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Structure of Chloro(2,2,4,4-tetramethylpiperidinyl-1-oxo-*O*,*N*)(triphenylphosphine)palladium(II), a Metal Complex of a Reduced Nitroxyl Radical

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The crystal and molecular structures of $PdCl(PPh_3)(TMPO^-)$ ($TMPO^-$ = 2,2,4,4-tetramethylpiperidinyl-1-oxo) have been determined by a single-crystal X-ray analysis. Crystals of this compound are monoclinic, space group $P2_1/n$, with four molecules in a unit cell of dimensions a = 8.881 (2) Å, b = 21.890 (4) Å, c = 13.676 (3) Å, and β = 95.00 (2)°. Full-matrix least-squares refinement, based upon 3459 nonzero intensity data and with phenyl rings treated as rigid groups, converged to a final conventional R factor of 0.049. The discrete monomeric molecules contain a palladium atom bound in a distorted square-planar configuration to a chloro ligand, a triphenylphosphine group, and a chelating N,O-bonded $TMPO^-$. The triphenylphosphine is trans to the coordinated nitrogen atom. Bond distances within the three-membered Pd–N–O metallacycle (Pd–N = 2.093 (4) Å, Pd–O = 2.023 (4) Å, N–O = 1.372 (6) Å) are compared with those in a series of related systems. Structural differences between the coordinated $TMPO^-$ and the metal-bound nitroxyl radicals in two copper(II) complexes are consistent with expectations based upon the electronic structures of these ligands.

Introduction

Recently, we reported the results of a crystal structure analysis of a copper(II) complex of the nitroxide free radical 2,2,6,6-tetramethylpiperidinyl-1-oxy (TMPO).[1] One of the principal structural observations of that study was the close similarity of the geometry of the coordinated nitroxyl radical in the copper complex to that of the free nitroxide.[2] This result was consistent with the view that the copper complex was best formulated as a copper(II) adduct of neutral TMPO, rather than as the product of an internal oxidation–reduction process.[3] The latter possibility required explicit consideration because of the relative ease of oxidation and reduction of nitroxide radicals.[4] As a further test of this interpretation, we felt it would be useful to investigate the structure of a metal complex in which the TMPO ligand had undergone formal one-electron reduction to $TMPO^-$. A series of palladium complexes of $TMPO^-$ has been reported by Okunaka et al.,[5] who proposed that the ligand was bound to the metal atom in a "side-on" fashion with formation of a three-membered Pd–N–O metallacycle. Similar ligand binding modes had previously been favored for closely related metal complexes derived from di-*tert*-butyl nitroxide.[6,7] We now report the results of our crystal structure analysis of one of these $TMPO^-$ complexes, $PdCl(PPh_3)(TMPO^-)$.

Experimental Section

Collection and Reduction of X-ray Data. The compound was synthesized by published methods.[5] Suitable crystals were grown by adding heptane to a benzene solution of the compound and allowing this mixture to evaporate slowly over a period of several days. An orange crystal of dimensions 0.40 × 0.46 × 0.42 mm was mounted on a glass fiber in a random orientation and was coated with a thin film of lacquer. Initial centering of reflections, generation of unit cell vectors, and assignment of indices were performed on a Syntex $P2_1$ diffractometer as previously described.[8] Interaxial angles suggested monoclinic symmetry; this was confirmed by axial rotation photographs. Refined cell parameters were obtained by our usual methods.[9] Crystal data are summarized in part A of Table I. The density measurement was performed by flotation in aqueous zinc bromide. Intensity data were collected by the 2θ–θ scan technique in bisecting geometry. Experimental parameters are listed in part B of Table I. Systematic absences in the data set ($h0l$, $h + l \neq 2n$; $0k0$, $k \neq 2n$) indicated space group $P2_1/n$.[10] Close spacing of reflections along b and broader than usual reflection profiles resulted in a few reflections showing asymmetric backgrounds caused by overlap with adjacent peaks. These were identified and corrected by analysis of peak profiles with the aid of a locally written computer program. Four standard reflections monitored after each 50 data declined by about 15% during data collection; the data were corrected accordingly. No reflections were intense enough to exceed the valid range of the coincidence correction. Data processing was performed as previously described.[9] The p factor in the expression[11] for the standard deviations of the observed intensities was set at 0.05. Sample calculations showed a maximum effect of absorption of ±2.5% on F^2; hence no absorption correction was made.

Table I. Crystal Data and Experimental Parameters

A. Crystal Data

formula	$PdC_{27}H_{33}ClNOP$	vol, Å^3	2648.4 (9)
fw	560.40	Z	4
a, Å	8.881 (2)	d(obsd), g cm^{-3}	1.40 (2)
b, Å	21.890 (4)	d(calcd), g cm^{-3}	1.41
c, Å	13.676 (3)	space group	$P2_1/n$
β, deg	95.00 (2)	μ(Mo Kα), cm^{-1}	8.73

B. Experimental Parameters

radiation	Mo Kα; λ(Kα) = 0.710 73 Å; graphite monochromator
temp, °C	24
receiving aperture	circular, 4-mm diam, 20 cm from crystal
scan rate, deg min^{-1}	variable, 2-12
scan range	−1.0° from Kα_1 to +1.2° from Kα_2
bkgd counting	stationary counts for $^1/_2$ of scan time at each end of scan
2θ(max), deg	50
data collected	4701
data with $F_o^2 > 3\sigma(F_o^2)$	3459

Structure Solution and Refinement. The structure was solved by conventional Patterson and Fourier methods.[12] Final full-matrix least-squares refinement employed anisotropic thermal parameters for all nonhydrogen atoms, except for the phenyl carbon atoms. The

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Table II. Positional Parameters of Nongroup Atoms

	x	*y*	*z*
Pd	0.33328 (5)[a]	0.13495 (2)	0.33531 (3)
Cl	0.4878 (2)	0.2163 (1)	0.3008 (2)
P	0.3910 (2)	0.0795 (1)	0.2047 (1)
O	0.1812 (5)	0.0934 (2)	0.4150 (3)
N	0.2272 (6)	0.1454 (2)	0.4651 (4)
C(1)	0.1038 (8)	0.1945 (3)	0.4647 (5)
C(2)	0.1731 (10)	0.2509 (3)	0.5150 (6)
C(3)	0.2605 (12)	0.2396 (4)	0.6148 (6)
C(4)	0.3814 (10)	0.1932 (4)	0.6045 (5)
C(5)	0.3240 (8)	0.1321 (3)	0.5604 (5)
C(6)	0.2335 (10)	0.0954 (4)	0.6334 (6)
C(7)	0.4575 (9)	0.0914 (4)	0.5353 (6)
C(8)	0.0511 (8)	0.2100 (3)	0.3579 (5)
C(9)	−0.0352 (9)	0.1706 (4)	0.5167 (7)

[a] Throughout this paper, numbers in parentheses are estimated standard deviations in the least significant figures.

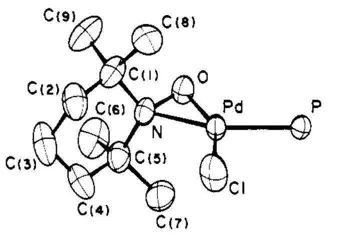

Figure 1. View of the molecular structure, with phenyl rings and hydrogen atoms omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level.

phenyl rings were treated as rigid groups (trigonal carbon atoms, C–C = 1.392 Å, C–H = 0.95 Å) with isotropic temperature factors for the carbon atoms. Methylene hydrogen atoms were included at their calculated positions; all hydrogen atoms were given fixed isotropic thermal parameters one unit greater than the final isotropic B value of the corresponding carbon atom. This refinement converged to conventional R factors $R_1 = 0.049$ and $R_2 = 0.070$; in the final cycle, no parameter shifted by more than one-third of its estimated standard deviation. The final standard deviation of an observation of unit weight was 1.97. Neutral atomic scattering factors, including anomalous terms for Pd, Cl, and P, were taken from ref 13. The function minimized in least-squares refinement was $\sum w(|F_o| - |F_c|)^2$, where $w = 4F_o^2/\sigma^2(F_o^2)$. Calculation of structure factors for the 1242 data with $F_o^2 \leq 3\sigma(F_o^2)$ showed 31 reflections with $\Delta F/\sigma \geq 3$; of these, 7 had $\Delta F/\sigma > 5$.

Final atomic positional parameters are listed in Table II and group parameters for the phenyl rings are given in Table III. Bond distances and angles are tabulated in Tables IV and V, respectively. Tables of structure factors, anisotropic thermal parameters, coordinates of group atoms, coordinates of hydrogen atoms, and least-squares planes are available as supplementary material.

Description of the Structure and Discussion

Views of the molecular structure of chloro(2,2,4,4-tetramethylpiperidinyl-1-oxo-*O*,*N*)(triphenylphosphine)palladium(II) are shown in Figures 1 and 2. The overall molecular structure is that proposed by Okunaka et al.,[5] with the palladium atom bound in a distorted square-planar configuration to the chloro ligand, the triphenylphosphine, and the N and O atoms of the $TMPO^-$. The triphenylphosphine is trans to the coordinated nitrogen atom, thus minimizing steric interactions between the phenyl groups and the tetramethylpiperidine ring. This particular compound was chosen for structural study because it yielded suitable single crystals; its structure is probably representative of those of the entire series of Pd(II)–R_2NO^- complexes.[5–7]

Structural parameters of the three-membered Pd–N–O ring include Pd–N = 2.093 (4) Å, Pd–O = 2.023 (4) Å, and N–O = 1.372 (6) Å. The existence of three-membered M–N–O metallacycles has only recently been structurally documented, although a number of examples are now known. A tabulation of these examples, together with bond length data, is given in Table VI. Two trends in the tabulated parameters are evident. Owing primarily to variation in the M–O distances, the difference between M–N and M–O distances tends to increase with increasing metal oxidation state. For complexes of V(V), Mo(VI), and V(VI), the M–N distance is longer by 0.10–0.23 Å than the M–O distance. These differences are greater than would be expected on the basis of covalent radii and are consistent with the greater affinity for oxygen ligands of metal ions in higher oxidation states. Lengthened M–O distances in complexes of lower valent metals give rise to smaller differences and in one case to a M–O distance *longer* by 0.05 Å than the M–N distance.[20] A second observation is that the two shortest N–O distances are found for complexes in which the N–O grouping is a part of an oximato ligand. The shortening is not highly significant, but the trend is clear. This may be indicative of a small degree of multiple bond character in the N–O bond of these complexes.

Three-membered metallacycles of the sort found here are strained, and potentially reactive, moieties; consequently, structural trends within these rings might be related to reactivity patterns. The most extensive chemical studies on a system containing a three-membered M–N–O ring are those of Otsuka et al.,[23] carried out on nitrosobenzene complexes of zerovalent nickel group atoms. These complexes were found to undergo N–O bond cleavage, followed by phenylnitrene and oxygen transfer reactions. Although no thorough investigation of the reactivity of the N–O bond in the Pd–$TMPO^-$ systems has been reported, it is known that triphenylphosphine cleaves the chlorine bridges of dimeric $[PdCl(TMPO^-)]_2$ without evident effect on the Pd–N–O ring system.[5] It would be of interest to determine whether these apparent differences in reactivity have any structural basis; however, no structural data are yet available for any of the nitrosobenzene complexes, the only systems for which N–O bond cleavage has been observed to date.

The comparative geometries of the $TMPO^-$ ligand in this complex and the coordinated TMPO· in $Cu(hfac)_2TMPO$ are consistent with the formulation of these ligands as a monoanion and a neutral radical, respectively. The N–O distance of 1.372 (6) Å in the present case is within the range expected for a single bond, while the shorter distance of 1.269 (7) Å in the copper complex is consistent with a bond order between 1 and 2, as is implicit in the conventional description of the electronic structure of nitroxide radicals. Also, the nitrogen atom is distinctly more pyramidal in the coordinated anion than in the radical, as measured by the distance of this atom from the plane of its three bonded atoms. This distance is 0.330 Å in the Pd^{2+}–$TMPO^-$ complex and 0.140 Å in the Cu^{2+}–TMPO· adduct. A comparison with the $Cu(hfac)_2$ complex of 4-OH-

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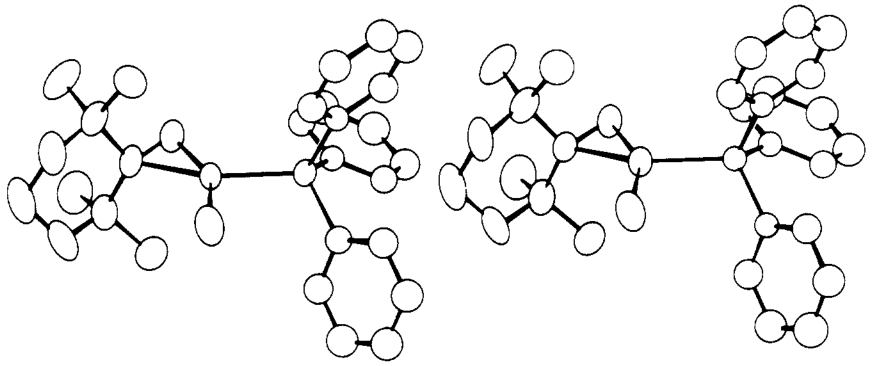

Figure 2. Stereoscopic view of the molecular structure, with hydrogen atoms not included.

Table III. Rigid Group Parameters[a]

	x	y	z	ϕ, deg	θ, deg	ρ, deg
phenyl 1	0.7464 (3)	0.0799 (1)	0.1766 (2)	−90.08 (16)	169.85 (12)	−102.59 (16)
phenyl 2	0.2176 (3)	0.1243 (1)	0.0014 (2)	56.28 (23)	125.26 (14)	−146.39 (24)
phenyl 3	0.3080 (3)	−0.0633 (1)	0.2164 (2)	164.69 (13)	−176.61 (14)	−143.74 (16)

[a] The fractional coordinates of the group center of gravity are designated x, y, and z. The orientation angles, ϕ, θ, and ρ, have previously been defined by: Doedens, R. J. In "Crystallographic Computing"; Ahmed, F. R., Ed.; Munksgaard: Copenhagen, 1970; pp 198–200. Since that reference is no longer readily available, the definition will be repeated here. An orthogonal set of unit axes (A_1, A_2, A_3) is defined relative to the crystal axes by the following: $A_2 \parallel b; A_1 \parallel (b \times c); A_3 \parallel (A_1 \times A_2)$. The angles ϕ, θ, and ρ bring this orthogonal system into alignment (except for translation) with the internal group axes by the following sequential rotations: ϕ about A_3; θ about new A_1; ρ about new A_2. The internal group axes (a_i, b_i, c_i) are defined such that c_i is perpendicular to the ring plane, $+b_i$ points toward C(1), and $+a_i$ points toward the midpoint of the C(2)–C(3) bond.

Table IV. Bond Distances (Å)

Pd–Cl	2.321 (2)	Pd–O	2.023 (4)
Pd–P	2.256 (2)	Pd–N	2.093 (4)
N–O	1.372 (6)	P–C(1–1)	1.822 (3)[a]
N–C(1)	1.533 (8)	P–C(2–1)	1.820 (4)
N–C(5)	1.526 (8)	P–C(3–1)	1.829 (3)
C(1)–C(2)	1.517 (11)	C(1)–C(8)	1.532 (10)
C(2)–C(3)	1.530 (11)	C(1)–C(9)	1.568 (10)
C(3)–C(4)	1.495 (12)	C(5)–C(6)	1.557 (10)
C(4)–C(5)	1.535 (10)	C(5)–C(7)	1.544 (10)

[a] Estimated standard deviations of distances and angles involving phenyl carbon atoms do not include effects of covariance and so may be underestimated.

Table V. Bond Angles (Deg)

Cl–Pd–P	94.2 (1)	P–Pd–O	113.2 (1)
Cl–Pd–O	152.6 (1)	P–Pd–N	151.7 (2)
Cl–Pd–N	113.9 (2)	O–Pd–N	38.9 (2)
Pd–N–O	67.8 (2)	Pd–N–C(1)	116.6 (4)
Pd–O–N	73.3 (2)	Pd–N–C(5)	116.2 (4)
Pd–P–C(1–1)	113.7 (1)	C(1–1)–P–C(1–2)	105.8 (2)
Pd–P–C(2–1)	114.0 (1)	C(1–1)–P–C(1–3)	102.7 (2)
Pd–P–C(3–1)	114.7 (1)	C(1–2)–P–C(1–3)	104.8 (2)
O–N–C(1)	113.4 (5)	C(2)–C(3)–C(4)	109.7 (6)
O–N–C(5)	112.9 (5)	C(3)–C(4)–C(5)	114.4 (7)
C(1)–N–C(5)	119.1 (5)	C(4)–C(5)–C(6)	111.6 (6)
N–C(1)–C(2)	107.9 (6)	C(4)–C(5)–C(7)	110.7 (7)
N–C(1)–C(8)	108.5 (5)	C(6)–C(5)–C(7)	107.1 (6)
N–C(1)–C(9)	110.8 (6)	N–C(5)–C(4)	108.1 (6)
C(8)–C(1)–C(9)	108.6 (6)	N–C(5)–C(6)	111.3 (6)
C(1)–C(2)–C(3)	115.3 (7)	N–C(5)–C(7)	107.9 (5)

Table VI. Bond Distances (Å) in M–N–O Metallacycles

M	R_1,R_2[a]	M–N[b]	M–O	N–O	ref
V(V)	Et,Et	2.078 (4)	1.863 (3)	1.402 (5)	14
V(III)	H,H	2.054 (17)	2.015 (12)	1.417 (26)	15
Mo(VI)	H,Me	2.093 (9)	1.961 (8)	1.402 (13)	16
Mo(VI)	H,Me	2.114 (4)	1.976 (3)	1.376 (7)	16
Mo(VI)	Me,Me	2.172 (4)	1.969 (3)	1.399 (4)	17
Mo(VI)	Et,Et	2.143 (2)	1.970 (2)	1.427 (3)	14
Mo(VI)	Ph,LP	2.036 (5)	1.944 (4)	1.416 (7)	18
Mo(IV)	$=CMe_2$	2.086 (8)	2.090 (6)	1.358 (10)	19
Mo(II)	$=CMe_2$	2.089 (12)	2.139 (12)	1.336 (27)	20
Pd(II)	pip	2.093 (4)	2.023 (4)	1.372 (6)	this work
U(VI)	H,H	2.436 (6)	2.292 (5)	1.465 (7)	21
U(VI)	H,H	2.41 (2)	2.30 (1)	1.41 (2)	22

[a] R_1 and R_2 specify the substituents on the nitrogen atom. The abbreviation LP signifies a lone pair, and pip denotes a nitrogen atom that is part of a 2,2,6,6-tetramethylpiperidinyl ring.
[b] Where more than one equivalent distance is present, average values are quoted with the estimated standard deviation for an individual distance.

TMPO yields similar results, though less definitively owing to an apparent disordering of the nitroxyl radical in that complex.[24]

Other features of the structure are unremarkable. The piperidinyl ring has the expected chair conformation. The four atoms bonded to Pd deviate slightly from coplanarity, with the largest displacements of ca. 0.06 Å involving the O and N atoms. Two of the methyl groups are involved in relatively short intramolecular contacts with the Pd atoms, as defined by Pd···C(7) = 3.013 (8) Å and Pd···C(8) = 3.035 (7) Å. In the absence of precise coordinates for the methyl hydrogen atoms, the nature of these interactions could not be explored in more detail. Bond distances fall within their expected ranges and there are no unusual intermolecular contacts.

In summary, the results of this crystal structure analysis have documented bidentate O,N binding of the reduced nitroxide ligand in the title complex and, by implication, in a series of closely related systems. Structural differences between this ligand and the metal-coordinated nitroxides in two copper(II) complexes are consistent with the presence of the nitroxide in its radical form in the copper systems.

Registry No. $PdCl(PPh_3)(TMPO^-)$, 63374-75-4.

Supplementary Material Available: A listing of observed and calculated structure amplitudes and tables of anisotropic thermal parameters, derived coordinates of group atoms, hydrogen atomic parameters, and least-squares planes (29 pages). Ordering information is given on any current masthead page.

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