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Preparation and Reaction of Some Di-*tert*-butylnitroxidopalladium(II) Complexes, $PdX(Bu^t_2NO)L$ ($L=PPh_3$, $AsPh_3$, $P(OPh)_3$; $X=Cl$, Br, I)

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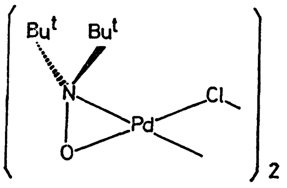
$PdX(Bu^t_2NO)L$ ($L=PPh_3$, $AsPh_3$, $P(OPh)_3$; X=Cl, Br, I) was isolated by the reactions of $[PdCl(Bu^t_2NO)]_2$ with L and by the halogen exchange reactions of the chloro complexes with $LiBr \cdot H_2O$ or NaI. PMR and IR spectra revealed that $PdX(Bu^t_2NO)(PPh_3)$ and $PdX(Bu^t_2NO)(AsPh_3)$ exist as only one geometrical isomer with the halogen atom *trans* to the oxygen atom of the nitroxide ligand, while two isomers of $PdX(Bu^t_2NO)[P(OPh)_3]$ coexist in solution. The reaction of $PdX(Bu^t_2NO)(PPh_3)$ (X=Cl, I) with triphenylphosphine was found to give $Pd(PPh_3)_4$ together with Pd $X_2(PPh_3)_2$ and $Bu_2NO\cdot$. A similar reaction proceeded between $PdCl(Bu^t_2NO)$-$[P(OPh)_3]$ and triphenylphosphite to yield $Pd[P(OPh)_3]_3$, while a not well-defined complex $[PdCl(AsPh_3)_2]_n$ was obtained in the reaction of $PdCl(Bu^t_2NO)(AsPh_3)$ with triphenylarsine.

The interactions between stable nitroxide radicals and metal halides have been studied by several workers.[1–8]

Some time ago, Beck and Schmidtner[2] reported that di-*tert*-butyl nitroxide reacts with palladium chloride to give a diamagnetic chloro-bridged complex $[PdCl(Bu^t_2NO)]_2$ (I), in which $Bu^t_2NO^-$ coordinates to the palladium through both the nitrogen and oxygen atoms to form a three-membered ring. The chloro-bridge is expected to undergo a cleavage reaction by nucleophiles. In addition, the unique three-membered ring moiety is supposed to be reactive.



I

In these respects, it is of interest to investigate the reaction of I with some nucleophiles. This paper reports the preparation of $PdX(Bu^t_2NO)L$ ($L=PPh_3$, $AsPh_3$, $P(OPh)_3$; X=Cl, Br, I), and the reactions of $PdX(Bu^t_2NO)L$ with L to give low-valent palladium complexes.

Experimental

Di-*tert*-butyl nitroxide radical was prepared as described by Hoffmann *et al.*[9] $[PdCl(Bu^t_2NO)]_2$ was prepared according to the literature.[2] All the manipulations in the reaction of $PdX(Bu^t_2NO)L$ with L ($L=PPh_3$, $AsPh_3$, $P(OPh)_3$; X=Cl, I) were carried out under dry nitrogen.

Preparation of $PdX(Bu^t_2NO)L$ ($L=PPh_3$, $AsPh_3$, $P(OPh)_3$; X=Cl, Br, I). To a benzene solution of $[PdCl(Bu^t_2NO)]_2$ (0.57 g, 1.0 mmol) was added dropwise a benzene solution of triphenylphosphine (0.53 g, 2.0 mmol) with stirring for 30 min at room temperature. The solvent was evaporated to dryness under reduced pressure. The product obtained was dissolved in diethyl ether to give a suspension. It was filtered, and the filtrate was evaporated to dryness again under reduced pressure. The resulting solid was recrystallized from a benzene solution by adding petroleum ether to afford orange crystals of $PdCl(Bu^t_2NO)(PPh_3)$ (0.74 g, yield 68%).

$PdCl(Bu^t_2NO)(PPh_3)$ and a large excess amount of $LiBr\cdot H_2O$ were mixed in ethanol. After stirring for 30 min, the solution was evaporated to dryness and the product was recrystallized from ligroin to give dark red needles of $PdBr(Bu^t_2NO)(PPh_3)$. $PdI(Bu^t_2NO)(PPh_3)$ was synthesized by

Table 1. Melting points, analytical data and molecular weights of the complexes

Complex	Mp (°C)	C% Found (Calcd)	H% Found (Calcd)	N% Found (Calcd)	M. W. Found (Calcd)
$PdCl(Bu^t_2NO)(PPh_3)$	152—153 (dec)	56.96 (56.71)	6.07 (6.30)	2.55 (2.69)	548 (503)
$PdBr(Bu^t_2NO)(PPh_3)$	175—183 (dec)	52.54 (52.68)	5.85 (5.61)	2.55 (2.36)	581 (593)
$PdI(Bu^t_2NO)(PPh_3)$	165—173 (dec)	49.18 (48.81)	5.47 (5.21)	2·34 (2.19)	646 (640)
$PdCl(Bu^t_2NO)(AsPh_3)$	155—156 (dec)	52.28 (52.71)	5.74 (5.63)	2.25 (2.37)	579 (592)
$PdBr(Bu^t_2NO)(AsPh_3)$	150—156 (dec)	48.98 (49.04)	5.25 (5.23)	2.40 (2.20)	608 (636)
$PdI(Bu^t_2NO)(AsPh_3)$	136—141 (dec)	45.48 (45.67)	4.93 (4.87)	2.24 (2.05)	645 (684)
$PdCl(Bu^t_2NO)[P(OPh)_3]$	104—105	52.15 (52.36)	5.68 (5.58)	2.36 (2.35)	579 (596)
$PdBr(Bu^t_2NO)[P(OPh)_3]$	123—126	48.79 (48.73)	5.37 (5.20)	2.29 (2.19)	638 (641)
$PdI(Bu^t_2NO)[P(OPh)_3]$	110—112	45.50 (45.40)	4.99 (4.85)	2.07 (2.03)	681 (689)

the reaction of the chloro complex with excess NaI in a similar manner. Six other complexes were similarly prepared. The melting points and analytical data are summarized in Table 1.

Reaction of $PdCl(Bu^t_2NO)(PPh_3)$ with Triphenylphosphine. To a benzene solution of $PdCl(Bu^t_2NO)(PPh_3)$ (0.55 g, 1.0 mmol) was added dropwise a benzene solution of triphenylphosphine (1.57 g, 6.0 mmol) with stirring at room temperature. The solution changed from orange to yellow *via* red, and finally a light yellow precipitate was obtained. Stirring was continued for 6 hr to force the reaction to completion. Then the solution was evaporated under reduced pressure, and the resulting solid was washed with diethyl ether to remove unreacted triphenylphosphine and liberated di-*tert*-butyl nitroxide. The product was recrystallized from ethanol to give pale yellow crystals of $Pd(PPh_3)_4$ (0.13 g, 0.11 mmol), mp 103—105 °C (decomp.) [lit,10) 100—105 °C (decomp.)]. Found: C, 72.97; H, 5.56%. Calcd for $Pd(PPh_3)_4$: C, 74.83; H, 5.24%. From the component insoluble in ethanol $PdCl_2(PPh_3)_2$ (0.33 g, 0.47 mmol) was obtained, mp above 220 °C. Found: C, 61.36; H, 4.38%. Calcd for $PdCl_2(PPh_3)_2$: C, 61.60; H, 4.32%. ν(Pd–Cl) 360 cm^{-1}.

An equimolar amounts of $PdCl(Bu^t_2NO)(PPh_3)$ and triphenylphosphine were mixed in benzene and stirred for 42 hr at room temperature. The solution was concentrated under reduced pressure to give a yellow precipitate, which was washed with diethyl ether and collected by filtration. The IR spectrum of this product showed ν(Pd–Cl) band at 303 and 360 cm^{-1} arising from $PdCl(Bu^t_2NO)(PPh_3)$ and $PdCl_2(PPh_3)_2$, respectively.

Reaction of $PdI(Bu^t_2NO)(PPh_3)$ with Triphenylphosphine. A benzene solution containing $PdI(Bu^t_2NO)(PPh_3)$ (0.30 g, 0.47 mmol) and triphenylphosphine (0.74 g, 2.82 mmol) was allowed to react overnight at room temperature to form pale yellow crystals of $Pd(PPh_3)_4$ (0.18 g, 0.16 mmol) and red brown crystals of $PdI_2(PPh_3)_2$ (0.20 g, 0.23 mmol). They were identified by IR spectra and decomposition points.

Reaction of $PdCl(Bu^t_2NO)[P(OPh)_3]$ with Triphenylphosphite. To a benzene solution of $PdCl(Bu^t_2NO)[P(OPh)_3]$ (0.45 g, 0.76 mmol) was added dropwise a benzene solution of triphenylphosphite (1.40 g, 4.53 mmol) with stirring at room temperature. Immediately, the yellow color of the solution faded away. The solution was concentrated under reduced pressure to give an oily product, which was dissolved in petroleum ether. The resulting white precipitate was collected by filtration and recrystallized from ethanol to give colorless crystals of $Pd[P(OPh)_3]_3$ (0.14 g, 0.14 mmol), mp 128—130 °C (decomp.) under dry nitrogen [lit,11) 118—129 °C (decomp.) under argon]. Found: C, 62.02; H, 4.35%. Calcd for $Pd[P(OPh)_3]_3$: C, 62.52; H, 4.38%. $PdCl_2[P(OPh)_3]_2$ (0.12 g, 0.14 mmol) was obtained from the petroleum ether solution, mp 177—179 °C (lit,12) 175—180 °C).

Reaction of $PdCl(Bu^t_2NO)(AsPh_3)$ with Triphenylarsine. $PdCl(Bu^t_2NO)(AsPh_3)$ (0.95 g, 1.60 mmol) and tripenylarsine (2.95 g, 9.63 mmol) were mixed in benzene and stirred for 7 days at room temperature to form a yellow precipitate, which was filtered, washed with diethyl ether and dried *in vacuo* (0.92 g), mp 154—156 °C (decomp.). Found: C, 57.14; H, 4.65%. Calcd for $[PdCl(AsPh_3)_2]_n$: C, 57.32; H, 4.02%. ν(Pd–Cl), 318 cm^{-1}.

Physical Measurements. IR spectra were recorded in Nujol mulls or in chloroform on a Hitachi EPI-L (700—200 cm^{-1}) spectrophotometer. PMR spectra were recorded on a JOEL JNM-PS-100 spectrometer, using tetramethylsilane as the internal reference. ESR spectra were recorded on a JOEL JES-ME-3X spectrometer. Molecular weights were determined in chloroform using a Mechrolab vapor pressure osmometer.

Results and Discussion

Preparation and Configuration of $PdX(Bu^t_2NO)L$ ($L=PPh_3$, $AsPh_3$, $P(OPh)_3$; $X=Cl$, Br, I). The reaction of $[PdCl(Bu^t_2NO)]_2$ with L ($L=PPh_3$, $AsPh_3$, $P(OPh)_3$) gave $PdCl(Bu^t_2NO)L$ (Eq. 1), which underwent halogen exchange reactions to yield the corresponding bromo and iodo complexes (Eq. 2). Molecular

$$[PdCl(Bu^t_2NO)]_2 + 2L \longrightarrow 2PdCl(Bu^t_2NO)L \quad (L=PPh_3,\ AsPh_3,\ P(OPh)_3) \tag{1}$$

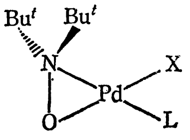
$$PdCl(Bu^t_2NO)L + \text{excess } LiBr\cdot H_2O \text{ or } NaI \longrightarrow PdX(Bu^t_2NO)L \quad (X=Br,\ I) \tag{2}$$

weight determination indicates that these complexes are essentially monomeric in chloroform (Table 1), which is consistent with the fact that the IR spectra of $PdCl(Bu^t_2NO)L$ show an intense band at 303—316 cm^{-1} assigned to the terminal Pd–Cl stretch as shown in Table 2. These facts reveal that the cleavage reaction took place at the bridging moiety.

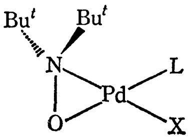
In these complexes obtained two geometrical isomers, *A* and *B*, are possible. PMR spectra of $PdX(Bu^t_2NO)(PPh_3)$ and $PdX(Bu^t_2NO)(AsPh_3)$ show only one *tert*-butyl signal (Table 2). In view of a large steric repulsion between *tert*-butyl and phenyl groups in *B*, but the insignificant one in *A*, this signal would be assigned to the isomer *A*. On the other hand, $PdX(Bu^t_2NO)[P(OPh)_3]$ exhibits another weak *tert*-butyl signal, which is probably arising from the isomer *B*. This is

TABLE 2. PMR AND IR DATA OF THE COMPLEXES

Complex	δ (Bu^t) in $CDCl_3$ at 23 °C	ν(Pd–Cl), cm^{-1}	
		in Nujol mull	in $CHCl_3$
$PdCl(Bu^t_2NO)(PPh_3)$	1.74	303	305
$PdBr(Bu^t_2NO)(PPh_3)$	1.67	—	—
$PdI(Bu^t_2NO)(PPh_3)$	1.78	—	—
$PdCl(Bu^t_2NO)(AsPh_3)$	1.75	304	305
$PdBr(Bu^t_2NO)(AsPh_3)$	1.80	—	—
$PdI(Bu^t_2NO)(AsPh_3)$	1.75	—	—
$PdCl(Bu^t_2NO)[P(OPh)_3]$	1.35, 1.31(w)	316	305, 312(w)
$PdBr(Bu^t_2NO)[P(OPh)_3]$	1.38, 1.34(w)	—	—
$PdI(Bu^t_2NO)[P(OPh)_3]$	1.35, 1.32(w)	—	—



A



B

supported from the smaller steric hindrance of triphenylphosphite than triphenylphosphine[13] (and probably triphenylarsine, too). In accordance with the PMR observations, IR spectra of $PdCl(Bu^t_2NO)(PPh_3)$ and $PdCl(Bu^t_2NO)(AsPh_3)$ in chloroform show only one ν(Pd–Cl) band, while two ν(Pd–Cl) bands appear in $PdCl(Bu^t_2NO)[P(OPh)_3]$ (Table 2).

ESR Spectra. The ESR spectrum of $PdCl(Bu^t_2NO)(PPh_3)$ in dichloromethane at room temperature shows a weak triplet with a spacing of 16.5 gauss (Fig. 1), which indicates a little dissociation of the complex in solution to produce di-*tert*-butyl nitroxide radical. The intensity of this signal is enourmously enhanced by the addition of triphenylphosphine as depicted in Fig. 1. These observations confirm that a redox reaction of the complex took place in the presence of triphenylphosphine. That is to say, $Bu^t_2NO^-$ which had coordinated as an anion was oxidized to $Bu^t_2NO\cdot$ radical, and, as an inevitable consequence, some reduced palladium species must be formed in solution. Thus, we investigated the reaction of $PdX(Bu^t_2NO)L$ with L in order to clarify the reduced palladium complex.

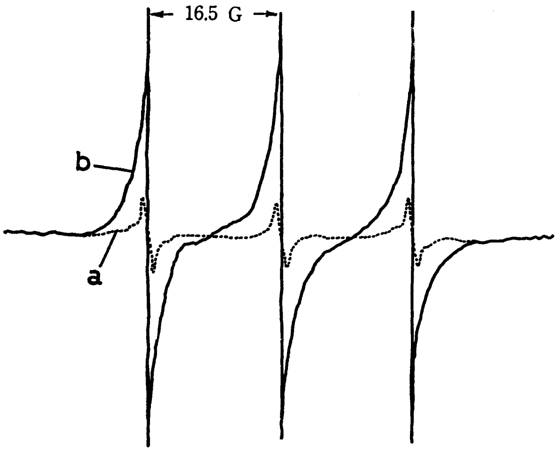
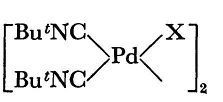


Fig. 1. ESR spectra of (a) $PdCl(Bu^t_2NO)(PPh_3)$ and (b) $PdCl(Bu^t_2NO)(PPh_3)+2PPh_3$, both in CH_2Cl_2 at 25 °C.
The concn. of the complex: 1.3×10^{-2} M; the signal is considered to be caused by $Bu^t_2NO\cdot$ produced by decomposition.

Reaction of $PdX(Bu^t_2NO)L$ with L. $PdX(Bu^t_2NO)(PPh_3)$ (X=Cl, I) reacted readily with triphenylphosphine to give $Pd(PPh_3)_4$ and $PdX_2(PPh_3)_2$. Since $Bu^t_2NO^-$ works clearly as a one electron reducing agent, a monovalent palladium complex must be formed as an intermediate in the course of the reaction (Path 3 in Scheme 1). Recently, Otsuka *et al*[14] reported the preparation of monovalent palladium complexes $[PdX(Bu^tNC)_2]_2$, for which they proposed a dimeric halide-bridged structure (II). Thus, an equilibrium 4 between monomer and dimer will be most probable in solution. Further, the dimeric complex may disproportionate to $Pd(PPh_3)_4$ and $PdCl_2(PPh_3)_2$ by assist of another triphenylphosphine molecule (Path 5). However, the assumed intermediate involving monovalent palladium could not be isolated even in the equimolar reaction of $PdCl(Bu^t_2NO)(PPh_3)$ with triphenylphosphine (see Experimental).



(X=Cl, Br, I)

II

Similarly, $Pd[P(OPh)_3]_3$ and $PdCl_2[P(OPh)_3]_2$ were obtained by the reaction of $PdCl(Bu^t_2NO)[P(OPh)_3]$ with excess triphenylphosphite. This reaction is thought to proceed through a similar way to Scheme 1.

In contrast to the results obtained for triphenylphosphine and triphenylphosphite complexes, no zerovalent complex could be isolated in the reaction of $PdCl(Bu^t_2NO)(AsPh_3)$ with excess triphenylarsine. Instead, a yellow complex whose IR spectrum shows a ν(Pd–Cl) band at 318 cm^{-1} was obtained. This complex is suggested to be $[PdCl(AsPh_3)_2]_n$ from analytical data. This complex is stable in air so far as it is in solid state. It is almost insoluble in common organic solvents, and at elevated temperatures decomposes in suspension in benzene even under dry nitrogen. The detailed structure of this complex has to await further studies in the solid state.

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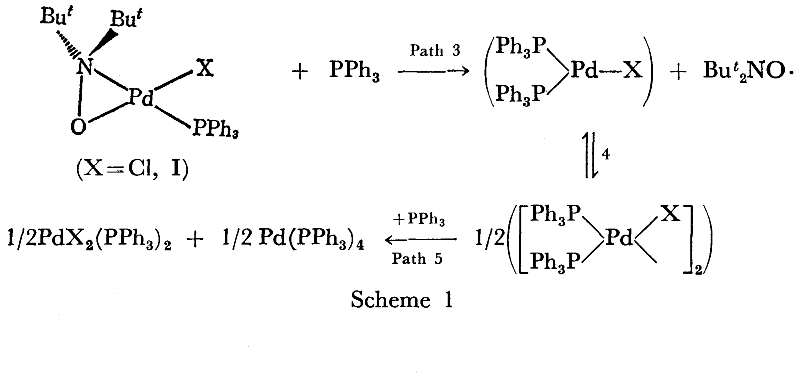

Scheme 1

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