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Contribution from the Laboratoire d'Oxydation, Institut Francais du Pétrole, 92506 Rueil-Malmaison, France,
Laboratoire de Chimie Minérale Moléculaire, Equipe de Recherche Associée au CNRS, Parc Valrose, 06034 Nice, France, and
Laboratoire de Cristallochimie, Institut Le Bel, Université Louis Pasteur, 67070 Strasbourg, France

Novel Unusually Stable Peroxotitanium(IV) Compounds. Molecular and Crystal Structure of Peroxobis(picolinato)(hexamethylphosphoric triamide)titanium(IV)

HUBERT MIMOUN,[1a] MICHELE POSTEL,*[1b] FRANCIS CASABIANCA,[1b] JEAN FISCHER,[1c] and ANDRE MITSCHLER[1c]

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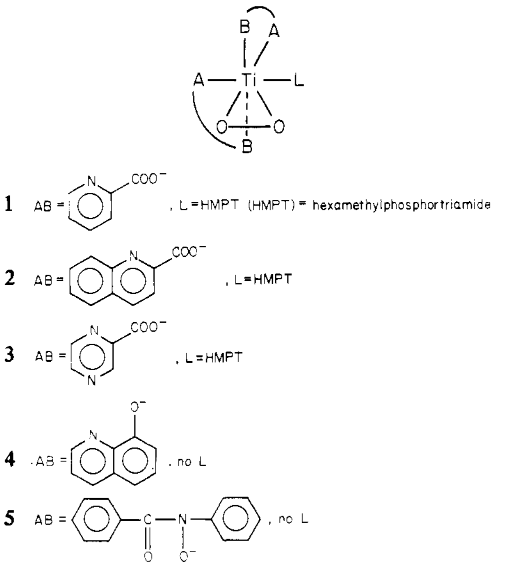
The synthesis, structure, and properties, with respect to oxygen transfer to various substrates, of peroxotitanium(IV) derivatives **1–5** are reported. The X-ray crystal structure of **1** essentially revealed that the O–O distance in the peroxo group is short and the HMPT molecule is weakly bonded to titanium. Strong stabilization of the peroxotitanium moiety by picolinato, hydroxyquinolino, or hydroximato ligands precluded oxygen transfer from the titanium compounds to olefins, allylic alcohols, cyclic ketones, or sulfides. Triphenylphosphine and tetracyanoethylene were found to react with **1–5**. These results are interpreted in terms of saturation of the metal which only very loosely coordinates strong donors such as HMPT.

Dioxygen complexes of the transition metals are the focus of active current research arising from their involvement in the activation and transfer of molecular oxygen to organic substrates.[2]

Peroxo complexes of group 6 metals in their high valence d^0 states have been reported as stoichiometric reagents and as catalysts in the oxidation of olefins.[3] Similarly, peroxovanadium species, although not isolated, have been suggested to be the active oxidizing species in the vanadium(V)-catalyzed oxidation of alkenes by H_2O_2.[4] Finally, the ability of titanium to transfer oxygen has recently been elegantly exemplified by Sharpless in the asymmetric transformation of allylic alcohols into epoxyalcohols by *t*-BuOOH in the presence of titanium tetraisopropoxide as a catalyst.[5]

We report here the synthesis, structure, and properties, with respect to oxygen transfer to various substrates, of the unusually stable new titanium(IV) peroxo complexes **1–5**.



Results and Discussion

Addition of H_2O_2 to a CH_2Cl_2 suspension of titanyl acetylacetonate in the presence of 2 equiv of picolinic acid and of an excess of HMPT resulted in a progressive dissolution, producing a deep orange CH_2Cl_2 solution. Workup of the organic phase afforded high yields of the deep orange crystalline compound **1**, which analyses as $Ti(O_2)(pic)_2HMPT$ (pic = picolinato).

The infrared spectrum of **1** exhibited three absorption bands at 895, 615, and 575 cm^{-1} assigned, by analogy with other peroxotitanium(IV) complexes,[6] to the O–O stretching vibration and to the symmetric and asymmetric M–O stretching vibrations of the peroxo group, respectively. The presence of the characteristic $\nu(C{=}O)_{asym}$ vibration at 1675 cm^{-1} and $\nu(C{=}N)$ vibration at 1600 cm^{-1} indicated that the picolinic anions are both bonded in a bidentate fashion through the oxygen atom of the carboxylic group and the heterocyclic nitrogen atom.[7] The coordination of HMPT to titanium in the solid phase was evidence by the lowering of the $\nu(P{=}O)$ vibration found at 1185 cm^{-1} ($\Delta\nu(P{=}O)$ = 25 cm^{-1}).

On the other hand, HMPT is dissociated from **1** in solution, as evidenced by the infrared spectrum (CH_2Cl_2) where the $\nu(P{=}O)$ vibration appears at 1205 cm^{-1} ($\Delta\nu$ = 0) and by the ^1H NMR spectra (CD_2Cl_2) in which only one doublet is measured at 2.65 ppm even at −60 °C; the picolinic protons appear in the NMR spectrum as a complex multiplet at ca. 8 ppm.

Single crystals of **1** were obtained by slow evaporation of CH_2Cl_2–Et_2O solutions at room temperature and were submitted to X-ray diffraction analysis (vide infra).

The same synthetic procedure was used with various other bidentate ligands in order to modify the basicity of the donor atoms and hence the electrophilicity of titanium in the peroxo adducts. The resulting compounds are listed in Table II.

The similarities of the infrared spectra measured on the solids (KBr disk) indicate that the structure established for **1** is valid for compounds **2** and **3**. The ^1H NMR data show that, in solution, HMPT also dissociates from **2** and **3**.

In the case of compounds **4** and **5**, no coordination of HMPT to titanium was observed probably because of the increase in steric hindrance of the bidentate ligand in these complexes compared to complexes **1–3**, where, as evidenced by NMR, the HMPT molecule is already very labile. Compounds **4** and

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(1) (a) Institut Francais du Pétrole. (b) Nice University. (c) Strasbourg University.

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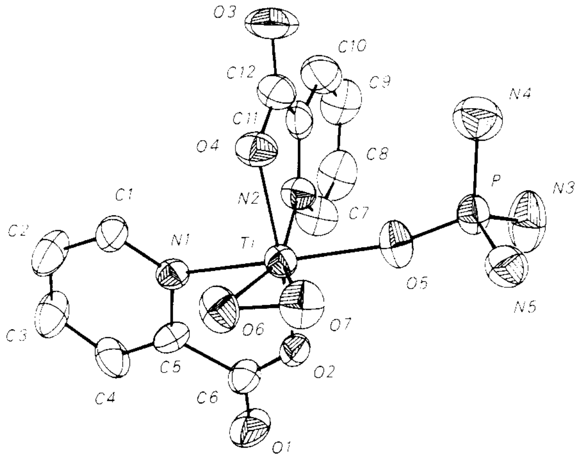

Figure 1. Molecular structure of $Ti(O_2)(C_6H_4NO_2)_2 \cdot OPN_3C_6H_{18}$ (**1**).

Table I. Selected Bond Distances (Å) and Angles (Deg) with Esd's for 1

Ti-O6	1.842 (4)	1.847 (3)	Ti-N1	2.207 (4)
Ti-O7	1.853 (4)		Ti-N2	2.340 (4)
Ti-O5	2.042 (4)		O6-O7	1.419 (6)
Ti-O4	1.968 (3)	1.977 (2)	P-O5	1.479 (4)
Ti-O2	1.986 (3)			
mean P-N	1.608 (3)		mean C-C	1.513 (5)
mean N-C	1.336 (3)		mean C-O	1.286 (4)
mean C-C	1.373 (3)		mean C=O	1.212 (4)

O6-Ti-O7	45.2 (2)	O7-Ti-O4	101.7 (2)
Ti-O6-O7	67.8 (2)	O7-Ti-O2	102.8 (2)
Ti-O7-O6	67.0 (2)	N1-Ti-N2	78.2 (1)
O6-Ti-N1	77.8 (2)	N1-Ti-O5	152.5 (1)
O6-Ti-N2	154.2 (2)	N1-Ti-O4	90.4 (1)
O6-Ti-O5	128.0 (2)	N1-Ti-O2	76.1 (1)
O6-Ti-O4	97.7 (2)	N2-Ti-O5	77.3 (1)
O6-Ti-O2	99.3 (2)	N2-Ti-O4	73.1 (1)
O7-Ti-N1	77.8 (2)	N2-Ti-O2	83.9 (1)
O7-Ti-N2	159.0 (2)	Ti-O5-P	154.5 (2)
O7-Ti-O5	82.9 (2)		

5 were best prepared in a two-step procedure from $TiO(acac)_2$: displacement of acetylacetonate gave the oxo derivatives $OTi(OC_9H_6N)_2$ (**6**) and $OTi[PhCON(Ph)O]_2$ (**7**), which were subsequently treated with an excess of H_2O_2 to afford **4** and **5**. The peroxo nature of adducts **4** and **5** and the bis(bidentate) behavior of the ligands toward titanium are clearly shown by the infrared spectra of the compounds (Table II).[6,8,9]

The peroxide infrared modes in all the five peroxo compounds appear to be essentially unaffected by changes in the donor strength of the ligands, but, as illustrated by Westland et al.[10] for a series of molybdenum peroxo complexes, it is rather difficult to interpret these values.

Crystal Structure of $TiO_2(HMPT)(py\text{-}2\text{-}CO_2^-)_2$ (1). The crystal structure of this complex consists of discrete molecules linked only by van der Waals contacts and hydrogen bonds. Figure 1 shows a molecule with the labeling scheme used; the hydrogen atoms and the carbon atoms of HMPT are omitted for clarity. Table I gives significant bond distances and angles.

The coordination polyhedron of titanium is a deformed pentagonal pyramid; the equatorial positions are occupied by the nitrogen atoms of the pyridine-2-carboxylate groups, the oxygen atom of HMPT, and the oxygen atoms of the peroxo group. The axial positions are occupied by one oxygen atom of each pyridine-2-carboxylate group. This coordination polyhedron is thus similar to those found by Schwarzenbach in two titanium(IV) dipicolinato peroxo complexes.[11] The peroxo group is π bonded to the titanium atom as usual and the two Ti-O6 and Ti-O7 bonds are equivalent, they are in the range found by Schwarzenbach[11] and not significantly different from those found by Guilard et al. in a peroxotitanium(IV) porphyrin adduct.[12] However, the O-O distance in the peroxo group of **1** is significantly shorter; consequently the O-Ti-O bond angle is smaller.

The two pyridine-2-carboxylate groups are not bonded with the same strength to titanium: the nitrogen atom N1 is trans to the HMPT group and nitrogen N2 is trans to the peroxo group, leading to different Ti-N bond lengths (2.207 (4) and 2.340 (4) Å). In contrast, the Ti-O2 and Ti-O4 bonds are in the same range.

The two pyridine-2-carboxylate ligands have a normal geometry: they are nearly planar. The HMPT group is weakly bonded to Ti, with a Ti-O5 bond length of 2.042 (4) Å. The Ti-O5-P bond angle differs from 180° as found in other complexes containing this ligand.[13]

Reactivity. The peroxo titanium derivatives **1**-**5** were found to be unusually stable, extremely "soft" peroxides. They can be kept in light at room temperature in open vessels without any visible change for months, and they do not decompose either under heating at 80 °C. None of them seems to be explosive. Their reduction by iodide is very slow and requires heating at ca. 60 °C to be initiated.

Complexes **1**-**5** are quite reluctant to react with simple olefins, allylic alcohols, and cyclic ketones. For example, no reaction was observed between **1** and a highly nucleophilic olefin such as tetramethylethylene (in a ca. 20/1 olefin/Ti ratio), after 48 h at 50 °C under anaerobic conditions; the unaltered peroxo complex was quantitatively recovered. The same absence of reactivity was observed when compounds **1**-**5** were added to large excesses of allylic alcohol or cyclohexanone under similar conditions, while related molybdenum complexes oxidize these substrates to a α,β epoxyalcohol[14] and to a lactone,[15] respectively.

Sharpless recently reported the titanium tetraisopropoxide-catalyzed asymmetric epoxidation of allylic alcohols by *tert*-butyl hydroperoxide.[5] Such a reaction is likely to involve an alkylperoxotitanium intermediate as the active catalyst.[16] We therefore attempted to generate more reactive hydroperoxo or alkylperoxo species in situ[17] by adding a stoichiometric amount (with respect to titanium) of an acid (HBF_4) or of an alkylating agent ($MeSO_3H$) to the peroxotitanium adducts **1**-**5**. But this resulted only in hydrolysis of the complexes, while no oxygenation of the organic substrates was detected.

Compounds **1**-**5** were found to react very smoothly with substrates which do not need to be coordinated to the metal prior to their insertion into the metal-oxygen bond.[2b,18] Thus, the reaction of **1** with tetracyanoethylene in methylene chloride, followed by addition of diethyl ether, yielded a brown solid which analyzed as $[Ti(O_2)(TCNE)(C_6H_4NO_2)_2 \cdot HMPT] \cdot CH_2Cl_2$ and which exhibited IR absorptions at 2170 and 2205 cm^{-1} ($\nu(C{\equiv}N)$) together with the disappearance of the titanium-dioxygen vibrations. These IR characteristics

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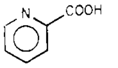
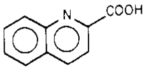
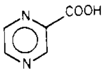
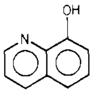
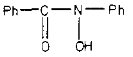
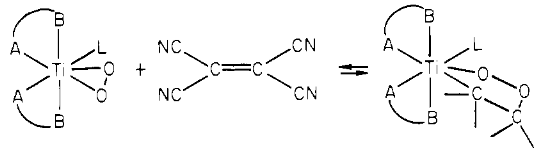
Table II. Elemental Analysis and Spectral Data on Titanium Peroxo Compounds **1-5**

		anal. found (calcd)					IR, cm^{-1} (KBr pellet)					
ligand	complex	% C	% H	% N	% P	% Ti	$\nu_1(OO)$	$\nu_{2_s}(MO)$	$\nu_{3_{as}}(MO)$	$\nu(C{=}O)$	$\nu(C{=}N)$	$\nu(P{=}O)$
	$Ti(\overline{ON})_2HMPT$ (1)	42.91 (42.96)	5.24 (5.20)	13.92 (13.84)	6.19 (6.15)	9.14 (9.52)	895	615	575	1675	1600	1185
	$Ti(\overline{ON})_2HMPT$ (2)	53.55 (52.83)	4.89 (5.02)	11.16 (11.62)	4.62 (5.14)	7.30 (7.95)	890	615	580	1690	1605	1185
	$Ti(\overline{ON})_2HMPT$ (3)	37.71 (38.04)	5.06 (4.78)	19.16 (19.40)	6.08 (6.13)		895	610	590	1680	1590	1185
	$Ti(\overline{ON})_2$ (4)	58.26 (58.72)	3.28 (3.28)	7.57 (7.60)		13.06 (13.01)	900	620	580	1390	1580	
	$Ti(\overline{OO})_2$ (5)	61.24 (61.90)	3.89 (3.99)	5.50 (5.55)			890	610	580	1580		

are similar to those of the known equivalent palladium[18] and rhodium[19] complexes. This therefore suggests the formation of the cyclic peroxo complex **8** according to reaction 1.


(1)

Triphenylphosphine was slowly converted (complete transformation required 12 h at room temperature) to the phosphine oxide by a stoichiometric amount of adducts **1-5** in CH_2Cl_2 under anaerobic conditions. Addition of excess diethyl ether, after completion of the reaction with **1**, yielded a yellow compound which analyzed as $TiO(C_6H_4NO_2)_2 \cdot {}^1/_2H_2O$. Its infrared spectra exhibited absorptions at 1680, 1605, and 800 cm^{-1} (very broad) characteristic of a bidentate coordination of the picolinate ligand and of the Ti-O-Ti pattern.

Surprisingly, adducts **1-5** were not found to react with sulfides: the starting materials (diethyl sulfide or thiophene and the the titanium peroxide adducts) were recovered unaltered after 3 days at 50 °C.

Conclusion. Contrary to what has been observed in the cases of molybdenum and tungsten,[14,15] the use of picolinato, hydroxyquinolino, or hydroximato ligands results in strong stabilization of the peroxotitanium moiety with, as a counterpart, the absence of oxygen transfer from the complexes to olefins, allylic alcohols, cyclic ketones, or sulfides.

HMPT, a very good donor ligand for early transition-metals peroxo derivatives, is only loosely bonded to titanium in **1-3** and does not coordinate to the metal in **4** and **5**. In seems, therefore, likely that coordination to titanium in **1-5** does not take place in the cases of organic substrates that are poorer ligands. This precludes oxygenation by **1-5** of nucleophilic substrates for which coordination to the metal is necessary prior to oxygen transfer.

On the other hand, the adducts **1-5** were found to oxidize triphenylphosphine and tetracyanoethylene, which can directly insert into the metal-peroxide bond.

Experimental Section

All chemicals and reagents were of reagent grade. The analytical and infrared data are gathered in Table II. The infrared spectra were recorded on a Perkin-Elmer 577 spectrometer and the NMR spectra on a Bruker WH 90 spectrometer.

Preparation of Peroxobis(pyridine-2-carboxylic acid)(hexamethylphosphoric triamide)titanium(IV) (1). Picolinic acid (2.7 g, 22 mmol) and HMPT (3.5 g, 20 mmol) were added to a suspension of $TiO(acac)_2$ (2.2 g, 8.4 mmol) in 100 mL of dichloromethane. Dropwise addition of 5 mL of H_2O_2 (20% solution) to this suspension at room temperature resulted in a deep orange solution. The organic phase was then separated, dried over Na_2SO_4, and concentrated to 10% to precipitate complex **1**. Recrystallization from a mixture of dichloromethane and diethyl ether (1:10) yielded 3.6 g of orange crystals of **1** (85%). **1** is soluble in most common solvents.

Table III. X-ray Experimental Data for 1

formula	$TiPO_7N_5C_{18}H_{26}$
mol wt	503
crystal system	orthorhombic
unit cell parameters (Å)	
a	20.834 (8)
b	11.248 (3)
c	10.229 (3)
V, Å^3	2397
space group	$P2_12_12_1$
$d_{obsd}/Z/d_{calcd}$	1.37 ± 0.02/4/1.39
F_{000}	1048
μ, cm^{-1}	41.7
diameter of sphere used, mm	0.320 (5)
diffractometer	Philips PW1100/16
λ	Cu
θ range	$2 < \theta < 57$
type of scan	$\theta/2\theta$ flying step scan
scan rate, deg min^{-1}	1.44
scan angle, θ	0.90 + $CuK\alpha_1\alpha_2$ splitting
step time, s	2.08
set measd	$hkl + \bar{h}kl$
std freq, h	2
stds decay, %	11
tot no. of measmts	3712
data set used ($I > 3\sigma(I)$)	1722
R_1/R_2	0.053/0.078
ignorance factor p	0.08
unit weight obsn	1.827

Preparation of $Ti(O_2)[C_{10}H_6NO_2]_2\{OP[N(CH_3)_2]_3\}$ (2). The same procedure applied to 1.1 g (4.2 mmol) of $TiO(acac)_2$, 2.18 g (12.6 mmol) of quinaldic acid, and 1.75 g (10 mmol) of HMPT gave 1.8 g (74%) of **2**. The solubility of **2** is good in all common solvents.

Preparation of $Ti(O_2)(C_5H_3N_2O_2)_2\{OP[N(CH_3)_2]_3\}$ (3). The analogous complex **3** was prepared similarly from 2.2 g (8.4 mmol) of $TiO(acac)_2$, 2.97 g (20 mmol) of pyrazinecarboxylic acid, and 3.5 g (24 mmol) of HMPA (70%).

Preparation of $TiO(OC_9H_6N)_2$ (6). A mixture of $TiO(acac)_2$ (1.06 g, 4 mmol) and 8-hydroxyquinoline (0.58 g, 4 mmol) in benzene (100 mL) was stirred for 2 h at room temperature. Addition of an excess of Et_2O and subsequent filtration of the precipitated solid gave **6** (1.1 g, 78%) almost insoluble in common solvents. Anal. Calcd: C, 61.38; H, 3.42; N, 7.95. Found: C, 61.25; H, 3.67; N, 7.42.

Preparation of TiO[PhCON(Ph)O]$_2$ (7). The same procedure applied to 0.85 g (4 mmol) of hydroxamic acid and 0.53 g (2 mmol) of $TiO(acac)_2$ afforded 0.93 g (1.8 mmol, 90%) of **7**.

Preparation of $Ti(O_2)(C_{10}H_6NO_2)_2$ (4). A suspension of the oxotitanium **6** (1 g, 2.8 mmol) in dichloromethane (50 mL) was treated

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Table IV. Positional and Thermal Parameters and Their Estimated Standard Deviations[a]

atom	x	y	z	$B(1,1)$	$B(2,2)$	$B(3,3)$	$B(1,2)$	$B(1,3)$	$B(2,3)$
Ti	0.38163 (4)	0.23522 (9)	0.5037 (1)	0.00132 (2)	0.00609 (8)	0.00600 (9)	0.00027 (7)	0.00009 (8)	−0.0004 (2)
P	0.33315 (8)	0.3558 (1)	0.2112 (2)	0.00223 (4)	0.0062 (1)	0.0062 (1)	0.0002 (1)	−0.0001 (1)	0.0007 (3)
O1	0.5744 (2)	0.1968 (5)	0.5384 (5)	0.00134 (9)	0.0125 (5)	0.0149 (6)	−0.0013 (4)	0.0010 (4)	0.0075 (10)
O2	0.4759 (2)	0.2440 (3)	0.4763 (4)	0.00156 (8)	0.0059 (3)	0.0067 (4)	−0.0006 (3)	0.0005 (3)	0.0020 (7)
O3	0.2237 (2)	0.0365 (5)	0.4272 (6)	0.00187 (10)	0.0142 (6)	0.0163 (7)	−0.0042 (4)	−0.0017 (5)	−0.0027 (12)
O4	0.2974 (2)	0.1562 (4)	0.5124 (4)	0.00136 (8)	0.0080 (3)	0.0096 (4)	0.0000 (3)	0.0002 (4)	−0.0024 (8)
O5	0.3689 (2)	0.2961 (4)	0.3174 (4)	0.00280 (12)	0.0072 (4)	0.0069 (4)	0.0026 (4)	−0.0004 (4)	0.0006 (8)
O6	0.3757 (2)	0.3196 (4)	0.6576 (4)	0.00253 (11)	0.0096 (4)	0.0070 (4)	0.0009 (4)	0.0014 (4)	−0.0030 (8)
O7	0.3605 (2)	0.3903 (4)	0.5469 (5)	0.00278 (11)	0.0067 (4)	0.0104 (5)	0.0017 (4)	0.0009 (4)	−0.0021 (8)
N1	0.4208 (2)	0.1082 (5)	0.6474 (5)	0.00107 (9)	0.0075 (4)	0.0068 (4)	−0.0004 (4)	0.0007 (4)	−0.0003 (9)
N2	0.3896 (2)	0.0615 (5)	0.3790 (5)	0.00170 (11)	0.0068 (4)	0.0078 (5)	−0.0005 (4)	−0.0001 (4)	−0.0018 (9)
N3	0.3685 (4)	0.3271 (6)	0.0770 (6)	0.00545 (25)	0.0099 (6)	0.0077 (6)	0.0030 (7)	0.0024 (7)	0.0008 (12)
N4	0.2593 (3)	0.3127 (6)	0.1912 (7)	0.00303 (16)	0.0093 (5)	0.0138 (8)	−0.0012 (6)	−0.0023 (6)	−0.0016 (13)
N5	0.3296 (2)	0.4961 (5)	0.2400 (6)	0.00207 (13)	0.0080 (5)	0.0112 (6)	0.0002 (5)	−0.0015 (5)	0.0017 (11)
C1	0.3912 (3)	0.0402 (7)	0.7317 (6)	0.0016 (1)	0.0105 (6)	0.0081 (6)	−0.0011 (6)	0.0002 (6)	0.005 (1)
C2	0.4224 (3)	−0.0268 (7)	0.8258 (8)	0.0027 (2)	0.0095 (6)	0.0132 (9)	−0.0001 (6)	0.0023 (7)	0.010 (1)
C3	0.4861 (3)	−0.0214 (7)	0.8331 (7)	0.0023 (2)	0.0101 (6)	0.0116 (8)	0.0023 (6)	0.0012 (6)	0.010 (1)
C4	0.5204 (3)	0.0491 (7)	0.7460 (7)	0.0020 (1)	0.0107 (7)	0.0087 (6)	0.0018 (6)	−0.0024 (6)	0.002 (1)
C5	0.4867 (3)	0.1125 (5)	0.6544 (7)	0.0014 (1)	0.0060 (5)	0.0098 (6)	−0.0010 (5)	0.0012 (6)	0.001 (1)
C6	0.5157 (3)	0.1910 (6)	0.5477 (6)	0.0018 (1)	0.0071 (5)	0.0074 (6)	−0.0008 (5)	0.0014 (5)	0.001 (1)
C7	0.4382 (3)	0.0145 (7)	0.3132 (8)	0.0026 (2)	0.0083 (6)	0.0126 (9)	0.0010 (6)	−0.0001 (7)	−0.003 (1)
C8	0.4343 (4)	−0.0730 (6)	0.2232 (8)	0.0047 (3)	0.0067 (6)	0.0107 (8)	0.0019 (7)	0.0043 (8)	−0.005 (1)
C9	0.3714 (4)	−0.1176 (6)	0.1964 (8)	0.0043 (3)	0.0048 (5)	0.0126 (8)	0.0001 (6)	0.0013 (9)	−0.004 (1)
C10	0.3220 (4)	−0.0744 (6)	0.2660 (8)	0.0034 (2)	0.0066 (6)	0.0134 (9)	−0.0017 (6)	−0.0039 (8)	−0.001 (1)
C11	0.3313 (3)	0.0153 (6)	0.3568 (6)	0.0030 (2)	0.0056 (5)	0.0063 (5)	−0.0012 (5)	−0.0019 (6)	0.004 (1)
C12	0.2779 (3)	0.0713 (6)	0.4330 (7)	0.0016 (1)	0.0085 (6)	0.0102 (7)	−0.0001 (5)	−0.0014 (6)	0.002 (1)
C13	0.3650 (10)	0.3852 (13)	−0.0375 (11)	0.0231 (11)	0.0219 (15)	0.0159 (10)	0.0189 (22)	0.0285 (15)	0.020 (2)
C14	0.4175 (11)	0.2702 (24)	0.0509 (15)	0.0162 (8)	0.0709 (43)	0.0147 (13)	0.0392 (27)	0.0143 (19)	0.007 (5)
C15	0.2135 (4)	0.3363 (10)	0.2991 (13)	0.0022 (2)	0.0185 (12)	0.0309 (19)	0.0018 (9)	0.0031 (11)	0.009 (3)
C16	0.2429 (7)	0.2239 (14)	0.1055 (12)	0.0083 (5)	0.0259 (19)	0.0191 (14)	−0.0075 (17)	−0.0124 (12)	−0.003 (3)
C17	0.3824 (4)	0.5601 (7)	0.3031 (9)	0.0032 (2)	0.0096 (7)	0.0162 (10)	−0.0022 (7)	−0.0017 (9)	0.004 (2)
C18	0.2867 (5)	0.5783 (8)	0.1694 (11)	0.0041 (3)	0.0091 (7)	0.0216 (15)	0.0023 (8)	−0.0022 (11)	0.005 (2)

[a] The form of the anisotropic thermal parameter is $\exp[-(B(1,1)h^2 + B(2,2)k^2 + B(3,3)l^2 + B(1,2)hk + B(1,3)hl + B(2,3)kl)]$.

with an excess of H_2O_2 (1 mL of 20% solution). After separation, the organic phase was concentrated (50%); **4** was precipitated by addition of diethyl ether, filtered, and recrystallized in CH_2Cl_2–Et_2O (1.10) mixtures (770 mg, 76%). **4** is poorly soluble in common solvents.

Preparation of $Ti(O_2)[PhCON(Ph)O]_2$ (5). By the same procedure, 520 mg (80%) of **5** were obtained from 650 mg (1.3 mmol) of **7**. **5** is very soluble in all common solvents.

Reaction of 1 with Tetracyanoethylene. A 350-mg (0.70-mmol) sample of **1** was reacted under argon with 95 mg (0.74 mmol) of tetracyanoethylene in dichloromethane at 0 °C. The orange solution immediately turned to purple. After 1 h of stirring, a brown powder was precipitated by addition of diethyl ether; filtration of the solution yielded 270 mg (0.38 mmol; 54%) of $[TiO_2(C_6N_4)(C_6H_4NO_2)_2\cdot HMPA]\cdot CH_2Cl_2$. Anal. Calcd: C, 42.00; H, 3.92; N, 17.60; P, 4.33. Found: C, 42.42; H, 3.90; N, 17.56; P, 3.64.

Reaction of 1 with Triphenylphosphine. A 530-mg (1.05-mmol) sample of **1** was reacted under argon with 276 mg (1.05 mmol) of triphenylphosphine in dichloromethane at room temperature. The deep orange solution slowly became clearer and a yellow precipitate appeared after 1 h. ^1H NMR showed that the reaction was completed within 12 h. The phosphine was converted entirely into triphenylphosphine oxide. Filtration of the solution yielded 280 mg (0.9 mmol) of $TiO(C_6H_4NO_2)_2\cdot{}^1/_2H_2O$. Anal. Calcd: C, 45.45; H, 2.85; N, 8.83. Found: C, 45.61; H, 2.85; N, 8.84.

X-ray Measurements. Suitable single crystals of **1** were obtained by slow evaporation of a dichloromethane–diethyl ether solution at room temperature. The crystals systems were determined with an automatic Philips PW1100/16 diffractometer with standard software. The unit cell parameters were refined with 25 carefully selected reflections. The results are summarized in Table III.

A single crystal was ground to a spherical shape, sealed in a Lindemann glass capillary, and mounted on an arc-free goniometer head. Intensities were recorded with the parameters listed in Table III.

The row step-scan data were converted to intensities with their standard deviation with the Lehman–Larsen algorithm.[20] These intensities were then corrected for Lorentz and polarization factors; spherical absorption corrections were applied.[21] A linear decay correction was applied. All computations were done with the Enraf-Nonius structure determination package;[22] the structure was solved with the MULTAN program.[23]

The structure was refined with full-matrix least squares and anisotropic temperature factors for all nonhydrogen atoms. The function minimized was $\sum w\|F_o| - |F_c\|^2$ with $w = 1/\sigma^2$ and $\sigma(F^2) = \sigma_{count}{}^2 + (pF^2)^2$. The coordinates of hydrogen atoms were computed with a C–H distance of 0.95 Å; their contributions were introduced in all final calculations, but they were not refined. Table III gives the final results. Final atomic coordinates with their estimated standard deviations are listed in Table IV.

Registry No. **1**, 80327-70-4; **2**, 80339-95-3; **3**, 80327-71-5; **4**, 80327-12-4; **5**, 80327-11-3; **6**, 24155-11-1; **7**, 47737-45-1; **8**, 80327-10-2; $TiO(C_6H_4NO_2)_2$, 80327-22-6; $TiO(acac)_2$, 14024-64-7; triphenylphosphine, 603-35-0; tetracyanoethylene, 670-54-2.

Supplementary Material Available: Table of the least-squares planes and listings of structure factor amplitudes and hydrogen atom parameters (10 pages). Ordering information is given on any current masthead page.

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