5.57 (W), 4.69 (VS), 4.39 (M), 4.31 (W), 3.83 (M), 3.69 (M), 3.44 (VW), 3.08 (VW), 2.82 (W), 2.67 (S), 2.60 (S), 2.43 (W), 2.37 (W), 2.29 (S), 2.10 (W), 2.04 (W).

$K[BH_4]$. ^{11}B NMR spectrum in D_2O: −43.0 ppm (quintet, $J = 80$ Hz). IR spectrum (KBr pellet): 1120 (vs), 2215 (s), 2289 (vs), 2379 (s) cm^{-1}.

$Rb[BH_4]$. ^{11}B NMR spectrum in D_2O: −42.5 ppm (quintet, $J = 80$ Hz). IR spectrum (KBr pellet): 1112 (vs), 2203 (vs), 2277 (vs), 2356 (s), 2356 (s) cm^{-1}.

$Cs[BH_4]$. ^{11}B NMR spectrum in D_2O: −42.0 ppm (quintet, $J = 81$ Hz). IR spectrum (KBr pellet): 1099 (vs), 2180 (s), 2249 (vs), 2289 (vs), 2334 (s) cm^{-1}.

Preparation of $Yb[B_3H_8]_2$. An amalgam of ytterbium metal was formed in the same manner as the alkali-metal amalgams with the exception that 15 h of stirring was required for complete formation. A 6:1 molar ratio of $BH_3{\cdot}THF$ to metal was used to form $(THF)_xYb[B_3H_8]_2$ complexes. By fractional crystallization at 0 °C $(THF)_xYb[B_3H_8]_2$ was removed from solution. ^{11}B NMR spectrum: in THF-d_8, −26.6 ppm (nonet, $J = 33$ Hz); in CH_3CN, −29.5 ppm (nonet, $J = 33$). ^1H NMR in CD_3CN: 0.0 ppm (decet, $J = 33$ Hz).

Preparation of B_4H_{10}. A 100-mg (1.27-mmol) sample of $K[B_3H_8]$ was placed in a 50-mL flask with a Teflon stir bar. The flask was evacuated, and 1.3 mmol of BCl_3 (measured as a gas) was condensed into the flask. The reaction was allowed to proceed at −78 °C for 90 min and then warmed to room temperature for an additional 20 min. The reaction mixture was a white slurry. Volatile materials were passed through traps maintained at −98, −140, and −196 °C. A yield of 0.52 mmol of B_4H_{10} (55% based on $[B_3H_8]^-$ boron) was collected in the −140 °C trap. ^{11}B NMR spectrum in benzene-d_6: −7.58 (triplet, $J = 132$ Hz), −42.4 ppm (doublet, $J = 135$ Hz). Both peaks decoupled to singlets. An identical procedure was performed on 0.103 g (1.3 mmol) of $K[B_3H_8]$ using 1.3 mmol of BF_3, affording 0.50 mmol of B_4H_{10} (51% yield).

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Contribution from the Departamento de Quimica
Inorgánica, Facultad de Ciencias Quimicas,
Universidad Complutense, 28040 Madrid, Spain

Intramolecular Carbonylation of $Ni(S_2COR')_2$ in Fused PR_3. An Improved Preparation of $Ni(CO)_2(PR_3)_2$

Loreto Ballester,* Angel Gutiérrez-Alonso,
Soledad Pérez-Serrano, and M. Felisa Perpiñán

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The ability of fused tertiary arylphosphines to participate in reduction reactions has permitted us to develop a new synthetic pathway to dicarbonylbis(tertiary phosphine)nickel(0) complexes from bis(alkyl xanthato)nickel(II) compounds (alkyl xanthate = *O*-alkyl dithiocarbonate). Depending on the phosphine and the alkyl xanthate used, different yields are achieved.

Several methods of preparation of $Ni(CO)_2(PR_3)_2$ complexes, all of them using carbon monoxide or highly toxic volatile carbonyls, are described in the literature. Thus the direct reaction between $Ni(CO)_4$ and the phosphine is still by far the most important synthetic method.[1,2]

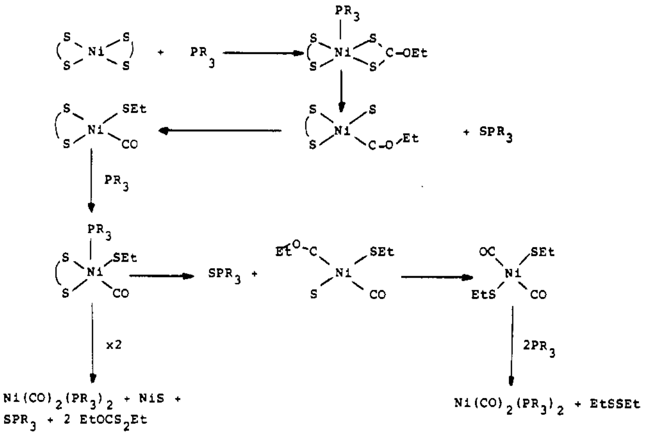
The reductive carbonylation of $NiX_2(PR_3)_2$ (X = halide) to give $Ni(CO)_2(PR_3)_2$ has also been carried out by using several reducing agents or by reaction with metal carbonyls or metal carbonyl anions.[2-5] The decarbonylation of methanol occurs in the reaction of PPh_3 and $Ni(cod)_2$ in the presence of a diene.[2,6] More recently, the partial formation of $Ni(CO)_4$, when the reaction of $Ni(S_2COR')_2$ with amines was carried out in the presence of CO, was proved.[7]

Table I. Reaction Conditions and Yields

$Ni(S_2COR')_2$ R′	PR_3 R	molar ratio PR_3/Ni	temp, °C	reacn time, h	yield, %[a]
Et	Ph	6	150–140	1	50
Et	Ph	3	150–120	0.7	30
Et	*p*-$CH_3C_6H_4$	4	150–140	1	4.2
Cy	Ph	6	170–160	1	15
Cy	*p*-$CH_3C_6H_4$	4	170–160	1	trace

[a] $Ni(CO)_2(PR_3)_2$ relative to $Ni(S_2COR')_2$.

Scheme I. Proposed Mechanism for the Formation of $Ni(CO)_2(PR_3)_2$



We have previously studied the reactivity of tertiary phosphines toward $Ni(S_2COR')_2$ (R′ = Et, C_6H_{11} (Cy)) compounds in several solvents to give mixed complexes. Under the reported conditions, no reaction was observed with PPh_3, but with $Ph_2PC_2H_4PPh_2$ (dppe), an adduct formation reaction or rupture of the O–R′ bond occurred to give dithiocarbonate complexes.[8] In the attempt to isolate derivatives of the PPh_3, the reaction was carried out in the fused phosphine. No adducts were isolated in the described reactions; instead, zerovalent nickel complexes were obtained.

As described below, the reaction occurs with formation of $Ni(CO)_2(PPh_3)_2$ in up to 50% yield, the best results being obtained when ethyl xanthate(1−) and triphenylphosphine are used. Table I shows the reaction conditions and the results obtained. Along with the main product, variable quantities of $SPPh_3$ are recovered. The reaction also produces a black amorphous residue that is analyzed to be a nickel sulfide. The analytical data are variable, depending on the conditions employed in the reaction, but all of them suggest the formation of a nonstoichiometric species $Ni_{1-x}S$ ($0 \leq x \leq 0.2$).

The organic products of this reaction condensed as colorless drops of liquid in the cooler parts of a Schlenk flask. They were collected, separated by alumina chromatography, and identified by comparison of their ^1H NMR spectra with those of authentic samples. From the mixtures we have been able to identify EtSEt (5%), EtSSEt (15%), and EtOCSSEt (30%). In some cases, we could also identify traces of phosphine adducts, similar to those previously reported by us,[8] as shown by the ν(COR) bands shifted to lower frequencies in the IR spectrum. A possible mechanism (Scheme I) would include the initial formation of a pentacoordinate phosphine adduct, followed by sulfur abstraction with liberation of $SPPh_3$.

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The previous formation of this adduct seems to be necessary for the reaction, and thus analogous reactions with $Ni(S_2COEt)_2(bpy)$ (bpy = 2,2′-bipyridine) give the dicarbonyl only as traces whereas with $Ni(S_2CNEt_2)_2$ no reaction is observed, in accordance with the lower tendency of these complexes to interact with a Lewis base.[9] The same tendency is observed for the $Ni(S_2COR')_2$ complexes, where it decreases in the order Et > Cy,[8] as shown for the lower yields obtained for the latter compound.

The abstraction of sulfur as $SPPh_3$ leaves a [Ni(SCOEt)] moiety that can undergo an ethyl migration to give the carbonyl and the SEt group. Dimerization of this group to EtSSEt or, alternatively, coupling to a SCOEt fragment to give EtOCSSEt would account for the observed organic products.

The formation of all the secondary products of this reaction has been well established in thermal decompositions of $Ni(S_2COR)_2$ to NiS, OCS, and ROCSSR[10] or in reactions between palladium or platinum bis(xanthates) and tertiary phosphines with formation of $Pt(S_2CO)(PR_3)_2$, EtOCSSEt, and EtSSEt.[11] The formation of EtSSEt is also possible by partial decomposition of EtOCSSEt.[12] In this case the overall stoichiometry would be

$$2Ni(S_2COEt)_2 + 5PPh_3 \rightarrow Ni(CO)_2(PPh_3)_2 + NiS + 3SPPh_3 + 2EtOC(S)SEt$$

Minor products, like EtSEt, have also been found in palladium xanthate thermolysis, and their appearance has been interpreted as being due to secondary reactions with elimination of COS and formation of PdS.[13] The use of phosphines other than PPh_3 gives lower yields as a consequence of the stronger reducing character of the latter phosphine. Bidentate phosphines do not react under these conditions.

Experimental Section

As a general procedure, the reaction of $Ni(S_2COEt)_2$[14] with PPh_3 is described. A 300-mL Schlenk flask was charged with 0.30 g (1 mmol) of $Ni(S_2COEt)_2$ and 1.57 g (6 mmol) of PPh_3 and evacuated. The closed flask was heated at 140–150 °C for 1 h, giving a black fused mixture, which was slowly cooled to room temperature, yielding a solid. The organic products that condensed on the glass walls were collected, chromatographed on alumina, and identified from their spectral data. The black solid that formed was stirred in Et_2O (150 mL) for 20 h, the mixture was then filtered and the solvent removed in vacuo. After addition of EtOH (50 mL), the mixture was stirred for another 1 h, leaving a gray solid that could be recrystallized from acetone with addition of charcoal to give $Ni(CO)_2(PPh_3)_2$, identified by its correct analysis, spectral data, and melting point. $SPPh_3$ was obtained from the solution by addition of water. The black residue from the Et_2O extraction was washed with acetone (3 × 30 mL), and the amorphous solid was identified as nickel sulfide. All the identified products gave correct analytical and spectral data.

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Registry No. $Ni(S_2COEt)_2$, 3269-24-7; $Ni(S_2COCy)_2$, 53566-81-7; $Ni(CO)_2(PPh_3)_2$, 13007-90-4; $Ni(CO)_2(P(p\text{-}CH_3C_6H_4)_3)_2$, 133551-21-0; $SPPh_3$, 3878-45-3; EtSEt, 352-93-2; EtSSEt, 110-81-6; EtOCSSEt, 623-79-0; nickel sulfide, 11113-75-0.

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Contribution from the Department of Chemistry,
University of Kentucky, Lexington, Kentucky 40506-0055

Convenient Syntheses of Unsymmetrically B-Substituted Borazines

J. Bai and K. Niedenzu*

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Literally hundreds of borazines, $(RBNR')_3$, are known, but only relatively few unsymmetrically substituted derivatives of the six-membered B_3N_3 heterocycle have been characterized and their chemistry has hardly been explored.[1] The most readily available unsymmetrically B-substituted borazine of the type $XR_2B_3N_3R'_3$ is the monochloro compound $Cl(CH_3)_2B_3N_3(CH_3)_3$, which can be prepared from $(ClBNCH_3)_3$ by a Grignard reaction. However, the purification of the product is fairly laborious, due to the presence of substantial amounts of byproducts.[2] It has now been found that a very convenient access to unsymmetrically B-substituted borazines is available by the reaction of a *B,B′,B″*-triorganylborazine with boron tribromide.

Initially, $(C_2H_5BNCH_3)_3$ and BBr_3 were reacted in a 3:1 molar ratio, in anticipation that all of the bromine of BBr_3 would exchange with the ethyl groups of the borazine to give $(C_2H_5)_3B$ and $Br(C_2H_5)_2B_3N_3(CH_3)_3$. However, even when a mixture of the two neat reagents was heated to reflux, the sole products of any significance were $Br(C_2H_5)_2B_3N_3(CH_3)_3$ and $C_2H_5BBr_2$ (besides unreacted $(C_2H_5BNCH_3)_3$). This result indicated that the Br/C_2H_5 exchange stops with the generation of $C_2H_5BBr_2$ rather than proceeding with the formation of $(C_2H_5)_3B$. Consequently, when equimolar amounts of the two reagents were reacted for several hours, and even at room temperature, $Br(C_2H_5)_2B_3N_3(CH_3)_3$ was formed in excellent yield according to eq 1; only $C_2H_5BBr_2$ and traces of $Br_2(C_2H_5)B_3N_3(CH_3)_3$ were obtained as byproducts.

$$(C_2H_5BNCH_3)_3 + BBr_3 \rightarrow Br(C_2H_5)_2B_3N_3(CH_3)_3 + C_2H_5BBr_2 \tag{1}$$

$Br(C_2H_5)_2B_3N_3(CH_3)_3$ was subsequently converted to $(CH_3S)(C_2H_5)_2B_3N_3(CH_3)_3$ by the reaction with $Pb(SCH_3)_2$ and to $(H_2N)(C_2H_5)_2B_3N_3(CH_3)_3$ by the reaction with anhydrous NH_3, as is shown in the following equations ($R = C_2H_5$, $R' = CH_3$):

$$2BrR_2B_3N_3R'_3 + Pb(SCH_3)_2 \rightarrow 2(CH_3S)R_2B_3N_3R'_3 + PbBr_2 \tag{2}$$

$$BrR_2B_3N_3R'_3 + 2NH_3 \rightarrow (H_2N)R_2B_3N_3R'_3 + NH_4Br \tag{3}$$

Similarly, when $(C_2H_5BNCH_3)_3$ was reacted with 2 molar equiv of BBr_3, the desired $Br_2(C_2H_5)B_3N_3(CH_3)_3$ was readily obtained. Formation of a precipitate was observed when the reaction was performed at room temperature or below, but the latter disappeared on gentle heating of the reaction mixture. In this case, the only byproduct, besides $C_2H_5BBr_2$, was some $(BrBNCH_3)_3$.

Subsequently, $Br_2(C_2H_5)B_3N_3(CH_3)_3$ was converted to $(H_2N)_2(C_2H_5)B_3N_3(CH_3)_3$ and $(CH_3S)_2(C_2H_5)B_3N_3(CH_3)_3$, as additional representatives of unsymmetrically B-substituted borazines.

All of the compounds were obtained in excellent purity and were characterized by their ^1H, ^{11}B, and ^{13}C NMR data. As yet, it is still uncertain if simple Br/C_2H_5 exchange occurs or if a BBr moiety is exchanged with a BC_2H_5 unit. The exclusive formation of $C_2H_5BBr_2$ as byproduct tends to support the latter assumption.

Experimental Section

Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY. Melting points (uncorrected) were determined on a Mel-Temp block.

NMR spectra were recorded for solutions in $CDCl_3$ on a Varian VXR-400 or XL-200 (^{11}B) or GEMINI-200 (^1H, ^{13}C) instrument. Chemical shift data are given in ppm with positive values indicating downfield from the reference (internal $(CH_3)_4Si$ for ^1H and ^{13}C NMR, external $(C_2H_5)_2O{\cdot}BF_3$ for ^{11}B NMR). Abbreviations are as follows: s = singlet, t = triplet, q = quartet, m = unresolved multiplet, and an asterisk denotes a broad signal. Coupling constants *J* are given in hertz. All ^{13}C NMR spectra were recorded in the proton-decoupled mode. Electron impact (EI) mass spectral data were obtained on a VG ZAB-2F spectrometer under standard operating conditions. Data are listed to *m/z* 30 for 5% or greater relative abundances (in parentheses) only.

Nonreferenced reagents were obtained from Aldrich Chemical Co., Milwaukee, WI, and used as received. All preparations were performed in an anhydrous atmosphere under argon cover; solvents were dried by standard procedures.

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