Reactivity of Nickel(II) Diphosphine Complexes towards Alkoxides: a New Route to the Synthesis of Nickel(0) Compounds through Nickel(II) Alkoxides

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Reaction of [Ni(L–L)Cl_2] [L–L = $Ph_2P(CH_2)_nPPh_2$, n = 2 (dppe) or 3 (dppp)] with NaOR (R = Me, Et or Pr^i) under a dinitrogen atmosphere afforded [Ni(L–L)$_2$], Ni(OR)$_2$ and aldehyde (or acetone when R = Pr^i) in 1 : 1 : 1 ratio, showing the peculiar reducing effect of alkoxide promoted by the chelating property of the phosphorus ligand. The reaction of NaOMe with [Ni(dcpe)Cl_2] [dcpe = 1,2-bis(dicyclohexylphosphino)-ethane] afforded mainly [Ni_2(dcpe)$_3$] when carried out in the absence of free diphosphine, and [Ni(dcpe)$_2$] in the presence of free diphosphine. The reaction always yields the nickel(0) species [Ni(L–L)(CO)$_2$] when it is carried out under a carbon monoxide atmosphere. The intermediate formation of unstable alkoxo(diphosphine)nickel(II) complexes has been demonstrated by recording the ^{31}P NMR spectra of the reacting solutions at low temperature; in the case of the reaction of [Ni(dcpe)Cl_2] with NaOMe only, it was possible to isolate as a solid the [Ni(dcpe)(OMe)$_2$] complex, which has been fully characterized by analytical and spectroscopic (IR and ^1H, ^{31}P NMR) methods. A possible route by which nickel(0) complexes could be formed is discussed.

A number of alkoxide derivatives of transition elements have been reported. The known nickel(II) alkoxides are polymeric substances, insoluble in common organic solvents,[1] easily hydrolysed on exposure to humidity and inert towards most organic ligands. Only a few alkoxo complexes of Ni, Pd and Pt are known;[2] they are generally unstable and easily undergo thermal decomposition also at room temperature, particularly the nickel compounds.[3]

In pursuit of our interest in the factors which influence the reactions of metal centres in the catalytic carbonylation of alcohols and amines, we have previously described the preparation and reactivity of the alkoxycarbonyl derivatives of several tertiary phosphine complexes of Ni^{II}, Pd^{II} and Pt^{II}.[4] Complexes of formula [$NiL_2X(O_2CR)$] (L = tertiary phosphine; X = Cl, Br or I; R = Et, Ph or CH_2Ph) were prepared by treating [NiL_2X_2] with the stoichiometric amount of sodium alkoxide in alcohol solution under a carbon monoxide atmosphere, but they rapidly decompose to nickel(0) derivatives in the presence of an excess of the alkoxide.

In this paper we describe the reactions of sodium alkoxides with some chelating diphosphine complexes of Ni^{II}, either under carbon monoxide or dinitrogen, and, on the basis of ^{31}P NMR results, suggest a mechanism for the alkoxide reduction to give nickel(0) diphosphine complexes.

Results and Discussion

The reaction of [Ni(L–L)Cl_2] [L–L = $Ph_2P(CH_2)_nPPh_2$, n = 2 (dppe) or 3 (dppp)] with alkoxides RO^- (R = Me, Et or Pr^i) in a 1:2 molar ratio in anhydrous alcohol under a dinitrogen atmosphere proceeded at ambient temperature to give [Ni(L–L)$_2$], Ni(OR)$_2$ and aldehyde (or acetone when R = Pr^i) in quantitative yields according to equation (1)

$$2[Ni(L\text{–}L)Cl_2] + 4R^1R^2CHO^- \longrightarrow [Ni(L\text{–}L)_2] + Ni(OCHR^1R^2)_2 + R^1R^2CO + R^1R^2CHOH + 4Cl^- \quad (1)$$

(R^1,R^2 = H or Me). It was very rapid giving, as soon as the alkoxide was added to the orange suspension of [Ni(L–L)Cl_2], a deep red solution which then lightened and from which a mixture of [Ni(L–L)$_2$] and Ni(OR)$_2$ precipitated. We were not able to isolate the very soluble deep red compounds formed in the first stage; indeed, the colour of the solution lightened, though more slowly, when the reaction was also carried out at low temperature (about −40 °C), and on evaporation of the solution *in vacuo* as quickly as possible a mixture of [Ni(L–L)$_2$] and Ni(OR)$_2$ was always obtained.

The reaction proceeded with the same stoichiometry also when the reagents were mixed in a 1 : 1 molar ratio; in this case the [Ni(L–L)Cl_2] present in excess was quantitatively recovered upon quickly filtering the initial red solution.

The reaction of [Ni(dcpe)Cl_2] [dcpe = 1,2-bis(dicyclohexylphosphino)ethane] with NaOMe in anhydrous methanol under a dinitrogen atmosphere proceeded in a similar way, giving mainly, as final products, [Ni_2(dcpe)$_3$] and green polymeric nickel dimethoxide, according to equation (2). In this case,

$$3[Ni(dcpe)Cl_2] + 6MeO^- \longrightarrow [Ni_2(dcpe)_3] + Ni(OMe)_2 + 2CH_2O + 2MeOH + 6Cl^- \quad (2)$$

however, the solution did not lighten even when it was left to stand for several days. Work-up gave [Ni_2(dcpe)$_3$], contaminated by some [Ni(dcpe)(CO)], besides Ni(OMe)$_2$ and NaCl. Evaporation *in vacuo* of the red solution obtained immediately after the mixing of the reagents afforded, besides NaCl, a red powder which was identified, by means of its elemental analysis, IR and NMR spectra, as [Ni(dcpe)(OMe)$_2$]. The IR spectrum in Nujol mull showed two strong absorption bands at 1081 and 1030 cm^{-1}, ascribable to the O–Me stretching,[3] and the ^1H NMR spectrum in $C_6D_5CD_3$ showed a singlet at δ_H 3.33, ascribable to the OMe resonance. The compound is not stable at room temperature, and slowly decomposes both in the solid state and in solution.

The reaction of [Ni(L–L)Cl_2] complexes with NaOMe in methanol in the presence of an excess of free diphosphine (L–L:Ni ⩾ 1:1) afforded the nickel(0) species [Ni(L–L)$_2$] (L–L = dppe, dppp or dcpe) according to equation (3). It was

$$[Ni(L\text{–}L)Cl_2] + L\text{–}L + 2MeO^- \longrightarrow [Ni(L\text{–}L)_2] + CH_2O + MeOH + 2Cl^- \quad (3)$$

rapid and essentially quantitative with the ligands dppe and dppp, but proceeded more slowly and in lower yields with dcpe. The same reaction, carried out under a carbon monoxide atmosphere (without free diphosphine), occurred rapidly giving [Ni(L–L)$(CO)_2$]. Also in this case the reactions were essentially quantitative, no other nickel phosphine complexes being observed according to the IR and ^{31}P spectra, giving isolated yields of about 80%.

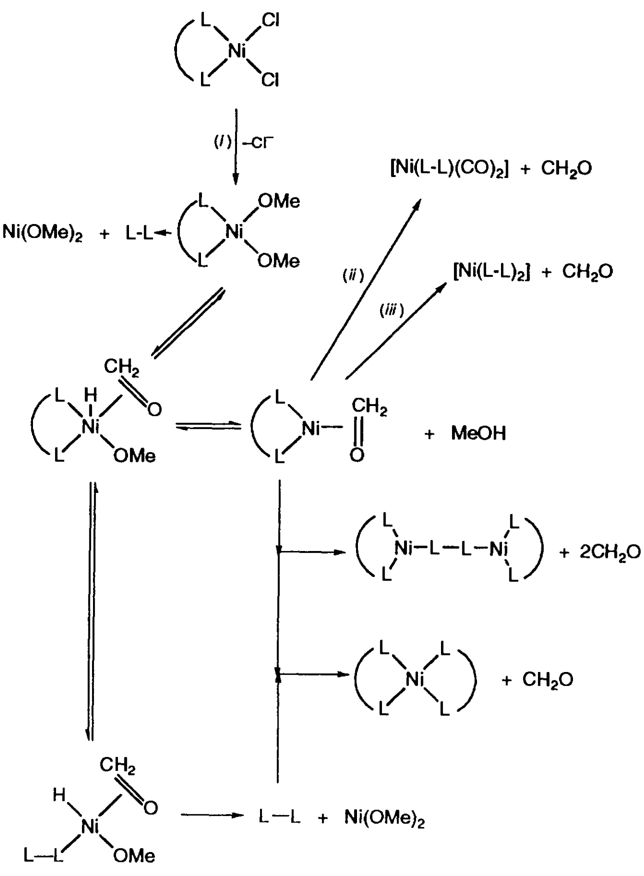
This alkoxide-promoted reduction of the nickel(II) complexes appears therefore to be, among the methods described in the literature,[5–8] the most simple, rapid and convenient for the preparation of [Ni(L–L)$_2$] and [Ni(L–L)$(CO)_2$] compounds when L–L = dppe, dppp or dcpe. However, this is not a general method for the preparation of nickel(0) phosphine complexes. For instance, [Ni(dppb)Cl_2] [dppb = 1,4-bis(diphenylphosphino)butane] and [Ni$(PPh_3)_2Cl_2$] decomposed rapidly when treated with NaOMe in toluene–methanol solution, yielding Ni$(OMe)_2$, NaCl and free phosphine. On the contrary, [Ni{P$(C_6H_{11})_3$}$_2Br_2$] did not react with the methoxide and was recovered unchanged after stirring for 4 d at room temperature.

With the aim of exploring the mechanism of the alkoxide-promoted reduction of the nickel(II) diphosphine complexes, we followed by ^{31}P NMR spectroscopy the reaction either of [Ni(dppe)Cl_2] and of [Ni(dcpe)Cl_2] with alkoxide in toluene–alcohol solution. The reaction of [Ni(dcpe)Cl_2] with NaOMe was studied at room temperature. The ^{31}P NMR spectrum showed initially only a sharp singlet at δ 69.4, characteristic of [Ni(dcpe)$(OMe)_2$]. The intensity of this signal slowly decreased, while a broad new singlet at δ 54.4 appears. A portion of this solution was filtered and evaporated *in vacuo*; the recovered solid showed in its IR spectrum (Nujol mull) a broad absorption band at 1060 cm^{-1}, assignable to the O–Me stretching, along with weak bands at 2780, 2740 and 1600 cm^{-1}, tentatively assigned to the co-ordinated aldehyde, and at 1900 cm^{-1}, assignable to a terminal co-ordinated CO. The ^{31}P NMR spectrum (in $C_6D_5CD_3$) showed, besides weak signals at δ 69.4 and 54.4, various other small peaks at about δ 50 and a signal of medium intensity at δ 46. The ^{31}P NMR spectrum of the initial reaction mixture, after filtration and about 50 h from the start, showed, besides various other small peaks, an intense signal at δ 46.1, characteristic of [Ni_2(dcpe)$_3$].

Since the reaction of [Ni(dppe)Cl_2] was too fast at room temperature, we poured the methoxide solution into a toluene suspension of the complex at −40 °C and immediately recorded the ^{31}P NMR spectrum of the red solution at this temperature. This showed initially only a sharp singlet at δ 46.6, but after about 15 min the intensity of the signal had strongly decreased, while signals at δ 42.4, 32.2 and −15.3 appeared. After 1 h at 0 °C the intensity of the last two signals had strongly decreased and the signal at δ 46.6 completely disappeared. After 1 d at room temperature the solution showed only a strong signal at δ 42.4.

An identical experiment was carried out using sodium ethoxide instead of methoxide: the ^{31}P NMR spectrum at −40 °C showed initially only a sharp singlet at δ 44.4, signals at δ 44.4, 42.4, 32.4 and −14.6 after 20 min and after 1 d at room temperature only the signal at δ 42.4.

These results are consistent with a mechanism involving rapid formation of the nickel(II) dialkoxo complexes [Ni(L–L)$(OR)_2$], moderately stable at room temperature when L–L = dcpe, but very unstable when L–L = dppe or dppp. These complexes, analogously to the more stable [Pt(dppe)$(OMe)_2$],[2b] easily undergo decomposition involving initial β-hydride migration from the alkoxide to the metal, generating an aldehyde. Examples of co-ordinated aldehydes and ketones in phosphine nickel(0) complexes are known,[9] and it is also known that the nickel diphosphine complexes in solution rapidly undergo ligand exchange through dissociation.[10] We therefore suggest that the formation of the nickel(0) diphosphine complexes proceeds mainly according to Scheme 1.



Scheme 1 (*i*) MeO^-; (*ii*) CO; (*iii*) L–L

The sharp singlet signal at δ 46.6 can be confidently assigned to the [Ni(dppe)$(OMe)_2$] complex, on the basis that it is the first which appears in the ^{31}P NMR spectrum of the red solution obtained at −40 °C from [Ni(dppe)Cl_2] and NaOMe and that the same signal shift (−11 ppm) is observed either on passing from [Ni(dppe)Cl_2] to [Ni(dppe)$(OMe)_2$] or from [Ni(dcpe)Cl_2] to the isolated [Ni(dcpe)$(OMe)_2$]. We tentatively assign the signals at δ 54.4 and 32.2 respectively to the relatively more stable [Ni(dcpe)(CH_2O)] and to the very unstable [Ni(dppe)(CH_2O)]. The decomposition path of the nickel(II) dimethoxo complexes depends greatly on the electronic and steric properties of the diphosphine ligand, and therefore it can lead, though in low yields, to products which are different from those shown in Scheme 1. Thus, the ^{31}P NMR spectrum of the deep red toluene–methanol solution obtained from [Ni(dcpe)Cl_2] and NaOMe showed, after 2 d at room temperature and when filtered immediately before the measurement, a broadening of the signals and a lowering of the signal-to-noise ratio, probably due the formation of soluble nickel(I) paramagnetic species.[11] Moreover, the IR spectrum of the solid recovered by evaporation showed an absorption band ascribable to [Ni(dcpe)(CO)]. This is not surprising, since a carbonylphosphine complex of Pt^0 is the major product of the rapid decomposition of the unstable formaldehyde complex [Pt$(PEt_3)_2(CH_2O)$],[12] while the thermolysis of [Pt(dppe)$(OMe)_2$] at room temperature in non-donor solvents generates formaldehyde and small amounts of carbon monoxide, resulting in the formation of stable methoxycarbonyl complexes of Pt^{II}.[2b] It is interesting that in the case of the analogous diphosphinedimethoxo complexes of Ni^{II} we never observed, not even under a carbon monoxide atmosphere, a carbonyl insertion in the Ni–OR bond to give methoxycarbonyl compounds, contrary to what could be expected on the basis of the reported reactions of [2,6-bis(diphenylphosphinomethyl)pyridine)]dichloronickel[4a] and of [Ni$(PR_3)_2Cl_2$] (R = Me or Et), [Ni$(PEt_2Ph)_2Br_2$] and [Ni$(PEtPh_2)_2Br_2$][4d] with NaOMe under CO, and of the facile carbonylation reaction of [Pt(dppe)$(OMe)_2$].[2d]

Experimental

All manipulations were carried out under a pure dinitrogen atmosphere and at room temperature, unless otherwise stated, using standard Schlenk techniques. The solvents used were anhydrous and freshly distilled under dinitrogen. The phosphines were obtained from Strem and used without further purification. The NMR solvents were dried over activated 5 Å molecular sieves and deoxygenated by repeated freezing and pumping cycles. The NMR spectra were recorded on a Varian XL200 spectrometer, ^{31}P shifts being measured with respect to external 85% H_3PO_4, IR spectra on a Perkin-Elmer 883 spectrophotometer. Elemental analysis were carried out with a Carlo Erba EA 1108 analyser.

Reactions of $[Ni(dppe)Cl_2]$.—*With* NaOMe. To a stirred suspension of $[Ni(dppe)Cl_2]$ (500 mg, 0.947 mmol) in methanol (3 cm^3) was added a 0.805 mol dm^{-3} methanolic solution (2.35 cm^3) of sodium methoxide (MeO : Ni = 2 : 1). Immediately a deep red solution formed, which soon lightened and after 15–20 min became a bright yellow suspension. Filtering afforded 457 mg of a solid comprising $[Ni(dppe)_2]^5$ **1** (402 mg, 0.470 mmol) and $Ni(OMe)_2$ **2** (55 mg, 0.455 mmol). The two compounds were separated by treating the recovered solid with toluene, which dissolves **1**. They were identified by comparison of their spectroscopic (IR, NMR) properties with those of pure samples and by elemental analysis (Found: C, 72.4; H, 5.6; Ni, 6.8; P, 14.3. Calc. for $C_{52}H_{48}NiP_4$ **1**: C, 73.0; H, 5.65; Ni, 6.9; P, 14.5. Found: Ni, 48.5. Calc. for $C_2H_6NiO_2$ **2**: Ni, 48.6%). IR (Nujol mull) of **2**: $\tilde{\nu}_{max}/cm^{-1}$ 1077 (OMe). NMR of **1**: $\delta_P(C_6D_5CD_3)$ 42.4 (s); $\delta_H(C_6D_6)$ 7.5 (16 H, m), 7.0 (24 H, m) and 2.12 (8 H, br s).

The reaction was carried out under the same conditions, but with a molar ratio of MeO^- to $[Ni(dppe)Cl_2]$ of 1 : 1. Filtering the reaction mixture 2 min after the addition of the sodium methoxide solution afforded a deep red solution and orange crystalline residue, identified as the starting nickel(II) complex (about the 50% of the initial amount). Complex **1** precipitated from the red methanolic solution in about 15 min.

The same reaction, carried out in toluene plus the stoichiometric amount of 0.805 mol dm^{-3} methanolic sodium methoxide (MeO^- : Ni = 2 : 1), was only slightly slower. Filtration of the crude product obtained after slight concentration of the reaction mixture led to the separation of NaCl and compound **2** from the yellow toluene solution of **1**. Addition of methanol to the toluene solution afforded orange crystals of **1** in good yield.

With NaOMe *in the presence of dppe*. To a stirred suspension of $[Ni(dppe)Cl_2]$ (500 mg, 0.947 mmol) and dppe (377 mg, 0.947 mmol) in methanol (3 cm^3) was added a 0.805 mol dm^{-3} methanolic solution (2.35 cm^3) of sodium methoxide (MeO^- : Ni = 2 : 1). The reaction mixture turned orange, soon lightening and forming a bright yellow suspension in about 10 min. Filtration afforded $[Ni(dppe)_2]$, which was washed with cold methanol and dried *in vacuo* (580 mg, 72% yield). Analysis of the filtrate showed the presence of only $[Ni(dppe)_2]$ and NaCl, consistent with quantitative reaction of the nickel(II) complex with methoxide and free diphosphine.

With NaOEt. To a stirred suspension of $[Ni(dppe)Cl_2]$ (500 mg, 0.947 mmol) in absolute ethanol (3 cm^3) was added a 0.535 mol dm^{-3} ethanolic solution (3.53 cm^3) of NaOEt (EtO^- : Ni = 2 : 1) at 0 °C. Immediately a brown solution formed, which slowly deposited a dark solid. The solid recovered by filtration was dissolved in toluene and pure $[Ni(dppe)_2]$ (252 mg, 62% yield) was isolated as a yellow powder by addition of methanol. The fraction insoluble in toluene was separated by extraction with 95% ethanol and found to be a mixture of NaCl and $Ni(OEt)_2$.

With NaOEt *in the presence of dppe*. The reaction was carried out as described above, but in the presence of free diphosphine {dppe : $[Ni(dppe)Cl_2]$ = 1 : 1}. The reaction mixture lightened immediately after addition of the ethoxide, yielding a bright yellow suspension in about 30 min. Filtration afforded $[Ni(dppe)_2]$, which was washed with cold ethanol and dried *in vacuo* (67% yield). Analysis of the filtrate showed the presence of only $[Ni(dppe)_2]$ and NaCl, consistent with quantitative formation of the nickel(0) complex. Acetaldehyde was detected in the filtrate, after distillation, both by a spot test using fuchsin–sulfurous acid acid reagent[13] and by GLC analysis.

With $NaOPr^i$. To a stirred suspension of $[Ni(dppe)Cl_2]$ (250 mg, 0.471 mmol) in toluene (4 cm^3) was added a 0.255 mol dm^{-3} isopropyl alcohol solution (3.7 cm^3) of $NaOPr^i$ (Pr^iO^- : Ni = 2 : 1) at 0 °C. Immediately a dark red-brown solution formed which slowly deposited a dark solid. The solid recovered by filtration was dissolved in toluene and pure $[Ni(dppe)_2]$ (82 mg, 41% yield) was obtained as a yellow powder by adding methanol to the concentrated solution. The fraction insoluble in toluene was found to be a mixture of NaCl and $Ni(OPr^i)_2$.

Reactions of $[Ni(dppp)Cl_2]$.—*With* NaOMe. To a stirred suspension of $[Ni(dppp)Cl_2]$ (494 mg, 0.91 mmol) in toluene (4 cm^3) was added a 0.505 mol dm^{-3} methanolic solution (3.6 cm^3) of NaOMe (MeO^- : Ni = 2 : 1). A yellow solution was obtained, from which orange crystals and a greenish powder deposited in about 6 h. After separation of the two fractions, carried out as before, the orange crystals were identified as $[Ni(dppp)_2]^6$ **3** (90% yield) (Found: C, 73.2; H, 5.8; Ni, 6.6; P, 13.9. Calc. for $C_{54}H_{52}NiP_4$: C, 73.4; H, 5.9; Ni, 6.6; P, 14.0%). IR (Nujol mull): $\tilde{\nu}_{max}/cm^{-1}$ 1569, 1145, 1083, 967, 960, 912, 832, 800, 749, 736, 692, 642, 509, 491 and 413. ^{31}P NMR (C_6D_6): δ 10.4 (s). The greenish powder was found to be a mixture of NaCl and compound **2**.

With NaOMe *in the presence of free dppp*. To a stirred suspension of $[Ni(dppp)Cl_2]$ (255 mg, 0.471 mmol) and dppp (194 mg, 0.471 mmol) in toluene (5 cm^3) was added a 0.805 mol dm^{-3} methanolic solution (1.17 cm^3) of NaOMe. The reaction mixture gradually lightened and in about 40 min a cloudy orange solution was obtained. Addition of methanol to the filtered solution afforded pure complex **3** (333 mg, 80% yield).

Reactions of $[Ni(dcpe)Cl_2]$.—*With* NaOMe. To a stirred suspension of $[Ni(dcpe)Cl_2]$ (400 mg, 0.74 mmol) in methanol (8 cm^3) was added a 0.805 mol dm^{-3} methanolic solution (1.85 cm^3) of NaOMe (MeO^- : Ni = 2 : 1) causing the formation of a deep red solution which was immediately evaporated *in vacuo*. The residue was redissolved in toluene, the solution filtered to separate NaCl and evaporated *in vacuo* to give a red solid, characterized as $[Ni(dcpe)(OMe)_2]$ **4** (Found: C, 61.5; H, 10.2; Ni, 10.6; P, 11.2. $C_{28}H_{54}NiO_2P_2$ requires C, 61.9; H, 10.0; Ni, 10.8; P, 11.4%). IR (Nujol mull): $\tilde{\nu}_{max}/cm^{-1}$ 1212, 1180, 1161, 1113, 1081 (OMe), 1030 (OMe), 1002, 914, 880, 850, 818, 765, 667, 625, 536 and 509. NMR: $\delta_P(C_6D_5CD_3)$ 69.4 (s); δ_H ($C_6D_5CD_3$) 3.33 (6 H, s, 2 OMe), 2.05 (4 H, br s, 2 CH_2), 1.91 [4 H, d, *J*(PH) 12 Hz, 4 CH] and 1.85–1.03 (40 H, m, 4 C_6H_{10}).

In another experiment the deep red solution obtained after the addition of the sodium methoxide was left under a nitrogen atmosphere at room temperature for 3 d. The very dark solution was then evaporated *in vacuo* and the residue was redissolved in light petroleum. After filtration from the insoluble NaCl and compound **2**, violet crystals of $[Ni_2(dcpe)_3]^7$ **5** were obtained by cooling the solution at −20 °C (Found: C, 67.5; H, 10.4; Ni, 8.4; P, 13.3. Calc. for $C_{78}H_{144}Ni_2P_6$: C, 67.6; H, 10.5; Ni, 8.5; P, 13.4%). IR (Nujol mull): $\tilde{\nu}_{max}/cm^{-1}$ 1210, 1180, 1161, 1113, 1002, 915, 887, 849, 817, 765, 738, 687, 636, 540 and 509. ^{31}P NMR ($C_6D_5CD_3$): δ 46.1 (br s). The IR spectrum of the dark solid recovered by evaporation of the deep red methanolic solution showed, beside bands due to $[Ni_2(dcpe)_3]$, a weak band at 1900 cm^{-1} ascribable to [Ni(dcpe)(CO)].[14]

With NaOMe *in the presence of dcpe*. To a stirred suspension of $[Ni(dcpe)Cl_2]$ (500 mg, 0.90 mmol) and dcpe (380 mg, 0.90 mmol) in toluene (5 cm^3) was added a 0.805 mol dm^{-3} methanolic solution (2.25 cm^3) of NaOMe (MeO^- : Ni = 2 : 1) causing the formation of a deep red solution. The dark residue obtained after evaporation was redissolved in toluene. After filtration and partial concentration of the brown solution, pure [Ni(dcpe)$_2$][7] **6** was recovered as a white solid (620 mg, 76% yield). IR (Nujol mull): $\tilde{\nu}_{max}$/cm^{-1} 1267, 1188, 1177, 1163, 1105, 999, 910, 886, 847, 814, 779, 775, 717 and 635. ^{31}P NMR (C_6D_6): δ 46.7 (s).

Reaction of [Ni(L–L)Cl$_2$] (L–L = *dppe, dppp or dcpe*) *with* NaOMe *in the Presence of Carbon Monoxide.*—To a stirred suspension of [Ni(dppe)Cl$_2$] (150 mg, 0.284 mmol) in methanol (5 cm^3) was added under a carbon monoxide stream at 0 °C a 0.480 mol dm^{-3} methanolic solution (1.20 cm^3) of NaOMe (MeO$^-$: Ni = 2 : 1). In a few seconds an orange solution was obtained, which rapidly lightened to pale yellow and deposited a white solid. The IR spectrum of the filtered solution showed, in the range 1600–2100 cm^{-1}, only the carbonylic bands of [Ni(dppe)(CO)$_2$] **7**. The white solid was identified as pure **7**[15] (mg 120, 82% yield). IR: (Nujol mull): $\tilde{\nu}_{max}$/cm^{-1} 1940 and 2000; (MeOH), 1945 and 2001. ^{31}P NMR ($C_6D_5CD_3$): δ 44.1 (s).

Analogously, starting from [Ni(dppp)Cl$_2$] and [Ni(dcpe)Cl$_2$], the complexes [Ni(dppp)(CO)$_2$] **8** (84% yield) and [Ni(dcpe)(CO)$_2$] **9** (78% yield) were obtained (Found: C, 65.54; H, 5.05; Ni, 11.0; P, 11.6. $C_{29}H_{26}NiO_2P_2$ **8** requires C, 66.05; H, 4.95; Ni, 11.15; P, 11.75; Found: C, 62.0; H, 9.10; Ni, 11.10; P, 11.4. $C_{28}H_{48}NiO_2P_2$ **9** requires C, 62.60; H, 9.00; Ni, 0.90; P, 11.55%). IR (toluene): v_{max}/cm^{-1} 1997 and 1938 (**8**); 1987 and 1926 (**9**). ^{31}P NMR ($C_6D_5CD_3$): δ 25.7 (s) (**8**), 45.9 (s) (**9**).

Reaction of [Ni(PPh$_3$)$_2$Cl$_2$] *and* [Ni(dppb)Cl$_2$] *with* NaOMe.—To a stirred suspension of [Ni(PPh$_3$)$_2$Cl$_2$] (200 mg, 0.30 mmol) in toluene (5 cm^3) was added a 0.505 mol dm^{-3} methanolic solution (1.2 cm^3) of NaOMe (MeO$^-$: Ni = 2 : 1). After a few seconds the suspension became pale green and a green solid deposited, which was filtered off, washed with methanol, dried under vacuum and identified as a mixture of NaCl and compound **2**. Evaporation of the filtrate gave a white solid, identified as pure PPh$_3$.

Analogously, the reaction of [Ni(dppb)Cl$_2$] with sodium methoxide, under the same conditions, yielded **2**, NaCl and free diphosphine.

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