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COMMUNICATION

EFFECTS OF AXIAL LIGAND ON THE OXIDATION OF TRIPHENYLPHOSPHINE CATALYZED BY NITRO(TETRAPHENYLPORPHYRINATO)COBALT COMPLEXES

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Abstract—Nitro(tetraphenylporphyrinato)cobalt complexes catalyze the oxidation of triphenylphosphine to triphenylphosphine oxide by molecular oxygen. The effects of axial ligands in the nitro cobalt complexes on this oxidation reaction were studied. 4-Cyanopyridine gave the best yield. This result suggests that the more unstable is nitro(tetraphenylporphyrinato)cobalt complex the better the yield obtained.

5,10,15,20 - Tetraphenylporphyrinatocobalt(II) ([Co(tpp)]) reacts with nitrogen monoxide and produces five-coordinate nitrosyl(tetraphenylporphyrinato)cobalt(II) ([Co(tpp)(NO)]).[1] In the presence of an axial ligand (L), this nitrosyl cobalt complex reacts with molecular oxygen to give a nitro(tetraphenylporphyrinato)cobalt complex ([Co(tpp)(NO_2)(L)]).[2] This [Co(tpp)(NO_2)(L)] reacts with triphenylphosphine, resulting in triphenylphosphine oxide. So, under an atmosphere of oxygen, [Co(tpp)(NO_2)(L)] catalyzes the oxidation of triphenylphosphine by molecular oxygen [eqns (1) and (2)]:[3]

$$[\mathrm{Co(tpp)(NO)}] + \mathrm{L} + \tfrac{1}{2}\mathrm{O_2} \rightarrow [\mathrm{Co(tpp)(NO_2)(L)}], \quad (1)$$

$$[\mathrm{Co(tpp)(NO_2)(L)}] + \mathrm{PPh_3} \rightarrow [\mathrm{Co(tpp)(NO)}] + \mathrm{Ph_3PO} + \mathrm{L}. \quad (2)$$

In this communication we present the effects of axial ligands such as 1-Meim,* 4-Mepy, py and 4-CNpy, which were used in the previous work,[4] on the yield in this oxidation reaction.

5,10,15,20-Tetraphenylporphyrin (H_2tpp) and [Co(tpp)] were synthesized by the literature methods, respectively.[5,6] Nitrosyl(tetraphenylporphyrinato)cobalt(II) was prepared from NO gas and [Co(tpp)] according to the literature method.[1] Nitro cobalt complexes were prepared from [Co(tpp)(NO)] and O_2 gas at a pressure of 1 atm in 1,2-dichloroethane (DCE) solution containing 5% (v/v) axial ligand in a reactor before the oxidation was started. A 5-cm³ three-necked round bottom flask equipped with a thermometer, a condenser, and a long syringe needle, by which O_2 was passed through the solution during the oxidation reaction, was used as a reactor. After the formation of the nitro cobalt complex, confirmed by monitoring the visible spectrum in the 350–700-nm range—([Co(tpp)(NO)]: λ_{max} (DCE) 413 nm ($\varepsilon = 1.40 \times 10^5$ mol^{-1} dm^3 cm^{-1}), 538 nm (1.68×10^4), 584 nm (sh, 2.81×10^3); [Co(tpp)(NO_2)(py)]: λ_{max} (DCE) 433 nm ($\varepsilon = 3.35 \times 10^5$ mol^{-1} dm^3 cm^{-1}), 512 nm (sh, 5.58×10^3), 549 nm (1.51×10^4), 588 nm (sh, 5.98×10^3)—triphenylphosphine was added to the solution. The oxidation was carried out at 60°C for 16 h with the solution being stirred magnetically on an oil bath. After 16 h, aliquots of the solution were taken by a micro syringe and analyzed by a liquid chromatography {column, 4.3 mm × 15 cm, packed with Partisil-5, ODS-3, Whatman Inc., U.S.A.; eluant CH_3OH and H_2O mixture [75:25 (v/v)]}. As the internal standard, the base involved in the reacted solution was used.

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*Abbreviations: py, pyridine; 4-Mepy, 4-methylpyridine; 1-Meim, 1-methylimidazole; pip, piperidine; 4-CNpy, 4-cyanopyridine.

Table 1. Oxidation of triphenylphosphine to triphenylphosphine oxide catalyzed by $[\mathrm{Co(tpp)(NO_2)(L)}]$

Experiment	Complex	$[\mathrm{Co}]^a$ (mol dm^{-3})	$[\mathrm{PPh_3}]/[\mathrm{Co}]^a$	Solvent	$\mathrm{Ph_3PO}$ yield^b (%)
1	$[\mathrm{Co(tpp)(NO_2)(4\text{-}CNpy)}]$	6.74×10^{-3}	10	DCE + 5% 4-CNpy	537
2	$[\mathrm{Co(tpp)(NO_2)(py)}]$	6.74×10^{-3}	10	DCE + 5% py	500
3	$[\mathrm{Co(tpp)(NO_2)(4\text{-}Mepy)}]$	6.74×10^{-3}	10	DCE + 5% 4-Mepy	404
4	$[\mathrm{Co(tpp)(NO_2)(1\text{-}Meim)}]$	6.74×10^{-3}	10	DCE + 5% 1-Meim	300
5	$[\mathrm{Co(tpp)(NO_2)(PPh_3)}]$	6.74×10^{-3}	10	DCE + 5% $\mathrm{PPh_3}$	157
6	$\mathrm{CoCl_2}$	6.74×10^{-3}	10	DCE	40

[a] [Co] and $[\mathrm{PPh_3}]$ represent the initial concentrations of $[\mathrm{Co(tpp)(NO_2)(L)}]$ and $\mathrm{PPh_3}$, respectively: temperature (60°C), reaction time (16 h), and dioxygen pressure (1 atm) were the same as in Ref. 3.

[b] Based on catalyst.

Table 2. IR data of $\mathrm{NO_2}$ group in $[\mathrm{Co(tpp)(NO_2)(L)}]$ complexes

Complex	ν_{as} (cm^{-1})	ν_{s} (cm^{-1})	δ (cm^{-1})	Reference
$\mathrm{NO_2}$ gas	1618	1320	750	8
$[\mathrm{Co(tpp)(NO_2)(py)}]^a$	1306	1210(m)^b	812	Present work
$[\mathrm{Co(tpp)(NO_2)(4\text{-}Mepy)}]^a$	1307	1205 (m)	810	Present work
$[\mathrm{Co(tpp)(NO_2)(1\text{-}Meim)}]^a$	1310	1200 (m)	810	Present work
$[\mathrm{Co(tpp)(NO_2)(pip)}]^a$	1304	1200 (m)	807	Present work
$[\mathrm{Co(tpp)(NO_2)(im)}]^c$	1310	1260	820	9
$\mathrm{CH_3NO_2}$	1582	1384	647	10
$\mathrm{NO_2^-}$ ion	1335	1250	830	11

[a] KBr disk.

[b] m stands for "masked" by the ligand absorptions, and the precise absorption frequencies were not clear.

[c] Solvent is benzene.

Table 1 shows the yields of triphenylphosphine oxide based on the catalyst. The yield depended apparently on the axial ligand (L) and decreased in order as follows:

4-CNpy > py > 4-Mepy > 1-Meim.

In this oxidation reaction, the following factors seem to be responsible for the yield: (a) the ease of formation of the nitro cobalt complex, (b) the ease of reproduction of the nitrosyl cobalt complex, and (c) the coordination geometry or the charge distribution of the nitro group in $[\mathrm{Co(tpp)(NO_2)(L)}]$. As is shown by eqns (1) and (2), the stronger the coordination of the axial ligand to the cobalt ion the more stable the nitro cobalt complex formed and reproduction of the nitrosyl cobalt complex becomes more difficult. As the measure of the coordinating ability of the ligand, the values of the equilibrium constants (K^{L}) (mol^{-1} dm^3) for the reaction shown in eqn (3):[4(c)]

$$[\mathrm{Co(tpp)}] + \mathrm{L} \overset{K^{\mathrm{L}}}{\rightleftharpoons} [\mathrm{Co(tpp)(L)}] \qquad (3)$$

were used. Though the log K^{L} values were obtained in DCE at room temperature (23°C), the sequence of the values may not be different at 60°C. The coordinating abilities of axial ligand decreased in the following order, 1-Meim (log $K^{\mathrm{L}} = 3.22$) > 4-Mepy (2.99) > py (2.92) > 4-Cpy (2.57). This sequence is in the reverse order to the yields of triphenylphosphine oxide shown above.

The IR spectra of the isolated nitro cobalt complexes were measured to study the IR spectra of the nitro groups in $[\mathrm{Co(tpp)(NO_2)(L)}]$.* The frequencies of the asymmetric [ν_{as} (cm^{-1})], symmetric [ν_{s} (cm^{-1})] and deformation vibrations [δ (cm^{-1})][2,7] are shown in Table 2. It indicates that

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* Solid $[\mathrm{Co(tpp)(NO_2)(L)}]$ complexes were isolated by a modification of the literature method[2] for the IR spectra sample (KBr tablets): L = 1-Meim, 4-Mepy, py and pip. The 4-CNpy complex could not be isolated, though it was formed in the solution.

the nitro groups seem to be nearly nitro anion forms in all the nitro cobalt complexes. The NO_2 group of the analogous

$$[Co(tpp)(NO_2)(3{,}5\text{-dimethylpyridine})]$$

was already shown as the NO_2^- form in the X-ray analysis data.[12] The differences in absorption frequencies among the different axial base complexes are small probably because all the $Co–NO_2$ bonds are nearly ionic. From the fact that the sequence of the yield is opposite to that of the coordinating ability of axial ligand, factor (b) seems to be the most effective on the yield of this oxidation reaction.

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