetone solution (15 ml) containing bipy (156 mg, 1.0 mmol) and sodium perchlorate monohydrate (140 mg, 1.0 mmol) with vigorous stirring at room temperature. The original brown solution changed immediately to a yellow suspension, which was filtered to remove the sodium chloride produced. The filtrate was evaporated to dryness under reduced pressure. The resulting product was recrystallized from acetone/petroleum ether to afford yellow crystals of $[Pd(Bu^t{}_2NO)(bipy)]ClO_4\cdot 1/2Me_2CO$ (427 mg, 80% yield). Other yellow perchlorate complexes were prepared by the same method (50—80% yields), and yellow tetraphenylborate complexes were similarly obtained using sodium tetraphenylborate in place of sodium perchlorate monohydrate (70—85% yields). The results of elemental analysis, the melting points and the molar electric conductances of the complexes are summarized in Table 1.

Reaction of $[Pd(Bu^t{}_2NO)(bipy)]ClO_4$ *with Dialkyl Disulfides in the Presence of bipy.* Dimethyl disulfide (470 mg, 5.0 mmol) was mixed with an acetone solution (15 ml) of $[Pd(Bu^t{}_2NO)(bipy)]ClO_4$ (268 mg, 0.5 mmol) in an atmosphere of dry nitrogen, followed by the addition of bipy (15.6 mg, 0.1 mmol) in acetone (5 ml) with stirring at room temperature. The solution was further stirred for 40 h to give a precipitate, which was collected by filtration. Recrystallization from acetonitrile gave yellow crystals of $[Pd(bipy)(SMe)]_2(ClO_4)_2$–MeCN (160 mg, 82% yield). Found: C, 33.46; H, 2.89; N, 8.21%. Calcd for $C_{24}H_{25}N_5O_8S_2Cl_2Pd_2$: C, 33.54; H, 2.94; N, 8.20%. $\Lambda_M=309\ ohm^{-1}\ cm^2\ mol^{-1}$ (1.0×10^{-3} M in acetonitrile). The propyl analog, $[Pd(bipy)(SPr)]_2(ClO_4)_2$, was prepared by the same method (75% yield). Found: C, 35.59; H, 3.42; N, 6.57%. Calcd for $C_{26}H_{30}N_4O_8S_2Cl_2Pd_2$: C, 35.71; H, 3.46; N, 6.41%. $\Lambda_M=328\ ohm^{-1}\ cm^2\ mol^{-1}$ (1.0×10^{-3} M in acetonitrile).

Physical Measurements. ^1H NMR and ESR spectra were measured as described previously,[10] and the electric con-

Table 1. Elemental analysis results, melting points and molar electric conductances[a)] of the complexes

No.	Complex[b)]	Mp (°C)	Found (Calcd) % C	H	N	Λ_M (ohm^{-1} cm^2 mol^{-1})
1a	$[Pd(Bu^t_2NO)(bipy)]ClO_4 \cdot 1/2Me_2CO$	—	43.72 (43.72)	5.49 (5.47)	7.81 (7.85)	148
1b	$[Pb(Bu^t_2NO)(bipy)]BPh_4$	169(d)	69.36 (69.47)	6.43 (6.40)	5.77 (5.79)	109
2	$[Pd(Bu^t_2NO)(phen)]BPh_4 \cdot Me_2CO$	175(d)	70.53 (69.84)	6.77 (6.50)	5.22 (5.20)	110
3a	$[Pd(Bu^t_2NO)$(pyma-Me)$]ClO_4$	—	38.23 (38.33)	5.77 (5.59)	8.89 (8.95)	152
3b	$[Pd(Bu^t_2NO)$(pyma-Et)$]ClO_4$	—	39.11 (39.68)	5.66 (5.84)	8.71 (8.68)	168
3c	$[Pd(Bu^t_2NO)$(pyma-Bu)$]BPh_4$	138(d)	68.38 (68.90)	7.21 (7.17)	5.89 (5.74)	94
3d	$[Pd(Bu^t_2NO)$(Pyma-*p*-tolyl)$]BPh_4 \cdot Me_2CO$	130(d)	69.93 (69.94)	6.89 (6.86)	5.22 (5.10)	98
4	$[Pd(Bu^t_2NO)(PPh_3)_2]ClO_4$	—	60.16 (60.41)	5.50 (5.54)	1.61 (1.60)	142

a) Measured in acetonitrile at 25 °C (1.65×10^{-3} M). b) pyma-R=*N*-substituted 2-pyridylmethyleneamine.

Table 2. ^{1}H NMR chemical shifts (δ, ppm) of $[Pd(Bu^t_2NO)(L\text{-}L)]X$ in acetonitrile at 24 °C[a)]

Complex[b)]	Configuration	Bu^t	H_{6a}	H_{6b}	N-CH$_n$-
1a	I	1.76	8.71(+0.09)	8.47(−0.15)	—
1b	I	1.75	8.68(+0.06)	8.45(−0.17)	—
2	I	1.82	9.05(−0.06)[e)]	8.84(−0.27)[e)]	—
3a	IIa	1.72	8.66(+0.06)	—	3.69(+0.18) [N-CH$_3$]
	IIb	1.72	—	8.46(−0.14)	3.82(+0.31) [N-CH$_3$]
3d[c)]	IIa	1.72	8.66(+0.04)	—	3.78(+0.11) [N-CH$_2$-]
	IIb	1.72	—	8.42(−0.20)	3.96(+0.29) [N-CH$_2$-]
3c	IIa	1.69	8.61(+0.01)	—	3.66(+0.04) [N-CH$_2$-]
3d	IIa	1.77	8.70(0)	—	—
4[d)]		1.46	—	—	—

a) The values in parentheses denote $\delta_{complexed} - \delta_{free}$. b) Refer to Table 1 for the number of complexes.
c) Measured in acetonitrile-d_3. d) Measured in acetone. e) H_2 or H_9 signal.

ductance was determined at 25 °C using a universal bridge, as has also been described elsewhere.[12)]

Results and Discussion

The complexes are stable in air in the solid state, however, they gradually decompose in solution. Electric conductance measurements appear to indicate that the complexes are 1 : 1 electrolytes in acetonitrile (Table 1). The assignment of the ^{1}H NMR spectra is easily carried out by refering to those of other metal complexes of bipy,[13)] phen,[13)] and 2-pyridylmethyleneamines,[11,14)] as summarized in Table 2.

Configuration of the $[Pd(Bu^t_2NO)(L\text{-}L)]^+$. Figure 1 shows a comparison of the ^{1}H NMR spectra of the bipy complex and free bipy in the bipy proton region in acetonitrile. The H_4 and H_5 signals of bipy move down-field upon complex formation with the former being observed near the H_3 signal. It is to be noted that two distinct H_6 signals appear separately with equal intensities; one of the H_6 signals undergoes a little down-field shift, while the other H_6 signal occurs at a higher field than does bipy itself. This result indicates a three-membered ring formed by the nitroxide and the palladium atom in a square planar configuration, as shown in I. The small shifts of the H_6 signals are ascribed to the counteraction of two opposite effects: a down-field shift due to a decrease in the electron density on the pyridine ring and an

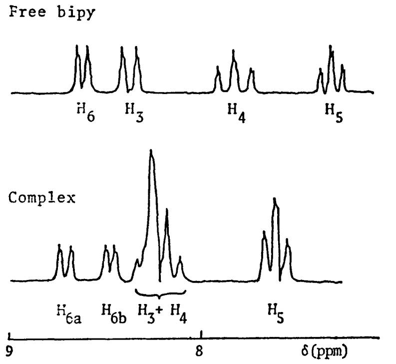
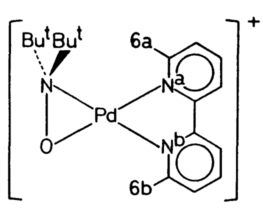


Fig. 1. ^{1}H NMR spectra of bipy and $[Pd(Bu^t_2NO)(bipy)]ClO_4$ in the bipy proton region, in acetonitrile at 24 °C.



I

up-field shift due to a decrease in the original paramagnetic anisotropy of lone pair electrons of the bipy nitrogen upon coordination, as was suggested for the pyridine complexes of triethylaluminum.[12] Steric repulsion between the *t*-butyl groups and the pyridine ring can possibly weaken the Pd–N^a bond compared with the Pd–N^b bond. Therefore, the larger paramagnetic anisotropy effect of the lone pair electrons may dominate more in N^a than in N^b. As a result, the H_{6a} signal is considered to occur at a lower field than the H_{6b} signal. The phen complex also exhibits two separated H_2 and H_9 signals, which suggests that the configuration is similar to I.

The ^{1}H NMR spectrum of the *N*-methyl-2-pyridylmethyleneamine complex shows two sets of H_6, *N*-methyl and *t*-butyl signals, as shown in Fig. 2; the intensity ratio of each pair is 1 : 1. This is due to the presence of two equimolar geometrical isomers, IIa and IIb, in solution. In the *N*-ethyl-2-pyridylmethyleneamine complex, the intensity ratio of each pair of H_6 and *N*-ethyl signals is 1 : 0.2, whereas the *N*-butyl and *N*-*p*-tolyl analogs exhibit only one set of signals. In view of the steric repulsion between the *t*-butyl and *N*-alkyl or *N*-aryl groups, configuration IIa would be more probable than IIb. This is consistent with the X-ray crystallographic analysis of $PdCl(Bu^t{}_2NO)(Me_2\overset{+}{S}\overset{-}{C}HC(O)Ph)$, in which the bulky phenacylide is located in the position *trans* to the di-*t*-butyl nitrogen.[15] The preference of IIa over IIb is also supported by failure to isolate the nitroxide–palladium(II) complex of *N*,*N'*-di-*p*-tolyl-2,3-butanediimine, in which the *p*-tolyl group should be located in the position *cis* to the di-*t*-butyl nitrogen.

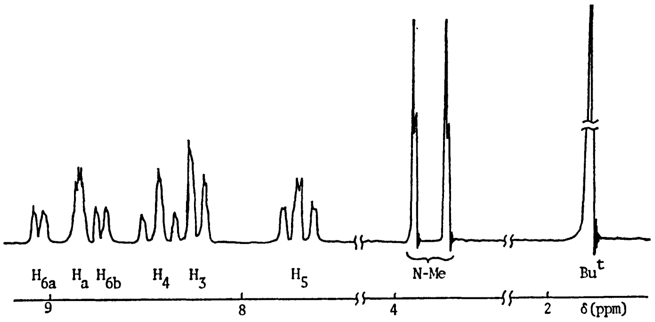
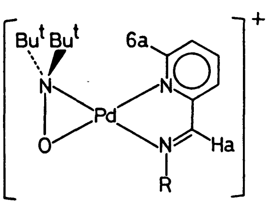
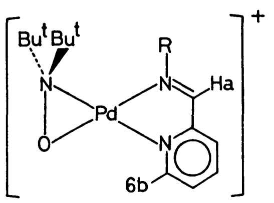


Fig. 2. The ^{1}H NMR spectrum of $[Pd(Bu^t{}_2NO)(pyma\text{-}Me)]ClO_4$ in acetone at 24 °C; the solvent signals are omitted.



IIa



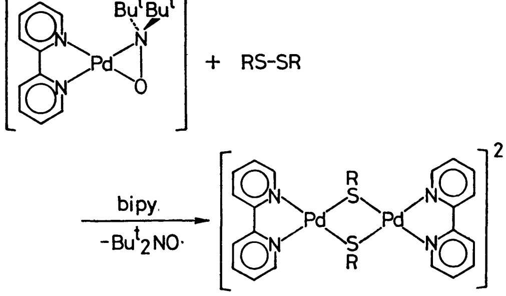
IIb

The bis(triphenylphosphine) complex is obtained in a high yield. On the other hand, the isolation of the corresponding 1,2-bis(diphenylphosphino)ethane complex was not successful possibly because the inflexibility of the bidentate ligand results in an unfavorable steric repulsion upon chelation.

Stability of the Complex to Nucleophiles. The ESR spectrum of $[Pd(Bu^t{}_2NO)(bipy)]ClO_4$ in degassed acetone shows a weak triplet signal due to a free di-*t*-butylnitroxide radical which may be produced by slight dissociation from the palladium atom. No appreciable enhancement of the ESR signal is observed upon the addition of bipy to a degassed acetone solution of the complex. These observations confirm that no reaction occurs between the complex and bipy. $[Pd(Bu^t{}_2NO)(PPh_3)_2]ClO_4$ does not react with excess PPh_3. This is in contrast to the facile reaction of $PdCl(Bu^t{}_2NO)(PPh_3)$ with PPh_3, generating a free nitroxide radical.[10]

Reaction of $[Pd(Bu^t{}_2NO)(bipy)]ClO_4$ with Some Oxidizing Reagents. When bipy is added to an acetone (not degassed) solution of $[Pd(Bu^t{}_2NO)(bipy)]ClO_4$ in air, an orange crystalline complex is obtained and a free nitroxide radical is generated as confirmed by the ESR spectrum of the reaction mixture. The ^{1}H NMR spectrum of the orange complex in DMSO-d_6 shows only the signals due to the coordinated bipy, but no signal for the di-*t*-butyl protons. The results of elemental analysis confirm the chemical formula, $[Pd(bipy)_2](ClO_4)_2 \cdot O_2$. Although details of the configuration are ambiguous, a redox reaction appears to occur between the $Bu^t{}_2NO^-$ moiety and dioxygen.

The redox reaction of $[Pd(Bu^t{}_2NO)(bipy)]ClO_4$ with dialkyl disulfides was further examined in the presence of catalytic amounts of bipy in an atmosphere of dry nitrogen. This reaction yields $[Pd(bipy)(SR)]_2(ClO_4)_2$ (R=Me and Pr) (Reaction 1),



(1)

III

(R=Me and Pr)

where the anionic nitroxide is oxidized to a neutral radical and dialkyl disulfides are reduced. Analogous complexes $[Pd(ethylenediamine)(SPh)]_2X_2$ (X=Cl and Br) were prepared by Boschi *et al.*,[16] who proposed a configuration similar to III.

References

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

2) D. L. Wilbur and R. Kreilick, *J. Chem. Phys.*, **52**, 1643 (1970).

3) T. B. Eames and R. Hoffman, *J. Am. Chem. Soc.*, **93**, 3140 (1971).

4) R. A. Zelonka and M. C. Baird, *J. Am. Chem. Soc.*, **93**, 6066 (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. Hoffmann, *Inorg. Chem.*, **13**, 1484 (1974).

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

9) M. Okunaka, G. Matsubayashi, and T. Tanaka, *Inorg. Nucl. Chem. Lett.*, **12**, 813 (1976).

10) M. Okunaka, G. Matsubayashi, and T. Tanaka, *Bull. Chem. Soc. Jpn.*, **48**, 1826 (1975).

11) K. Kawakami, T. Ohara, G. Matsubayashi, and T. Tanaka, *Bull. Chem. Soc. Jpn.*, **48**, 1440 (1975).

12) G. Matsubayashi, K. Wakatsuki, and T. Tanaka, *Org. Magn. Reson.*, **3**, 703 (1971).

13) G. Matsubayashi and T. Tanaka, *J. Organomet. Chem.*, **120**, 347 (1976).

14) G. Matsubayashi, M. Okunaka, and T. Tanaka, *J. Organomet. Chem.*, **56**, 215 (1973).

15) N. Kasai and N. Yasuoka, private communication.

16) T. Boschi, B. Crociani, L. Toniolo, and U. Belluco, *Inorg. Chem.*, **9**, 532 (1970).