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The reactivity of Ni(II)–tertiary phosphine complexes towards alkoxides under carbon monoxide: methoxo–carbonyl complexes, synthesis and reactivity

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Abstract

The reactivity of some Ni(II)–tertiary phosphine complexes, NiX_2L_2 (X = Cl, Br, I; L = tertiary alkylphosphine), towards the RONa (R = Me, Et, Ph, $PhCH_2$) alkoxides under carbon monoxide, has been studied. Whereas their reactions with methoxide yield *trans*-$NiXL_2COOCH_3$ methoxo–carbonyl complexes, those with the other alkoxides lead to the formation of organic and inorganic products such as aldehydes, hydrocarbons, CO_2 or derivatives, Ni(II) and Ni(0) compounds. This behaviour could be explained by assuming that the reactions lead to the formation of unstable $NiXL_2(OR)$ alkoxo complexes, which can either react with CO to yield the alkoxo–carbonyls $NiXL_2COOR$, or else decompose to Ni compounds and organic products. The alkoxo complexes have not been isolated but in some cases spectroscopic evidence of their formation has been obtained. Furthermore, we have studied the reactivity of methoxo–carbonyl complexes towards amines and alkoxides: under CO they are not very reactive either in mild or in drastic conditions, and above all yield compounds which derive from decarbonylative and decarboxylative decomposition.

Introduction

Our studies [1] on the carbonylation reactions promoted by transition metal complexes show that the phosphine complexes of Ni(II) can easily be reduced to Ni(0) compounds, and that the reduction can occur either at the expense of the phosphine ligand or of the carbon monoxide (reactions (1) and (2)).

$$Ni(II) + H_2O + L \longrightarrow Ni(0) + LO + 2H^+ \qquad (1)$$

$$NI(II) + CO + H_2O \longrightarrow Ni(O) + CO_2 + 2H^+ \qquad (2)$$

In the course of these studies, it has in some cases been possible to isolate alkoxo–carbonyl compounds [2].

In recent years special attention has been paid to alkoxo–carbonyls since the alkoxo–carbonyl ligand constitutes a fragment common to several organic molecules, such as esters, alkyl- and aryl-carbonates, carbamates and oxalates, into which it could be transformed in opportune conditions. Therefore, alkoxo–carbonyls are considered key intermediates both in the carbonylation processes of alcohols, amines and organic halides and in the oxo-type processes [3]. The alkoxo–carbonyl ligand has been generated either by oxidative addition of substances already including the alkoxo–carbonyl group (haloformates), (eqn. (3)) [4] or by direct interaction on the metals between CO and an alcohol molecule in the presence of a base (eqn. (4)) [5].

$$M(0) + X\text{–}COOR \longrightarrow MXCOOR \qquad (3)$$

$$M^{n+} + CO + ROH \xrightarrow{B} M^{(n-1)+}COOR + BH^+ \qquad (4)$$

It has also been obtained by ester interchange and by the alcoholysis of a carbamoyl ligand (reactions (5) and (6)) [6].

$$M\text{–}COOR + R'OH \longrightarrow M\text{–}COOR' + ROH \qquad (5)$$

$$M\text{–}CONHR' + ROH \longrightarrow M\text{–}COOR + NH_2R' \qquad (6)$$

From the point of view of the synthesis of the ligand, the most interesting method is the alkoxo-carbonylation of alcohols (reaction (4)). In the Ni, Pd

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and Pt triad, this method has been used to prepare several alkoxo–carbonyl complexes of palladium and platinum [7, 5]. In the case of nickel, of which few alkoxo–carbonyl complexes are known [8, 4], in a very few cases the alkoxo–carbonyl ligand has been obtained by alkoxo-carbonylation [8].

Otsuka and coworkers' studies [4] on nickel alkoxo–carbonyls prepared by oxidative addition, point out that the different behaviour of nickel towards Pd and Pt should be ascribed to the inferior stability of the alkoxo–carbonyl ligand with respect to the alkyl ligand, into which it evolves through decarboxylative decomposition (eqn. (7)).

$$\text{Ni–COOR} \longrightarrow \text{Ni–R} + CO_2 \qquad (7)$$

In this work we report the results of a study on the interaction between some phosphine complexes of Ni(II) and alkoxides under CO atmosphere and the reactivity of isolated compounds.

Results

Reactions with methoxide: methoxo–carbonyl complexes

By adding an equivalent quantity of sodium methoxide to NiX_2L_2 complexes (X = Cl, Br, I; L = tertiary alkyl-aryl-phosphine) in CH_2Cl_2, alcohol or THF solution at room temperature under a carbon monoxide atmosphere, methoxo–carbonyl complexes *trans*-$NiXL_2COOCH_3$ (L = PPh_2Et, $PPhEt_2$, PEt_3, PMe_3) have been obtained in the form of orange-yellow or brownish-red crystals (Table 1). In all the reactions, some quantities of a mixture of Ni(0)–carbonyl complexes ($NiL_2(CO)_2$ and $NiL(CO)_3$) have been obtained, evidenced by IR spectra of reaction solutions. The spectra display three bands: the first one centred at 2070 cm^{-1}, and the other in the 1998–1990 and 1940–1930 cm^{-1} range [1, 9].

In solution the methoxo complexes are unstable to oxygen, whereas the ones with the PMe_3 are unstable even under nitrogen; in the solid state they can be manipulated in the air for brief periods. The compounds have been characterized by elemental analysis, spectroscopic data (IR, NMR, Tables 1 and 2), and by some reactions. Their IR spectra display two absorptions, in the 1635–1630 and 1050–1030 cm^{-1} regions, typical of the stretching frequencies of C=O and C–O–C of the alkoxo–carbonyl ligand. The presence of the methoxo fragment in the methoxo–carbonyl ligand has also been confirmed by ^1H NMR spectra which, in the case of compounds with PEt_3, present a signal at 3.42 ppm (Table 2), in agreement with the values reported for other methoxo–carbonyl complexes [3–5]. In the case of PEt_3 complexes, the ^{31}P NMR spectra show the presence of a single signal centered at 17.45, 17.40 and 15.04 ppm, for the iodide, bromide and chloride complexes, respectively, indicative of a *trans* structure.

The compounds have also been characterized by analyzing the products of decomposition with HCl (eqn. (8)). The amounts of methanol developed are almost quantitative (see 'Experimental'), whereas those of CO do not exceed 60% of the theoretical value.

$$NiX(PEt_3)_2COOCH_3 + HCl \longrightarrow NiXCl(PEt_3)_2 + CO + CH_3OH \qquad (8)$$

Trace amounts of CO_2, probably formed via reaction (2), have also been observed.

The reactivity of methoxo–carbonyls towards amines or alkoxides has been studied in order to obtain information about their use in the synthesis of organic products containing the alkoxo–carbonyl group. The compounds react with methoxide in the 100–120 °C temperature range, either under 1 atm. of CO or under pressure (P(CO) > 20 atm.), yielding trace amounts of dimethylcarbonate or dimethyloxalate, respectively. The main products are a

TABLE 1

Analytical data of methoxo–carbonyl complexes

Compound	Yield (%)	Colour	Found (%)			Calculated (%)		
			Ni	P	X	Ni	P	X
$(PEt_3)_2NiClCOOCH_3$	70	red–orange	14.9	15.8	9.2	15.09	15.93	9.11
$(PEt_3)_2NiBrCOOCH_3$	70	red–orange	13.4	14.2	18.3	13.54	14.30	18.43
$(PEt_3)_2NiICOOCH_3$	68	dark red	11.9	12.5	25.8	12.22	12.90	26.40
$(PEt_2Ph)_2NiBrCOOCH_3$	50	yellow–orange	11.0	11.5	15.7	11.09	11.71	15.09
$(PEtPh_2)_2NiBrCOOCH_3$	40	yellow–orange	9.1	9.5	12.4	9.38	9.91	12.77
$(PMe_3)_2NiClCOOCH_3$	50	yellow	19.4	19.1	11.4	19.24	20.32	11.62
$(PMe_3)_2NiBrCOOCH_3$	52	yellow	16.9	17.1	19.2	16.79	17.73	22.84

TABLE 2

Spectral data of methoxo-carbonyl complexes

Compound	IR bands cm^{-1}[a]		NMR			
	$\nu(C{=}O)$	$\nu(C{-}OC)$	^1H[b]			^{31}P[c]
			OCH_3	CH_2	CH_3	
$Ni(PEt_3)_2ClCOOCH_3$	1630(vs)	1043(vs)	3.42(s)	1.75(m)	1.16(m)	15.04(s)
$Ni(PEt_3)_2BrCOOCH_3$	1634(vs)	1040(sh)1032(vs)	3.42(s)	1.66(m)	1.13(m)	17.40(s)
$Ni(PEt_3)_2ICOOCH_3$	1630(vs)	1040(sh)1030(vs)	3.42(s)	1.75(m)	1.07(m)	17.47(s)
$Ni(PEt_2Ph)_2BrCOOCH_3$	1635(vs)	1032(vs)	3.43(s)			
$Ni(PEtPh_2)_2BrCOOCH_3$	1635(vs)	1032(vs)	3.43(s)			
$Ni(PMe_3)_2ClCOOCH_3$	1640(vs)	1055(vs)	3.39(s)		1.10(m)	
$Ni(PMe_3)_2BrCOOCH_3$	1628(vs)	1050(vs)	3.39(s)		1.10(m)	
$Ni(PEt_3)_2ClCOOC_2H_5$[d]	1630(vs)					

[a] Unless otherwise indicated, the spectra were recorded in nujol. [b] In CD_2Cl_2, chemical shifts in ppm relative to Me_4Si. [c] In C_6H_6/C_6D_6 (1:1), chemical shifts in ppm relative to 85% H_3PO_4. [d] In CH_2Cl_2 solution.

Ni(0)–carbonyl mixture and a greenish product, consisting of a mixture of sodium and nickel methylcarbonate. Similar behaviour has been observed in the reaction with amines ($BuNH_2$ and $PhNH_2$). Under 1 atm. of CO, there is no formation of products containing the alkoxo–carbonyl or carbamoyl group. Only when the reactions are carried out under pressure ($P(CO) > 20$ atm.) do the carbamates $BuNHCOOCH_3$ or $PhNHCOOCH_3$ form in traces. The reactions with aniline require the additional presence of a strong base.

Reaction with ethoxide, benzoxide and phenoxide

The reactions between the NiL_2X_2 complexes and other alkoxides ($C_2H_5O^-$, $C_6H_5CH_2O^-$, $C_6H_5O^-$) do not yield the corresponding alkoxo–carbonyl complexes.

A Ni(0)–carbonyl mixture, phosphine oxide and differing amounts of organic products, depending on the alkoxide, have been obtained. An insoluble greenish precipitate not containing the phosphine ligand has also been observed. Its elemental analysis is similar to that of the compound produced by the reaction between NiX_2 and the corresponding alkoxide.

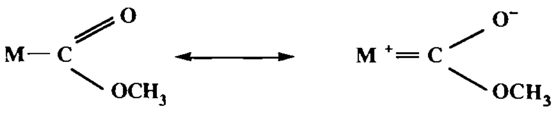
In the case of the reactions with ethoxide we obtain small amounts of acetaldehyde and dimethylcarbonate as organic products. The IR spectrum of the reaction solution between $NiBr_2(PEt_3)_2$ and C_2H_5ONa shows the presence of a strong sharp band at 1640 cm^{-1} which could be ascribed to the ethoxo–carbonyl complex, but we have not been able to separate it from the Ni(0)–carbonyl mixture.

In the reactions with benzoxide we have obtained small amounts of diphenylethane and trace amounts of benzaldehyde, whereas in the ones with phenoxide, traces of diphenylcarbonate have been found. The reaction between $NiBr_2(PEt_3)_2$ and phenoxide may be of interest from the point of view of the mechanism. The resulting orange–yellow reaction product shows a spectrum which can justify a mixture of $NiBr(PEt_3)_2(COOPh)$ and $NiBr(PEt_3)_2(OPh)$. Its IR spectrum displays bands at 1640(m) and 1055(m) cm^{-1}, ascribable to the phenoxo–carbonyl ligand, whose intensities vary from one preparation to another. The band intensity decreases every time we try to crystallize the product, even under CO atmosphere. This behaviour could be interpreted as an irreversible evolution from $NiBr(PEt_3)_2COOPh$ to $NiBr(PEt_3)_2(OPh)$. The analytical data are not significant, given that the compounds differ only in a CO molecule.

Discussion

The great stability of structure **II** (Scheme 1), promoted by the basicity of the phosphine ligand, can justify the trend in the yields of the methoxo–carbonyl complexes in the ligand series $PEt_x(PPh)_{3-x}$ ($x=3$, 2, 1) (Table 1), but it cannot explain the behaviour of the other alkoxides, which in any case give rise to corresponding alkoxo–carbonyl complexes.

It is not possible to invoke their instability, since some of them have been prepared by oxidative addition [4], and the ethoxo–carbonyl complex, with



I II

Scheme 1.

the PPh_3 ligand, is found to be stable up to 130 °C. Therefore, the behaviour observed may depend above all on the mechanism of the formation of the alkoxo–carbonyl ligand.

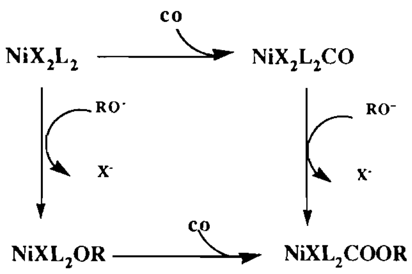
It is possible to rationalize our results by supposing that the interaction between the Ni(II)–phosphine complexes and the alkoxides occurs through the formation of the unstable alkoxo $NiL_2X(OR)$, rather than through the commonly accepted nucleophilic attack of a RO^- molecule on the CO of NiL_2X_2CO [19] (Scheme 2).

The alkoxo intermediate could: (i) react with CO giving the alkoxo–carbonyl complexes; (ii) dissociate, freeing the ligand and Ni(II); (iii) decompose to products deriving from the alkoxo group.

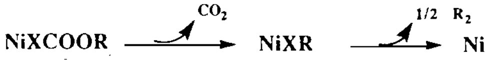
The possibility of synthesizing the alkoxo–carbonyl ligand and isolating the related complexes would depend therefore on the lifetime of the alkoxo complex. This should be sufficient to allow the coordination of CO and its insertion in the Ni–OR bond (Scheme 2). The insertion of a CO molecule in the metal–alkoxo bond is not unusual [11a] and, together with the nucleophilic attack of the alkoxo ion on the CO coordinated to metal, constitutes the commonly accepted mechanism for the synthesis of the alkoxo–carbonyl ligand.

We have not been able to isolate the NiL_2XOR alkoxo compounds but, with the PMe_3 complexes, in some cases, strong evidence for the formation of $NiCl(PMe_3)_2(OCH_3)$ has been obtained. In fact, when $NiCl(PMe_3)_2COOCH_3$ is heated under vacuum to 70 °C, the IR bands of the $-COOCH_3$ group disappear. Suspending the resulting product in Et_2O, under CO, the bands reappear with a lower intensity than the initial value. The minor intensity of the bands could be attributed to a partial irreversible decomposition of the compound according to the presence of phosphine oxide bands in the IR spectrum of the product.

However, alkoxo complexes are not very common with these metals and the first alkoxo complexes of Pt, Pd [11] and Ni [12] have only recently been isolated under mild conditions. Monomeric and bridged methoxo complexes of Ni(II) have been also prepared at −70 °C, by a reaction between methylnickel compounds and methanol [13].



Scheme 2.



Scheme 3.

Even in the case of the reaction with ethoxide and benzoxide the alkoxo intermediate has not been isolated, although the nature of the organic products obtained may be an indirect proof of its formation. Thus the acetaldehyde and benzaldehyde produced, respectively, in these reactions could derive from the evolution of the alkoxo compound, probably via migration of a hydrogen atom from the carbon in α to the oxygen of the alkoxo group, to nickel and successive reductive elimination of HX to give a Ni(0) compound and aldehyde.

All the other products observed in the reactions can be justified by the decarboxylative decomposition of the alkoxo–carbonyl ligand. So the diphenylethane obtained in the reaction with benzoxide should be ascribed to this reaction according to the sequence of Scheme 3.

Even if CO_2 is not present among the reaction products, decarboxylative decomposition could be more or less active in all those reactions in which the alkoxo group succeeds in evolving as far as alkoxo–carbonyl. Control experiments show that RONa ($R = CH_3$, C_2H_5) and CO_2 react at room temperature giving sodium alkylcarbonate, whose IR spectrum (nujol and solution) displays absorptions centered at 1620 and 1090 cm^{-1}.

Formation of the alkylcarbonate might be taken as an indirect test of the instability of the alkoxo–carbonyl with respect to decarboxylative decomposition. Unfortunately, this is not possible as they could also form by a CO_2 reaction having a different origin. In fact, trace amounts of H_2O, which are hard to remove from the alcohol solvent, can produce CO_2 via reductive carbonylation [1].

In order to minimize this reduction, the reactions between Ni complexes and alkoxides were not carried out in alcohol, as this not only increases the reduction but also promotes the dissociation of the initial NiX_2L_2 complex into the free ligand and NiX_2. The reactions were achieved in a benzene–alcohol mixture, THF or CH_2Cl_2, although the last solvent seems not to be consistent in reactions with alkoxides. However, the experimental data show that the best methoxo–carbonyl complex yields are obtained in CH_2Cl_2. Control experiments show that CH_2Cl_2 and alkoxides left to react either under CO or under nitrogen do not produce the carbonylated products which form when the Ni complexes are present.

Experimental

All the solvents were pure reagents and were dried and distilled before use. The gas chromatographic analyses were made with a gas chromatograph Varian Vista 6000, connected to a Varian 4270 integrator, using a 2 m 80/120 Carbopack 3% SP-1500 column and a 1.5 m 80/100 chromosorb 3% SP-2250 column. The gas analysis (CO_2, C_2H_4) was made with a Carlo Erba Fractvap Model C, using a porapak Q Column. The IR spectra were recorded with a Perkin-Elmer spectrophotometer 883. The NMR spectra (^1H, ^{31}P) were recorded with a Varian XL 200, working in the FT mode. The Ni(II)–phosphine complexes were prepared according to the methods described in the literature [14, 10].

Preparation of $NiCl(COOCH_3)(PEt_3)_2$

To $NiCl_2(PEt_3)_2$ (2.82 mmol) in 15 ml of CH_2Cl_2, 3 ml of a methanol solution of sodium methoxide (1 N) were added at room temperature under a carbon monoxide atmosphere. After the methoxide addition, which determined a variation in colour of the solution from brownish-red to orange–yellow, the solution was stirred for a further half an hour and an absorption of gas was observed. The solution was dried *in vacuo* and the residue was extracted by C_6H_6 (10 ml) and filtered. The resulting solution was concentrated (4 ml), and after hexane addition (10 ml) was kept cold (2 °C) overnight. The resulting deposit of orange–red crystals was filtered off (0.84 g, 70%).

The other methoxo–carbonyl complexes were prepared in the same way. The yields are reported in Table 1.

Reaction with ethoxide

(a) To $NiBr_2(PEt_3)_2$ (2.42 mmol) in 20 ml of CH_2Cl_2, 2.5 ml of an ethanol solution of ethoxide (1 N) were added at room temperature under CO atmosphere. The system was stirred for 30 min and after filtration a yellowish-green residue and an orange–yellow solution were obtained. The IR spectrum of the solution presents bands at 2070(w), 1990(s) and 1935(s) cm^{-1} ($Ni(CO)_3(PEt_3) + Ni(CO)_2(PEt_3)_2$), two weak bands at 1775 and 1725 cm^{-1} ($CO(OCH_3)_2 + CH_3CHO$) and a strong band at 1635 cm^{-1} ($NiBr(COOC_2H_5)(PEt_3)_2$). The GC analysis revealed the presence of $CO(OCH_3)_2$ and of CH_3CHO in traces. The solution was concentrated and after cooling to −5 °C yielded a yellow semi-solid product, which, in the IR spectrum (nujol), showed bands centered at 1990, 1935, 1635, 1050 cm^{-1} ($Ni(CO)_2(PEt_3)_2 + NiBr(COOC_2H_5)(PEt_3)_2$) and a band at 1180 cm^{-1} (phosphine oxide).

The yellowish-green residue of the filtered reaction solution was washed with acetone/H_2O (5:2), dried and analysed. IR (nujol): 1630(s, br) cm^{-1}. *Anal.* Found: Ni, 41.3; Br, 2.1* P, trace, Calc. for $Ni(OC_2H_5)_2$: Ni, 39.48. Calc. for $Ni(OH)(OC_2H_5)$:Ni, 48.63%. The product, decomposed by HCl, does not yield CO_2 and presents ethanol to GC analysis.

(b) In a two-branch glass reactor, a solution of $NiBr_2(PEt_3)_2$ (2.31 mmol) in 5 ml CH_2Cl_2, and 2.5 ml of an ethanol solution of ethoxide (1 N) were charged separately. The reactor was closed with a rubber stopper and the solutions were mixed. After 30 min of stirring, the gas phase was analyzed. Only traces of ethylene were observed.

Reaction with benzoxide

To $NiBr_2(PEt_3)_2$ (2.31 mmol) in 10 ml of CH_2Cl_2, $C_6H_5CH_2ONa$ (2.46 mmol) was added under CO at room temperature. After 3 h, the reaction solution was filtered and a greenish residue was separated from the orange–yellow solution. IR (solution): bands at 2075(w), 1990(s), 1935(s) cm^{-1} ($Ni(PEt_3)_2(CO)_2 + NiPEt_3(CO)_3$) and bands at 1710(w) ($C_6H_5CHO$) and 1635(s) ($NiBr(PEt_3)_2COOCH_2Ph$) cm^{-1}. During the spectrum recording the intensity of this last band decreases, whereas the 1990 and 1935 cm^{-1} bands slightly increase. The GC analysis of the solution highlights the presence of benzaldehyde (10 mg) and diphenylethane (20 mg). By drying the reaction solution, a semi-solid oil was obtained; in the IR spectrum it presented bands characteristic of phosphine oxide and Ni(0)–carbonyl complexes. The green residue obtained in the reaction was washed with acetone/H_2O (5:2) and analyzed. *Anal.* Found: Ni, 22.2; Br, 1.5*. Calc. for $Ni(OCH_2C_6H_5)_2$: Ni, 21.53. Calc. for $Ni(OH)(OCH_2C_6H_5)$: Ni, 32.19%.

Reaction with phenoxide

(a) To $NiBr_2(PEt_3)_2$ (3.08 mmol) in 15 ml of CH_2Cl_2, C_6H_5ONa (3.10 mmol) dissolved in absolute ethanol (5 ml) was added under a CO atmosphere at room temperature. The filtered reaction solution shows bands at 1990(s), 1935(s) cm^{-1} and at 1755(w) ($CO(OC_6H_5)_2$) and 1635 ($NiBr(PEt_3)_2COOPh$) cm^{-1}. The GC analysis reveals traces of $CO(OC_6H_5)_2$ (8 mg). The reaction solution was partially evaporated *in vacuo*. Addition of hexane (10 ml) and cooling to −5 °C gave an orange–yellow product which was filtered off and washed with cold hexane (0.45 g). IR (nujol): 1640(s) and 1055(s) cm^{-1}. *Anal.* Found: Ni, 11.9; Br, 16.2; P, 12.4. Calc. for $NiBr(COOPh)(PEt_3)_2$: Ni, 11.85; Br, 16.12: P, 12.51. Calc. for $NiBr(OPh)(PEt_3)_2$: Ni, 12.56; Br, 17.09; P, 13.26%. The product was crystallized from CH_2Cl_2/

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*The bromine might be ascribable to some impurities of NiBr(OH) or NiBr(OR)).

hexane. The intensities of the bands at 1640 and 1055 cm^{-1} decreased, whereas the elemental analysis did not change substantially.

Characterization of the complexes

Methanol analysis

To $NiBr(COOCH_3)(PEt_3)_2$ (0.55 mmol) at 0 °C, a toluene solution (10 ml) saturated with gaseous HCl, containing C_6H_6 (0.855 g) as internal standard was added. The solution was warmed ($T > 50$ °C) and analyzed. The GC analysis reveals the presence of 16.7 mg of methanol, corresponding to 94.9% of the theoretical value (eqn. (8)).

The other samples of $NiX(COOCH_3)(PEt_3)_2$, were analyzed in the same way and the methanol obtained was between 80 and 85% of the theoretical value.

CO analysis

The CO analysis was carried out by decomposing a weighted quantity of samples with HCl in a glass tube. In a typical experiment $NiCl(COOCH_3)(PEt_3))_2$ (0.123 mmol) developed CO (0.072 mmol) and CO_2 (0.003 mmol). The CO values obtained with the other complexes were found to be between 60 and 65% of the theoretical value.

Reactions of $NiX(COOCH_3)(PEt_3)_2$ with methoxide

Under 1 atm. of carbon monoxide

To $NiCl(COOCH_3)(PEt_3)_2$ (0.77 mmol) in THF (10 ml), 2 ml of a methanol solution of CH_3ONa (1 N) were added. The reactor was heated to 120 °C for 1 h and the resulting light yellow solution was analyzed (IR and GC). IR: bands at 1990, 1935 and at 1755 cm^{-1}. GC analysis: presence of $CO(OCH_3)_2$ (6.5 mg). The reaction mixture was filtered and the greenish-yellow residue was washed with warm methanol, then with an acetone/H_2O (2:1) mixture and dried. *Anal* Found: Ni, 26.3; Na and Cl traces. Calc. for $(Ni(OCO_2CH_3)_2)$: Ni, 28.13%. The compound reacts with HCl developing CO_2.

Under CO pressures

$NiCl(COOCH_3)(PEt_3)_2$ (0.98 mmol), THF or methanol (6 ml) and CH_3ONa (2 ml of 1 N methanol solution) were placed in a stainless steel autoclave (56.5 ml). The autoclave was charged with CO up to 20 atm. and then heated for 1 h to 130 °C. The resulting mixture was analysed (IR and GC). IR: bands at 1990 and 1935 (Ni(0)carbonyl complexes), 1755 ($CO(OCH_3)_2$), 1740 ($(COOCH_3)_2$), and 1725 ($HCOOCH_3$) cm^{-1}. GC analysis: presence of dimethylcarbonate (9 mg), dimethyloxalate (10 mg) and methylformate (15 mg). A blank test shows that a methanol solution of CH_3ONa produces $HCOOCH_3$ in the same temperature and CO pressure conditions. The reaction mixture was filtered and the greenish-yellow residue, which developed CO_2 by reaction with HCl, was analyzed. *Anal.* Found: Ni, 27.2%; Na and Cl traces.

Reactions of $NiX(COOCH_3)(PEt_3)_2$ with amines

$NiCl(COOCH_3)(PEt_3)_2$ (0.72 mmol), THF (5 ml) and a test-tube containing $BuNH_2$ (1 ml) were placed in the autoclave which was charged with CO pressure (20 atm.) and heated to 130 °C. When the temperature reached the required level, the autoclave was turned upside down in order to allow the amine to react with the methoxo-carbonyl. The system was left to react for 1 h and then the mixture was analyzed (IR and GC). IR: bands at 1990, 1935 (Ni(0) carbonyls) and 1660 ($BuNHCOOCH_3$) cm^{-1}. The GC analysis reveals the presence of $BuNHCOOCH_3$ (12 mg).

The reaction with aniline was carried out using the procedure described above. The presence of a strong base (NEt_3, Na_2CO_3) was also required. In a typical experiment $NiBrCOOCH_3(PEt_3)_2$ (0.76 mmol) produced 14 mg. of $PhNHCOOCH_3$.

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