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SYNTHESIS AND CHARACTERIZATION OF SOME NEW ORGANOMETALLIC COMPLEXES OF NICKEL(II) CONTAINING TRIMETHYLPHOSPHINE

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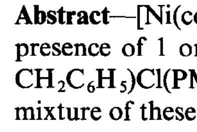
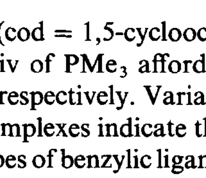
Abstract—[Ni(cod)$_2$]$_2$ (cod = 1,5-cyclooctadiene) oxidatively adds $C_6H_5CH_2Cl$ in the presence of 1 or 2 equiv of PMe_3 affording [Ni(η^3-$CH_2C_6H_5$)Cl(PMe_3)] or *trans*-[Ni(η^1-$CH_2C_6H_5$)Cl(PMe_3)$_2$], respectively. Variable temperature NMR studies carried out with a mixture of these two complexes indicate that both are involved in a fast equilibrium which interchanges the two types of benzylic ligands. The above mentioned compounds decompose in the presence of excess PMe_3 with the formation of [$NiCl_2$(PMe_3)$_3$], [Ni(PMe_3)$_4$] and the reductive elimination product ($C_6H_5CH_2$)$_2$. In addition, the synthesis and spectral characterization of the new complexes *trans*-[Ni(C_6H_5)X(PMe_3)$_2$] (X = Cl, Br), *trans*-[Ni(2,4,6-$C_6H_2Me_3$)X(PMe_3)$_2$] (X = Cl, Br) and [(η^5-C_5H_5)Ni(2,4,6-$C_6H_2Me_3$)(PMe_3)], are also described.

It is well known that the benzyl ligand, $C_6H_5CH_2$, can adopt a variety of coordination modes (which include the alkyl-type coordination, **A**, as well as the pseudoallylic η^3-bonding, **B**) and that the adoption of a particular coordination mode is strongly influenced by the nature of the ML_n fragment to which the benzyl group is bonded. While η^1-interactions are commonly found among transition metal–benzyl complexes,[1] relatively few η^3-structures are known[2] and for nickel only a few examples have been reported to date, among them the η^3-*o*-methylbenzyl derivative, [Ni(η^3-$CH_2C_6H_4$-*o*-Me)Cl(PMe_3)], recently prepared in our laboratory.[3]



A



B

As an extension of this and previous work concerning the chemistry of nickel alkyl and acyl complexes,[4] we now report the formation of η^1- and η^3-benzyl complexes of the compositions [Ni(η^1-$CH_2C_6H_5$)Cl(PMe_3)$_2$] (**1a**) and [Ni(η^3-$CH_2C_6H_5$)Cl(PMe_3)] (**2**), that of the aryl derivatives [NiX(Ar)(PMe_3)$_2$], [Ar = C_6H_5, X = Cl (**3a**); X = Br (**4a**); Ar = 2,4,6-$C_6H_2Me_3$ (mesityl), X = Cl (**5**); X = Br (**6**)] and [Ni(η^5-C_5H_5)(2,4,6-$C_6H_2Me_3$)PMe_3] (**7**) and their reactions with CO to afford the acyl compounds [NiX(η^1-COR)(PMe_3)$_2$], [R = $CH_2C_6H_5$, X = Cl (**1b**); R = C_6H_5, X = Cl (**3b**); X = Br (**4b**)]. Variable temperature NMR studies on the benzyl complexes, **1a** and **2**, have been carried out, and are also reported.

RESULTS AND DISCUSSION

Synthesis and spectroscopic characterization of the benzyl complexes trans-[Ni(η^1-$CH_2C_6H_5$)Cl(PMe_3)$_2$] (1a) *and* [Ni(η^3-$CH_2C_6H_5$)Cl(PMe_3)] (2)

The room temperature reaction of the dichloride, [$NiCl_2$(PMe_3)$_2$], with *ca* 2 equiv of Mg($CH_2C_6H_5$)Cl, produces a brown suspension from which a brown crystalline material can be obtained after work-up. Spectroscopic studies reveal the presence of a mixture of the benzyl derivatives *trans*-[Ni(η^1-$CH_2C_6H_5$)Cl(PMe_3)$_2$] (**1a**) and [Ni(η^3-$CH_2C_6H_5$)Cl(PMe_3)] (**2**). In addition to these products, formation of a very dark, sparingly soluble

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crystalline species is sometimes observed. The latter displays an IR absorption at 3580 cm^{-1}, which indicates the presence of hydroxo ligands, and this, together with the similarity in colour, solubility and other properties with those found for the recently prepared *o*-methylbenzyl compound $[Ni_3(CH_2C_6H_4\text{-}o\text{-}Me)_4(PMe_3)_2(\mu_3\text{-}OH)_2]$,[3] whose structure was determined by X-ray crystallography, suggest an analogous formulation as $[Ni_3(\eta^1\text{-}CH_2C_6H_5)_4(PMe_3)_2(\mu_3\text{-}OH)_2]$. No satisfactory analytical data can however be obtained for this complex which, as with the related *o*-methylbenzyl derivative, decomposes upon attempted recrystallization, even under an inert atmosphere. For these reasons its investigation has not been pursued any further.

Compounds **1a** and **2** are best prepared by the oxidative addition of $C_6H_5CH_2Cl$ to $[Ni(cod)_2]$ in the presence of the required amount of PMe_3, as shown in eqs (1) and (2).

$$[Ni(cod)_2] + C_6H_5CH_2Cl + 2PMe_3 \longrightarrow [Ni(\eta^1\text{-}CH_2C_6H_5)Cl(PMe_3)_2] + 2cod \quad (1)$$

$$[Ni(cod)_2] + C_6H_5CH_2Cl + PMe_3 \longrightarrow [Ni(\eta^3\text{-}CH_2C_6H_5)Cl(PMe_3)] + 2cod. \quad (2)$$

They have been found to be related by an intermolecular process which involves PMe_3 association and dissociation [eq. (3)], and indeed, on a macroscopic scale, compound **2** can be obtained by addition of 1 equiv of PMe_3 to solutions of **2**, while the latter is formed by PMe_3 abstraction from **1a** using $[Ni(cod)_2]$.

$$[Ni(\eta^1\text{-}CH_2C_6H_5)Cl(PMe_3)_2] \underset{+PMe_3}{\overset{-PMe_3}{\rightleftharpoons}} [Ni(\eta^3\text{-}CH_2C_6H_5)Cl(PMe_3)]. \quad (3)$$

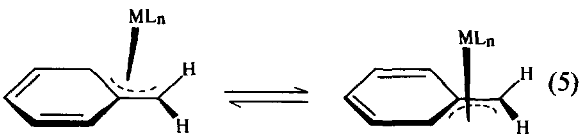
Both compounds have been characterized by IR and ^1H, ^{13}C and ^{31}P NMR spectroscopy. The ^1H NMR spectrum of **1a** shows two singlets at δ 0.98 (18H) and 1.71 (2H) ppm corresponding to the PMe_3 and the methylene benzylic protons, respectively. The lack of observation of coupling is clearly due to an exchange process involving PMe_3 dissociation. A similar situation has been found in other nickel alkyl complexes of related composition, and has been explained in terms of a fast exchange between traces of free PMe_3 and complexed PMe_3, possibly through the intermediacy of a five-coordinate species.[4] Such a process, however, could not be operative in the present system, since addition of free PMe_3 to solutions of **1a** does not increase the rate of PMe_3 exchange, but it rather induces decomposition, with formation of $[NiCl_2(PMe_3)_3]$, $[Ni(PMe_3)_4]$ and $C_{14}H_{14}$ (1,2-diphenylethane) as shown in eq. (4).

$$2[Ni(\eta^1\text{-}CH_2C_6H_5)Cl(PMe_3)_2] + 3PMe_3 \longrightarrow [NiCl_2(PMe_3)_3] + [Ni(PMe_3)_4] + C_{14}H_{14}. \quad (4)$$

Hence, it seems more likely that the process responsible for the observed NMR features implies phosphine dissociation and re-association through the intermediacy of the pseudoallylic complex **2**, and this is not only in accord with the above comments regarding the reversible transformation **1a** $\rightleftharpoons$ **2** but also with the observation of only one set of proton resonances for mixtures of **1a** and **2**, with chemical shifts being an average of those corresponding to compounds **1a** and **2** (see below). As expected, **1a** exhibits a single $^{31}P\{^1H\}$ NMR signal, while in the $^{13}C\{^1H\}$ NMR spectrum a singlet is observed for each of the carbon atoms of the benzyl ligand as well as for those of the PMe_3 groups (Table 1).

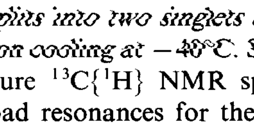
A related situation is found in the η^3-benzyl complex, **2**. The fluxionality of this species is clearly indicated by the appearance of broad, unresolved signals in the NMR spectra. Thus, the $^{31}P\{^1H\}$ NMR exhibits a broad singlet at -7.9 ppm, while the ^1H NMR spectrum displays a broad singlet at 1.0 ppm for the methylene benzylic protons. In the room temperature $^{13}C\{^1H\}$ NMR spectrum, a doublet is observed at δ 15.0 ppm for the PMe_3 ($^1J_{CP} = 30.2$ Hz), a broad singlet at 22.0 ppm for the methylene carbon atom and three resonances (intensity ratio *ca* 2 : 2 : 1) between 117–134 ppm for the *ortho*, *meta* and *para* benzyl carbon atoms. No signal can be found for the *ipso* carbon atom of the benzyl ligand. In order to gain further information on the fluxionality of these species and on their interconversion process, variable temperature NMR studies have been carried out with complex **2** and with approximately equimolar mixtures of **1a** and **2**.

Upon cooling a toluene-d_8 solution of **2** at -60°C, a doublet at 0.9 ppm is observed for the PMe_3 protons ($^2J_{HP} = 9.8$ Hz) and a second doublet at 1.1 ppm ($^3J_{HP} = 21.3$ Hz) for the two benzyl protons, which remain equivalent under these conditions. Only broad, partially resolved signals are found for the aromatic protons. These features are maintained at temperatures down to -90°C, the spectrum becoming less resolved due possibly to viscosity effects. Similarly, the methylene carbon atom gives rise to a doublet at 23.7 ppm ($^2J_{CP} = 11.3$ Hz) due to coupling to the phosphorus nucleus, while four resonances at 133.5 (2C), 128.2 (1C) and 117.7 (2C) are observed in the aromatic region, along with a singlet at 114.6 ppm which is due to the quaternary carbon atom. The equivalence of the two benzyl methylene protons and that of the two *ortho* and the two *meta* carbon atoms can be explained in terms of a fast suprafacial rearrangement,[5] as shown in eq. (5).



This process, however, would not account for the loss of coupling, observed at temperatures above $-10°C$, between the methylene carbon or hydrogen atoms and the ^{31}P nucleus of the phosphine ligand. A second fluxional process, which is very slow in the NMR time scale at temperatures of $-10°C$ and below, must therefore operate at temperatures above $-10°C$, and this is proposed to be the intermolecular process depicted in eq. (3), that, as already indicated, interrelates complexes **1a** and **2** through a PMe_3 dissociation and association process. Its occurrence can be conclusively demonstrated by variable temperature NMR studies. Thus, the $^{31}P\{^1H\}$ NMR of a *ca* 1 : 1 mixture of **1a** and **2** exhibits, at room temperature, a very broad signal, which splits into two singlets at -7.9 (**1a**) and -16.4 (**2**) on cooling at $-40°C$. Similarly, the room temperature $^{13}C\{^1H\}$ NMR spectrum displays three broad resonances for the *ortho*, *meta* and *para* carbon atoms of species **1a** and **2**, present in the frozen equilibrium of eq. (3). This temperature-dependent behaviour clearly demonstrates the existence of the equilibrium between the η^1-benzyl complexes **1a** and the pseudoallylic species **2**.

In conclusion, two different types of fluxional processes are observed for complex **2**. A suprafacial jump, similar to that observed in other benzyl complexes,[5,6] which is very fast even at $-90°C$, and an intermolecular phosphine exchange with traces of PMe_3 present in solution. From the above data and by similarity with the structure found for the *o*-methylbenzyl analogue by X-ray studies,[3] structure **C** can be proposed for this compound.



C

Aryl derivatives of composition $[NiAr(X)(PMe_3)_2]$ *and* $[(\eta^5\text{-}C_5H_5)Ni(Ar)(PMe_3)]$. *Preparation and spectral properties*

The addition of *ca* 1 equiv of the Grignard reagent $Mg(C_6H_5)Br$ to a suspension of $[NiCl_2(PMe_3)_2]$ in diethyl ether, produces extensive decomposition and formation of the desired aryl derivative only in very low yields. The chloride complex $[Ni(C_6H_5)Cl(PMe_3)_2]$ (**3a**), and its bromide analogue, $[Ni(C_6H_5)Br(PMe_3)_2]$ (**4a**), can be obtained in good yields by the oxidative addition of C_6H_5X (X = Cl, Br), to $[Ni(cod)_2]$, in the presence of 2 equiv of PMe_3. While the reaction with bromobenzene takes place readily under ambient conditions, that of chlorobenzene requires heating at 60°C, for 24 h, for completion.

NMR studies for the complexes $[Ni(C_6H_5)X(PMe_3)_2]$ indicate a square-planar structure with *trans* phosphine ligands. Thus, the ^1H NMR spectrum for complex **4a** shows a virtually coupled triplet at 0.9 ppm, characteristic of bisphosphine compounds with strong coupling between the phosphorus nuclei ($^2J_{HP_{app}} = 3.6$ Hz). In addition, the phosphine ligands give rise to a singlet in the $^{31}P\{^1H\}$ NMR spectrum and to a triplet at 13.6 ppm in the $^{13}C\{^1H\}$ NMR. Other pertinent NMR data for these aryl derivatives are included in Table 1 and require no further comment.

Upon addition of 1 equiv of the Grignard reagent derived from the mesityl ligand, $Mg(2,4,6\text{-}C_6H_2Me_3)Br$, to a suspension of $[NiCl_2(PMe_3)_2]$, a fairly clean and fast reaction takes place which provides good yields (*ca* 60%) of the mesityl derivative $[Ni(2,4,6\text{-}C_6H_2Me_3)Br(PMe_3)_2]$ (**6**). Formation of this bromo derivative is obviously due to a metathetical replacement of the chloride ligand in complex $[Ni(2,4,6\text{-}C_6H_2Me_3)Cl(PMe_3)_2]$ (**5**) by the bromide present in solution. Similar M—X to M—X′ exchanges (X′ = heavier halogen) are frequently observed during alkylation reactions.[7,8] For instance, alkylation of $[M(\eta^5\text{-}C_5H_5)_2Cl_2]$ (M = Ti, Zr, Hf) with $Mg(CH_2SiMe_3)Br$, gives the bromo-alkyl product $[M(\eta^5\text{-}C_5H_5)_2Br(CH_2SiMe_3)]$, without contamination of the chloro complex, and the driving force for this exchange has been associated with the "hard" nature of the Mg^{2+} ion. The chloride derivative $[Ni(2,4,6\text{-}C_6H_2Me_3)Cl(PMe_3)_2]$ (**5**) can be obtained by reaction of the dichloride, $[NiCl_2(PMe_3)_2]$, with 1 equiv of the diaryl magnesium reagent, $Mg(2,4,6\text{-}C_6H_2Me_3)_2$. Compounds **5** and **6** are highly crystalline materials, soluble in common organic solvents and fairly air stable, even in solution. Spectroscopic data for these compounds (Table 1) are also in accord with their formulation as *trans*-$[Ni(2,4,6\text{-}C_6H_2Me_3)X(PMe_3)_2]$.

Interaction of **5** or **6** with an excess of NaCp (1.5 equiv), produces the cyclopentadienyl derivative $[Ni(\eta^5\text{-}C_5H_5)(2,4,6\text{-}C_6H_2Me_3)(PMe_3)]$ (**7**) in high yields [eq. (6)].

$$[Ni(2,4,6\text{-}C_6H_2Me_3)X(PMe_3)_2] + NaCp \longrightarrow [CpNi(2,4,6\text{-}C_6H_2Me_3)(PMe_3)] + NaX + PMe_3. \quad (6)$$

Table 1. Selected NMR data for the new complexes

	^{1}H[a]				^{31}P{^{1}H}	^{13}C{^{1}H}[b]			
		R					R		
Compound	PMe$_3$	CH$_3$	CH$_2$	Aromatic		PMe$_3$	CH$_3$	CH$_2$	Aromatic
Ni(η^1-CH$_2$C$_6$H$_5$)Cl(PMe$_3$)$_2$ (**1a**)[c]	0.98s	—	1.71s	7.0–7.7m	−16.45s	12.9s	—	7.2s	146.2s (C) 123.9 s (CH) 127.8s (CH) 129.3s (CH)
Ni(η^3-CH$_2$C$_6$H$_5$)Cl(PMe$_3$) (**2**)[c]	0.87pst (6.4)	—	1.03brs	6.5–7.5m	−7.73brs	15.0d (30.2)	—	22.0bs	117.4s (2CH) 127.8s (CH) 133.4s (2CH)
Ni(C$_6$H$_5$)Cl(PMe$_3$)$_2$ (**3a**)[d,e]	0.80brs	—	—	6.7–7.4m	−14.5s	12.4brs	—	—	121.5s (CH) 126.7s (2CH) 136.0s (2CH)
Ni(C$_6$H$_5$)Br(PMe$_3$)$_2$ (**4a**)[c]	0.87pst (3.6)	—	—	6.6–7.4m	+12.7s	13.6pst (13.6)	—	—	121.6s (CH) 126.9s (2CH) 135.9s (2CH) 156.4t (*C*—Ni) (34.5)
Ni(2,4,6-C$_6$H$_2$Me$_3$)Cl(PMe$_3$)$_2$ (**5**)[f]	0.87pst (3.6)	2.20s 2.70s (2Me)	—	6.58s	−13.6s	13.4t (13.8)	20.6s 25.6s (2Me)	—	125.9t (2CH) (3.4) 131.2s (*C*Me) 140.6s (2*C*Me)
Ni(2,4,6-C$_6$H$_2$Me$_3$)Br(PMe$_3$)$_2$ (**6**)[f]	1.08pst (3.5)	2.12s 2.70s (2Me)	—	6.49s	−13.6s	14.8t (14.2)	20.6s 25.4s (2Me)	—	126.3s (2CH) 131.8s (*C*Me) 140.6s (2*C*Me) 149.7t (*C*—Ni) (34.5)

$(C_5H_5)Ni(2,4,6\text{-}C_6H_2Me_3)(PMe_3)$ (**7**)[d,g]	0.62s (9.3)	2.27s 2.70s (2Me)	—	6.79brs	−2.6s	18.3d (29.5)	20.6s	—	125.8s (2CH) 130.9s (*C*Me) 138.5d (C—Ni) (36.1) 145.7s (2*C*Me)
$Ni(COCH_2C_6H_5)Cl(PMe_3)_2$ (**1b**)[c]	0.78s	—	3.81s	7.0–7.6m	−16.0s	13.1s	—	58.4s	126.4s (CH) 128.4s (CH) 129.7s (CH) 134.7s (C)
$Ni(COC_6H_5)Cl(PMe_3)_2$ (**3b**)[c,h]	1.11pst (3.7)	—	—	7.44m 8.30m	−14.1s	12.9pst (14.1)	—	—	127.5s (2CH) 128.5s (2CH) 131.7s (CH) 140.9s (C)
$Ni(COC_6H_5)Br(PMe_3)_2$ (**4b**)[c,i]	1.10pst (3.3)	—	—	7.43m 8.28m	−16.5s	13.6pst (14.1)	—	—	127.3s (2CH) 128.5s (2CH) 131.6s (CH) 140.9s (C)

Coupling constants in Hz. pst = pseudotriplet.

[a] In parentheses J(HP).

[b] In parentheses J(CP).

[c] In CD_2Cl_2.

[d] In C_6D_6.

[e] Fluxional at r.t.

[f] In $CDCl_3$.

[g] δC_5H_5 5.17s; C_5H_5 90.3s.

[h] δNi—CO 253.0t (26.5).

[i] δNi—CO 253.4t (23.7).

As expected, the Cp protons give rise to a singlet at 5.17 ppm, indicating pentahapto coordination to the nickel atom. ^{13}C and ^{31}P NMR studies are also in agreement with the proposed formulation. Compound **7** is very thermally stable and can be sublimed under vacuum (0.1 mm), at 100°C, without decomposition.

Carbonylation reactions

Interaction of carbon monoxide (20°C, 1 atm) with compounds **1a**, **3a** and **4a**, produces the corresponding insertion products, **1b**, **3b** and **4b**, as exemplified in eq. (7) for the benzyl derivative **1b**.

$$[Ni(\eta^1\text{-}CH_2C_6H_5)Cl(PMe_3)_2] + CO \longrightarrow [Ni(\eta^1\text{-}COCH_2C_6H_5)Cl(PMe_3)_2]. \quad (7)$$

All these carbonyl species are orange crystalline solids, which show no tendency towards CO dissociation under ambient conditions. The presence of an acyl ligand is indicated by the appearance of a medium intensity IR band in the region 1600–1630 cm^{-1}, due to the CO stretching of the coordinated acyl group. The similarity of their NMR spectra with those of the parent compounds **1a**, **3a** and **4a**, clearly suggests conservation of the *trans* geometry. At variance with the behaviour found for these compounds, carbonylation of the mesityl derivatives **6** and **7**, cannot be achieved even under rather forcing conditions (4–5 atm of CO, 50–60°C). This is likely due to steric hindrance of the *o*-methyl groups of the mesityl ligand,[9] which may prevent association of CO to yield the aryl–carbonyl intermediate species proposed for the carbonylation reaction.

EXPERIMENTAL

Microanalyses were by Pascher Microanalytical Laboratory, Bonn and the Microanalytical Service of the University of Sevilla. The spectroscopic instruments used were Perkin–Elmer models 577 and 684 for IR spectra and Varian XL-200 for ^1H, ^{13}C and ^{31}P NMR spectra. All preparations and other operations were carried out under oxygen-free nitrogen, following conventional Schlenk techniques. Solvents were dried and degassed before use. The light petroleum used had b.p. 40–60°C. PMe_3,[10] $NiCl_2(PMe_3)_2$[11] and $Ni(cod)_2$[12] were prepared according to literature methods.

$[Ni(\eta^1\text{-}CH_2C_6H_5)Cl(PMe_3)_2]$ (**1a**) *and* $[Ni(\eta^3\text{-}CH_2C_6H_5)Cl(PMe_3)]$ (**2**)

Since the conventional Grignard route does not provide reproducible and efficient procedures for the independent preparation of compounds **1a** and **2** (see Results and Discussion), only the oxidative addition of $C_6H_5CH_2Cl$ to $[Ni(cod)_2]$ procedure is reported.

To a stirred suspension of $[Ni(cod)_2]$ (0.274 g, *ca* 1 mmol) in 30 cm^3 of diethyl ether, cooled to -70°C, an excess of $C_6H_5CH_2Cl$ (0.15 cm^3, 1.3 mmol) and 0.2 cm^3 of PMe_3 (2 mmol) were added. The reaction mixture was warmed and stirred at room temperature for 20 h, when a yellow–brown solution was obtained. The solvent was removed under vacuum, the residue extracted with 20 cm^3 of diethyl ether and filtered to give a clear solution from which yellow–brown crystals of the desired product were collected after partial removal of the solvent and cooling overnight. Yield 0.2 g, *ca* 60%.

A similar reaction, using 1 equiv of PMe_3, provided the pseudoallyl complex **2** in *ca* 50% yield. Complex **2** is obtained as red crystals from diethyl ether. Found: C, 45.9; H, 6.2. Calc. for $C_{10}H_{16}PClNi$: C, 45.9; H, 6.1%.

Interconversion reactions of **1a** *and* **2**

(a) To a suspension of $[Ni(\eta^3\text{-}CH_2C_6H_5)Cl(PMe_3)]$ (**2**) (0.26 g, *ca* 1 mmol) in Et_2O (20 cm^3), PMe_3 was added (0.1 cm^3, 1 mmol). The mixture was stirred for 30 min, during which time the red starting material dissolved forming a brown solution. The solvent was evaporated to dryness and the residue crystallized from Et_2O to afford yellow crystals of **1a** in 60% yield.

(b) To a mixture of $[Ni(\eta^1\text{-}CH_2C_6H_5)Cl(PMe_3)_2]$ (**1a**) (0.1 g, *ca* 0.3 mmol) and $[Ni(cod)_2]$ (0.05 g, *ca* 0.15 mmol), Et_2O (10 ml) was added. The solution, initially brown–yellow, darkened to red. After stirring for 10 min, the solution was cooled to produce compound **2** in 20% yield.

Reaction of $[Ni(\eta^1\text{-}CH_2C_6H_5)Cl(PMe_3)_2]$ (**1a**) *with an excess of* PMe_3

A solution of **1a** (0.33 g, *ca* 1 mmol) in Et_2O (20 cm^3) was treated with 0.5 cm^3 of PMe_3. The mixture was stirred at room temperature for 3 h and cooled at -30°C. Crystalline dark blue $[NiCl_2(PMe_3)_3]$ (0.15 g, 0.4 mmol) was filtered off and the remaining pale solution was evaporated to dryness. ^1H, $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ studies, carried out with a C_6D_6 solution of the residue, reveal the presence of $[Ni(PMe_3)_4]$ and $C_{14}H_{14}$ (1,2-diphenylethane, identified by comparison of its IR, ^1H and ^{13}C NMR spectra with those of an authentic sample) as the major species in solution.

$[Ni(C_6H_5)X(PMe_3)_2]$ [X = Cl (**3a**); Br (**3b**)]

These compounds are prepared as described above for the benzyl derivative **1a**, using C_6H_5X (X = Cl, Br). The reaction of $[Ni(cod)_2]$ with C_6H_5Br was complete within about 4 h, while that with C_6H_5Cl required stirring in tetrahydrofuran, at 50–60°C for 20–24 h. Yields were about 50–65%, and the compounds could be crystallized from diethyl ether. $[Ni(C_6H_5)Cl(PMe_3)_2]$. Found: C, 44.8; H, 7.2. Calc. for $C_{12}H_{23}P_2ClNi$: C, 44.6; H, 7.1%. $[Ni(C_6H_5)Br(PMe_3)_2]$. Found: C, 39.1; H, 6.3. Calc. for $C_{12}H_{23}P_2BrNi$: C, 39.2; H, 6.3%.

$[Ni(2,4,6\text{-}C_6H_2Me_3)X(PMe_3)_2]$, [X = Cl (**5**); Br (**6**)] *and* $[Ni(2,4,6\text{-}C_6H_2Me_3)(C_5H_5)PMe_3]$ (**7**)

2.7 cm^3 of a 0.55 N solution of $Mg(2,4,6\text{-}Me_3C_6H_2)_2$ in tetrahydrofuran (*ca* 1.5 eq) were added to a cold (−60°C) suspension of $[NiCl_2(PMe_3)_2]$ (0.42 g, 1.5 mmol) in Et_2O (30 cm^3). The solution was allowed to reach room temperature and stirred for 5 h. The solvent was then stripped off under reduced pressure and the residue extracted with 25 cm^3 of Et_2O and centrifuged. Upon cooling at −30°C overnight the product was obtained as brown–yellow crystals (0.33 g, 60% yield).

The bromide derivative, **6**, was prepared similarly, but using $Mg(2,4,6\text{-}C_6H_2Me_3)Br$ as the alkylating reagent. The reaction mixture, composed of 2 mmol of $[NiCl_2(PMe_3)_2]$ and 2 mmol of the Grignard reagent was stirred at −60°C for 30 min and at room temperature for an additional 20 min (Yield 0.51 g, 62%). Found: C, 44.0; H, 7.2. Calc. for $C_{15}H_{29}P_2BrNi$: C, 43.9; H, 7.1%.

The reaction of **5** or **6** with an excess of NaCp (1.5 equiv) at 20°C for 12 h, produces complex **7** in 80% yield as red–brown needles. Found: C, 64.0; H, 8.6. Calc. for $C_{17}H_{25}PNi$: C, 64.0; H, 7.8%.

$[Ni(COR)X(PMe_3)_2]$, [R = $C_6H_5CH_2$, X = Cl (**1b**); R = C_6H_5, X = Cl (**3b**); X = Br (**4b**)]

Carbon monoxide was bubbled at room temperature through a solution of the alkyl or aryl precursors, **1a**, **3a** or **4a**, in diethyl ether (*ca* 0.5 mmol; 25 cm^3) for about 5 min, after which time an orange crystalline precipitate of the carbonylation product was obtained. The solvent was removed under reduced pressure and the resulting solid recrystallized from diethyl ether at 0°C, to provide orange crystals of the desired products in *ca* 90% yield. $[Ni(COCH_2C_6H_5)Cl(PMe_3)_2]$. IR (Nujol mull) 1600 cm^{-1} (CO). $[Ni(COC_6H_5)Cl(PMe_3)_2]$. Found: C, 44.7; H, 6.8. Calc. for $C_{13}H_{23}P_2ClONi$: C, 44.4; H, 6.6%. IR (Nujol mull) 1610 cm^{-1} (CO). $[Ni(COC_6H_5)Br(PMe_3)_2]$. Found: C, 39.8; H, 5.9. Calc. for $C_{13}H_{23}P_2BrONi$: C, 39.4; H, 5.8%. IR (Nujol mull) 1625 cm^{-1} (CO).

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