N_2O Oxidation of Phosphines Catalyzed by Low-Valent Nickel Complexes

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In the presence of a catalytic amount of the nickel(0) complex derived from $Ni(acac)_2$ or $NiCl_2$ with DIBAL or BuLi, nitrous oxide (N_2O) was captured and activated to oxidize phosphine(III) into the corresponding phosphine oxide. Bidentate phosphines, for example, 1,3-bis(diphenylphosphino)propane (dppp), were employed as effective ligands for N_2O oxidation and were recovered after the reaction.

Various oxides of nitrogen, *e.g.*, NO,[1] NO_2 and N_2O, have received considerable attention in the field of biochemistry, medical science and environment science. Nitrogen monoxide (NO) is enzymatically produced *in vivo* and their important role was revealed as a mediator in the circulatory, immune, and nervous systems of the human body, whereas it is emitted in the exhaust gas of internal-combustion engines and closely related to air pollution. Therefore, many studies have been conducted to develop efficient removal systems[2] for the reductive transformation of nitrogen monoxide into harmless reduced species. Nitrous oxide (N_2O) has been medically employed as an anesthetic gas, while a vast amount of N_2O is emitted as a byproduct of the industrial manufacture of nylon[3] and it have been recently implicated with the global warming as a greenhouse gas. In the field of synthetic organic chemistry, nitrogen dioxide (NO_2) has been industrially produced for the production of nitric acid, and a nitration reaction with NO_2[4] has recently proposed, while only several trials involving nitrogen monoxide (NO)[5] or nitrous oxide (N_2O)[6] were given as practical reactions. Because nitrous oxide is an extremely inert gaseous molecule, the few known reactions of this gaseous molecule include the stoichiometric oxidation of a metal-carbon bond,[7] the direct oxygen atom transfer reaction catalyzed by a ruthenium-porphyrin complex,[8] and the catalytic oxidation of phosphine using cobalt(I) complexes.[9] In this communication, we would like to report that in the presence of a catalytic amount of low-valent nickel complexes with bidentate ligands, dinitrogen monoxide (N_2O) was effectively captured and activated in order to oxidize phosphine(III) to phosphine(V) oxide in high yields.

The low-valent metal complexes were expected to capture and activate nitrous oxide and then the valence of the metals increased to form tentative oxo-metal intermediates, which were reported to oxidize the substrates. It was reported that the combined use of a cobalt complex with a hydride reductant was an effective system for the asymmetric reductions of ketones,[10] immines,[11] and α,β-unsaturated carboxamides,[12] and the selective 1,4-reduction of α,β-unsaturated carbonyl compounds.[13] In the latter reaction,[13] a cobalt hydride intermediate was generated from the bis(1,3-diketonato)cobalt complex and diisobutylaluminum hydride (DIBAL), therefore, these low-valent cobalt complexes were first examined as a catalyst for the capture and activation of N_2O. It was found that in the presence of a catalytic amount of the cobalt hydride intermediate prepared from cobalt(II) acetylacetonate and 2 equivalents of DIBAL, triphenylphosphine(III) were readily oxidized to triphenylphosphine(V) oxide in high yield (Entry 1 in Table 1). Various transition-metal acetylacetonates other than cobalt were screened under the same reaction conditions. Ruthenium and iron complexes were less effective catalysts (Entries 3 and 4), and palladium could not be employed at all as a catalyst (Entry 5). In the presence of 20 mol% of the nickel catalyst, the oxidation of triphenylphosphine was completed in 0.5 h to obtain triphenylphosphine oxide in 89% yield (Entry 6). The nickel complex gave higher yields than the cobalt complex during the N_2O oxidation reactions at 0 °C (Entries 2 and 7), although the cobalt complex and nickel complex showed a similar catalytic activity at room temperature. It should be noted that the low-valent nickel complex derived from $Ni(acac)_2$ with DIBAL could be employed as a highly active catalyst for the capture and activation of N_2O.

Table 1. Various low-valent metal catalysts for N_2O oxidation

$$PPh_3 \xrightarrow[N_2O\ (1\ atm)]{cat.\ M(acac)_n,\ cat.\ DIBAL} O{=}PPh_3$$

Entry[a]	$M(acac)_n$	Temp	Time/h	Yield/%[c]
1	Co $(acac)_2$	rt	0.25	98
2[b]		0 °C	4	30[d]
3	Ru $(acac)_3$	rt	28	43
4	Fe $(acac)_3$	rt	24	18
5	Pd $(acac)_2$	rt	24	No reaction
6	Ni $(acac)_2$	rt	0.5	89
7[b]		0 °C	4	85[d]

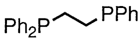
[a]Reaction conditions; 20 mol% of $M(acac)_2$ and 40 mol% of DIBAL, 0.4 mmol of PPh_3, solvent(toluene) 1.5 ml. $M(acac)_2$ was treated with DIBAL at 0 °C and then N_2O oxidation was carried out at rt. [b]10 mol% of $M(acac)_2$ and 20 mol% of DIBAL was used. [c]Isolated yield. [d]Starting material was recovered in 70%(Entry 2) and 12%(Entry 7).

In the present N_2O oxidation reaction, the catalysts prepared from $NiCl_2$·(dppe) and DIBAL or *n*-BuLi were employed as an efficient catalyst while no reaction occurred using the nickel(II) dichloride alone (Entry 1 in Table 2). As shown in Entry 6, the nickel(0) species prepared from 10 mol% $NiCl_2$·(dppp) and 30 mol% *n*-BuLi effectively catalyzed the N_2O oxidation and triphenylphosphine was completely consumed in 1 h to afford the corresponding phosphine oxide in 99% yield. The catalyst prepared from $NiCl_2$·(dppp) and *n*-BuLi showed high activity for capturing N_2O and oxidizing phosphine.[14] Even under the low partial pressure, N_2O (0.5 atm and 0.1 atm of N_2O in N_2) was effectively captured and activated to oxidize phosphine to phosphine oxide in high yield (Entries 7 and 8). Also, at low temperature (-40 °C), the low-valent nickel complex[15] retained its activity to produce phosphine oxide in 94% yield (Entry 9).

The present N_2O oxidation reaction catalyzed by the low-valent nickel complex was successfully applied to the oxidation

Table 2. Combination of bidentate ligands and reductants for Ni-catalyzed N_2O oxidation

$$PPh_3 \xrightarrow[N_2O\ (1\ atm)]{10\ mol\%\ NiCl_2\bullet L,\ cat.\ Reductant} O{=}PPh_3$$

Entry[a]	Ligand	Reductant (eq. vs PPh_3)	Pres./atm	Yield/%[c]
1[b]	None (Ph_3P)	*n*-BuLi (30 mol%)	1	No reaction
2	 (dppe)	DIBAL (20 mol%)	1	44
3		(80 mol%)	1	51
4	 (dppp)	*n*-BuLi (23 mol%)	1	33
5		DIBAL (20 mol%)	1	32
6		*n*-BuLi (30 mol%)[d]	1	99
7			0.5	95
8			0.1	98
9[e]			1	94

[a]Reaction conditions; 0.4 mmol of PPh_3 and 10 mol% of $NiCl_2\bullet L$ in toluene(1.5 ml) was treated with DIBAL or *n*-BuLi at rt under N_2 and then N_2O gas was introduced. [b]Reaction conditions; 10 mol%(0.04 mmol) of $NiCl_2$ and 0.4 mmol of PPh_3 in toluene(1.5 ml) was treated with *n*-BuLi at rt and then N_2O gas was introduced. [c]Isolated yield. [d]Reaction time 1 h(Entry 6), 2 h(Entry 7), 3 h(Entry 8), 4.5 h(Entry 9). [e]Reaction temperature -40 °C.

of various phosphines[16] (Figure 1). A toluene solution of the low-valent Ni(dppp) complex and phosphines was exposed to nitrous oxide, the gas, which was expected to be N_2 gas, was vigorously evolved for 15-60 min and phosphines were almost completely oxidized to their oxides. Various triarylphosphines were smoothly oxidized to their phosphine oxides in quantitative yields. Trialkylphosphines, such as tributylphosphine and tricyclohexylphosphine, were also converted to their oxides in good to quantitative yields. It should be pointed out here that about half of the dppp ligand was recovered when the reaction was quenched by treatment with excess 2,2'-dipyridyl immediately after the complete consumption of the triphenylphosphine.[17] These observations suggested that triphenylphosphine in the low-valent Ni(dppp)·Ph_3P complex should be preferentially oxidized by nitrous oxide and could be utilized for designing the efficient ligands of complex catalysts for N_2O oxidation.

It is noted that low-valent nickel complexes coordinated by the bidentate ligands can be employed as highly active catalysts for the capture and activation of N_2O to oxidize phosphine(III) to phospine(V) oxide. Investigations to expand the present clean and catalytic oxidation system to various substrates other than phosphines are currently ongoing.

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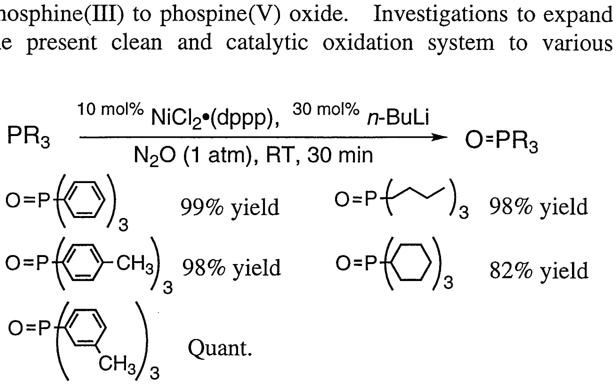

Figure 1. N_2O oxidation of various phosphines.

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14 The catalyst prepared from $CoCl_2$·(dppp) and *n*-BuLi was not efficiently employed to capture and to activate nitrous oxide. Triphenyl-phosphine oxide was obtained only in 16% yield at room temperature.

15 It was considered that the active intermediate could be 16-electron Ni(dppp)·PPh_3 and was coordinated by nitrous oxide to generate Ni(dppp)·PPh_3·N_2O. Then, triphenylphosphine was preferentially oxidized by nitrous oxide with evolution of nitrogen, and triphenylphosphine oxide was released from the complex catalyst to regenerate Ni(dppp)·PPh_3 by coordination of another triphenylphosphine.

16 Typical procedure is as follows: To a solution of $NiCl_2$·(dppp) (21.7 mg, 0.040 mmol) and triphenylphosphine (10.5 mg, 0.40 mmol) in toluene (1.5 ml) was added 1.57 M *n*-BuLi hexane solution (0.059 ml, 0.92 mmol) at room temperature under a N_2 atmosphere. After 30 min, gas phase was replaced with an atmosphere of N_2O. The red-colored suspension gradually turned to a brown solution with gas evolution. After stirring for 1 h at room temperature, the reaction was quenched by 1 M HCl (8 ml) and the products were extracted three times with ether (10 ml). The combined extracts were washed with brine and dried over anhydrous sodium sulfate. The solvents were removed under reduced pressure and the crude product was purified by silica-gel column chromatography to afford triphenylphosphine oxide in 99% yield.

17 Partial oxidation of the bidentate phosphine ligand to 1,3-bis(diphenyl-phosphino)propane monoxide and dioxides were observed.