Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

PRELIMINARY COMMUNICATION

NITROGENBIS(TRIETHYLPHOSPHINE) NICKEL HYDRIDE: A NEW NICKEL(0) COMPLEX CONTAINING MOLECULAR NITROGEN

SURESH C. SRIVASTAVA and M. BIGORGNE*
Laboratoire de Chimie Minérale, Ecole Nationale Supérieure de Chimie, Paris, (France)

(Received July 15th, 1969)

During the past two years, organo-transition metal compounds of the general formula $H_xM(N_2)(PR_3)_y$ containing molecular nitrogen as a ligand have been reported (Co^1, Fe^2, Ru^3). These compounds have been isolated in a pure state and fairly well characterized. Except for a report by Jolly and Jonas[4] who prepared a binuclear compound, $N_2[Ni(P(C_6H_{11})_3)_2]_2$, containing nitrogen as a bridging group, analogous nickel–nitrogen complexes have not been described.

We report here the preparation of a new compound of nickel containing coordinated nitrogen formed according to the following reaction:

$$Ni(acac)_2 + (C_2H_5)_3P + (i\text{-}C_4H_9)_3Al \xrightarrow[-70^\circ]{\text{Toluene or ether}} HNi(N_2)[(C_2H_5)_3P]_2$$

2.5 mmoles (0.64 g) of nickel(II) acetylacetonate were added to 10 mmoles (2.02 g) of triethylphosphine in 100 ml of ether. After purging the mixture with pure nitrogen for two hours, 2.0 ml of triisobutylaluminum were added dropwise at -70°. The temperature was allowed to rise gradually after 4 hours and thereafter maintained between 0° and -5° for a day. The contents were left stirring under nitrogen at room temperature for another 24 hours when all the reactants dissolved giving a clear deep-red solution. Upon surrounding the homogeneous mixture with dry ice and leaving it undisturbed for three days, orange-yellow crystals of the compound separated. The crystals were washed with a minimum of petroleum ether and dried under nitrogen.

An analogous compound was obtained when tributylphosphine was used instead of triethylphosphine as a ligand. However, when a similar reaction was carried out with triphenylphosphine or ethyldiphenylphosphine as ligands, the nitrogen compound could not be obtained. When the reactions were carried out at room temperature, the complex did not form.

The complex is very soluble in most common solvents and many times it was obtained only as a dark viscous material or as an oil when solvents like toluene, THF,

---

*Author to whom correspondence should be addressed.

pentane, hexane and petroleum ether were used. Only after most careful and repeated efforts was it possible to obtain the solid crystalline material from ether or toluene.

The orange-yellow solid is quite air and moisture sensitive and loses nitrogen slowly; it is even less stable in solution. However, it can be stored under nitrogen for several days without decomposition. The loss of the coordinated N_2 from the complex was shown by the slow disappearance of the $\nu(N_2)$ band in the IR spectrum.

The results of elemental analysis support a formula $Ni(N_2)(PR_3)_n$ or $HNi(N_2)(PR_3)_n$ ($n = 2$) for the compound. The analysis is quite inconsistent with any other formulation (*e.g.*, $n = 3$ etc.).

The IR spectra of the compound in different solvents are summarized in Table 1. The complex in solution or the crude product isolated as a viscous material, as well as the crystals obtained from ether or toluene, gave a sharp intense band in the 2064—2076 cm^{-1} region assignable to the coordinated N–N stretch. Another sharp band of medium intensity was observed at 1900—1914 cm^{-1}, which can be assigned to the Ni–H frequency by analogy with the compound *trans*-$HClNi[(C_6H_{11})_3P]_2$ prepared by Green *et al.*[5]. Their compound shows a Ni–H frequency at 1916 cm^{-1} in the IR spectrum; the existence of this bond was confirmed further by NMR studies[5].

It is interesting that contrary to the analogous cobalt nitrogen complex[1] and the ruthenium nitrogen complex[3] reported recently, the present nickel compound does show a metal–hydrogen frequency in the infrared spectrum. Also it appears that the Ni–H bond is relatively more stable than the Ni–N_2 bond, since upon exposure to air the band at 2075 cm^{-1} (N–N; nujol) slowly disappears while the Ni–H band (1911 cm^{-1}; nujol) is seen to persist for a longer period. Efforts are underway to obtain other evidence, *e.g.*, NMR to characterize the nickel – hydrogen bond.

Due to the extremely unstable nature of the complex, studies on the molecular weight and the magnetic moment have not been successful so far. Attempts are being made, however, to obtain this information.

On the basis of analytical results and the IR spectra, the compound has thus tentatively been formulated as $HNi(N_2)(PR_3)_2$ ($R = C_2H_5$, n-C_4H_9). Although this structure seems most likely on the basis of our results, other possibilities cannot be entirely excluded. A definitive assignment of the structure must await completion of further studies which are currently in progress. The exchange reactions of this complex with H_2, CO, CO_2, ethylene and CH_3I etc., are also under investigation.

TABLE 1

IR FREQUENCIES[a] OF THE NITROGEN COMPOUND OF NICKEL, $HNi(N_2)(PR_3)_2$ (cm^{-1})

Solvent	$HNi(N_2)(PEt_3)_2$		$HNi(N_2)(PBu_3)_2$	
	$\nu(N_2)$	ν(Ni–H)	$\nu(N_2)$	ν(Ni–H)
Toluene	2065 vs	1900 m	2065 vs	1900 (sh)
Ether	2067 s	1905 (sh)	2068 s	1900 (sh)
Hexane	2076 vs	1914 m	–	–
Nujol (mull)	2075 vs	1911 s	2074 vs	1914 s
Hexachlorobutadiene	2063 s	1912 m	–	–

[a] vs very strong; s strong; m medium; (sh) shoulder.

ACKNOWLEDGEMENT

Financial support for this research by the Institut Français du Pétrole is gratefully acknowledged.

REFERENCES

1(a) A. Yamamoto, L.S. Pu, S. Kitazume and S. Ikeda, *J. Amer Chem. Soc.*, 89 (1967) 3071, and references cited therein.
(b) A Misono, Y. Uchida, T. Saito, M. Hidai and M. Araki, *Inorg. Chem.*, 8 (1969) 168, and references cited therein.
(c) A. Sacco and M. Rossi, *Chem. Commun.*, (1967) 316; *Inorg. Chim. Acta*, 2 (1968) 127.
(d) J.H. Enemark, B.R. Davis, J.A. McGinnety and J.A. Ibers, *Chem. Commun.*, (1968) 96; B.R. Davis, N.C. Payne and J.A. Ibers, *J. Amer. Chem. Soc.*, 91 (1969) 1241.
2 A. Sacco and M. Aresta, *Chem. Commun.*, (1968) 1223; C.H. Campbell, A.R. Dias, M.L.H. Green, T. Saito and M.G. Swanwick, *J. Organometal. Chem.*, 14 (1968) 349.
3 A. Yamamoto, S. Kitazume and S. Ikeda, *J. Amer. Chem. Soc.*, 90 (1968) 1090; W.H. Knoth, *J. Amer. Chem. Soc.*, 90 (1968) 7172.
4 P.W. Jolly and K. Jonas, *Angew. Chem.*, 80 (1968) 705.
5 M.L.H. Green and T. Saito, *Chem. Commun.*, (1969) 208.