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SYNTHESIS AND REACTIVITY TOWARD REDUCING AGENTS OF THE ETHOXYCARBONYL COMPLEX $[(np_3)Ni(CO_2Et)]BPh_4$ (np_3 = tris(2-diphenylphosphinoethyl)amine)

CLAUDIO BIANCHINI and ANDREA MELI

Istituto per lo Studio della Stereochimica ed Energetica dei Composti di Coordinazione, CNR, Via F.D. Guerrazzi, 27, 50132 Firenze (Italy)

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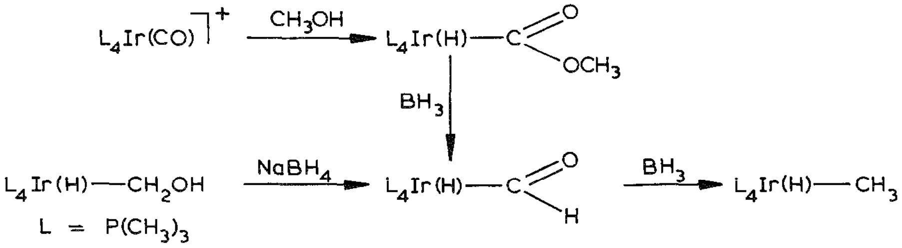
Summary

The ethoxycarbonyl complex $[(np_3)Ni(CO_2Et)]BPh_4$ (**2**) [np_3 = tris(2-diphenylphosphinoethyl)amine] has been synthesized by ethoxide ion attack on $(np_3)Ni(CO)$ (**3**) or $[(np_3)Ni(CO)]BPh_4$ (**4**). Compound **2** reacts with $LiHBEt_3$, $NaBH_4$, MeMgI, $NaC_{10}H_8$, or MeLi to give the carbonyl **3**, whereas with $BH_3 \cdot THF$ it gives the complexes $[(Hnp_3)Ni(CO)]BPh_4$ (**6**) and $[(np_3)NiH]BPh_4$ (**7**). The mechanism of the reactions leading to the formation of the last two compounds is briefly discussed.

Introduction

Increasing attention has been directed recently towards the chemistry of (alkoxycarbonyl)metal complexes. Both the formation and the reactions of these compounds give an insight into several important processes, such as the metal-mediated reduction of carbon oxides and of other carbonyl-derived functional groups [1–6]. The following set of reactions reported by Thorn [4] illustrates the significant role of a methoxycarbonyl complex as an intermediate in the transformation of M–CO into M–CH_3 or M–CH_2OH (Scheme 1).



SCHEME 1

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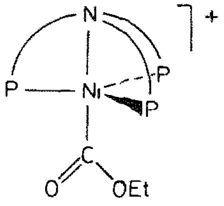
In the course of recent investigations on the reactivity of the d^{10} trigonal pyramidal complex $(np_3)Ni$ (**1**) (np_3 = tris(2-diphenylphosphinoethyl)amine) toward CO_2 and related groups, we have synthesized the stable ethoxycarbonyl compound $[(np_3)Ni(CO_2Et)]BPh_4$ through the oxidative addition of ethyl cyanoformate, $NCCO_2Et$, to **1** [7]. A complete X-ray structure determination of **2** has shown that the nickel atom is five-coordinate, being linked to np_3 and the $-CO_2Et$ group in a trigonal bipyramidal arrangement.



(2)

In this paper we report on two alternative syntheses of **2**, and describe its reactions with the reducing agents $LiHBEt_3$, $NaBH_4$, MeMgI, $NaC_{10}H_8$, MeLi, and $BH_3 \cdot THF$.

Experimental

All reactions and manipulations were performed under a nitrogen atmosphere except where otherwise stated. The complexes were collected on a sintered-glass frit and were washed successively with ethanol and petroleum ether (b.p. 40–70 °C) before being dried in a stream of nitrogen. The complexes $(np_3)Ni(CO)$ and $[(np_3)Ni(CO)]BPh_4$ were prepared according to literature methods [8]. Reagents $BH_3 \cdot THF$, $NaBH_4$, $LiHBEt_3$, and $NCCO_2Et$ were obtained from Aldrich and were used as supplied. THF was dried over sodium diphenyl ketyl and distilled. All other solvents and materials were of reagent grade quality and were used without further purification.

Preparation of $[(np_3)Ni(CO_2Et)]BPh_4$ (2)

Method A. A 1 *M* solution of sodium ethoxide in ethanol (5 ml) was added to a solution of $(np_3)Ni(CO)$, **3**, (0.37 g, 0.5 mmol) in THF (30 ml) and the resulting mixture was stirred magnetically for 1 h. During this time no reaction took place. A solution of $NaBPh_4$ (0.34 g, 1 mmol) in ethanol (20 ml) was then added and the yellow reaction mixture was exposed to air. Within 4 h the color of the solution had changed to orange, and red-orange crystals of **2** formed when the solution was left overnight; yield 20%.

Method B. To a suspension of $[(np_3)Ni(CO)]BPh_4$, **4**, (0.32 g, 0.3 mmol) in THF (20 ml) was added a 1 *M* solution of sodium ethoxide in ethanol (1.5 ml), which caused the solid to dissolve to give an orange solution. On the addition of butanol (25 ml), followed by partial evaporation of the solvent, yellow crystals of **3** were obtained in 70% yield. After further concentration of the solution, red-orange crystals of **2** separated in 15% yield.

Reaction of 2 with $LiHBEt_3$

A solution of **2** (0.55 g, 0.5 mmol) in THF (30 ml) was treated with 0.5 ml of a solution of $LiHBEt_3$ (1 *M*) in THF, and the color immediately changed from orange to yellow. Addition of butanol (30 ml) gave yellow crystals of **3** in 80% yield.

Reaction of 2 with $NaBH_4$

A solution of $NaBH_4$ (0.04 g, 1 mmol) in THF/H_2O (15 ml) was added to a THF (30 ml) solution of **2** (0.55 g, 0.5 mmol). The resulting mixture was stirred for 2 h, and ethanol (20 ml) was added. On concentration of the solution, yellow crystals of **3** separated in 70% yield.

Reaction of 2 with $BH_3 \cdot THF$

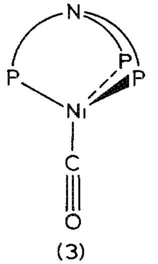
A solution of $BH_3 \cdot THF$ (1 *M*) in THF (3 ml) was added to a solution of **2** (0.55 g, 0.5 mmol) in THF (40 ml), and the mixture was refluxed for 5 h. The reaction mixture was then allowed to cool. On the addition of butanol and evaporation of the THF, orange crystals of $[(np_3)NiH]BPh_4$ separated in 40% yield. They were filtered off and the mother liquor was then concentrated to 10 ml and allowed to stand. White crystals of $[(Hnp_3)Ni(CO)]BPh_4$ formed; yield 35%.

Results and discussion

Current synthetic routes to alkoxycarbonyl complexes exploit either the reaction of alkoxide ions with metal carbonyls [3] or the oxidative addition of chloroformates [3] or cyanoformates [7] to metal complexes. The first route involves nucleophilic attack by the alkoxide ion on the M–CO carbon atom (eq. 1):

$$L_nMC{\equiv}O + RO^- \rightarrow L_nMCOOR \qquad (1)$$

This requires that, in order to enhance its electrophilic nature the carbonyl ligand should not be heavily involved in back-bonding from the metal [9]. A diagnostic tool for discriminating between electrophilic and nucleophilic CO ligands is provided by IR spectroscopy [3]. In particular, carbonyl complexes with $\nu(CO)$ values below approximately 2000 cm^{-1} do not yield alkoxycarbonyl complexes. Accordingly, a THF solution of the d^{10} complex $(np_3)Ni(CO)$, **3**, ($\nu(CO)$ 1890 cm^{-1}) [8] does not react with an ethanol solution of NaOEt, but when the reaction mixture is exposed to air, and $NaBPh_4$ is then added, the color changes from yellow to red-orange within a few hours, and crystals of **2** are formed:

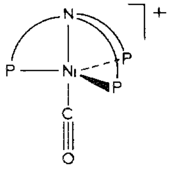


(3)

$$(np_3)Ni(CO) + EtO^- \xrightarrow[NaBPh_4]{air} [(np_3)Ni(CO_2Et)]BPh_4 \qquad (2)$$

Alternatively, **2** may be obtained by treatment of a THF solution of the green d^9

complex $[(np_3)Ni(CO)]BPh_4$, **4**, (ν(CO) 2000 cm^{-1}) [8] with EtO^- (eq. 3). In this case the reaction is immediate and does not require exposure to air.



(4)

$$[(np_3)Ni(CO)]BPh_4 + EtO^- \rightarrow 0\,2\,[(np_3)Ni(CO_2Et)]BPh_4 + 0\,8\,(np_3)Ni(CO) \qquad (3)$$

The formation of **2** through the reaction shown in eq. 2 may occur following a preliminary oxidation of the metal by atmospheric oxygen: the increased oxidation state of the metal, and the consequent decrease of electron transfer into the CO antibonding π^* orbitals, may enhance the electrophilic character of the carbonyl carbon atom [9]. These suggestions are supported by the fact that reaction of the nickel(I) complex **4** with EtO^- (eq. 3), leads to alkoxycarbonyl formation without exposure to the air. The stretching frequencies of the CO groups in **3** and **4** are in agreement with the observed reactivity toward EtO^-. The low yield of **2** from the route summarised in eq. 2 can be explained tentatively by taking into account all the chemical processes which might accompany the exposure of the reaction mixture to the air (oxidation of phosphines to phosphine oxides, competing reaction of EtO^- with atmospheric components, partial decomposition of the final product). Conversely, the low yield of **2** from the route shown in eq. 3 may be due to well known reducing capability of the enthoxide ion. This could account for the formation of a sizable amount of the nickel(0) carbonyl, **3**.

Compound **2** reacts with $LiHBEt_3$ or $NaBH_4$ in THF to give almost quantitative yields of the carbonyl complex **3**:

$$[(np_3)Ni(CO_2Et)]BPh_4 \xrightarrow{LiHBEt_3 \text{ or } NaBH_4} (np_3)Ni(CO) \qquad (4)$$

The transformation into metal carbonyls is a general feature of alkoxycarbonyl complexes [3]. It occurs always by the treatment of the latter compounds with strong acids like HCl of HBF_4, through a mechanism similar to that of the acid-catalyzed hydrolysis of organic esters [10]. However, **2** is quite inert towards strong acids, thus representing the classical exception to the rule. Although a mechanistic investigation has not been conducted, it appears reasonable to consider the process occurring in reaction 4 as a classical electronic reduction. The intermediacy of formyl or hydrido carbonyl species seems, in fact, to be ruled out for at least two reasons. (a) The carbonyl **3** is also obtained by the treatment of **2** with reducing agents such as $NaC_{10}H_8$, $MeC_{10}H_8$, MeMgI, or LiMe, which do not contain hydridic hydrogen atoms. (b) The formyl ligand can be stabilized by the $(np_3)Ni$ fragment, as shown by the formation of $(np_3)Ni(CHO)$ (**5**), which has recently been obtained by the reaction of the nickel(0) trigonal pyramidal complex **1** with gaseous H_2CO [11]. Furthermore it is symptomatic that $LiHBEt_3$ reduces the nickel(I) carbonyl complex **4** quantitatively to **3** (see eq. 5), instead of giving the formyl complex **5**. By analogy

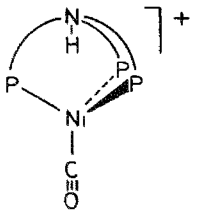
$$(np_3)Ni(CO)]^+ \xrightarrow{LiHBEt_3} (np_3)Ni(CO) \qquad (5)$$

with the nucleophilic attack by EtO^- on **4**, which affords the ethoxycarbonyl compound **2**, it would have been reasonable to expect the formation of a formyl complex from reaction [5].

The reactivity of **2** toward $BH_3 \cdot THF$ has also been examined. This reagent functions as a reducing agent in attacking groups at positions of high electron density, whereas $LiHBEt_3$ and $NaBH_4$ prefer to attack centres of low electron density [12].

Diborane in THF has been found to reduce methoxycarbonyl ligands to formyl groups and formyl groups to methyl groups [4]. However, **2** reacts with $BH_3 \cdot THF$ to give almost equivalent amounts of the complexes $[(Hnp_3)Ni(CO)]BPh_4$ (**6**) and $[(np_3)NiH]BPh_4$ (**7**):

$$[(np_3)Ni(CO_2Et)]BPh_4 + BH_3 \cdot THF \rightarrow 0.5\ [(Hnp_3)Ni(CO)]BPh_4 + 0.5\ [(np_3)NiH]BPh_4 + BH_2OEt \qquad (6)$$



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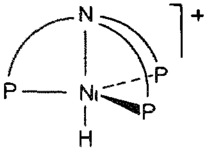
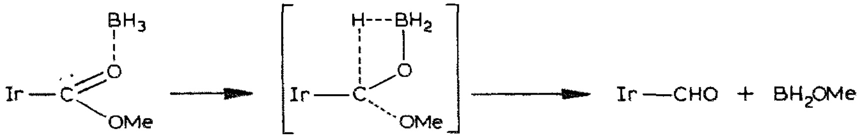


(7)

Both compounds **6** and **7** have been prepared by alternative routes [8,9].

Several proposals have been made in the literature as to the likely mechanisms for reduction of carbonyl-derived functional groups with the electrophilic BH_3 molecule [4,14]. It is generally accepted that reduction by BH_3 involves attack at centres of high electron density. Two centres of this type are present in the alkoxycarbonyl group: the carbonyl oxygen and the alkoxy oxygen. So far, studies on BH_3 reductions of alkoxycarbonyl groups have not demonstrated for certain which site is preferentially attacked by the borane.

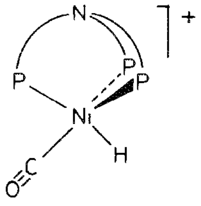
For the reduction to the formyl group, Thorn suggested that attack at the carbonyl oxygen is more plausible than at the ether oxygen:



(7)

As for our system, the ambiguity regarding the preferred site of BH_3 attack remains to throw doubt on any suggested reaction mechanism. By analogy with eq. 7, and with the reductions of organic esters with BH_3 [12], a reasonable pathway is that depicted in Scheme 2.

We suggest that the initial interaction involves BH_3 coordination at the carbonyl oxygen, followed by hydride migration. Which species to being formed at this stage (formyl or hydrido(carbonyl)) is hard to assess in absence of information on the intermediates [15]. However, the formation of both the carbonyl complex **6** and the hydrido complex **7** seems to be satisfactorily explained by assuming the intermediacy of the hydridometal carbonyl $[(np_3)Ni(H)(CO)]^+$ (**8**).



(8)

An intermediate of the latter type has been, in fact, suggested to play a fundamental role in the formation of the nickel(0) carbonyl complex **6** by attack of CO on the nickel(I) hydride **7** (see eq. 8) [13].

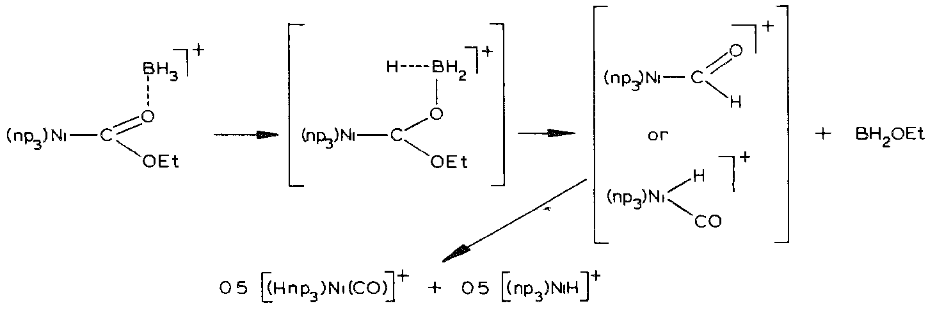
$$[(np_3)NiH]^+ + CO \rightarrow [(Hnp_3)Ni(CO)]^+ \qquad (8)$$

Most important for both reactions 6 and 8 to occur is the flexibility of the $(np_3)Ni$ fragment, which can interconvert easily, as shown in eq. 9. Such a deformation of the

(I) (II)

(9)

np_3 ligand is a necessary requirement since only conformation II provides a new coordination site to give the carbonyl (reaction 8) or the hydride (reaction 6), and hence allow the formation of **8**. The conversion of the latter intermediate into the carbonyl **6** may then occur through the migration of H, as a proton, to the amine group, a process which corresponds in practice to a reduction of the metal [13]. Finally, it is necessary to explain the simultaneous formation along with **6** of an almost equivalent amount of the hydride **7** in the reaction 6, a fact which apparently seems contrary to the proposed reaction pathway. On the basis of the above considerations, only the formation of **6** would be expected. Tentatively we suggest that both the departure of CO and of H^+ from the intermediate **8** occur by equally probable pathways. A factor which could favour which route is followed seems to be the concentration of CO in the reaction mixture. Reaction 8, in fact, requires a large



SCHEME 2

excess of carbon monoxide [13], whereas in reaction 6 the carbonyl ligand is formed by degradation of the ethoxycarbonyl group.

Acknowledgment

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