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## The Addition of Nitrosyl Chloride to Nickel(0) Complexes. The Preparation of Nitrosyl Nickel Complexes

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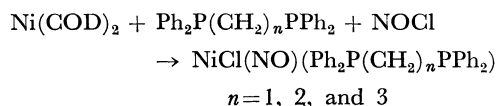
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Several methods for preparing nitrosyl nickel complexes have been established.<sup>1-5)</sup> During the course of a study of oxidative-addition reactions of covalent molecules to nickel(0) complexes,<sup>6)</sup> we have found that nitrosyl chloride adds to nickel(0) complexes to yield a series of nitrosyl nickel complexes.

The nitrosyl complex,  $\text{NiCl}(\text{NO})(\text{PPh}_3)_2$ , prepared by the reaction of  $\text{NiCl}_2(\text{PPh}_3)_2$  with  $\text{NaNO}_2$ ,<sup>4)</sup> was obtained by the addition reaction of nitrosyl chloride to nickel(0) complexes such as  $\text{Ni}(\text{PPh}_3)_4$  and  $\text{Ni}(\text{PPh}_3)_2(\text{COD})$  ( $\text{COD}=1,5\text{-cyclooctadiene}$ ). The use of excess nitrosyl chloride afforded only  $\text{NiCl}_2(\text{PPh}_3)_2$ . The  $\text{NiCl}(\text{NO})(\text{P}(\text{OPh})_3)_2$  complex was also prepared from  $\text{Ni}(\text{COD})_2$ , triphenyl phosphite, and nitrosyl chloride. Hieber *et al.*<sup>3)</sup> prepared similar nitrosyl complexes,  $\text{NiX}(\text{NO})(\text{P}(\text{OPh})_3)_2$  ( $\text{X}=\text{Br}, \text{I}$ ), by the reaction of triphenyl phosphite with  $[\text{NiX}(\text{NO})\text{P}(\text{OPh})_3]_2$ .

Nitrosyl chloride also added to  $\text{Ni}(\text{COD})_2$  in the presence of equimolar ditertiary phosphines in ether to afford new nitrosyl complexes,  $\text{NiCl}(\text{NO})(\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2)$  ( $n=1, 2$ , and  $3$ ). These nitrosyl complexes are fairly



air-stable, but easily decompose in toluene or benzene at an ambient temperature. The nitrosyl complexes were, therefore, not obtained when the above reactions were carried out in benzene or toluene. Table 1 shows that  $\nu_{\text{N-O}}$  shifts to a lower frequency with an increase in the length of the methylene chain of the ditertiary phosphines, as in the case of  $\nu_{\text{N-N}}$  of  $\text{Mo}(\text{N}_2)_2(\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2)_2$ .<sup>7)</sup> The reaction of nitrosyl chloride with  $\text{Ni}(\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2)_2$  ( $n=1$  and  $2$ ) at  $90^\circ\text{C}$  did

TABLE 1. ANALYTICAL AND PHYSICAL DATA FOR  $\text{NiCl}(\text{NO})(\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2)$ 

<i>n</i>	Mp (decomp.) °C	$\nu_{\text{N-O}}$ $\text{cm}^{-1}$	Analysis found (Calcd) (%)			
			C	H	N	Cl
1	180	1750	60.45 (59.05)	4.48 (4.36)	2.62 (2.75)	7.01 (6.97)
2	198—199	1735	60.04 (59.76)	4.55 (4.63)	2.43 (2.68)	6.70 (6.78)
3 <sup>a)</sup>		1725				

a) The complex was not obtained in a pure state.

not yield the nitrosyl complexes.

### Experimental

All the reactions were carried out under a nitrogen atmosphere in a small Schlenk-type flask containing a magnetic stirring bar. Tetrakis(triphenylphosphine)nickel(0)  $\text{Ni}(\text{PPh}_3)_4$ <sup>8)</sup> and bis(1,5-cyclooctadiene)nickel(0)  $\text{Ni}(\text{COD})_2$ <sup>9)</sup> were prepared by the published methods. All the operations for preparing nitrosyl nickel complexes are very similar, so only a few typical examples will be described below.

**Preparation of  $\text{NiCl}(\text{NO})(\text{PPh}_3)_2$ .** To a solution of  $\text{Ni}(\text{PPh}_3)_4$  (0.374 g, 0.337 mmol) in benzene (10 ml) was added a solution of nitrosyl chloride (0.337 mmol) in toluene (0.1 ml) at an ambient temperature. The colour of the solution turned dark blue. After stirring the solution for 2 hr at that temperature, hexane (20 ml) was added to the solution and  $\text{NiCl}(\text{NO})(\text{PPh}_3)_2$  was precipitated as blue crystals (0.139 g, 65%).

Found: C, 66.85; H, 4.84; N, 2.02; Cl, 5.84%. Calcd for  $\text{C}_{36}\text{H}_{30}\text{NOClNi}$ : C, 66.67; H, 4.63; N, 2.16; Cl, 5.47%.

**Preparation of  $\text{NiCl}(\text{NO})(\text{Ph}_2\text{PCH}_2\text{PPh}_2)$ .** A suspension of  $\text{Ni}(\text{COD})_2$  (0.155 g, 0.56 mmol) and bis(diphenylphosphino)methane (0.215 g, 0.56 mmol) in ether (20 ml) was stirred at  $-15$ — $-20^\circ\text{C}$  for 2 hr. To this yellow suspension was then added a solution of nitrosyl chloride (0.56 mmol) in toluene (0.17 ml) at that temperature, after which the reaction mixture was stirred for 2 hr. The colour of the mixture thus changed into purple. The purple precipitate was separated by filtration and recrystallized from tetrahydrofuran-hexane, thus affording  $\text{NiCl}(\text{NO})(\text{Ph}_2\text{PCH}_2\text{PPh}_2)$  as reddish-purple crystals (0.156 g, 53.5%).

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