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

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

The nitrosyl complex, $NiCl(NO)(PPh_3)_2$, prepared by the reaction of $NiCl_2(PPh_3)_2$ with $NaNO_2$,[4] was obtained by the addition reaction of nitrosyl chloride to nickel(0) complexes such as $Ni(PPh_3)_4$ and $Ni(PPh_3)_2(COD)$ (COD=1,5-cyclooctadiene). The use of excess nitrosyl chloride afforded only $NiCl_2(PPh_3)_2$. The $NiCl(NO)(P(OPh)_3)_2$ complex was also prepared from $Ni(COD)_2$, triphenyl phosphite, and nitrosyl chloride. Hieber *et al.*[3] prepared similar nitrosyl complexes, $NiX(NO)(P(OPh)_3)_2$ (X=Br, I), by the reaction of triphenyl phosphite with $[NiX(NO)P(OPh)_3]_2$.

Nitrosyl chloride also added to $Ni(COD)_2$ in the presence of equimolar ditertiary phosphines *in ether* to afford new nitrosyl complexes, $NiCl(NO)(Ph_2P(CH_2)_nPPh_2)$ (n=1, 2, and 3). These nitrosyl complexes are fairly

$$Ni(COD)_2 + Ph_2P(CH_2)_nPPh_2 + NOCl \rightarrow NiCl(NO)(Ph_2P(CH_2)_nPPh_2)$$
$$n = 1,\ 2,\ \text{and}\ 3$$

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 ν_{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 ν_{N-N} of $Mo(N_2)_2(Ph_2P(CH_2)_nPPh_2)_2$.[7] The reaction of nitrosyl chloride with $Ni(Ph_2P(CH_2)_nPPh_2)_2$ (n=1 and 2) at 90°C did not yield the nitrosyl complexes.

Table 1. Analytical and physical data for $NiCl(NO)(Ph_2P(CH_2)_nPPh_2)$

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

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

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) $Ni(PPh_3)_4$[8] and bis(1,5-cyclooctadiene)nickel(0) $Ni(COD)_2$[9] 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 $NiCl(NO)(PPh_3)_2$. To a solution of $Ni(PPh_3)_4$ (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 $NiCl(NO)(PPh_3)_2$ was precipitated as blue crystals (0.139 g, 65%).

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

Preparation of $NiCl(NO)(Ph_2PCH_2PPh_2)$. A suspension of $Ni(COD)_2$ (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°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 $NiCl(NO)(Ph_2PCH_2PPh_2)$ as reddish-purple crystals (0.156 g, 53.5%).

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