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Journal of Organometallic Chemistry 643–644 (2002) 331–341

Journal of Organo metallic Chemistry

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Synthesis and reactivity studies on alkyl–aryloxo complexes of nickel containing chelating diphosphines: cyclometallation and carbonylation reactions

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Received 16 July 2001; accepted 27 September 2001

Dedicated to Professor F. Mathey on the occasion of his 60th birthday

Abstract

Nickel alkyl–aryloxo complexes of composition $Ni(R)(O\text{–}C_6H_3\text{–}2,6\text{-}Me_2)(P\text{–}P)$ ($R = CH_2SiMe_3$, CH_3, CH_2CMe_2Ph; $P\text{–}P{=}PPr^i_2(CH_2)_nPPr^i_2$, $n = 2$ (dippe) or 3 (dippp)) have been synthesized. While the (trimethylsilyl)methyl and the methyl derivatives are stable in solution at room temperature, the bis-neophyl ($R = CH_2CMe_2Ph$) complexes undergo a cyclometallation reaction that leads to the metallacycles $\overline{Ni(CH_2CMe_2\text{-}o\text{-}C}_6H_4)(P\text{–}P)$ together with 2,6-dimethylphenol. The alkyl–aryloxo complexes cleanly react with carbon monoxide giving products resulting from CO insertion and reductive elimination, i.e. $Ni(CO)_2(P\text{–}P)$ and the corresponding 2,6-dimethylphenyl carboxylates quantitatively. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Alkyl; Aryloxide; Carbonylation; Nickel; Metallacycle

1. Introduction

Late transition metal complexes containing alkoxide ligands often display interesting reactivity patterns that are relevant to the mechanism of several important catalytic processes [1]. However, the synthesis of these compounds is often hampered by their low stability and their tendency to form alkoxo-bridged dimers or even to polymerize into highly insoluble solids [2]. In contrast, aryloxide ligands usually provide higher thermal stability and tend to coordinate in a terminal form. Perhaps for this reason, many aryloxides of the Group 10 metals have been prepared and their reactivity studied in some detail, among these, several (aryloxo)alkyl complexes of Ni that contain monodentate phosphine [3] or chelating nitrogen ligands [4]. This type of compound is involved in C–O bond forming and cleavage reactions [5]. In the present contribution, we describe the synthesis of some new nickel derivatives of the bulky ligand 2,6-dimethylphenoxide, stabilized by the chelating diphosphines 1,2-bis(diisopropylphosphino)-ethane (dippe) or 1,3-bis(diisopropylphosphino)propane (dippp), and our first results in the study of their chemical reactivity.

2. Results and discussion

The reaction of alkyl complexes with alcohols constitutes a mild and efficient method for the synthesis of metal alkoxides [2,5,6]. Following this approach, we have attempted the preparation of the desired (aryloxo)alkyl complexes by means of the reaction of nickel dialkyl complexes of composition NiR_2(dippe) and NiR_2(dippp) with 2,6-dimethylphenol. The required alkyl derivatives **2**–**3**, are actually synthesized by ligand exchange reactions, using the corresponding pyridine

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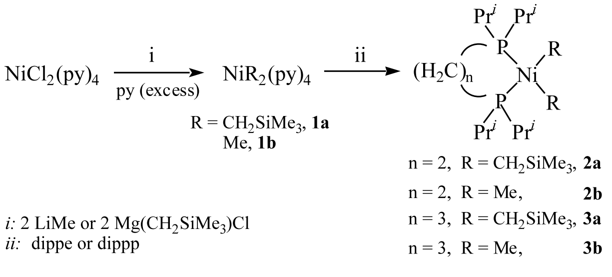
0022-328X/02/$ - see front matter
PII: S0022-328X(01)01323-7

(py) [7] or *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (tmed) [8] complexes as starting materials. The low thermal stability of these precursors and their high reactivity toward O_2 and H_2O pose some experimental difficulties to this procedure. However, considerable simplification is introduced by the use of the pyridine dialkyls **1a**,**b** without previous isolation, so that compounds **2** and **3** may be readily obtained in 50–65% overall yield (Scheme 1). Attempts to prepare the corresponding 2-methyl-2-phenylpropyl (neophyl) derivatives proved unsuccessful and gave no isolable product. However, the failure of this procedure has been noted previously [7], and may be due to the poor thermal stability of the $Ni(CH_2CMe_2Ph)_2(py)_2$ complex intermediate.

NMR studies on compounds **2** and **3** are in accord with the proposed structures. As expected, their $^{31}P\{^1H\}$ spectra consist of a single peak, while in the $^{13}C\{^1H\}$ spectra, a more complex resonance is observed for the Ni-bound C atoms. This appears as an apparent doublet of doublets in the spectra of the dippe derivatives **2a**,**b**, and as a multiplet in those of the dippp complexes **3a**,**b**, due to the coupling to the two magnetically inequivalent ^{31}P nuclei. The simulation of the spin system in the dippe and dippp derivatives shows that, whereas, for the former it approaches a first order coupling situation ($J_{PP'} \approx 5$ Hz), in the case of the latter the coupling of the ^{31}P nuclei has a significantly larger value of ca. 25 Hz (Table 1).

Somewhat disappointingly, the dialkyl derivatives **2** and **3** are remarkably inert toward reaction with 2,6-dimethylphenol, even after prolonged heating at 60 °C in THF. Therefore, in order to prepare the desired (aryloxo)alkyl compounds, we have considered as precursors related complexes of the monodentate phosphine PMe_3, **4** and **5** (Scheme 2). Use of the known compounds $Ni(CH_2SiMe_3)_2(PMe_3)_2$ [7a] and $Ni(R)Cl(PMe_3)_2$ (R = Me, **5b** [9]; CH_2CMe_2Ph, **5c** [10]) leads initially to aryloxide complexes **6** and then to the diphosphine species **7** and **8** (Scheme 2). At variance with **2a** and **3a**, the bis(trimethylsilyl) complex **4** reacts cleanly with 2,6-dimethylphenol at room temperature, giving rise to **6a**. In turn, the analogous methyl (**6b**) and neophyl (**6c**) derivatives are obtained when **5b** or **5c** are treated with sodium 2,6-dimethylphenolate. As anticipated, complexes **6a**–**c** undergo ligand exchange reactions with dippe or dippp providing **7a**–**c** and **8a**–**c** in nearly quantitative yield. All these compounds can be isolated as red or brown crystalline solids, soluble in hydrocarbon solvents. The X-ray structure of the trimethylsilyl derivatives **7a** and **8a** have been determined, and will be discussed at a later stage (Figs. 1 and 2).



Scheme 1.

The $^{31}P\{^1H\}$-NMR spectra of complexes **7a**–**b** and **8a**–**b** display AX spin systems with small (0–5 Hz) J_{PP} values for the dippe derivatives and close to 30 Hz for those of dippp, as previously noted for the dialkyl complexes. It is likely that these differences are a reflection of a deviation of the P–Ni–P angle in compounds **8** from the ideal value of 90° (vide infra). In spite of the relatively large bulk of the ligands attached to the Ni center, the ^1H and ^{13}C spectra of **7**–**8** display two sets of signals for the isopropyl groups, and a single methyl resonance for the 2,6-dimethylphenolate, indicating that the aryloxide unit rotates freely about the Ni–O and C–O bonds (Tables 2 and 3).

In contrast with the trimethylsilyl and methyl complexes **7a**,**b** and **8a**,**b**, the neophyl complexes **7c** and **8c** are not stable in solution at room temperature. Instead, they undergo a cyclometallation reaction that cleanly leads to the metallacycles **9** and **10**, together with 2,6-dimethylphenol (Scheme 3). As shown, these complexes can be prepared by an alternative route consisting of a ligand exchange reaction from the previously known PMe_3 derivative **11** [11] (Table 4).

We have shown recently that palladium neophyl complexes bearing PMe_3 ligands can be readily cyclometallated under a variety of experimental conditions [12,13]. These studies have provided mechanistic evidence that suggests the intermediacy of a cationic π-arene intermediate. It is therefore reasonable to assume that the cyclometallation of the Ni compounds **7c** and **8c** follows a similar reaction pathway (Scheme 4), consisting in the dissociation of the 2,6-dimethylphenolate ligand, which subsequently acts as a base, deprotonating the cationic intermediate **12**. In this regard, it should be mentioned however, that complex **6c**, that is, the PMe_3 analogue of **7c** and **8c**, is more stable in solution and does not undergo the cyclometallation reaction under similar conditions.

The carbonylation of aryloxo(methyl) nickel complexes has been studied by Yamamoto [5], who showed that it involves the migratory insertion of CO into the Ni–C bond followed by reductive elimination of the corresponding aryl acetate. The aryloxo complexes **7a**–**c** and **8a**–**c** also react cleanly with CO (20°, 1 atm) affording the carbonyl complexes $Ni(CO)_2(P–P)$ (P–P=dippe or dippp) together with the expected 2,2-dimethylphenyl carboxylates in nearly quantitative yield (Scheme 5). Interestingly, the carbonylation of the CH_2SiMe_3 derivatives **7a** and **8a** also yields the aryl

Table 1
$^{31}P\{^{1}H\}$-, ^{1}H- and $^{13}C\{^{1}H\}$-NMR data for complexes **2a**, **2b**, **3a** and **3b**

	$^{31}P\{^{1}H\}$ [a]	^{1}H		$^{3}C\{^{1}H\}$ [a]	
		Ni–R	$Pr^i_2P(CH)_nPPr^i_2$	Ni–R	$Pr^i_2P(CH)_nPPr^i_2$
$Ni(CH_2SiMe_3)_2$-(dippe) (**2a**)	71.8	0.30 (m, 4H, $^{*}J_{HP} = 5.7$, 14.0, CH_2) 0.50 (s, 9H, $SiCH_3$)	0.87 (dd, 12H, $^{3}J_{HH} = 7.2$, $^{3}J_{HP} = 11.7$, CH_3) 0.93 (m, 4H, CH_2) 1.12 (dd, 12H, $^{3}J_{HH} = 7.0$, $^{3}J_{HP} = 14.2$, CH_3) 1.99 (h, 4H, $^{3}J_{HH} = 7.2$, CH)	−2.4 (m, $^{*}J_{CP} = 19$, 66, CH_2) 5.4 (CH_3)	18.1 (4C, CH_3), 19.7 (4C, CH_3) 20.1 (pt, 2C, $^{*}J_{CP} = 19$, CH_2) 24.2 (d, 4C, $^{1}J_{CP} = 18$, CH)
$NiMe_2$(dippe) (**2b**)	76.4	0.54 (m, 6H, $^{*}J_{HP} = 4.1$, 9.3,CH_3)	0.85 (dd, 12H, $^{3}J_{HH} = 7.0$, $^{3}J_{HP} = 11.7$, CH_3) 1.01 (m, 4H, CH_2) 1.11 (dd, 12H, $^{3}J_{HH} = 7.2$, $^{3}J_{HP} = 14.6$, CH_3) 1.95 (h, 4H, $^{3}J_{HH} = 7.8$, CH)	1.6 (m, $^{*}J_{CP} =$ 20, 74, CH_3)	18.2 (4C, CH_3), 19.4 (4C, CH_3) 21.1 (dd, 2C, $^{1}J_{CP} = 21$, $^{2}J_{CP} = 17$, CH_2) 24.4 (d, 4C, $^{1}J_{CP} = 19$, CH)
$Ni(CH_2SiMe_3)_2$-(dippp) (**3a**)	17.3	0.06 (m, 4H, $^{*}J_{HP} = 9.7$, CH_2) 0.51 (s, 9H, $SiCH_3$)	0.77 (m, 4H, CH_2) 0.95 (dd, 12H, $^{3}J_{HH} = 7.1$, $^{3}J_{HP} = 10.5$, CH_3) 1.20 (dd, 12H, $^{3}J_{HH} = 7.4$, $^{3}J_{HP} = 13.7$, CH_3) 1.42 (m, 2H, CH_2) 2.01 (m, 4H, CH)	−0.2 (m, CH_2) 5.2 (CH_3)	17.7 (4C, CH_3) 17.9 (pt, 2C, $^{*}J_{CP} = 9$, CH_2), 20.7 (4C, CH_3) 21.8 (1C, CH_2), 25.0 (4C, CH)
$NiMe_2$(dippp) (**3b**)	24.2	0.31 (m, 6H, $^{*}J_{HP} = 6.1$, CH_3)	0.94 (m, 16H, CH_3, CH_2) 1.23 (dd, 12H, $^{3}J_{HH} = 6.8$, $^{3}J_{HP} = 13.2$, CH_3) 1.52 (m, 2H, CH_2) 1.95 (h, 4H, $^{3}J_{HH} = 6.5$, CH)	3.8 (m, $^{*}J_{CP} =$ 30, 74, CH_3)	18.0 (4C, CH_3) 18.2 (pt, 2C, $^{*}J_{CP} = 12$, CH_2), 20.7 (4C, CH_3) 21.9 (1C, CH_2) 25.5 (t, 4C, $^{1}J_{CP} = 11$, CH)

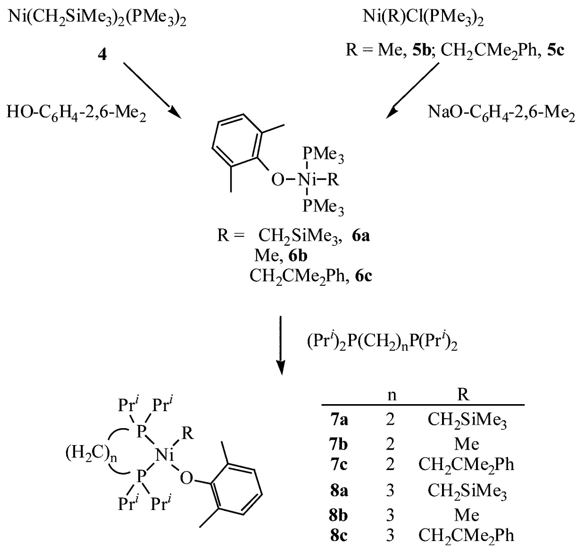
C_6D_6, δ en ppm, J en Hz.

[a] Singlets unless otherwise indicated.

acetate **13b**, instead of the expected α-trimethysilylacetate, due to the hydrolytic cleavage of the $SiMe_3$ group. Since α-trimethylsilyl esters are fairly resistant to hydrolysis [14], it seems likely that the intermediate trimethylsilylacetyl complexes are unstable and react with trace amounts of water to give the observed products. Hydrolytic cleavage of C–Si bonds in transition metal α-trimethylsilylacetyl or -trimethylsilyliminoacetyl complexes to give the corresponding desilylated products has been observed previously [15].

3. Crystal structure of compounds 7a and 8a

The crystal structures of the aryloxides **7a** and **8a** are shown on Figs. 1 and 2. Selected bond lengths and angles are listed in Tables 5 and 6. In both molecules, the Ni atoms occupy approximately square planar environments, with virtually no tetrahedral distortion, the sum of the *cis* L–Ni–L′ angles around the nickel center amount 359.7° in **7a** and 360.1° in **8a**. As expected for the different bite angles of the dippe and dippp ligands, the P–Ni–P angle in **8a** (97.36(13)°) is wider (ca. 9°) than in **7a** (88.52(1)°). This has a noticeable influence on the disposition of the alkyl and aryloxide ligands, which are closer in **8a** (C–Ni–O = 87.8(3)°) than in **7a** (C–Ni–O = 91.0(4)°). Apart from this, both molecules have similar structural parameters. In both complexes, the Ni–P bonds placed in *trans* to carbon are ca. 0.1 Å longer than those in *trans* to oxygen, suggesting a larger *trans* influence of the alkyl group as compared with the aryloxide ligand. Both the alkyl and the aryloxide groups adopt an alternated conformation that minimizes the steric repulsions with the bulky phosphine ligands, while the isopropyl substituents are found in a nearly identical disposition. Several metric features of the aryloxide ligands evidence some degree of steric crowding. Thus, the Ni–O bond length is 1.907(8) Å in **7a** and 1.915(7) Å in **8a**. These values are significantly longer than in other aryloxides of Ni [16], where they usually cluster within the narrow range of 1.85–1.87 Å [17]. The M–O–C angles in **7a** and **8a** are 135.0(7) and 133.1(6)°, respectively, which are somewhat wider than those encountered in other Group 10 aryloxides, usually close to 120° [3a,6b–6d,16].



Scheme 2.

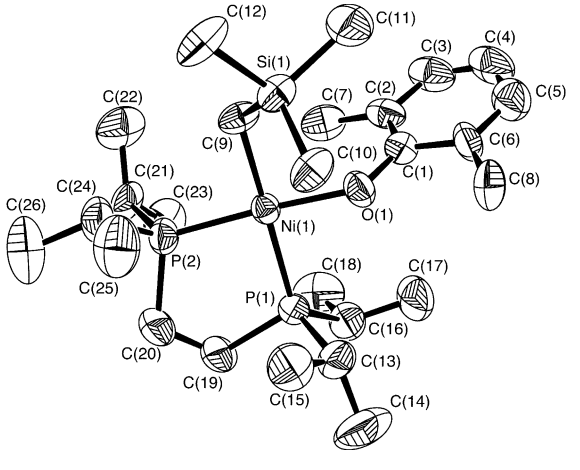


Fig. 1. X-ray structure of compound **7a**.

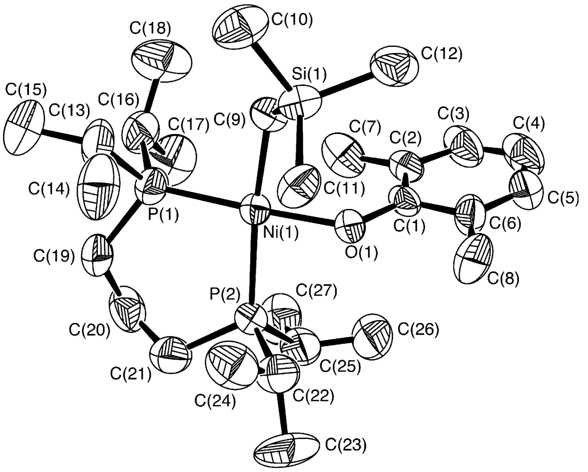


Fig. 2. X-ray structure of compound **8a**.

We believe that the relatively large values of the M–O distances and M–O–C angles in compounds **7a** and **8a** are due to the steric repulsions between the bulky aryloxide and dippe or dippp ligands.

As already pointed out, the NMR spectra of the aryloxides **7**–**8** are consistent with unrestricted rotation of the aryloxide ligand around the C–O bond. Hence, the above solid-state effects noted in the structures of **7a** and **8a** appear to have no significant influence in solution. Nevertheless, steric encumbrance could be important in promoting the dissociation of the aryloxide ligand that allows cyclometalation of the neophyl complexes **7c** and **8c** to **9** and **10**.

4. Concluding remarks

Although the Ni dialkyl complexes **2a**,**b** and **3a**,**b** do not react with the bulky 2,6-dimethyl phenol, alkyl–aryloxide complexes **7**–**8**, bearing the chelating diphosphines dippe or dippp may be readily prepared from the corresponding PMe_3 derivatives by metathetical exchange of the phosphine ligands. In general the alkyl aryloxides exhibit good thermal stability, although when $R = CH_2CMe_2Ph$ (neophyl group) they undergo facile cyclometallation, releasing the free phenol. At variance with the related Pd and Pt alkyl aryloxides, this is a relatively uncommon process in Ni chemistry, and its mechanism might involve the heterolytic dissociation of the aryloxide ligand. The carbonylation of complexes **7**–**8** takes place cleanly, giving rise to the corresponding aryl esters quantitatively.

5. Experimental

Microanalyses were performed by the Analytical Service of the University of Seville and the Instituto de Investigaciones Químicas. The spectroscopic instruments used were Perkin–Elmer Models 684 and 883 and Bruker Model Vector 22 for IR spectra, and Bruker AMX-300, DRX-400, AMX-500 and DRX-500 for NMR spectroscopy. The ^{13}C resonance of the solvent was used as an internal standard, but chemical shifts are reported with respect to $SiMe_4$. The $^{13}C\{^1H\}$-NMR assignments were helped in most cases with the use of gate-decoupling techniques. $^{31}P\{^1H\}$-NMR shifts are referenced to external 85% H_3PO_4. All preparations and other operations were carried out under oxygen-free nitrogen by conventional Schlenk techniques. Solvents were dried and degassed before use. The petroleum ether used had a b.p. of 40–60 °C. The compound $\overline{\mathrm{Ni}(\mathrm{CH_2CMe_2}\text{-}o\text{-}\mathrm{C}}\mathrm{_6H_4})\text{–}(\mathrm{PMe_3})_2$ [11] and phosphines PMe_3 [18] and $Pr^i_2PCH_2CH_2PPr^i_2$ (dippp) [19] were prepared according to literature methods.

Table 2
^{31}P{^{1}H}- and ^{1}H-NMR data for complexes **6a**–**c**, **7a**–**c** and **8a**–**c**

	^{31}P{^{1}H} [a]	^{1}H		
		Ni–R	PMe$_3$/Pr$^i_2$P(CH)$_n$PPr$^i_2$	OAr [b]
Ni(CH$_2$SiMe$_3$)(OAr)(PMe$_3$)$_2$ (**6a**)	−20.9	−1.31 (t, 2H, $^3J_{\mathrm{HP}} = 13.8$, CH$_2$)	0.81 (sa, 18H, PMe$_3$)	2.98 (s, 6H, Me)
		0.28 (s, 9H, SiCH$_3$)		6.65 (t, 1H, $^3J_{\mathrm{HH}} = 6.9$, CH$_{\mathrm{ar}}$)
				7.17 (d, 2H, $^3J_{\mathrm{HH}} = 7.0$, CH$_{\mathrm{ar}}$)
Ni(Me)(OAr)(PMe$_3$)$_2$ (**6b**)	−18.0	−1.07 (sa, 3H, CH$_3$)	0.74 (s, 18H, PMe$_3$)	3.0 (sa, 6H, Me)
				6.66 (t, 1H, $^3J_{\mathrm{HH}} = 7.2$, CH$_{\mathrm{ar}}$)
				7.23 (d, 2H, $^3J_{\mathrm{HH}} = 7.2$, CH$_{\mathrm{ar}}$)
Ni(CH$_2$CMe$_2$Ph)(OAr)-(PMe$_3$)$_2$ (**6c**)	−22.2	0.41 (t, 2H, $^3J_{\mathrm{HP}} = 13.0$, CH$_2$)	0.77 (sa, 18H, PMe$_3$)	2.94 (sa, 6H, Me)
		1.64 (s, 6H, CMe$_2$)		6.65 (t, 1H, $^3J_{\mathrm{HH}} = 6.8$, CH$_{\mathrm{ar}}$)
		7.06 (t, 1H, $^3J_{\mathrm{HP}} = 7.3$, CH$_{\mathrm{ar}}$)		7.19 (d, 2H, $^3J_{\mathrm{HH}} = 6.2$, CH$_{\mathrm{ar}}$)
		7.26 (m, 2H, CH$_{\mathrm{ar}}$)		
		7.61 (d, 2H, $^3J_{\mathrm{HP}} = 7.3$, CH$_{\mathrm{ar}}$)		
Ni(CH$_2$SiMe$_3$)(OAr)(dippe) (**7a**)	59.4	0.06 (t, 2H, *$J_{\mathrm{HP}} = 7.6$, CH$_2$)	0.70 (m, 2H, CH$_2$)	2.94 (s, 6H, Me)
	70.6	0.42 (sa, 9H, SiCH$_3$)	0.80 (m, 12H, CH$_3$)	6.70 (t, 1H, $^3J_{\mathrm{HH}} = 6.9$, CH$_{\mathrm{ar}}$)
		.	0.90 (m, 2H, CH$_2$)	7.25 (d, 2H, $^3J_{\mathrm{HH}} = 7.0$, CH$_{\mathrm{ar}}$)
			1.15 (m, 12H, CH$_3$)	
			1.75 (m, 4H, CH)	
Ni(Me)(OAr)(dippe) (**7b**)	63.0d	−0.39 (t, 3H, *$J_{\mathrm{HP}} = 4.7$, CH$_3$)	0.77 (m, 2H, CH$_2$)	2.66 (s, 6H, Me)
	75.8d		0.80 (dd, 6H, $^3J_{\mathrm{HP}} = 13.0$, $^3J_{\mathrm{HH}} = 7.0$, CH$_3$)	6.86 (t, 1H, $^3J_{\mathrm{HH}} = 7.3$, CH$_{\mathrm{ar}}$)
	$^2J_{\mathrm{PP}} = 10$		0.98 (m, 2H, CH$_2$)	7.34 (d, 2H, $^3J_{\mathrm{HH}} = 7.3$, CH$_{\mathrm{ar}}$)
			1.05 (m, 12H, CH$_3$)	
			1.37 (dd, 6H, $^3J_{\mathrm{HP}} = 14.7$, $^3J_{\mathrm{HH}} = 7.2$, CH$_3$)	
			1.58 (m, 2H, CH)	
			1.98 (m, 2H, CH)	
Ni(CH$_2$CMe$_2$Ph)(OAr)(dippe) (**7c**)	57.7	1.49 (dd, 2H, $^3J_{\mathrm{HP}} = 4.8$, 12.6, CH$_2$)	0.60 (m, 2H, CH$_2$)	2.95 (s, 6H, Me)
	65.7	1.66 (s, 6H, CMe$_2$)	0.73 (dd, 6H, $^3J_{\mathrm{HP}} = 12.6$, $^3J_{\mathrm{HH}} = 6.8$, CH$_3$)	6.53 (t, 1H, $^3J_{\mathrm{HH}} = 7.0$, CH$_{\mathrm{ar}}$)
		7.02 (t, 1H, $^3J_{\mathrm{HP}} = 7.2$, CH$_{\mathrm{ar}}$)	0.89 (m, 8H, CH$_3$, CH$_2$)	7.31 (d, 2H, $^3J_{\mathrm{HH}} = 7.2$, CH$_{\mathrm{ar}}$)
		7.16 (t, 2H, $^3J_{\mathrm{HP}} = 7.2$, CH$_{\mathrm{ar}}$)	1.03 (dd, 6H, $^3J_{\mathrm{HP}} = 15.3$, $^3J_{\mathrm{HH}} = 7.2$, CH$_3$)	
		7.33 (d, 2H, $^3J_{\mathrm{HP}} = 7.3$, CH$_{\mathrm{ar}}$)	1.29 (dd, 6H, $^2J_{\mathrm{HP}} = 14.9$, $^3J_{\mathrm{HH}} = 7.2$ CH$_3$)	
			1.90 (m, 4H, CH)	
Ni(CH$_2$SiMe$_3$)(OAr)(dippp) (**8a**)	5.1d	−0.08 (dd, 2H, $^3J_{\mathrm{HP}} = 6.2$, 8.8, CH$_2$)	0.60 (m, 4H, CH$_2$)	2.98 (s, 6H, Me)
	29.4d	0.30 (sa, 9H, SiCH$_3$)	0.90 (m, 12H, CH$_3$)	6.76 (t, 1H, $^3J_{\mathrm{HH}} = 7.2$, CH$_{\mathrm{ar}}$)
	$^2J_{\mathrm{PP}} = 37$		1.32 (m, 14H, CH$_3$, CH$_2$)	7.27 (d, 2H, $^3J_{\mathrm{HH}} = 7.3$, CH$_{\mathrm{ar}}$)
			1.80 (m, 2H, CH)	
			2.17 (m, 2H, CH)	
Ni(Me)(OAr)(dippp) (**8b**)	9.0d	−0.40 (t, 3H, *$J_{\mathrm{HP}} = 4.2$, CH$_3$)	0.64 (m, 2H, CH$_2$)	2.65 (s, 6H, Me)
	37.1d		0.80 (m, 2H, CH$_2$)	6.86 (t, 1H, $^3J_{\mathrm{HH}} = 7.0$, CH$_{\mathrm{ar}}$)
	$^2J_{\mathrm{PP}} = 34$		0.85 (m, 6H, CH$_3$)	7.33 (d, 2H, $^3J_{\mathrm{HH}} = 7.1$, CH$_{\mathrm{ar}}$)
			0.90 (m, 2H, CH$_2$)	
			1.05 (dd, 6H, $^3J_{\mathrm{HP}} = 12.3$, $^3J_{\mathrm{HH}} = 6.7$, CH$_3$)	
			1.27 (dd, 6H, $^3J_{\mathrm{HP}} = 15.6$, $^3J_{\mathrm{HH}} = 6.5$, CH$_3$)	
			1.47 (dd, 6H, $^3J_{\mathrm{HP}} = 14.7$, $^3J_{\mathrm{HH}} = 6.7$, CH$_3$)	
			1.54 (m, 2H, CH)	
			2.15 (m, 2H, CH)	
Ni(CH$_2$CMe$_2$Ph)(OAr)(dippp) (**8c**)	4.6d	1.50 (dd, 2H, $^3J_{\mathrm{HP}} = 4.3$, 8.0, CH$_2$)	0.55 (pt, 2H, CH$_2$)	2.99 (s, 6H, Me)

Table 2 (*Continued*)

	$^{31}P\{^1H\}$ [a]	^1H		
		Ni–R	$PMe_3/Pr^i_2P(CH)_nPPr^i_2$	OAr [b]
	27.9d	1.62 (s, 6H, CMe_2)	0.73 (dd, 6H, $^3J_{HP} = 12.2$, $^3J_{HH} = 6.8$, CH_3)	6.79 (t, 1H, $^3J_{HH} = 7.2$, CH_{ar})
	$^2J_{PP} = 29$	6.97 (t, 1H, $^3J_{HP} = 7.2$, CH_{ar})	0.95 (dd, 6H, $^3J_{HP} = 12.1$, $^3J_{HH} = 7.1$, CH_3)	7.31 (d, 2H, $^3J_{HH} = 7.3$, CH_{ar})
		7.11 (t, 2H, $^3J_{HP} = 7.8$, CH_{ar})	0.96 (m, 4H, CH_2)	
		7.43 (d, 2H, $^3J_{HP} = 7.6$, CH_{ar})	1.15 (dd, 6H, $^3J_{HP} = 14.6$, $^3J_{HH} = 7.1$, CH_3)	
			1.28 (m, 2H, CH)	
			1.44 (dd, 6H, $^3J_{HP} = 14.6$, $^3J_{HH} = 7.2$, CH_3)	
			2.23 (m, 2H, CH)	

C_6D_6, δ en ppm, J en Hz.

[a] Singlets unless otherwise indicated.

[b] $OAr{=}OC_5H_3$–2,6-Me_2.

$Pr^i_2PCH_2CH_2PPr^i_2$ was obtained by reacting $Cl_2PCH_2CH_2PCl_2$ with the Grignard $Mg(Pr^i)Cl$.

5.1. Synthesis of $Ni(CH_2SiMe_3)_2$(dippe) (**2a**)

To a cooled (−80 °C) suspension of $NiCl_2(py)_4$ (0.44 g, 1 mmol) in 50 ml of Et_2O was added 0.75 ml (9 mmol) of Py and 2.15 ml (2 mmol) of a 0.93 M solution of $Mg(CH_2SiMe_3)Cl$ in Et_2O. The mixture was allowed to reach room temperature (r.t.) and stirred for 1 h. Then it was cooled again at −50 °C, treated with 0.3 ml (1 mmol) of dippe and stirred at r.t. for 2 h. The solvent was evaporated under reduced pressure and the residue extracted with 60 ml of petroleum ether. After centrifugation and partial concentration of the solvent, cooling to −30 °C provided complex **2a** as red crystals in 63% yield. Anal. Calc. for $C_{22}H_{54}NiP_2Si_2$: C, 53.33; H, 10.98. Found: C, 53.13; H, 10.84%.

The compound $Ni(CH_2SiMe_3)_2$(dippp) (**3a**) was similarly prepared and isolated as yellow crystals in 65% yield. Anal. Calc. for $C_{23}H_{56}NiP_2Si_2$: C, 54.22; H, 11.08. Found: C, 54.24; H, 11.37%.

5.2. Synthesis of $Ni(Me)_2$(dippe) (**2b**)

Pyridine (0.75 ml, 9 mmol) and 1.25 ml (2 mmol) of a 1.6 M solution of LiMe in Et_2O were added to a cold (−80 °C) suspension of $NiCl_2(py)_4$ (0.44 g, 1 mmol) in Et_2O (50 ml). After removing the cold bath the mixture was stirred at r.t. for 2 h and cooled again at −50 °C for the addition of 0.3 ml (1 mmol) of dippe. The suspension was stirred at r.t. for 1 h and then taken to dryness. The residue was extracted with 50 ml of petroleum ether and centrifuged. After partial concentration of the solution, cooling to −30 °C furnished compound **2b** as yellow crystals in 55% yield. Anal. Calc. for $C_{16}H_{38}NiP_2$: C, 54.73; H, 10.91. Found: C, 54.84; H, 10.84%.

The complex $Ni(Me)_2$(dippp) (**3b**) was identically prepared and obtained as brown crystals in 53% yield. Anal. Calc. for $C_{17}H_{40}NiP_2$: C, 55.92; H, 11.04. Found: C, 56.10; H, 11.09%.

5.3. Synthesis of $Ni(CH_2SiMe_3)(OC_6H_3$–2,6-$Me_2)(PMe_3)_2$ (**6a**)

A suspension of $NiCl_2(py)_4$ (0.44 g, 1 mmol) in 50 ml of Et_2O was cooled at −80 °C and Py (0.35 ml, 4.5 mmol) and 2.2 ml (2 mmol) of a 0.93 M solution of $Mg(CH_2SiMe_3)Cl$ in Et_2O were added. The mixture was warmed to r.t. and stirred for 2 h, cooled to −80 °C, and 2 ml (2 mmol) of a 1 M solution of PMe_3 in Et_2O were added. The resulting suspension was then stirred at r.t. for 1 h, during which time the initial red color due to $Ni(CH_2SiMe_3)_2(py)_2$ turned yellow. The solvent was evaporated under vacuum and the residue extracted with 50 ml of Et_2O and centrifuged. The solution was evaporated and the solid, $Ni(CH_2SiMe_3)_2(PMe_3)_2$ (0.32 g, 0.84 mmol) dissolved in 30 ml of Et_2O and treated with 0.10 g (0.84 mmol) of 2,6-dimethylphenol and stirred at r.t. for 1 h. The solvent was stripped off and the residue extracted with 30 ml of petroleum ether and filtered. After partial evaporation of the solvent and cooling at −30 °C, complex **6a** was isolated as yellow crystals in 69% yield. Anal. Calc. for $C_{18}H_{38}NiOP_2Si$: C, 51.57; H, 9.14. Found: C, 52.12; H, 8.86%.

5.4. Synthesis of $Ni(Me)(OC_6H_3$–2,6-$Me_2)(PMe_3)_2$ (**6b**)

To a cooled (−20 °C) suspension of $NiCl_2(PMe_3)_2$ (0.282 g, 1 mmol) in 40 ml of Et_2O, were added 0.65 ml

Table 3
^{13}C{^{1}H}-NMR data for complexes **6a**–**c**, **7a**–**c** and **8a**–**c**

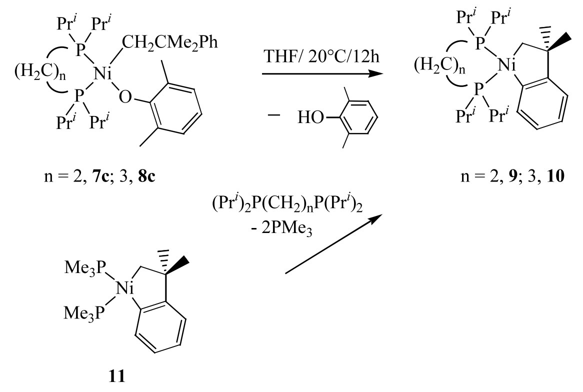
	^{13}C{^{1}H} [a]		
	Ni–R	PMe$_3$/Pr$^i_2$P(CH)$_n$PPr$^i_2$	OAr [b]
Ni(CH$_2$SiMe$_3$)(OAr)(PMe$_3$)$_2$ (**6a**)	-20.4 (t, $^2J_{CP} = 23$, CH$_2$) 2.8 (SiCH$_3$)	12.4 (t, 6C, $^1J_{CP} = 11$, PMe$_3$)	19.3 (s, 2C, Me) 112.2 (s, 1C, C$_{ar}$H) 124.9 (s, 2C, C$_{ar}$) 128.4 (s, 2C, C$_{ar}$H) 165.0 (s, 1C, C$_{ar}$)
Ni(Me)(Oar)(PMe$_3$)$_2$ (**6b**)	23.5 (sa, CH$_3$)	11.5 (sa, 6C, PMe$_3$)	19.1 (s, 2C, Me) 111.8 (s, 1C, C$_{ar}$H) 124.8 (s, 2C, C$_{ar}$) 128.4 (s, 2C, C$_{ar}$H) 166.6 (s, 1C, C$_{ar}$)
Ni(CH$_2$Cme$_2$Ph)(OAr)(PMe$_3$)$_2$ (**6c**)	10.8 (t, $^2J_{CP} = 24$, CH$_2$) 32.4 (C*Me*$_2$) 40.2 (*C*Me$_2$) 124.8 (s, 1C, C$_{ar}$H) 125.6 (s, 2C, C$_{ar}$H) 127.8 (s, 2C, C$_{ar}$H) 153.2 (s, 1C, C$_{ar}$)	12.8 (t, 6C, $^1J_{CP} = 11$, PMe$_3$)	19.5 (s, 2C, Me) 112.2 (s, 1C, C$_{ar}$H) 124.9 (s, 2C, C$_{ar}$) 128.5 (s, 2C, C$_{ar}$H) 165.2 (s, 1C, C$_{ar)}$
Ni(CH$_2$SiMe$_3$)(OAr)(dippe) (**7a**)	2.17 (dd, $^2J_{CP} = 31, 67$, CH$_2$) 3.8 (SiCH$_3$)	16.6 (dd, 1C, $^1J_{CP} = 19$, $^2J_{CP} = 11$, CH$_2$) 17.8 (s, 2C, CH$_3$) 17.9 (s, 2C, CH$_3$) 18.8 (d, 2C, $^2J_{CP} = 5$, CH$_3$) 20.9 (s, 2C, CH$_3$) 23.3 (pt, 1C, $^*J_{CP} = 23$, CH$_2$) 23.9 (d, 2C, $^1J_{CP} = 13$, CH) 25.5 (d, 2C, $^1J_{CP} = 27$, CH)	19.6 (s, 2C, Me) 112.2 (s, 1C, C$_{ar}$H) 125.5 (s, 2C, C$_{ar}$) 128.4 (s, 2C, C$_{ar}$H) 166.5 (s, 1C, C$_{ar}$)
Ni(Me)(OAr)(dippe) (**7b**)	-0.7 (dd, $^2J_{CP} = 35, 68$, CH$_3$)	16.0 (dd, 1C, $^1J_{CP} = 19$, $^2J_{CP} = 11$, CH$_2$) 18.1 (s, 2C, CH$_3$) 18.3 (s, 2C, CH$_3$) 19.0 (d, 2C, $^2J_{CP} = 5$, CH$_3$) 19.5 (d, 2C, $^2J_{CP} = 3$, CH$_3$) 23.6 (d, 2C, $^1J_{CP} = 13$, CH) 23.9 (pt, 1C, $^*J_{CP} = 24$, CH$_2$) 25.3 (d, 2C, $^1J_{CP} = 27$, CH)	19.2 (s, 2C, Me) 114.2 (s, 1C, C$_{ar}$H) 128.2 (s, 2C, C$_{ar}$) 128.4 (s, 2C, C$_{ar}$H) 165.3 (s, 1C, C$_{ar}$)
Ni(CH$_2$CMe$_2$Ph)(OAr)(dippe) [c] (**7c**)	26.1 (dd, $^2J_{CP} = 31, 77$, CH$_2$) 32.4 (C*Me*$_2$) 40.9 (*C*Me$_2$) 126.1 (s, 2C, C$_{ar}$H) 127.6 (s, 2C, C$_{ar}$H) 127.9 (s, 1C, C$_{ar}$H) 156.1 (s, 1C, C$_{ar}$)	17.0 (dd, 1C, $^1J_{CP} = 19$, $^2J_{CP} = 10$, CH$_2$) 18.3 (sa, 4C, CH$_3$) 19.2 (s, 2C, $^2J_{CP} = 4$, CH$_3$) 20.9 (s, 2C, CH$_3$) 23.2 (pt, 1C, $^*J_{CP} = 24$, CH$_2$) 23.9 (d, 2C, $^1J_{CP} = 14$, CH) 25.4 (d, 2C, $^1J_{CP} = 25$, CH)	19.9 (s, 2C, Me) 111.1 (s, 1C, C$_{ar}$H) 124.5 (s, 2C, C$_{ar}$) 126.3 (s, 2C, C$_{ar}$H) 165.5 (2, 1C, C$_{ar}$)
Ni(CH$_2$SiMe$_3$)(OAr)(dippp) (**8a**)	1.6 (dd, $^2J_{CP} = 31, 63$, CH$_2$) 3.6 (SiCH$_3$)	17.2 (sa, 2C, CH$_3$) 17.5 (m, 2C, CH$_2$) 17.7 (sa, 2C, CH$_3$) 19.7 (s, 2C, $^2J_{CP} = 4$, CH$_3$) 20.9 (sa, 2C, CH$_3$) 21.3 (d, 1C, $^2J_{CP} = 6$, CH$_2$) 23.6 (d, 2C, $^1J_{CP} = 17$, CH) 26.4 (d, 2C, $^1J_{CP} = 28$, CH)	20.6 (s, 2C, Me) 113.1 (s, 1C, C$_{ar}$H) 125.9 (s, 2C, C$_{ar}$) 128.7 (s, 2C, C$_{ar}$H) 164.5 (2, 1C, C$_{ar}$)
Ni(Me)(OAr)(dippp) (**8b**)	1.20 (dd, $^2J_{CP} = 38, 61$, CH$_3$)	17.6 (s, 2C, CH$_3$) 17.9 (m, 2C, CH$_2$) 18.1 (s, 2C, CH$_3$) 19.8 (d, 2C, $^2J_{CP} = 5$, CH$_3$) 21.2 (d, 2C, $^2J_{CP} = 3$, CH$_3$) 22.3 (m, 1C, CH$_2$) 24.0 (d, 2C, $^1J_{CP} = 16$, CH) 26.3 (d, 2C, $^1J_{CP} = 29$, CH)	19.2 (s, 2C, Me) 114.3 (s, 1C, C$_{ar}$H) 128.1 (s, 2C, C$_{ar}$H) 128.5 (s, 2C, C$_{ar}$) 164.2 (s, 1C, C$_{ar}$)

C$_6$D$_6$, δ en ppm, J en Hz.

[a] Singlets unless otherwise indicated.

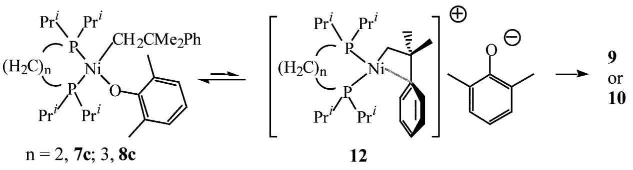
[b] OAr=OC$_5$H$_3$–2,6-Me$_2$.

[c] CD$_2$Cl$_2$ (−30 °C).



Scheme 3.

(1 mmol) of a 1.6 M solution of LiMe in Et_2O. The mixture was stirred 30 min at this temperature, 45 min at r.t. and then taken to dryness. The residue was extracted with Et_2O (40 ml) and centrifuged. The solution was evaporated under vacuum, and the resulting solid residue, $Ni(Me)Cl(PMe_3)_2$ (0.23 g, 0.88 mmol) dissolved in 30 ml of Et_2O and the solution cooled at −50 °C and treated with 1.2 ml (0.88 mmol) of a 0.74 M solution of $Na(2,6\text{-}OC_6H_3Me_2)$ in THF. The mixture was allowed to reach r.t. and stirred for 1 h. The solvent was evaporated under reduced pressure and the residue extracted with 45 ml of Et_2O. The

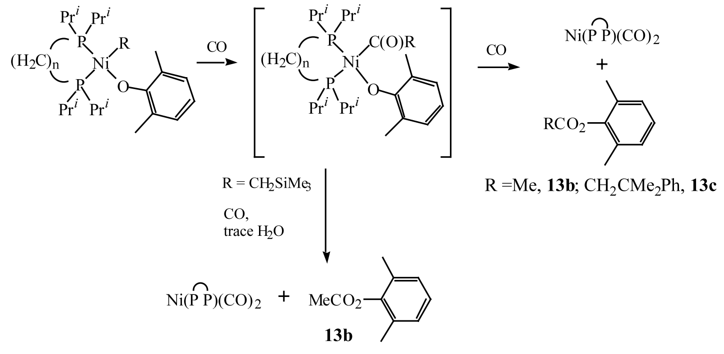


Scheme 4.

Table 4
$^{31}P\{^1H\}$-, ^1H- and $^{13}C\{^1H\}$-NMR data for complexes **9** and **10**

	$^{31}P\{^1H\}$	^1H		$^{13}C\{^1H\}$	
		Ni–R	$Pr^i_2P(CH)_nPPr^i_2$	Ni–R	$Pr^i_2P(CH)_nPPr^i_2$
$\overline{\mathrm{Ni(CH_2CMe_2}\text{-}o\text{-}\mathrm{C}}\mathrm{_6H_4)}$-(dippe) (**9**)	68.1d	2.01 (dd, 2H, $^3J_{HP} = 3.2$, 9.9, CH_2)	0.86 (m, 12H, CH_3)	46.1 (dd, $^2J_{CP} = 18$, 61, CH_2)	18.4 (d, 2C, $^2J_{CP} = 6$, CH_3)
	71.5d	1.74 (s, 6H, CMe_2)	1.06 (m, 12H, CH_3)	35.8 (d, $^4J_{CP} = 4$, CMe_2)	19.2 (d, 2C, $^2J_{CP} = 5$, CH_3)
	$^2J_{PP} = 5$	7.29 (m, 3H, CH_{ar})	1.09 (m, 4H, CH_2)	51.2 (d, $^3J_{CP} = 5$, CMe_2)	20.3 (m, 2C, CH_2)
		7.77 (t, 1H, $^3J_{HH} = 6.2$, CH_{ar})	1.85 (h, 2H, CH)	121.8 (s, $C_{ar}H$)	20.6 (s, 2C, CH_3)
			2.09 (h, 2H, CH)	122.9 (d, $J_{CP} = 6$, $C_{ar}H$)	20.7 (s, 2C, CH_3)
				123.2 (s, $C_{ar}H$)	24.7 (d, 2C, $^2J_{CP} = 19$, CH)
				140.8 (dd, $J_{CP} = 4$, 9, $C_{ar}H$)	25.1 (d, 2C, $^2J_{CP} = 13$, CH)
				167.7 (dd, $^2J_{CP} = 15$, 81, C_{ar})	
				168.6 (d, $^3J_{CP} = 5$, C_{ar})	
$\overline{\mathrm{Ni(CH_2CMe_2}\text{-}o\text{-}\mathrm{C}}\mathrm{_6H_4)}$-(dippp) (**10**)	21.1d	1.83 (dd, 2H, $^3J_{HP} = 2.2$, 10.6, CH_2)	0.90 (m, 12H, CH_3)	47.8 (dd, $^2J_{CP} = 20$, 58, CH_2)	16.7 (dd, 1C, $^1J_{CP} = 13$, $^2J_{CP} = 9$, CH_2)
	19.1d	1.77 (s, 6H, CMe_2)	0.98 (m, 2H, CH_2)	35.3 (d, $^4J_{CP} = 4$, CMe_2)	17.7 (d, 2C, CH_3)
	$^2J_{PP} = 23$	7.26 (m, 3H, CH_{ar})	1.19 (m, 14H, CH_3, CH_2)	50.8 (t, $^*J_{CP} = 4$, CMe_2)	17.8 (s, 2C, CH_3)
		7.77 (t, 1H, $^3J_{HH} = 6.7$, CH_{ar})	1.42 (m, 2H, CH_2)	121.8 (s, $C_{ar}H$)	19.0 (dd, 1C, $^1J_{CP} = 11$, $^2J_{CP} = 5$, CH_2)
			1.92 (h, 2H, CH)	122.8 (d, $J_{CP} = 6$, $C_{ar}H$)	20.0 (d, 2C, $^2J_{CP} = 5$, CH_3)
			2.25 (h, 2H, CH)	123.1 (s, $C_{ar}H$)	21.2 (t, 1C, $^2J_{CP} = 4$, CH_2)
				138.7 (dd, $J_{CP} = 5$, 9, $C_{ar}H$)	21.5 (d, 2C, $^2J_{CP} = 9$, CH_3)
				166.9 (dd, $^2J_{CP} = 18$, 74, C_{ar})	25.2 (d, 2C, $^1J_{CP} = 14$, CH)
				168.0 (d, $^3J_{CP} = 5$, C_{ar})	25.8 (d, 2C, $^1J_{CP} = 20$, CH)

C_6D_6, δ en ppm, J en Hz.



Scheme 5.

suspension was centrifuged and the solution partially evaporated and cooled to − 30 °C. Compound **6b** was obtained as yellow crystals in 65% yield. Anal. Calc. for $C_{15}H_{30}NiOP_2$: C, 51.91; H, 8.71. Found: C, 51.76; H, 8.35%.

5.5. *Synthesis of $Ni(CH_2CMe_2Ph)(OC_6H_3\text{–}2,6\text{-}Me_2)(PMe_3)_2$ (**6c**)*

A suspension of $NiCl_2(PMe_3)_2$ (0.56 g, 2 mmol) in Et_2O (80 ml) was cooled at − 50 °C and 2.22 ml (2 mmol) of a 0.9 M solution of $Mg(CH_2CMe_2Ph)Cl$ in Et_2O was added. The mixture was warmed to r.t. and stirred for 5 h. The solvent was evaporated under vacuum and the residue extracted with 40 ml of Et_2O and centrifuged. The solution was evaporated and the solid residue, compound $Ni(CH_2CMe_2Ph)Cl(PMe_3)_2$ (0.62 g, 1.65 mmol) dissolved in 30 ml of Et_2O and the solution cooled at − 50 °C and $Na(2,6\text{-}OC_6H_3Me_2)$ (1.65 mmol, 2.4 ml of a 0.74 M solution in THF) added. The resulting suspension was stirred at r.t. for 2 h and then taken to dryness. The residue was extracted with 60 ml of petroleum ether and the solution filtered. After partial concentration of the solvent, cooling to − 30 °C provided compound **6c** as yellow crystals in 50% yield. Anal. Calc. for $C_{24}H_{40}NiOP_2$: C, 61.96; H, 8.67. Found: C, 61.32; H, 8.67%.

The preparation of compounds **7a**–**c** and **8a**–**c** involves the reaction of $Ni(R)(2,6\text{-}OC_6H_3Me_2)(PMe_3)_2$ ($R = CH_2SiMe_3$, Me, CH_2CMe_2Ph) with the appropriate phosphine, dippe or dippp. A representative example of the experimental procedure employed to synthesize **7b** is as follows.

Dippe (0.15 ml, 0.5 mmol) was added to a cooled (− 50 °C) solution of complex **6b** (0.18 g, 0.5 mmol) in Et_2O (40 ml). After removing the cold bath, the mixture was stirred at r.t. for 1 h. The solvent was evaporated under reduced pressure and the residue extracted with 30 ml of petroleum ether. After partial concentration of the solvent and cooling to − 30 °C, compound **7b** was isolated as yellow crystals in quantitative yield.

7a: Anal. Calc. for $C_{26}H_{52}NiOP_2Si$: C, 58.99; H, 9.90. Found: C, 58.55; H, 10.01%.

7b: Anal. Calc. for $C_{23}H_{44}NiOP_2$: C, 60.42; H, 9.70. Found: C, 60.67; H, 9.82%.

7c: Anal. Calc. for $C_{32}H_{54}NiOP_2$: C, 66.79; H, 9.46. Found: C, 66.24; H, 9.38%.

8a: Anal. Calc. for $C_{27}H_{54}NiOP_2Si$: C, 59.67; H, 10.02. Found: C, 58.97; H, 10.24%.

8b: Anal. Calc. for $C_{24}H_{46}NiOP_2$: C, 61.17; H, 9.84. Found: C, 60.73; H, 9.80%.

8c: Anal. Calc. for $C_{33}H_{56}NiOP_2$: C, 67.24; H, 9.58. Found: C, 66.61; H, 9.95%.

5.6. *Synthesis of $\overline{Ni(CH_2CMe_2\text{-}o\text{-}C}_6H_4)$(dippe) (**9**)*

5.6.1. *Method a*

A solution of complex **7c** (0.29 g, 0.5 mmol) in 20 ml of THF was stirred at r.t. for 12 h. The solvent was

Table 5
Selected bond lengths (Å) and angles (°) for compound **7a**

Bond lengths			
Ni(1)–P(1)	2.225(3)	Ni(1)–C(9)	2.001(10)
Ni(1)–P(2)	2.122(5)	Si(1)–C(9)	1.855(10)
Ni(1)–O(1)	1.907(8)	O(1)–C(1)	1.32(1)
Bond angles			
P(1)–Ni(1)–P(2)	88.52(14)	O(1)–Ni(1)–C(9)	91.0(4)
P(1)–Ni(1)–O(1)	88.9(2)	Ni(1)–O(1)–C(1)	135.0(7)
P(2)–Ni(1)–C(9)	91.3(4)	Ni(1)–C(9)–Si(1)	115.1(5)

Table 6
Selected bond lengths (Å) and angles (°) for compound **8a**

Bond lengths			
Ni(1)–P(1)	2.151(5)	Ni(1)–C(9)	1.988(9)
Ni(1)–P(2)	2.264(3)	O(1)–C(1)	1.309(10)
Ni(1)–O(1)	1.915(7)	Si(1)–C(9)	1.858(9)
Bond angles			
P(1)–Ni(1)–P(2)	97.36(13)	O(1)–Ni(1)–C(9)	87.8(3)
P(1)–Ni(1)–C(9)	89.8(3)	Ni(1)–O(1)–C(1)	133.1(6)
P(2)–Ni(1)–O(1)	85.1(2)	Ni(1)–C(9)–Si(1)	116.8(5)

Table 7
Crystal and refinement data for compounds **7a** and **8a**

	7a	**8a**
Empirical formula	$C_{26}H_{52}NiOP_2Si$	$C_{27}H_{54}NiOP_2Si$
Molecular weight	529.42	543.46
Temperature (K)	290	290
λ (Å) (Mo–K_α)	0.71069	0.71069
Color and habit	Orange plate	Red prism
Crystal system	Orthorhombic	Orthorhombic
Space group	$P2_12_12_1$ (No. 19)	$P2_12_12_1$ (No. 19)
Unit cell dimensions		
a (Å)	17.210(4)	17.704(4)
b (Å)	18.080(4)	18.347(4)
c (Å)	9.600(4)	9.475(3)
V (Å^3)	2987(2)	3077(2)
Z	4	4
D_{calc} (g cm^{-3})	1.177	1.173
Diffractometer	MSC-Rigaku AFC6S	MSC-Rigaku AFC6S
Monochromator	Graphite	Graphite
μ (mm^{-1})	0.81	0.79
Crystal size (mm)	$0.15\times0.25\times0.37$	$0.14\times0.17\times0.26$
Scan type	ω–2θ	ω–2θ
2θ range (°)	5.0–50.1	5.0–50.1
Decay (three standards every 100 reflections) (%)	−1.30	−0.71
Absorption correction (F_{min}, F_{max})	ϕ-scan, 0.95–1.00	ϕ-scan, 0.97–1.00
No. of reflections	2666	2576
No. of refined parameters	280	289
R factor all	0.0980	0.1125
R factor [$I>2\sigma(I)$]	0.0499	0.0483
wR	0.1775	0.1365
wR [$I>2\sigma(I)$]	0.1310 [a]	0.1142 [b]
Goodness-of-fit	1.045	0.964

[a] $w=1/[\sigma^2(F_o^2)+(0.1057P)^2]$; $P=([F_o]^2+2[F_c]^2)/3$.

[b] $w=1/[\sigma^2(F_o^2)+(0.0557P)^2]$; $P=([F_o]^2+2[F_c]^2)/3$.

evaporated under vacuum, the residue extracted with Et_2O (25 ml) and the solution filtered. The filtrate was concentrated and some petroleum ether added. Cooling to −30 °C furnished complex **9** as orange crystals in 94% yield. Anal. Calc. for $C_{24}H_{44}NiP_2$: C, 63.60; H, 9.78. Found: C, 63.63; H, 10.01%.

5.6.2. Method b

A solution of complex **11** (0.17 g, 0.5 mmol) in 30 ml of Et_2O was cooled at −30 °C and 0.15 ml (0.5 mmol) of dippe were added. The mixture was stirred at r.t. for 1 h. The solvent was stripped off and the residue extracted with 20 ml of Et_2O. After filtration, partial evaporation of the solvent and cooling to −30 °C, compound **9** was obtained as orange crystals in quantitative yield.

Complex $\overline{\mathrm{Ni(CH_2CMe_2}\text{-}o\text{-}\mathrm{C}}\mathrm{_6H_4)}$dippp (**10**) was similarly prepared and isolated as red crystals in quantitave yield. Anal. Calc. for $C_{24}H_{44}NiP_2$: C, 64.26; H, 9.92. Found: C, 64.10; H, 9.61%.

5.7. Reactions of compounds **7a–c** and **8a–c** with CO

The carbonylation of complexes **7a–c** and **8a–c** gives rise to the formation of carbonyls $Ni(CO)_2$(dippe) (or $Ni(CO)_2$(dippp)) and the organic esters $RCO_2C_6H_3$–2,6-Me_2 (R = Me, CH_2CMe_2Ph), as a result of the reductive elimination reaction. An example of the reaction of complex **7b** is as follows.

CO was bubbled through a solution of compound **7b** (0.23 g, 0.5 mmol) in 20 ml of Et_2O at r.t. for 5 min (a ^{1}H-NMR spectrum of the crude mixture showed quantitative conversion to the products). The resulting colorless solution was evaporated and the oily residue extracted with Et_2O and filtered. From the filtrate, ester **13b** was isolated by spinning band chromatography, using the mixture petroleum ether–Et_2O (9.5:0.5) as eluant.

5.7.1. $MeCO_2C_6H_3$–2,6-Me_2

^{1}H-NMR (C_6D_6, 20 °C) δ 1.82 (s, 3H, Me), 2.03 (s, 6H, Me_2), 6.89 (s, 3H, CH_{ar}); $^{13}C\{^1H\}$ (C_6D_6, 20 °C) δ 15.9 (s, Me), 19.5 (s, Me_2), 125.6 (s, $C_{ar}H$), 128.5 (s, $C_{ar}H$), 130.3 (s, C_{ar}), 152.9 (s, C_{ar}), 168.0 (s, CO). EI–HRMS: m/z 164.08372 [M^+] (exact mass calculated for $C_{10}H_{12}O_2$ 164.08373).

5.7.2. $PhMe_2CCH_2CO_2C_6H_3$–2,6-Me_2

^{1}H-NMR (C_6D_6, 20 °C) δ 1.40 (s, 6H, Me_2), 1.87 (s, 6H, Me_2), 2.68 (s, 2H, CH_2), 6.85 (s, 3H, CH_{ar}), 7.05 (t, 1H, $^3J_{HH}=7.3$ Hz, CH_{ar}), 7.15 (t, 2H, $^3J_{HH}=7.7$ Hz, CH_{ar}), 7.26 (d, 2H, $^3J_{HH}=7.6$ Hz, CH_{ar}); $^{13}C\{^1H\}$ (C_6D_6, 20 °C) δ 16.1 (s, CMe_2), 29.0 (s, CMe_2), 36.8 (s, CMe_2), 47.0 (s, CH_2), 125.4, 125.7, 126.0, 128.2, 128.4 (s, $C_{ar}H$), 130.2, 147.8, 148.7 (s, C_{ar}), 168.3 (s, CO). EI–HRMS: m/z 282.1617 [M^+] (exact mass calculated for $C_{19}H_{22}O_2$ 282.16198).

5.8. X-ray structure determination of compounds **7a** and **8a**

A summary of crystal and refinement data is reported in Table 7. Data were collected on a MSC-Rigaku AFC6S diffractometer and corrected for absorption and Lorentz-polarization effects. The structures were solved by Patterson method using TEXSAN, Single Crystal Structure Analysis Software [20]. Refinements were performed using SHELXL-97 program [21]. In both structures all non-hydrogen atoms were anisotropically refined. The hydrogen atoms were treated by the SHELX riding model. Calculations for data reduction and structure solution were performed on a VAX 3520 station at the 'Servicio Central de Ciencia y Tecnología de la Universidad de Cádiz'.

6. Supplementary material

Tables of atomic coordinates, thermal parameters and bond lengths and angles for **7a** and **8a**.

Acknowledgements

Financial support from the Dirección General de Enseñanza Superior e Investigación Científica (M.E.C) (Research grant to C.M. and Project 1FD97-019-C02-01), Dirección General de Investigación (M.C.T.) (Project BQU2000-1169) and Junta de Andalucía is gratefully acknowledged. J.A.L. thanks the CONACYT and the University of Guanajuato (Mexico) for a fellowship.

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