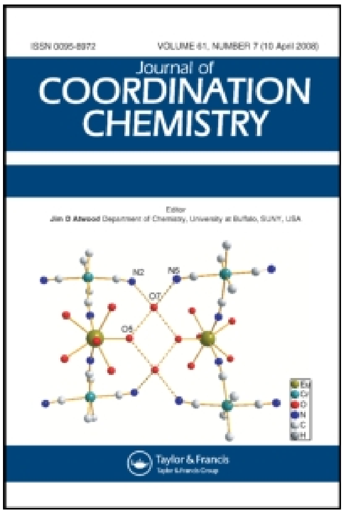

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Reaction of [Co$(PMe_3)_4$]BPh_4 with Oxygen: Crystal and Molecular Structure of [Co$(MeCN)_2(OPMe_3)_4$]$(BPh_4)_2$

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REACTION OF $[Co(PMe_3)_4]BPh_4$ WITH OXYGEN: CRYSTAL AND MOLECULAR STRUCTURE OF $[Co(MeCN)_2(OPMe_3)_4](BPh_4)_2$

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Reaction of molecular oxygen with the cobalt(I) cationic complex $[Co(PMe_3)_4]BPh_4$ in acetonitrile yields pink crystals of the cobalt(II) compound $[Co(MeCN)_2(OPMe_3)_4](BPh_4)_2$. X-ray diffraction ($P2_1/c$, $a = 12.580$, $b = 18.54$, $c = 18.684$ Å, $\beta = 130.76°$, $R = 0.041$) shows that the cation is an octahedral d^7 Co(II) monomer with two *trans* acetonitrile ligands. This compound is one of the few examples of octahedral Co(II) complexes containing phosphine oxide ligands. The peroxocobalt(III) compound $[Co(PMe_3)_4(O_2)]BPh_4$, showing an infrared ν(O–O) absorption at $880\,cm^{-1}$, has been obtained as an intermediate.

Keywords: Cobalt(I), phosphine, X-ray structure, oxygen binding

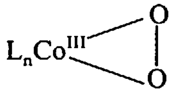
INTRODUCTION

The binding of dioxygen to cobalt(II) phosphine complexes has attracted considerable attention. In many cases, such as with $CoCl_2(PEt_3)_2$, quantitative oxidation to the phosphine oxide complex has been found to take place.[1] On the other hand, depending on the phosphine present, various dioxygen adducts have been isolated, in which the O_2 ligand is end-on bonded, side-on bonded or bridging.[2] It is now generally admitted that the reactions with Co(II) occur as follows:

$$[L5Co^{II}] \xrightarrow{O_2} [L5Co^{III}\text{–O–O}] \xrightarrow{L_5Co} [L_5Co^{III}\text{–O–O–}Co^{III}L_5]$$

$$\text{Superoxo Co(III)} \qquad \mu\text{-Peroxo Co(III)}$$

Since the first step includes a thermodynamically unfavoured one-electron reduction of the O_2 molecule, the more nucleophilic Co(I) or Co(0) centres should favour O_2 fixation. This is indeed observed, as indicated by the high affinity of the Co(I) and Co(0) phosphine complexes for O_2. However, the only products of addition of oxygen to Co(I) complexes reported so far are the Co(III) peroxo species $[CoL(O_2)]^+$, where L is a tetraarsine,[3] and $[CoL_2(O_2)]^+$, where L = diphos.[4]



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We had observed that $CoX(PMe_3)_3$ (X = Cl, Br, I) reacted instantly with O_2, giving exclusively Co(II) tertiary phosphine oxide species.[5] However, when the cationic $[Co(PMe_3)_4]BPh_4$ complex was used, the reaction proceeded differently, giving rise in a first step to a peroxocobalt(III) complex. Nevertheless, the final product was the cobalt(II) phosphine oxide species $[Co(MeCN)_2(OPMe_3)_4]^{2+}$, whose crystal structure is described below.

EXPERIMENTAL

The preparation of $CoBr(PMe_3)_3$ and $[Co(PMe_3)_4]BPh_4$, as well as the physicochemical methods used, have been described previously.[6]

Synthesis of $[Co(MeCN)_2(OPMe_3)_4](BPh_4)_2$ *(1) and* $[Co(PMe_3)_4(O_2)]BPh_4$ *(2)*

To a mixture of $CoBr(PMe_3)_3$ (1 g, 2.7 mmol) and excess PMe_3 (0.5 cm^3, 5 mmol) in acetonitrile (10 cm^3) was added $NaBPh_4$ (0.93 g, 2.7 mmol) in methanol (30 cm^3). The resulting green solution, cooled to −80°C, was kept under an oxygen atmosphere. The green colour turned brown, and brown crystals of **2** deposited slowly, They were filtered off and dried under oxygen. Anal: Calcd. for $CoBC_{36}H_{56}O_2P_4$: Co, 8.25; B, 1.51; C, 60.52; H, 7.90; P, 17.34%. Found: Co, 7.58; B, 1.46; C, 60.20; H, 7.84; P, 16.59%. Recrystallization of **2** overnight at −30°C from acetonitrile gave a small quantity of pink crystals of $[Co(MeCN)_2(OPMe_3)_4](BPh_4)_2$, **1**, which were filtered off and dried in air. Anal: Calcd. for $CoB_2C_{64}H_{82}N_2O_4P_4$: C, 66.97; H, 7.20; N, 2.44%. Found: C, 67.03; H, 7.27; N, 2.35%.

Crystallographic Measurements and Structure Resolution of $[Co(MeCN)_2(OPMe_3)_4](BPh_4)_2$ *(1)*

Crystal data: $C_{64}H_{82}B_2CoN_2P_4O_4$, *fw* = 1147.8, monoclinic, $P2_1/c$, a = 12.580(8) Å, b = 18.54(2) Å, c = 18.684(4) Å; β = 130.76(4)°, V = 3301 Å^3, D_c = 1.155 g cm^{-3}, Z = 2; $\lambda(CuK\bar{\alpha})$ = 1.54178 Å (graphite monochromator), $\mu(CuK\alpha)$ = 33.9 cm^{-1}, T = 23°C.

The pink crystals slowly turn blue in air. The X-ray work was therefore carried out on a specimen sealed in a Lindemann capillary under nitrogen. A roughly spherical fragment of mean diameter 0.30 mm was selected for the structure determination. A total of 4898 independent hkl and $hk\bar{l}$ reflections ($2\theta \leq 120°$) were collected with an Enraf-Nonius CAD4 diffractometer, following the procedure described previously.[7] A set of 2081 reflections with intensity significantly above background ($I \geq 2.5\,\sigma(I)$) was retained to solve the structure. No absorption correction was applied owing to the nearly spherical shape and low absorption coefficient of the crystal.

The heavy-atom method was used. Full-matrix refinement of the positional and isotropic temperature parameters of all non-hydrogen atoms converged to $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.099$. The refinement was continued by block-diagonal least-squares methods. The hydrogen atoms on the aromatic rings were fixed at ideal positions (isotropic B = 7.0 Å^2). At least one hydrogen was visible on the ΔF map for each methyl group. These positions were used to calculate ideal coordinates for the three hydrogens of each group (P–C–H = 109.5°, C–H = 0.95 Å, B = 9.0 Å^2). The parameters of the hydrogens were not refined, but their coordinates were recalculated after each least-squares cycle. Individual weights based on counting statistics were applied to each reflection in the last cycles. Refinement converged to $R = 0.041$ and $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2} = 0.044$. The goodness-of-fit ratio was 1.42. The final ΔF map was essentially featureless, with a general background lower than ± 0.19 e/Å^3. The refined coordinates are listed in Table I.

The scattering factors used were those of Cromer and Waber,[8] except for hydrogen.[9] The real and imaginary contributions to anomalous dispersion were included in the calculations for Co and P.[10] The programs used are listed elsewhere.[11]

TABLE I

Final atomic coordinates (× 10^4, P × 10^5) and equivalent isotopic temperature factors (Å^2 × 10^3).

Atom	x/a	y/b	z/c	U_{eq}
Co	0	0	0	52
P1	18370(13)	4690(8)	22160(9)	67
P2	−5680(14)	17560(8)	−4850(10)	73
O1	1244(3)	−72(2)	1449(2)	65
O2	141(3)	1102(2)	110(2)	61
N	−1882(4)	19(2)	−178(3)	72
C1	542(7)	1026(4)	2036(4)	125
C2	2766(6)	55(3)	3335(3)	100
C3	3036(6)	1052(3)	2308(4)	117
C4	−534(6)	1817(3)	−1411(4)	114
C5	238(8)	2542(3)	190(5)	139
C6	−2340(6)	1792(4)	−998(5)	163
C7	−2938(4)	43(2)	−384(3)	61
C8	−4307(5)	94(3)	−650(4)	91
C11	6436(4)	2971(2)	549(3)	56
C12	6031(5)	3562(3)	−41(3)	73
C13	6968(6)	3989(3)	−9(3)	84
C14	8382(5)	3850(3)	664(4)	91
C15	8832(5)	3299(3)	1273(3)	84
C16	7879(5)	2860(3)	1214(3)	64
C21	4332(4)	2018(2)	−566(3)	56
C22	4464(5)	2088(3)	−1249(3)	68
C23	3640(5)	1701(3)	−2085(3)	82
C24	2659(5)	1232(3)	−2272(3)	90
C25	2495(5)	1137(3)	−1625(4)	84
C26	3332(4)	1526(3)	−776(3)	68
C31	5932(4)	1914(2)	1289(3)	58
C32	5678(5)	1889(3)	1919(3)	72
C33	6355(6)	1409(3)	2672(3)	91
C34	7275(6)	929(3)	2821(4)	97
C35	7556(5)	911(3)	2220(4)	85
C36	6864(5)	1387(3)	1475(3)	71
C41	4181(5)	3052(2)	372(3)	66
C42	2766(5)	3139(3)	−380(3)	77
C43	1920(6)	3639(3)	−397(4)	99
C44	2499(7)	4072(3)	359(5)	114
C45	3885(7)	4029(3)	1110(4)	110
C46	4717(6)	3519(3)	1117(4)	91
B	5235(5)	2483(3)	420(4)	56

RESULTS AND DISCUSSION

The green crystals of $[Co(PMe_3)_4]BPh_4$ turned brown when they were left in air for a short time. Colour change was accompanied by the appearance of an infrared band at $880\,cm^{-1}$, in the region expected for the ν(O–O) band of a side-bonded peroxo ligand.[12] The phosphine oxide P=O stretching band normally found near $1140\,cm^{-1}$ was not observed. A brown powder with a similar IR spectrum was obtained by bubbling O_2 in a suspension of $[Co(PMe_3)_4]BPh_4$ in benzene. However, a medium intensity band at $1150\,cm^{-1}$, belonging to $OPMe_3$, was then also detected. When O_2 was bubbled at −80°C in an acetonitrile/methanol solution containing $CoBr(PMe_3)_3$, PMe_3 and $NaBPh_4$, brown crystals of composition $[Co(PMe_3)_4(O_2)]BPh_4$, **2**, precipitated. Their ^{31}P NMR spectrum at −90°C in acetone in the presence of O_2 showed triplets at 11 ppm and 8 ppm, characteristic of an A_2B_2 spin system. The solid-state IR spectrum showed no ν(O=P) band, but the stretching band of coordinated $(O_2)^{2-}$ was present at $880\,cm^{-1}$. Dissolution of **2** in acetonitrile at −30°C yielded pink crystals of a new compound $[Co(MeCN)_2(OPMe_3)_4](BPh_4)_2$ (**1**). The presence of coordinated acetonitrile was indicated by a doublet at 2290/2300 cm^{-1}, in which at least one component originates from a C≡N stretching vibration shifted upward from free acetonitrile ($2250\,cm^{-1}$).[13] There was no IR band near $880\,cm^{-1}$; only the strong ν(P=O) vibration of phosphine oxide at $1130\,cm^{-1}$ was found. Since the existence of a superoxo Co-(O–O$^-$) group which would appear at $\sim 1150\,cm^{-1}$, could not be ruled out by the above results, the X-ray structure of **1** was determined.

The pink compound is the BPh_4^- salt of the cobalt(II) complex cation *trans* $[Co(MeCN)_2(OPMe_3)_4]^{2+}$ shown in Figure 1. The Co atom sits on a crystallographic inversion centre. The departure from octahedral geometry in the CoO_2N_4 coordination sphere is within 1.1° (Table II).

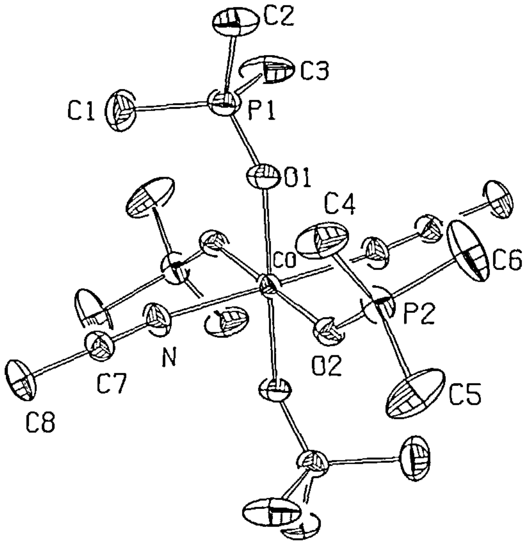

FIGURE. 1. Geometry of the $[Co(MeCN)_2(OPMe_3)_4]^{2+}$ ion with the numbering scheme. The cation has a crystallographically-imposed inversion centre at the Co atom. Ellipsoids correspond to 50% probability. Hydrogens are omitted for simplicity.

TABLE II
Interatomic distances and bond angles.

Distances (Å)			
Co–O1	2.065(3)	P1–C3	1.770(8)
Co–O2	2.049(3)	P2–C4	1.762(7)
Co–N	2.165(5)	P2–C5	1.753(7)
P1–O1	1.490(3)	P2–C6	1.761(10)
P2–O2	1.486(3)	N–C7	1.117(8)
P1–C1	1.766(9)	C7–C8	1.451(10)
P1–C2	1.771(5)		
Angles (deg)			
O1–Co–O2	89.5(1)	O1–P1–C2	111.9(3)
O1–Co–N	91.1(2)	O1–P1–C3	111.4(3)
O1–Co–O2[a]	90.5(1)	O2–P2–C4	113.5(3)
O1–Co–N[a]	88.9(2)	O2–P2–C5	110.9(3)
O2–Co–N	90.8(2)	O2–P2–C6	111.5(3)
O2–Co–N[a]	89.2(2)	C1–P1–C2	107.1(3)
Co–N–C7	171.4(4)	C1–P1–C3	106.4(3)
N–C7–C8	178.5(6)	C2–P1–C3	106.6(3)
Co–O1–P1	133.8(2)	C4–P2–C5	106.2(4)
Co–O2–P2	140.2(2)	C4–P2–C6	107.3(4)
O1–P1–C1	113.0(3)	C5–P2–C6	107.0(4)

[a] Related to molecules at x, y, z by $\bar{x}, \bar{y}, \bar{z}$.

The Co–O distances (av. 2.057(3) Å) are significantly greater than those found for *cis*-$Co(NO_3)_2(OPMe_3)_2$ (1.96 Å), which also contains a six-coordinate Co(II) atom.[14] The short bonds in the latter case can be explained by the low steric demand of the bidentate nitrate ligands. The remaining Co(II) complexes with phosphine oxides are tetrahedral and their shorter Co–O bonds can be ascribed to the lower coordination number.[5,15,16] The longer Co–N bonds (2.165(5) Å) compared with those of the $[Co(NO_3)_3(MeCN)]^-$ ion (2.054(12) Å)[17] can also be related to steric effects.

TABLE III
Geometry of the $OPMe_3$ ligand.

	a	This work
P–O	1.495(11)	1.488(3)
P–C	1.793(18)	1.764(8)
O–P–C	111.3(9)	112.0(3)
C–P–C	107.5(16)	106.8(4)
M–O–P	129.0–173.7	133.8(2), 140.2(2)

[a] Refs. 5, 13, 15, 17. Individual values are listed in the supplementary material.

Crystallographic work has been carried out on *ca* 10 trimethylphosphine oxide complexes.[5,14,16,18] Typical values for the distances and angles in the coordinated $OPMe_3$ unit are provided in Table III. In many of these studies, the accuracy is lower than in the present case, because of the presence of very heavy atoms and/or higher R

factors. Nevertheless, our results are in good general agreement with those of Table III. For instance, our O–P–C angles (av. 112.0(3°) are 5–6° greater than the C–P–C angles (av. 106.8(4)°). The P–O distances (av. 1.488(3) Å) compare well with those of the other structures, whereas our slightly shorter P–C bonds (av. 1.764(8) Å) are probably related to the fact that the methyl hydrogen atoms have not been taken into account in many of the earlier structures. The Co–O–P angles (133.8(2)°) and 140.2(2)°) are on the low side of the range given in Table III. This angle is likely to vary widely depending on steric interactions between non-bonded groups.

The acetonitrile ligand shows the usual linear geometry[6] and is "end-on" coordinated as expected. The Co–N–C7 angle of 171.4(4)° indicates a large departure from perfect linearity, but this is not unreasonable for this tube-like ligand which is particularly sensitive to intermolecular steric effects. The BPh_4^- ion shows no unusual features. The B–C bonds average 1.640 Å and the common pattern of internal angles in the phenyl rings is observed: boron-bonded carbon, 114.1°; *ortho*, 123.2°; others, 119.8°. Cohesion between the anions and the cations is achieved by normal van der Waals contacts.

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SUPPLEMENTARY MATERIAL AVAILABLE

Tables of anisotropic temperature factors, hydrogen coordinates, distances and angles in the BPh_4^- ion, atom-to-plane distances, and structure factor amplitudes for the present structure, together with the distances and angles in other $OPMe_3$ complexes (31 pages) are available from the authors upon request.

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