ELSEVIER

Journal of Organometallic Chemistry 632 (2001) 164–174

Journal of Organometallic Chemistry

www.elsevier.com/locate/jorganchem

Synthesis and characterisation of ring-coupled cyclopentadienyl and indenyl bimetallic derivatives of nickel

José R. Ascenso, Alberto R. Dias, M. Teresa Duarte, Pedro T. Gomes *, Joaquim N. Marote, Alejandro F.G. Ribeiro

Centro de Química Estrutural, Complexo I, Instituto Superior Técnico, Av. Rovisco Pais, 1049-001 Lisbon, Portugal

Received 1 March 2001; accepted 29 March 2001

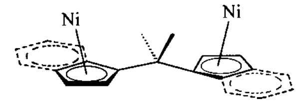
Abstract

The reaction of $NiCl_2(PPh_3)_2$ with 0.5 equivalents of the salts $Li_2[CMe_2(C_5H_4)_2]$ (**1**), $Li_2[CMe_2(C_9H_6)_2]$ (**2**) or $Li_2[(C_5H_4)CMe_2(C_9H_6)]$ (**3**) is an efficient route to the synthesis of ring-coupled cyclopentadienyl and indenyl homobimetallic nickel derivatives. The new binuclear complexes $[Cl(PPh_3)Ni\{\mu\text{-}(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}Ni(PPh_3)Cl]$ (**4**), $[(PPh_3)_2Ni\{\mu\text{-}(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}Ni(PPh_3)_2][PF_6]_2$ (**5**), $[(PPh_3)_2Ni\{\mu\text{-}(\eta\text{-}C_9H_6)CMe_2(\eta\text{-}C_9H_6)\}Ni(PPh_3)_2][PF_6]_2$ (**6**), $[Cl(PPh_3)Ni\{\mu\text{-}(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_9H_6)\}Ni(PPh_3)Cl]$ (**7**), $[(PPh_3)_2Ni\{\mu\text{-}(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_9H_6)\}Ni(PPh_3)Cl][PF_6]$ (**8**), $[(PPh_3)_2Ni\{\mu\text{-}(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_9H_6)\}Ni(PPh_3)_2][PF_6]_2$ (**9**) have been prepared and characterised. The X-ray crystal structure of **5** is reported. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Nickel; Ring-coupled derivatives; Cyclopentadienyl; Indenyl; Bimetallic compounds; Crystal structures

1. Introduction

Homo- and heterobinuclear metal complexes containing metal centres in adjacent positions may lead to the observation of cooperative chemical behaviour, thus modifying the stoichiometric or catalytic reactivity of the isolated mononuclear counterparts [1]. One of the most common ligand frameworks that has been used to hold two metal centres in vicinal positions is that of *ansa*-bridged ligands, where two cyclopentadienyl, two indenyl or both type of rings are coupled by CH_2, CMe_2, $C(CH_2)_5$ or $SiMe_2$ bridges. Many homo- and heterobimetallic compounds of this type have been described [2–9] but, to the best of our knowledge, no Group 10 derivatives containing such ligands have been reported so far. In this paper we describe the synthesis and characterisation of new ring-coupled cyclopentadienyl and indenyl binuclear complexes of nickel, in which the bridging ligands 2,2-bis(cyclopentadienyl)propane, 2,2-bis(1-indenyl)propane and 2-cyclopentadienyl-2-(1-indenyl)-propane are co-ordinated to NiCl(PPh_3) or $Ni(PPh_3)_2$ fragments.



2. Results and discussion

The metathetical reaction of the dilithium salts $Li_2[CMe_2(C_5H_4)_2]$ (**1**), $Li_2[CMe_2(C_9H_6)_2]$ (**2**) and $Li_2[(C_5H_4)CMe_2(C_9H_6)]$ (**3**) with $NiCl_2(PPh_3)_2$ is a convenient starting point for the preparation of ring-coupled binuclear complexes of nickel. All reactions described below are depicted in Scheme 1 and the analytical and NMR data for the resulting compounds are given in Table 1.

Treatment of $NiCl_2(PPh_3)_2$ with 0.5 equivalents of $Li_2[CMe_2(C_5H_4)_2]$ (**1**) in diethyl ether affords deep red $[Cl(PPh_3)Ni\{\mu\text{-}(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}Ni(PPh_3)Cl]$ (**4**) in 30% yield. This compound is relatively stable to air or moisture as a microcrystalline powder, and is readily soluble in toluene, dichloromethane and THF, spar-

---

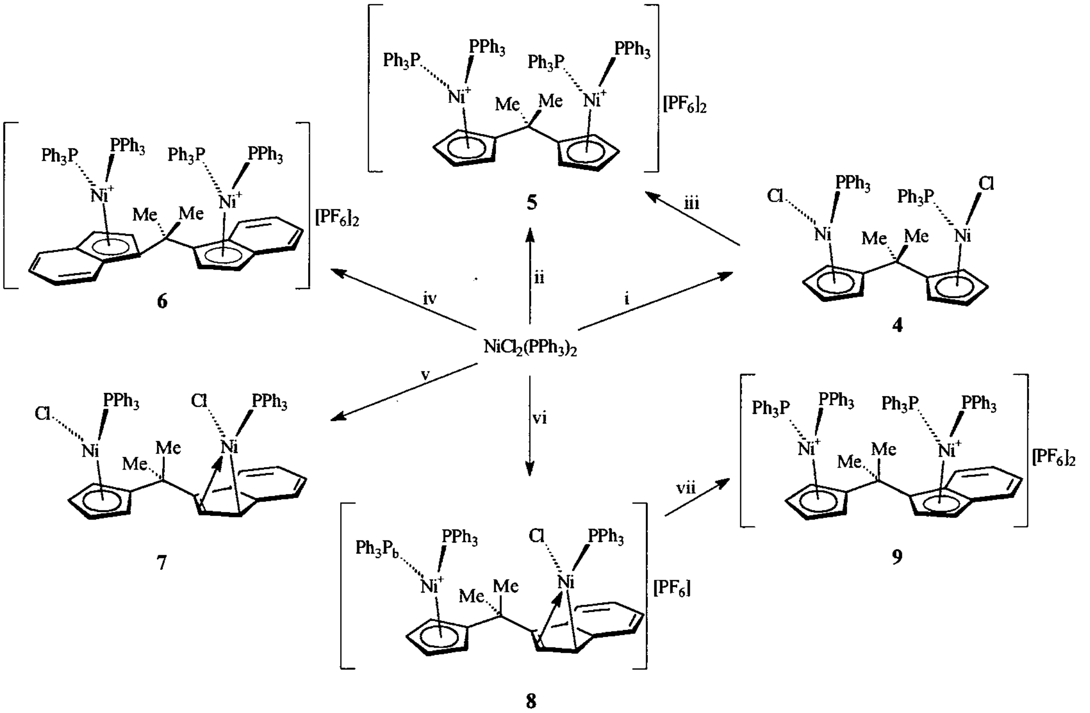
* Corresponding author. Tel.: + 351-218419232; fax: + 351-218464457.

E-mail address: pedro.gomes@ist.utl.pt (P.T. Gomes).

0022-328X/01/$ - see front matter © 2001 Elsevier Science B.V. All rights reserved.
PII: S0022-328X(01)00842-7

ingly soluble in diethyl ether and insoluble in *n*-hexane. However, it revealed to be unstable in solution while trying to grow crystals in toluene for two days, at room temperature. The ^{1}H-NMR spectrum shows a single resonance at δ 2.10 for both bridging methyl protons and only two triplets at δ 4.40 and 5.17 ($J_{HH} = 2.0$ Hz) for the Cp ring protons, assigned by NOE experiments to the equivalent proximal (H2′/H5′, closer to the bridge) and distal (H3′/H4′) protons, respectively. These triplets are somewhat broadened presumably due to weak coupling with the phosphorus atom. This deceptively simple AA′XX′ pattern, typical of monosubstituted cyclopentadienyl ligands [10], is due to the existence of a pseudo-plane of symmetry containing the Cp ring centroids and the bridging quaternary carbon, and also to a mirror plane perpendicular to the latter, defined by the three carbons of the CMe$_2$ bridge. This pattern together with the observation of a single resonance in the ^{31}P spectrum at δ 29.8 point out to unrestricted rotation of the NiCl(PPh$_3$) groups around each Cp–Ni bond. The overall symmetry of the molecule is thus C_{2v}, which is further confirmed by the ^{13}C{^{1}H} spectrum that exhibits one methyl resonance at δ 30.2, two peaks at δ 89.3 and 93.3 for the Cp CH carbons and one peak at δ 131.1 corresponding to the Cp *ipso* carbon resonance (C1′). These NMR features are close to those observed for the related mononuclear complexes [Ni(η-MeC$_5$H$_4$)(PPh$_3$)X] (X = Cl, Br, I, NCS) [11].

Halide abstraction from **4** with two equivalents of TlPF$_6$, in the presence of two equivalents of PPh$_3$, in THF, affords brownish yellow crystals of the dicationic compound [(PPh$_3$)$_2$Ni{μ-(η-C$_5$H$_4$)CMe$_2$(η-C$_5$H$_4$)}Ni(PPh$_3$)$_2$][PF$_6$]$_2$ (**5**) in a quantitative yield. Alternatively, compound **5** may be obtained in a much higher global yield (74%) if **4** is not isolated, hence by reacting one equivalent of NiCl$_2$(PPh$_3$)$_2$ with 0.5 equivalents of **1**, in Et$_2$O, and then the subsequent addition of two equivalents of TlPF$_6$ after changing the solvent to THF. Compound **5** is soluble in CH$_2$Cl$_2$ or THF and, as for all the compounds mentioned in this work, it is fairly stable when exposed to air or moisture when in the solid state. The NMR data show that C_{2v} symmetry is maintained in **5**. The Cp resonances observed in the ^{1}H-NMR spectrum are two triplets centred at δ 3.85 and 5.67 ($J_{HH} = 2.0$ Hz) the difference between their chemical shifts ($\Delta = \delta$(H2′/H5′) − δ(H3′/H4′) = 1.82) being higher than for **4** ($\Delta = 0.77$). These values are of the same order of magnitude of those verified for the previously mentioned mononuclear compounds [Ni(η-MeC$_5$H$_4$)(PPh$_3$)X] (X = Cl, Br, I, NCS), with Δ ranging from 0.90 to 1.66 [11], but they are significantly higher than for other mononuclear substituted cyclopentadienyl complexes of nickel such as [Ni(η-



Scheme 1. Synthesis of compounds **4**–**9**. Reagents: (i) **1** (0.5 equivalents) in diethyl ether, room temperature, 12 h; (ii) **1** (0.5 equivalents) in diethyl ether, room temperature, 3 h, then TlPF$_6$ (two equivalents), in THF, 1 h; (iii) PPh$_3$ (two equivalents) in THF, room temperature, 5 min, then TlPF$_6$ (two equivalents), 2 h; (iv) **2** (0.5 equivalents) in THF, room temperature, 0.5 h, then TlPF$_6$ (two equivalents), 1 h; (v) **3** (0.5 equivalents) in diethyl ether, room temperature, 3 h; (vi) **3** (0.5 equivalents) in diethyl ether, room temperature, 1 h, then TlPF$_6$ (two equivalents), in THF, 1 h; (vii) PPh$_3$ (one equivalent) in THF, room temperature, 5 min, then TlPF$_6$ (one equivalent), 2 h.

Table 1
Analytical and spectroscopic data for compounds **4**–**9**

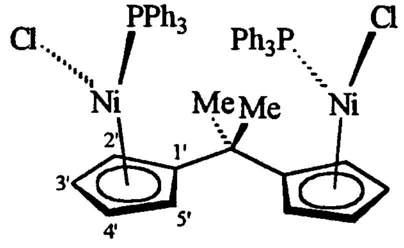
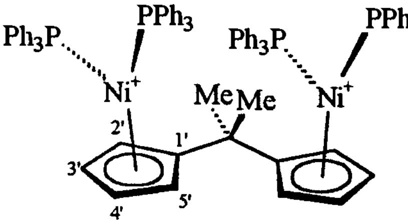
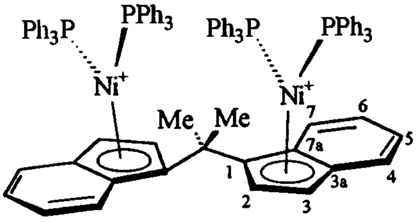
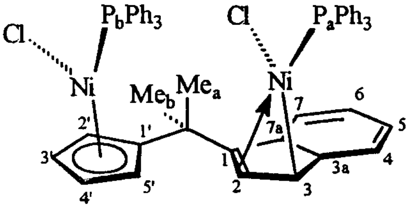
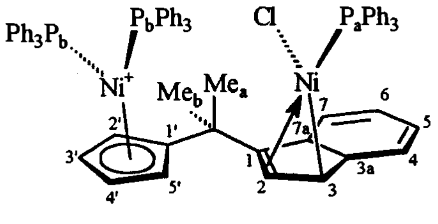
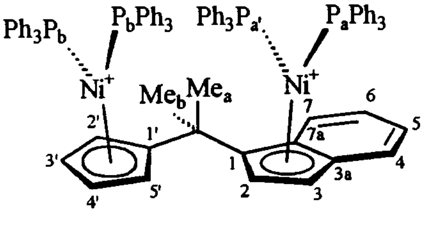
Compound[a]	NMR data[b]
4$[Cl(PPh_3)Ni\{\mu\text{-}(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}Ni(PPh_3)Cl]\cdot 2CH_3C_6H_5$ (**4**); deep red; C, 70.35 (70.89); H, 5.34 (5.67)  	$^1H^c$: 7.93 (br m, 12H, PPh_3 *ortho*), 7.2–6.9 (br, 28H, PPh_3 *meta* and *para* and $C_6\mathit{H}_5$ of toluene), 5.17 (br t, 4H, $J_{HH} = 2.1$, H2′ and H5′), 4.40 (br t, 4H, $J_{HH} = 2.1$, H3 and H4), 2.13 (s, 6H, $C\mathit{H}_3$ of toluene), 2.10 (s, 6H, $C(C\mathit{H}_3)_2$) $^{13}C\{^1H\}^c$: 134.5 (d, $^2J_{CP} = 10$, PPh_3 *ortho*), 133.5 (d, $^1J_{CP} = 45$, PPh_3 *ipso*), 131.1 (C1′), 130.3 (PPh_3 *para*), 128.4 (d, $^3J_{CP} = 9$, PPh_3 *meta*), 93.3 (C2′ and C5′ or C3′ and C4′), 89.3 (C3′ and C4′ or C2′ and C5′), 36.0 ($\mathit{C}(CH_3)_2$), 30.2 ($C(\mathit{C}H_3)_2$) $^{31}P^c$: 29.8 (s, $\mathit{P}Ph_3$)
5$[(PPh_3)_2Ni\{\mu\text{-}(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}Ni(PPh_3)_2][PF_6]_2\cdot CH_2Cl_2$ (**5**); brownish yellow; C, 59.88 (60.35); H, 4.39 (4.48)  	$^1H^d$: 7.73 (br m, 24H, PPh_3 *ortho*), 7.42–7.26 (br, 36H, PPh_3 *meta* and *para*), 5.67 (br t, 4H, $J_{HH} = 2.0$, H2′ and H5′), 5.33 (s, 2H, $C\mathit{H}_2Cl_2$), 3.85 (br t, 4H, $J_{HH} = 2.0$, H3′ and H4′), 1.22 (s, 6H, $C(C\mathit{H}_3)_2$) $^{13}C\{^1H\}^d$: 136.2 (PPh_3 *ipso*), 134.3 (PPh_3 *ortho*), 131.8 (PPh_3 *para*), 130.5 (C1′), 130.5 (d, $^1J_{CP} = 49$, PPh_3 *ipso*), 129.2 (PPh_3 *meta*), 97.2 (C3′ and C4′ or C2′ and C5′), 94.7 (C2′ and C5′ or C3′ and C4′), 35.3 ($\mathit{C}(CH_3)_2$), 30.7 ($C(\mathit{C}H_3)_2$) $^{31}P^d$: 32.5 (s, 4P, $\mathit{P}Ph_3$), −143.7 (sept, 2P, $^1J_{PF} = 712$, $\mathit{P}F_6^-$)
6$[(PPh_3)_2Ni\{\mu\text{-}(\eta\text{-}C_9H_6)CMe_2(\eta\text{-}C_9H_6)\}Ni(PPh_3)_2][PF_6]_2\cdot 3CH_2Cl_2$ (**6**); deep red; C, 57.75 (58.19); H, 4.87 (4.27)  	$^1H^d$: 8.06 (d, $^3J_{HH} = 8.1$, 1H, H7 or H4), 7.6–7.1 (br, 60H, $P(C_6\mathit{H}_5)_3$), 7.52 (t, $^3J_{HH} = 8.1$, 1H, H6 or H5), 7.14 (m, 1H, H5 or H6), 6.78 (d, $^3J_{HH} = 2.4$, 1H, H2), 6.75 (d, $^3J_{HH} = 8.1$, 1H, H4 or H7), 5.33 (s, 6H, $C\mathit{H}_2Cl_2$), 3.87 (m, 1H, H3), 2.08 (s, 6H, $C(C\mathit{H}_3)_2$ $^{13}C\{^1H\}^d$: 133.6 (d, $^2J_{CP} = 11$, PPh_3 *ortho*), 131.1 (PPh_3 *para*), 130.0 (d, $^1J_{CP} = 46$, PPh_3 *ipso*), 129.7 (C6 or C5), 128.8 (d, $^3J_{CP} = 11$, PPh_3 *meta*), 126.6 (C5 or C6), 126.4 (d, $^2J_{CP} = 15$, C1), 125.4 (C7a or C3a), 124.6 (C3a or C7a), 120.2 (C7 or C4), 119.7 (C4 or C7), 104.4 (C2), 67.8 (C3), 36.2 ($\mathit{C}(CH_3)_2$), 28.7 ($C(\mathit{C}H_3)_2$) $^{31}P^d$: 29.1 (s, 4P, $\mathit{P}Ph_3$), −143.7 (sept, $^1J_{PF} = 712$, 2P, $\mathit{P}F_6^-$)
7$[Cl(PPh_3)Ni\{\mu\text{-}(\eta\text{-}C_5H_4)CMe_2(\eta^2{:}\eta^1\text{-}C_9H_6)\}Ni(PPh_3)Cl]$ (**7**); deep red; C, 68.42 (68.22); H, 5.22 (4.97)  	$^1H^c$: 7.89 (br, 6H, P_bPh_3 *ortho*), 7.7–7.5 (br, 6H, P_aPh_3 *ortho*), 7.61 (d, $^3J_{HH} = 8.1$, 1H, H7), 7.05 (t, $J_{HH} = 7.6$, 1H, H6), 7.15–6.9 (br, 18H, P_aPh_3 and P_bPh_3 *meta* and *para*), 6.83 (t, $J_{HH} = 7.6$, 1H, H5), 6.80 (d, $^3J_{HH} = 3.1$, 1H, H2), 6.22 (d, $^3J_{HH} = 7.8$, 1H, H4), 5.39 (br q, $J_{HH} = 4.4$, 1H, H2′), 5.04 (br q, $J_{HH} = 4.4$, 1H, H5′), 4.76 (br q, $J_{HH} = 4.4$, 1H, H3′), 4.36 (br q, $J_{HH} = 4.4$, 1H, H4′), 3.01 (dd, $^3J_{HH} = 3.1$, $^3J_{PH} = 4.8$, 1H, H3), 2.48 (s, 3H, $C(C\mathit{H}_3)_a(CH_3)_b)$, 2.30 (s, 3H, $C(CH_3)_a(C\mathit{H}_3)_b)$ $^1H^e$: 7.86 (br, 6H, P_bPh_3 *ortho*), 7.5–7.7 (br, 6H, P_aPh_3), 7.58 (d, $^3J_{HH} = 8.4$, 1H, H7), 7.04 (t, $J_{HH} = 7.8$, 1H, H6), 7.15–6.9 (br, 18H, PPh_3 P_aPh_3 and P_bPh_3 *meta* and *para*), 6.82 (t, $J_{HH} = 7.5$, 1H, H_5), 6.76 (d, $^3J_{HH} = 3.0$, 1H, H2), 6.19 (d, $J_{HH} = 7.5$, 1H, H4), 5.34 (br q, $J_{HH} = 4.4$, 1H, H2′), 4.98 (br q, $J_{HH} = 3.8$, H5′), 4.82 (br q, $J_{HH} = 4.4$, 1H, H3′), 4.29 (br q, $J_{HH} = 3.8$, H4′), 2.97 (dd, $^3J_{HH} = 3.0$, $^3J_{PH} = 4.8$, 1H, H3), 2.42 (s, 3H, $C(C\mathit{H}_3)_a(CH_3)_b)$, 2.22 (s, 3H, $C(CH_3)_a(C\mathit{H}_3)_b)$ $^{13}C\{^1H\}^e$: 134.7 (P_aPh_3 *ortho*), 134.6 (P_bPh_3 *ortho*), 133.3 (d, $^1J_{CP} = 45$, P_aPh_3 or P_bPh_3 *ipso*), 132.6 (d, $^1J_{CP} = 43$, P_bPh_3 or P_aPh_3 *ipso*), 131.5 (C1′), 130.2 (P_aPh_3 and P_bPh_3 *para*), 129.8 (C3a or C7a), 128.4 (P_aPh_3 and P_bPh_3 *meta*), 127.2 (C7a or C3a), 126.8 (C6), 125.2 (C5), 121.3 (C7), 117.5 (C4), 115.5 (d, C1, $^2J_{CP} = 17$), 104.1 (C2), 94.5 (C2′), 91.8 (C3′), 91.1 (C5′),

Table 1 (*Continued*)

Compound[a]	NMR data[b]
	89.2 (C4′), 66.2 (C3), 39.1 ($\mathit{C}(\mathrm{CH_3})_\mathrm{a}(\mathrm{CH_3})_\mathrm{b}$), 28.9 ($\mathrm{C}(\mathit{C}\mathrm{H_3})_\mathrm{a}(\mathrm{CH_3})_\mathrm{b}$), 28.6 ($\mathrm{C}(\mathrm{CH_3})_\mathrm{a}(\mathit{C}\mathrm{H_3})_\mathrm{b}$) $^{31}\mathrm{P}^{e}$: 30.7 (s, 1P, $P_\mathrm{b}\mathrm{Ph_3}$), 28.7 (s, 1P, $P_\mathrm{a}\mathrm{Ph_3}$)
8[$(\mathrm{PPh_3})_2\mathrm{Ni}\{\mu\text{-}(\eta\text{-}\mathrm{C_5H_4})\mathrm{CMe_2}(\eta^2{:}\eta^1\text{-}\mathrm{C_9H_6})\}\mathrm{Ni(PPh_3)Cl}][\mathrm{PF_6}]\cdot 0.33\mathrm{CH_2Cl_2}\cdot 0.5\mathrm{Et_2O}$ (**8**); brownish red; C, 64.47 (64.80); H, 4.69 (4.93) 	$^{1}\mathrm{H}^{d}$: 7.49–7.30 (br, 46H, PPh$_3$ and H7 or H4), 7.18 (br, 1H, H6 or H5), 6.95 (t, $^3J_\mathrm{HH} = 8.1$, 1H, H5 or H6), 6.34 (d, $^3J_\mathrm{HH} = 7.8$, 1H, H4 or H7), 5.99 (d, $^3J_\mathrm{HH} = 3.3$, 1H, H2), 5.63 (br q, $J_\mathrm{HH} = 2.1$, 2H, H2′ and H5′), 5.33 (s, 0.66H, $\mathrm{C}\mathit{H}_2\mathrm{Cl_2}$), 4.79 (br q, $J_\mathrm{HH} = 2.1$, 1H, H4′ or H3′), 4.48 (br q, $J_\mathrm{HH} = 2.1$, 1H, H3′ or H4′), 3.44 (q, $^3J_\mathrm{HH} = 6.9$, 2H, $\mathrm{O(C}\mathit{H}_2\mathrm{CH_3)_2}$), 3.23 (dd, $^3J_\mathrm{HH} = 3.3$, $^3J_\mathrm{PH} = 5.1$, 1H, H3), 1.89 (s, 3H, $\mathrm{C(C}\mathit{H}_3)_\mathrm{a}(\mathrm{CH_3})_\mathrm{b}$), 1.66 (s, 3H, $\mathrm{C(CH_3)_a(C}\mathit{H}_3)_\mathrm{b}$), 1.16 (t, $^3J_\mathrm{HH} = 6.9$, 3H, $\mathrm{O(CH_2C}\mathit{H}_3)_2$) $^{13}\mathrm{C}\{^1\mathrm{H}\}^{d}$: 134.3 (P$_\mathrm{a}Ph_3$ and P$_\mathrm{a}$Ph$_3$ *ortho*), 132.0 (d, $^1J_\mathrm{CP} = 44$, P$_\mathrm{b}$Ph$_3$ *ipso*), 131.7 (P$_\mathrm{b}$Ph$_3$ *para*), 131.4 (C1′), 131.2 (d, $^1J_\mathrm{CP} = 47$, P$_\mathrm{a}$Ph$_3$ *ipso*), 130.8 (P$_\mathrm{a}$Ph$_3$ *para*), 130.2 (C7a or C3a), 129.1 (P$_\mathrm{b}$Ph$_3$ *meta*), 128.7 (d, $^3J_\mathrm{CP} = 11$, P$_\mathrm{a}$Ph$_3$ *meta*), 127.9 (C3a or C7a), 127.4 (C6 or C5), 126.0 (C5 or C6), 119.8 (C7 or C4), 118.4 (C4 or C7), 112.8 (d, $^2J_\mathrm{CP} = 16$, C1), 102.5 (C2), 98.1 (C4′or C3′), 97.1 (C3′ or C4′), 95.3 (C5′ or C2′), 94.8 (C2′ or C5′), 66.5 (C3), 38.6 ($\mathit{C}(\mathrm{CH_3})_\mathrm{a}(\mathrm{CH_3})_\mathrm{b}$), 27.5 ($\mathrm{C}(\mathit{C}\mathrm{H_3})_\mathrm{a}(\mathit{C}\mathrm{H_3})_\mathrm{b}$) $^{31}\mathrm{P}^{d}$: 33.5 (s, 2P, $P_\mathrm{b}\mathrm{Ph_3}$), 29.3 (s, 1P, $P_\mathrm{a}\mathrm{Ph_3}$), −143.7 (sept, $^1J_\mathrm{PF} = 712$, 1P, $P\mathrm{F}_6^-$)
9[$(\mathrm{PPh_3})_2\mathrm{Ni}\{\mu\text{-}(\eta\text{-}\mathrm{C_5H_4})\mathrm{CMe_2}(\eta\text{-}\mathrm{C_9H_6})\}\mathrm{Ni(PPh_3)_2}][\mathrm{PF_6}]_2\cdot 0.5\mathrm{Et_2O}$ (**9**); brownish yellow; C, 63.51 (63.75); H, 4.56 (4.57) 	$^{1}\mathrm{H}^{d}$: 7.6–7.0 (br, 62H, PPh$_3$ and H5 and H6), 6.58 (d, $^3J_\mathrm{HH} = 7.2$, 1H, H7 or H4), 6.35 (d, $^3J_\mathrm{HH} = 7.8$, 1H, H4 or H7), 6.08 (d, $^3J_\mathrm{HH} = 3.0$, 1H, H2), 5.60 (br s, 1H, H5′ or H2′), 5.34 (br s, 1H, H2′ or H5′), 4.74 (br s, 1H, H3), 3.99 (br s, 2H, H3′ and H4′), 3.43 (q, $^3J_\mathrm{HH} = 6.9$, 2H, $\mathrm{O(C}\mathit{H}_2\mathrm{CH_3)_2}$), 1.53 (s, 3H, $\mathrm{C(C}\mathit{H}_3)_\mathrm{a}(\mathrm{CH_3})_\mathrm{b}$), 1.16 (t, $^3J_\mathrm{HH} = 6.9$, 3H, $\mathrm{O(CH_2C}\mathit{H}_3)_2$), 0.45 (s, 3H, $\mathrm{C(CH_3)_a(C}\mathit{H}_3)_\mathrm{b}$) $^{13}\mathrm{C}\{^1\mathrm{H}\}^{d}$: 134.2 (PPh$_3$ *ortho*), 131.8 (PPh$_3$ *para*), 131.2 (C1′), 130.9 (d, $^1J_\mathrm{CP} = 44$, P$_\mathrm{b}$Ph$_3$ *ipso*), 130.6 (d, $^1J_\mathrm{CP} = 45$, P$_\mathrm{a}$Ph$_3$ and P$'_\mathrm{a}$Ph$_3$ *ipso*), 129.2 (PPh$_3$ *meta*), 127.8 (C1), 124.9 (C7a or C3a), 124.5 (C3a or C7a), 121.6 (C4–C7), 104.4 (C2), 97.3 (C4′ or C3′), 96.4 (C3′ or C4′), 95.7 (C5′ or C2′), 94.9 (C2′ or C5′), 78.9 (C3), 38.1 ($\mathit{C}(\mathrm{CH_3})_\mathrm{a}(\mathrm{CH_3})_\mathrm{b}$), 26.8 ($\mathrm{C}(\mathit{C}\mathrm{H_3})_\mathrm{a}(\mathit{C}\mathrm{H_3})_\mathrm{b}$) $^{31}\mathrm{P}^{d}$: 32.5 (s, 2P, $P_\mathrm{b}\mathrm{Ph_3}$), 31.5 (v br, $P_\mathrm{a}\mathrm{Ph_3}$ or $P_{a'}\mathrm{Ph_3}$), 28.1 (v br, $P_{a'}\mathrm{Ph_3}$ or $P_a\mathrm{Ph_3}$), −143.7 (sept, $^1J_\mathrm{PF} = 712$, 2P, $P\mathrm{F}_6^-$)

[a] Analytical data given as: found (calculated)%.

[b] ^{1}H NMR at 300 MHz, ^{13}C at 75.43 MHz, ^{31}P at 121.44 MHz; room temperature. Data given as: chemical shift (δ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, sept = septet, m = multiplet, br = broad; v = very), coupling constant (in Hz), relative intensity and assignment.

[c] In C_6D_6.

[d] In CD_2Cl_2.

[e] In toluene-d_8.

$\mathrm{MeC_5H_4)(dppe)]X}$ (X = Cl, I, NCS) [11] with values of Δ between 0.09 and 0.12, $[\mathrm{Ni}(\eta\text{-RC_5H_4})\mathrm{L_2}]\mathrm{BF_4}$ (R = Me, ^{t}Bu; L$_2$ = norbornadiene, 1,5-cyclooctadiene) [12] with Δ varying from 0 to 0.41, or $[\mathrm{Ni}(\eta\text{-MeC_5H_4})(\mathrm{CO})]_2$ ($\Delta = 0.06$) [13]. Also in the last two cases, where no PPh$_3$ ligands are present, the distal protons (H3′/H4′) resonate in the normal range of Cp protons (δ ca. 5.6 for the cationic complexes, and δ 5.22 for the neutral dimer, respectively). Therefore, it is possible that the low-field shifts observed in our binuclear compounds for H3′/H4′ are caused by ring current anisotropy induced by the phosphine phenyl rings, by the vicinal Cp ring or by both effects simultaneously. The same type of argument may explain why the bridge methyl resonance at δ 1.22 appears considerably more shielded in relation to **4**, but the corresponding ^{13}C resonance at δ 35.3 is not particularly sensitive to the increase in the number of PPh$_3$ ligands in **5**. The CH ring ^{13}C reso-

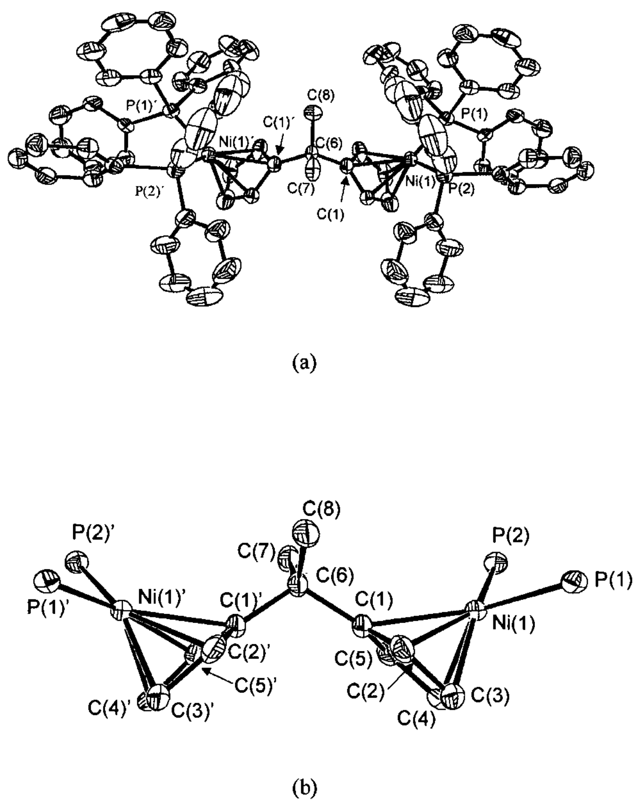


Fig. 1. ORTEPIII diagram of dication **5**, using 30% probability level ellipsoids. (a) Global view. (b) Side view (the phenyl groups have been omitted for clarity).

nances, at δ 94.7 and 97.2, as well as the ^{31}P resonance, at δ 32.5, are shifted low-field in relation to the corresponding resonances in **4** due to the cationic nature of the nickel centres, while the Cp *ipso* C1′ resonance at δ 130.5 remains virtually unchanged.

Recrystallisation of **5** from CH_2Cl_2–Et_2O gave crystals suitable for X-ray diffraction. The crystal structure of **5** reveals that only one half of the binuclear dication is found in the asymmetric unit as atoms C6, C7 and C8 (from the CMe_2 bridge) are located in a mirror plane and the remaining is generated by a symmetry operation (see Section 3). The molecular structure of the dication is shown in Fig. 1 and selected interatomic distances and angles are listed in Table 2. The $Ni(PPh_3)_2$ fragments are positioned on the C_5H_4 faces of the bridging ligand so that inter-ring repulsions are minimised. As a consequence there is a long interatomic separation Ni(1)···Ni(1)′ of 6.750(1) Å. In contrast to the observed structure of **5** in solution, the plane defined by atoms C(1)–C(6)–C(1)′ is not a mirror plane in the solid state as its dihedral angle with the Cp ring planes is 81.8(6)°. This corresponds to a 8.2° anti-clockwise rotation of the Cp ring around the C(1)–C(6) bond (or clockwise rotation around C(1)′–C(6)) which is probably a result of the minimisation of the repulsions between the CMe_2 bridge and the closer P(2) PPh_3 group. The geometry at nickel is trigonal planar (sum of bond angles using Cp ring centroid = 359.7(9)°) but, due to the same reason, the Cp plane is slightly shifted from perpendicularity to the P(2)–Ni(1)–P(1) plane (dihedral angle = 83.9(2)°). This is also observed in other existing X-ray structures of monosubstituted cyclopentadienyl complexes of nickel [11,14,15]. The Ni–C_{Cp} and Ni–P distances are slightly longer than the values observed for [Ni(η-MeC_5H_4)(PPh_3)I] [11] which is another consequence of high steric crowding in compound

Table 2
Selected bond lengths (Å) and bond angles (°) for the dication $\{(PPh_3)_2Ni[\mu\text{-}(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)]Ni(PPh_3)_2\}^{2+}$ (**5**)

Bond lengths (Å)			
Ni(1)–P(1)	2.211(2)	C(5)–C(1)	1.429(11)
Ni(1)–P(2)	2.214(2)	C(5)–C(4)	1.428(12)
Ni(1)–C(2)	2.121(8)	C(2)–C(3)	1.429(13)
Ni(1)–C(4)	2.136(9)	C(2)–C(1)	1.382(11)
Ni(1)–C(5)	2.098(8)	C(3)–C(4)	1.371(15)
Ni(1)–C(1)	2.186(7)	C(1)–C(6)	1.534(9)
Ni(1)–C(3)	2.103(9)	Ni(1)–$Cp_{cent.}$	1.76(8)
Bond angles (°)			
P(1)–Ni(1)–C(2)	100.0(3)	P(2)–Ni(1)–C(1)	115.0(2)
P(1)–Ni(1)–C(4)	127.1(3)	P(2)–Ni(1)–C(3)	148.2(4)
P(1)–Ni(1)–C(5)	161.4(2)	P(2)–Ni(1)–P(1)	103.0(8)
P(1)–Ni(1)–C(1)	131.4(2)	C(1)–C(6)–C(1)′ [a]	105.2(6)
P(1)–Ni(1)–C(3)	97.5(3)	C(6)–C(1)–Ni(1)	134.3(5)
P(2)–Ni(1)–C(2)	152.3(2)	C(7)–C(6)–C(8)	111.1(11)
P(2)–Ni(1)–C(4)	111.2(4)	$Cp_{cent.}$–Ni(1)–P(1)	127.6(9)
P(2)–Ni(1)–C(5)	95.2(2)	$Cp_{cent.}$–Ni(1)–P(2)	129.1(9)
Dihedral angle between Cps (°)	88.5(2)		
Dihedral angle between Cp and P(2)–Ni(1)–P(1) (°)	83.9(2)		
Nearest Cp carbon (C(5)) to P(2)–Ni(1)–P(1) plane (Å)	0.143(8)		

[a] Atom C (1)′ generated by symmetry operation (x, y, −z+1).

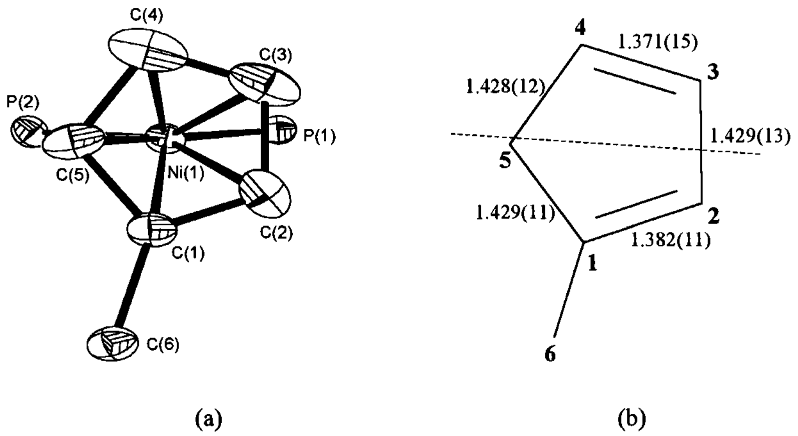


Fig. 2. (a) Top view of one of the $CpNi(PPh_3)_2$ moieties of dication **5**. (b) Diene distortion observed in the cyclopentadienyl ligands of **5** (the P(2)–Ni(1)–P(1) plane is indicated by a dashed line; distances in Å).

5 that has a bulkier Cp substituent and ligands (PPh_3 instead of I).The Cp ring has two internal non-adjacent bonds C(1)–C(2) (1.382(11) Å) and C(3)–C(4) (1.371(15) Å) markedly shorter than C(1)–C(5) (1.429(11) Å), C(4)–C(5) (1.428(12) Å) and C(2)–C(3) (1.429(13) Å) (Fig. 2), and the shortest Ni–C_{Cp} distance Ni-C(5) (2.098(8) Å) is that of the carbon that stays on the P(2)–Ni(1)–P(1) plane, lying over P(2). According to the classification introduced by Andersen and coworkers [16], this is characteristic of a η^5 co-ordinated cyclopentadienyl ligand with a diene-type distortion, and the geometry at nickel may be re-interpreted as pseudo-square-planar. This distortion arises from the preference of Ni(II) to form square-planar 16-electron complexes.

The one-pot reaction of $NiCl_2(PPh_3)_2$ with 0.5 equivalents of $Li_2[CMe_2(C_9H_6)_2]$ (**2**) in THF followed by treatment with an equimolar amount of $TlPF_6$ gave a deep red powder $[(PPh_3)_2Ni\{\mu\text{-}(\eta\text{-}C_9H_6)CMe_2(\eta\text{-}C_9H_6)\}Ni(PPh_3)_2][PF_6]_2$ (**6**) in 68% yield. Attempts to synthesise the neutral compound $[Cl(PPh_3)Ni\{\mu\text{-}(\eta\text{-}C_9H_6)CMe_2(\eta\text{-}C_9H_6)\}Ni(PPh_3)Cl]$, analogous to **4**, were unrewarding leading to unidentified products independent of the reaction conditions used (temperature, solvent and time), which contrasts with the successful synthesis of the mononuclear indenyl nickel derivatives $[Ni(\eta\text{-}1\text{-}R\text{–}Ind)(PPh_3)Cl]$ (R = H, Me) by Zargarian and co-workers [17a,c]. These authors had already synthesised the mononuclear cationic derivative $[Ni(\eta\text{-}1\text{-}Me\text{–}Ind)(PPh_3)_2][AlCl_4]$, by reaction of the previous neutral compound (R = Me) with $AlCl_3$ in the presence of an equimolar amount of PPh_3 [17b]. The ^1H-NMR spectrum of the binuclear dication **6** shows only a single resonance at δ 2.08 for both bridge methyl protons and one peak for each type of indenyl protons C2–C7. These features denote a structure conformationally similar to **5** where only the *rac*-isomer is observed (in the *rac*-isomer the indenyl bezenoid rings alternate in relation to the plane containing the indenyl C_5 ring centroids and the bridging quaternary carbon; the *meso*-isomer would lead to two different resonances for the Me groups). The indenyl protons H4 and H7 appear at δ 8.06 and 7.75 as two doublets ($J = 8.1$ Hz), while at δ 7.52 and 7.14 the H5 and H6 protons are superimposed on the broad PPh_3 resonances. Protons H2 and H3 correspond, respectively, to the doublet at δ 6.78 ($^3J_{HH} = 2.4$ Hz) and to the multiplet at δ 3.87, which is broadened by weak coupling to the phosphorus atoms. This overall C_2 symmetry is confirmed in the $^{13}C\{^1H\}$ spectrum that exhibits one methyl resonance at δ 28.7. The comparison of the ^{13}C chemical shifts of the indenyl ring-junction carbons (C3a and C7a) of a complex with those of sodium indenyl correlate well with the indenyl hapticity, and a solution hapticity parameter, $\Delta\delta_{av}C$, can be defined ($\Delta\delta_{av}C = \delta_{av}(C3a/C7a)$ (η-Ind) $- \delta(C3a/C7a)$ (NaInd)); values of $\Delta\delta C \ll 0$ are typical of η^5 hapticity, $\Delta\delta C \gg 0$ reveal a η^3 behaviour, while $\Delta\delta_{av}C \approx 0$ indicate an intermediate character [18]. For complex **6** a value of $\Delta\delta_{av}C = -6.7$ is determined, pointing to an intermediate η^5–η^3 hapticity for the indenyl ligands, in agreement with the same type of hapticity determined by X-ray crystallography for $[Ni(\eta\text{-}1\text{-}Me\text{–}Ind)(PPh_3)(PMe_3)][AlCl_4]$ [17b]. Noteworthy are the relatively shielded values of chemical shift observed for C3 and H3, at δ 67.8 and 3.87, respectively, which are positioned very closely to those found for the only other cationic C1 substituted indenyl complex of Ni characterised simultaneously by ^1H- and ^{13}C-NMR spectroscopy, $[Ni(\eta^3{:}\eta^1\text{-}Ind(CH_2)_2NMe_2)(PPh_3)][BPh_4]$) [17d]. The variable-temperature ^{31}P-NMR spectra show a single sharp resonance at ca. δ 29.1 throughout the range of temperatures studied (room temperature to -80°C), and a proper integration of this peak shows a ratio 2:1 compared to the PF_6^- septet at δ -143.7. This result is unexpected since each Ni moiety is locally asymmetric due to the indenyl substitution in carbon C1, which should give rise to two ^{31}P resonances corresponding to two magnetically inequivalent PPh_3 ligands, as in the already mentioned [Ni(η-1-Me–Ind)$(PPh_3)_2$][$AlCl_4$] [17b] or in compound **9** (see below). Therefore, the only possible explanation is given by a rapid (in the NMR time-scale) unrestricted rotation of the $Ni(PPh_3)_2$ groups around each Ind–Ni bond, similar to the observation made for **4**.

Employment of an identical synthetic procedure used for **4**, reacting $NiCl_2(PPh_3)_2$ with 0.5 equivalents of the ligand precursor $Li_2[(C_5H_4)CMe_2(C_9H_6)]$ (**3**) in Et_2O, afforded [Cl(PPh_3)Ni{μ-(η-C_5H_4)CMe_2(η-C_9H_6)}Ni(PPh_3)Cl] (**7**) as a deep red powder in 47% yield. This mixed-ring binuclear complex has no elements of symmetry (C_1) with all proton, carbon and phosphorus nuclei being inequivalent in the corresponding NMR spectra. The use of $^{1}H-^{1}H$ 2D correlations (COSY and NOESY) and $^{13}C-^{1}H$ single bond correlation (HETCOR) allowed the full assignment of all the spectra resonances as shown in Table 1. Although now consisting of four different broadened pseudo-quartets, five different ^{13}C resonances and one ^{31}P peak (δ 30.7), all the chemical shifts of the cyclopentadienyl moiety are very close to the values found for compound **4**. The neutral indenyl moiety has NMR features similar to those of compound [Ni(η-1-Me–Ind)(PPh_3)Cl] [17c]. The proton H2 resonance at δ 6.76 and a very shielded H3 resonance at δ 2.97 appear, respectively, as a doublet ($^{3}J_{HH} = 3.0$ Hz) and a doublet of doublets due to additional coupling with the phosphorus ($^{3}J_{PH} = 4.8$ Hz). The carbon C2 comes as a doublet ($^{2}J_{CP} = 17$ Hz) at δ 104.1 and C3 is also very shielded at δ 66.2. On the other side, carbons C3a and C7a, at δ 127.2 and 129.8, determine a hapticity parameter of $\Delta\delta_{av}C = -2.2$ ppm, lower than the value obtained in the dicationic derivative **6**. This corresponds to a higher degree of distortion (slippage) of the indenyl bonding to Ni in the neutral complex **7**, although maintaining an intermediate a $\eta^5-\eta^3$ character. Similar to its mononuclear analogue, a second type of distortion may be envisaged to take place in **7** due to different *trans* influences of the Cl and PPh_3 ($PPh_3 > Cl$). As a consequence, the distance Ni–C1 is larger than Ni–C3 and partial localisation of bonding in the allyl part of the C_5 ring is observed, resulting in an asymmetric η^2: η^1 co-ordination of indenyl to Ni [17a,c].

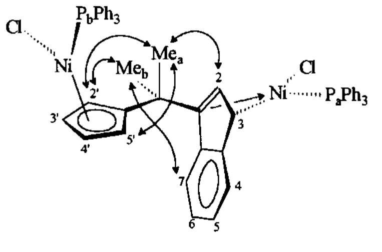


Fig. 3. Average conformation of **7** in solution according to some of the most relevant nuclear Overhauser (NOE) correlations observed in the room temperature NOESY spectrum.

A NOESY spectrum at room temperature (22°C), using a $\tau_{mix} = 1$ s, provided some spatial assignments and enabled an approximate picture of the average relative conformation of both moieties in **7** to be drawn (Fig. 3). In the previous compounds **4**–**6** it was demonstrated that the plane defined by C1′–C6–C1 is perpendicular to both ring planes. The strong cross-peaks correlating the Me_a group (δ 2.42) with H2 (δ 6.76) and H5′ (δ 4.98), and less intense ones with H2′ (δ 5.34) and H7 (δ 7.58) show that, in relation to this plane, there has been a clockwise rotation of both Cp and Ind rings around the C1′–C6 and C1–C6 bonds, respectively. These rotations, approaching the bridging C–Me_b and C–Me_a bonds to coplanarity with Cp and Ind planes respectively, are a consequence of the minimisation of inter-ring repulsions. This hypothetical conformation is validated by the fact that Me_b (δ 2.22) correlates strongly with H2′ and H7, and virtually no correlation is observed with H2 and H5′.

In an attempt to isolate the mixed-ring dicationic complex [$(PPh_3)_2$Ni{μ-(η-C_5H_4)CMe_2(η-C_9H_6)}Ni$(PPh_3)_2$][PF_6]$_2$ (**9**), the reaction of $NiCl_2(PPh_3)_2$ with 0.5 equivalents of $Li_2[(C_5H_4)CMe_2(C_9H_6)]$ (**3**) in Et_2O was carried out. After 1 h, one equivalent of $TlPF_6$ was added in THF, and the reaction was allowed to proceed for a further hour, giving rise to a brownish red powder of the monocationic product [$(PPh_3)_2$Ni{μ-(η-C_5H_4)-CMe_2(η-C_9H_6)}Ni(PPh_3)Cl][PF_6] (**8**), in high yield (73%). In this unexpected reaction, the metathetical exchange of Cl^- by PF_6^- occurred selectively in the cyclopentadienylic nickel moiety, which can be explained by a considerably higher ionic character of the Ni–Cl bond in the CpNi fragment. This marked difference in the reactivity is probably the result of a stronger co-ordination of the Cp versus Ind [19]. The higher degree of metal electronic unsaturation in the IndNi moiety gives a more covalent character to the indenyl Ni–Cl bond when compared with its cyclopentadienyl counterpart, being the driving force for their different kinetic behaviour. Halide abstraction of the remaining halide occurs by reacting **8** with equimolar amounts of PPh_3 and $TlPF_6$, in THF, with the formation of a brownish yellow powder of the binuclear dicationic complex **9**, in 90% yield.

Both compounds are asymmetric, with the ^{1}H-NMR spectra containing four typical, slightly broadened pseudo-quartet resonances belonging to the Cp part of the ligand. For complex **9**, these resonances appear at chemical shifts near to those of the dicationic complex **5**. In the case of **8**, the H3′ and H4′ resonances are less shielded than in **9**, due to smaller ring current effects of the single PPh_3 ligand co-ordinated to the adjacent IndNi unit. Both Cp ^{13}C chemical shift values are similar to those found for complex **5**. As for **7**, the neutral indenyl moiety of **8** shows a η^5–η^3 intermediate hapticity ($\Delta\delta_{av}C = -1.7$ ppm) with η^2: η^1 asymmetric co-ordination to nickel. In fact, the H3 proton is found to be shifted upfield to δ 3.23 as a doublet of doublets ($^3J_{HH} = 3.3$ and $^3J_{PH} = 5.1$ Hz), and H2 appears at δ 5.99 as a doublet. The localised bond character is also visible in the ^{13}C spectrum where values of δ 66.5, 102.5 and 112.8 ($^2J_{CP} = 16$ Hz) are found for C3, C2 and C1, respectively. Compared to **8**, the cationic indenyl moiety of **9** is, as expected, less distorted ($\Delta\delta_{av}C = -6.0$ ppm), and has a very similar hapticity parameter to **6**, since two PPh_3 ligands are co-ordinating to Ni. A more delocalised indenyl bonding mode is evident from the ^1H chemical shifts of δ 6.08 ($^3J_{HH} = 3.0$ Hz) and 4.74 for H2 and H3, respectively, and from the ^{13}C spectrum with resonances at δ 78.9, 104.4 and 127.8, for C3, C2 and C1.

In the ^{31}P spectra, the fact that both compounds **8** and **9** present two singlets at δ 33.5 and 32.5, respectively, implies the existence of rapid rotation of the $Ni(PPh_3)_2$ fragments about the Ni–Cp bonds. In the indenyl neutral fragment of **8** the ^{31}P resonates at δ 29.3, while for the cationic indenyl fragment of **9** two very broad peaks at δ 31.5 and 28.1 are observed. These broad features are assigned to the slow rotation of the $Ni(PPh_3)_2$ fragments around the Ni–Ind bond. Variable-temperature NMR spectra allow the observation, at -80°C, of an AX spectrum with two doublets at δ 30.6 and 28.0 ($^2J_{PP} = 28$ Hz). These resonances broaden and coalesce at $T_C = 308$ K. At this temperature, the rate constant (k) and free energy of activation ($\Delta G^\ddagger$) of this fluxional process can be estimated [20] as 733 s^{-1} and 14.0 kcal mol^{-1}, respectively. This value is 2 kcal mol^{-1} lower than the one obtained for the neutral $[Ni(\eta^2{:}\eta^1\text{-Ind})(PPh_3)Cl]$ [17a], which is in agreement with a less distorted indenyl ligand [21].

3. Experimental

All manipulations and reactions were carried out under an atmosphere of dinitrogen (<10 ppm oxygen or water) using standard Schlenk vessel and vacuum-line techniques or in a dry-box. Solvents were pre-dried over activated 4 Å molecular sieves and then distilled under an atmosphere of dinitrogen from Na/benzophenone (Et_2O, THF and $C_6H_5CH_3$) or CaH_2 (CH_2Cl_2 and n-hexane), and stored under dinitrogen. Deuteriated solvents (C_6D_6, toluene-d_8, CD_2Cl_2 and $CDCl_3$) for NMR samples were dried with molecular sieves, degassed by freeze–pump–thaw cycles and stored in ampoules over activated molecular sieves.

The NMR spectra were recorded on Varian Unity 300 and Inova spectrometers (^1H, 300 MHz; ^{13}C, 75.43 MHz; ^{31}P, 121.44 MHz) and referenced internally using residual protio-solvent (^1H) or solvent (^{13}C) resonances relative to Me_4Si ($\delta = 0$), or referenced externally (^{31}P) to 85% H_3PO_4 ($\delta = 0$). Assignments were supported by Nuclear Overhauser Effect (one- and two-dimensional) experiments and one- and two-dimensional homo- and heterocorrelations, as appropriate. Elemental analyses were performed by the Laboratório de Análises at this Institute. Reagents as ^{n}BuLi or PPh_3 were purchased from Aldrich, and used as received. The $NiCl_2(PPh_3)_2$ [22] and the ligand precursors 2,2-bis(cyclopentadiene)propane [23a], 2,2-bis(1-indene)propane [23b] and 2-cyclopentadiene-2-(1-indene) propane [23a] and their corresponding dilithium salts, respectively, $Li_2[CMe_2(C_5H_4)_2]$ (**1**) [23a], $Li_2[CMe_2(C_9H_6)_2]$ (**2**) [23b] and $Li_2[(C_5H_4)CMe_2(C_9H_6)]$ **3** [9b] were prepared according to literature methods.

3.1. Synthesis of $[Cl(PPh_3)Ni\{\mu\text{-}(\eta\text{-}C_5H_4)CMe_2\text{-}(\eta\text{-}C_5H_4)\}Ni(PPh_3)Cl]_2\cdot CH_3C_6H_5$ (4)

A suspension of **1** (0.44 g; 2.39 mmol) in Et_2O (30 ml) was slowly added to a suspension of $NiCl_2(PPh_3)_2$ (2.78 g; 4.25 mmol) in Et_2O (30 ml), at room temperature (r.t.), and the reaction mixture was stirred for 12 h. Filtration of the deep red supernatant solution left a mixture of deep red and off-white solids that was further washed with Et_2O (3 × 50 ml). Extraction of the residue with toluene (3 × 50 ml) afforded a deep red solution. Partial evaporation of the solvent under vacuum induced the formation of small needles, and the compound was allowed to crystallise overnight, at -20°C. The resulting deep red microcrystals of **4** (0.24 g) were filtered and dried under dynamic vacuum. Reduction of the mother liquor volume under vacuum and cooling to -20°C for two days further gave a second crop of microcrystals of **4** (0.44 g) that were dried under vacuum. Global yield: 30%.

3.2. Synthesis of $[(PPh_3)_2Ni\{\mu\text{-}(\eta\text{-}C_5H_4)CMe_2\text{-}(\eta\text{-}C_5H_4)\}Ni(PPh_3)_2][PF_6]_2\cdot CH_2Cl_2$ (5)

A suspension of **1** (0.534 g; 2.89 mmol) in Et_2O (30 ml) was slowly added to a suspension of $NiCl_2(PPh_3)_2$ (3.85 g; 5.79 mmol) in Et_2O (30 ml), at r.t., and the reaction mixture was stirred for 3 h. The resulting precipitate was filtrated and washed with Et_2O (3 × 40 ml). THF (50 ml) was added to the residue followed by $TlPF_6$ (2.10 g; 6 mmol) and the mixture was further stirred for 1 h. The solvent was removed under vacuum and the residue extracted with CH_2Cl_2. The brownish yellow solution was filtrated through a Celite bed, concentrated under vacuum and layered with Et_2O at -20°C. After three days, brownish yellow needles of **5** (3.77 g) were filtrated and dried under vacuum. Yield: 74%. Crystals suitable for X-ray diffraction were obtained. Alternatively, addition of two equivalents of

PPh_3 to a solution of **4** in THF, at r.t., followed by addition of $TlPF_6$ (two equivalents) and similar work-up of the product gave **5** in an almost quantitative yield.

3.3. Synthesis of $[(PPh_3)_2Ni\{\mu\text{-}(\eta\text{-}C_9H_6)CMe_2\text{-}(\eta\text{-}C_9H_6)\}Ni(PPh_3)_2][PF_6]_2\cdot 3CH_2Cl_2$ (**6**)

A solution of **2** (0.300 g; 0.68 mmol) in THF (30 ml) was slowly added to a suspension of $NiCl_2(PPh_3)_2$ (0.89 g; 1.36 mmol) in THF (30 ml), at r.t. The resulting deep red solution was stirred for 0.5 h prior to the addition of $TlPF_6$ (0.475 g; 1.36 mmol). After 1 h, the solvent was removed under vacuum and the residue washed with Et_2O (2 × 30 ml). Extraction with CH_2Cl_2 gave a dark red solution that was filtrated through a Celite bed, concentrated under vacuum and layered with Et_2O at −20°C. After three days, the deep red powder of **6** (1.83 g) was filtered and dried under vacuum. Yield: 68%.

3.4. Synthesis of $[Cl(PPh_3)Ni\{\mu\text{-}(\eta\text{-}C_5H_4)CMe_2\text{-}(\eta^2{:}\eta^1\text{-}C_9H_6)\}Ni(PPh_3)Cl]$ (7)

A suspension of **3** (0.51 g; 2.179 mmol) in Et_2O (30 ml) was slowly added to a suspension of $NiCl_2(PPh_3)_2$ (2.85 g; 4.35 mmol) in Et_2O (30 ml), at r.t., and the deep red reaction mixture was stirred for 3 h. Filtration of the deep red supernatant solution left a mixture of deep red and off-white solids that was further washed with Et_2O (3 × 50 ml). Extraction of the residue with toluene (3 × 30 ml) afforded a deep red solution. Evaporation of the solvent under vacuum to ca. 20 ml and dropwise addition of *n*-hexane induced the precipitation of a deep red powder of **7** (0.96 g), that was further washed with *n*-hexane (3 × 30 ml) and dried under dynamic vacuum. Yield: 47%.

3.5. Synthesis of $[(PPh_3)_2Ni\{\mu\text{-}(\eta\text{-}C_5H_4)CMe_2\text{-}(\eta^2{:}\eta^1\text{-}C_9H_6)\}Ni(PPh_3)Cl][PF_6]\cdot 0.33CH_2Cl_2\cdot 0.5Et_2O$ (**8**)

A suspension of **3** (0.236 g; 1 mmol) in Et_2O (30 ml) was slowly added to a suspension of $NiCl_2(PPh_3)_2$ (1.32 g; 2 mmol) in Et_2O (30 ml), at r.t., and the deep red reaction mixture was stirred for 1 h. The solvent was evaporated to drieness and THF (50 ml) added to the residue followed by $TlPF_6$ (0.718 g; 2.05 mmol), and the mixture further stirred for 1 h. The solvent was removed under vacuum and the residue washed with Et_2O (2 × 30 ml) and extracted with CH_2Cl_2. The resulting solution was filtrated through a Celite bed and concentrated under vacuum. Dropwise addition of Et_2O induced the precipitation of a brownish red powder that was dried under vacuum. Redissolution of the powder in CH_2Cl_2 and layering with Et_2O gave a brownish red powder of **8** (0.95 g). Yield: 73%.

3.6. Synthesis of $[(PPh_3)_2Ni\{\mu\text{-}(\eta\text{-}C_5H_4)CMe_2\text{-}(\eta\text{-}C_9H_6)\}Ni(PPh_3)_2][PF_6]_2\cdot 0.5Et_2O$ (**9**)

A solution of PPh_3 (0.026 g; 0.1 mmol) in THF (5 ml) was slowly added to a solution of **8** (0.131 g; 0.1 mmol) in THF (20 ml), at r.t. After 5 min, $TlPF_6$ (0.037 g; 0.105 mmol) was added and the reaction mixture was stirred for 2 h. The solvent was removed under vacuum and the residue extracted with CH_2Cl_2. The brownish yellow solution was filtrated through a Celite bed and concentrated under vacuum. Dropwise addition of Et_2O induced the precipitation of a deep red powder that was dried under vacuum. Redissolution of the powder in CH_2Cl_2 and layering with Et_2O gave a brownish yellow powder of **9** (0.151 g). Yield: 90%.

3.7. X-ray structure determination of **5**

Crystals of **5** suitable for diffraction measurements were sealed in glass capillaries under dinitrogen.

Data were collected in a TURBO CAD4 rotating anode equipped with Mo–Kα ($\lambda = 0.71069$ Å) radiation by the ω–2θ scan mode. Unit cell dimensions were obtained from the refinement of the setting angles of 25 reflections $15 < \theta < 17°$. Data was corrected for Lorentz polarisation, linear decay as well as empirically for absorption (using the ψ scan mode). The MOLEN software from Enraf–Nonius was used in the data reduction.

The position of the Ni atom was obtained from a three-dimensional Patterson synthesis and all other non-hydrogen atoms were located in subsequent difference Fourier maps and refined with anisotropic thermal motion parameters based on F^2. Only half of the binuclear dication is found in the asymmetric unit as atoms C6, C7 and C8 (from the CMe_2 bridge) are located in a mirror plane (x, y, 0.5), and the remaining is generated by the symmetry operation x, y, $-z+1$. Two disordered PF_6^- anions were found, both being in special positions, one in the mirror plane (x, y, 0.5) and the other in a two-fold axis (0.5, 0, z). Both anions have large thermal parameters for the F atoms. Two disorder models with different geometries were tried, but showed no improvement in the refinement. The F atoms were allowed to refine with anisotropic thermal parameters. A solvent molecule (CH_2Cl_2) was also found in the structure. The CH_2Cl_2 molecule was found to be both thermally and positionally disordered, with the two chlorine atoms also located in the plane (x, y, 0.5), and near the centre of symmetry at (0.5, 0.5, 0.5). Several trial refinements were used with different disorder models, but none of the tested models gave satisfactory results either in terms of a reasonable overall geometry or pronounced decrease in the R values. The poor diffracting pattern and unresolved disorder in the anions and solvent molecules precluded a structural analy-

Table 3
Crystal data and structure refinement parameters for **5**

Empirical formula	$C_{43}H_{38}ClF_6NiP_3$
Formula weight	860.80
Temperature (K)	293(2)
Wavelength (Å)	0.71069
Crystal system	Orthorhombic
Space group	*Pnnm* (no. 58)
Unit cell dimensions	
a (Å)	13.5006(16)
b (Å)	19.7952(13)
c (Å)	30.843(2)
α (°)	90
β (°)	90
γ (°)	90
V (Å^3)	8242.8(13)
Z	8
D_{calc} (Mg m^3)	1.387
Absorption coefficient (mm^{-1})	0.710
F(000)	3536
Theta range for data collection (°)	1.65–25.97
Index ranges	$-16 \leq h \leq 1$, $-24 \leq k \leq 0$, $-1 \leq l \leq 37$
Reflections collected	9317
Reflections observed [$I > 2\sigma(I)$]	4251
Independent reflections	8236 [$R_{int} = 0.0417$]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	8236/0/499
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0888$, $wR_2 = 0.2089$
R indices (all data)	$R_1 = 0.1778$, $wR_2 = 0.2851$
Goodness-of-fit on F^2	1.051
Largest difference peak and hole (e Å^{-3})	1.079 and −0.620

sis with the high accuracy we expected. All remaining crystal data and refinement parameters are presented in Table 3.

Solution and refinement were performed using SHELXS-97 [24a] and SHELXL-97 [24b]. Molecular diagrams were drawn with ORTEPIII [24c]. OSCAIL-8 package was used [24d].

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 157845 for compound **5**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

We wish to thank the Fundação para a Ciência e Tecnologia, Portugal, for financial support (Project PRAXIS 2/2.1/QUI/143/94) and for the award of a doctoral PRAXIS XXI grant (BD/5669/95) to A.F.G.R. We also thank the Secretaria Regional da Educação da Madeira, the Serviços de Acção Social da Universidade da Madeira and the Acção Social da Universidade Técnica de Lisboa, Portugal, for an undergraduate scholarship to J.N.M.

References

[1] (a) E.L. Muetterties, R.N. Rhodin, E. Band, C.F. Brucker, W.R. Pretzer, Chem. Rev. 79 (1991) 91;
(b) E.L. Muetterties, M.J. Krause, Angew. Chem. Int. Ed. Engl. 22 (1983) 147;
(c) T.J. Marks, Acc. Chem. Res. 25 (1992) 57;
(d) G. Süss-Fink, G. Meister, Adv. Organomet. Chem. 35 (1993) 41;
(e) W. Beck, B. Niemer, M. Wieser, Angew. Chem. Int. Ed. Engl. 32 (1993) 923;
(f) N. Wheatley, P. Kalck, Chem. Rev. 99 (1999) 3379;
(g) N. Wheatley, P. Kalck, Chem. Rev. 101 (2001) 207.

[2] (a) T.E. Bitterwolf, J. Organomet. Chem. 312 (1986) 197;
(b) T.E. Bitterwolf, A.L. Rheingold, Organometallics 6 (1987) 2138;
(c) T.E. Bitterwolf, J. Organomet. Chem. 320 (1987) 121;
(d) R. Fierro, T.E. Bitterwolf, A.L. Rheingold, G.P.A. Yap, L.M. Liable-Sands, J. Organomet. Chem. 524 (1996) 19;
(e) T.E. Bitterwolf, A.A. Saygh, J.T. Bays, C.A. Weiss, W.B. Scallorn, J.E. Shade, A.L. Rheingold, L.L. Sands, J. Organomet. Chem. 583 (1999) 152;
(f) T.E. Bitterwolf, A.A. Saygh, J.E. Shade, A.L. Rheingold, G.P.A. Yap, L.M. Liable-Sands, Inorg. Chim. Acta 300 (2000) 800.

[3] (a) H. Werner, M. Treiber, A. Nessel, F. Lippert, P. Betz, C. Kruger, Chem. Ber. 125 (1992) 337;
(b) H. Werner, D. Schneider, M. Schulz, Chem. Ber. 125 (1992) 1017;
(c) D. Schneider, H. Werner, Organometallics 12 (1993) 4420.

[4] (a) P.A. Wegner, V.A. Usky, Inorg. Chem. 18 (1979) 646;
(b) S. Jungling, R. Mulhaupt, H. Plenio, J. Organomet. Chem. 460 (1993) 191.

[5] (a) K.P. Reddy, J.L. Petersen, Organometallics 8 (1989) 2107;
(b) K.P. Reddy, J.L. Petersen, Organometallics 8 (1989) 547.

[6] (a) R. Gomez, T. Cuenca, P. Royo, W.A. Herrmann, E. Herdtweck, J. Organomet. Chem. 382 (1990) 103;
(b) S. Ciruelos, T. Cuenca, J.C. Flores, R. Gomez, P. Gomez-Sal, P. Royo, Organometallics 12 (1993) 944;
(c) P. Gomez-Sal, E. de Jesús, A.I. Pérez, P. Royo, Organometallics 12 (1993) 4633.

[7] (a) I.E. Nifant'ev, K.A. Butakov, Z.G. Aliev, I.F. Urazovskii, Organomet. Chem. USSR 4 (1991) 622;
(b) I.E. Nifant'ev, M.V. Borsov, A.V. Churakov, S.G. Mkoyan, L.O. Atovmyan, Organometallics 11 (1992) 3942.

[8] U. Siemeling, P. Jutzi, Chem. Ber. 125 (1992) 31.

[9] (a) G.M. Diamond, M.L.H. Green, N.A. Popham, A.N. Chernega, J. Chem. Soc. Chem. Commun. (1994) 727;
(b) G.M. Diamond, A.N. Chernega, P. Mountford, M.L.H. Green, J. Chem. Soc. Dalton Trans. (1996) 921;
(c) T. Ushioda, M.L.H. Green, J. Hagitt, X.F. Yan, J. Organomet. Chem. 518 (1996) 155;
(d) X.F. Yan, A.N. Chernega, M.L.H. Green, J. Sanders, J. Souters, T. Ushioda, J. Mol. Catal. A — Chem. 118 (1998) 119;
(e) M.L.H. Green, N.H. Popham, J. Chem. Soc. Dalton Trans. (1999) 1049.

[10] N.J. Coville, K.E. du Plooy, W. Pickl, Coord. Chem. Rev. 116 (1992) 1.

[11] L. Ballester, S. Perez, A. Gutierrez, M.F. Perpiñan, E. Gutierrez-Puebla, A. Monge, C. Ruiz, J. Organomet. Chem. 414 (1991) 411.

[12] A. Salzer, T.L. Court, H. Werner, J. Organomet. Chem. 54 (1973) 325.

[13] L.R. Byers, L.F. Dahl, Inorg. Chem. 19 (1980) 680.

[14] J. Darkwa, R.M. Moutloali, T. Nyokong, J. Organomet. Chem. 564 (1998) 37.

[15] I.L.C. Campbell, F.S. Stephens, J. Chem. Soc. Dalton Trans. (1975) 337.

[16] P.L. Holland, M.E. Smith, R.A. Andersen, R.G. Bergman, J. Am. Chem. Soc. 119 (1997) 12815.

[17] (a) T.A Huber, F. Bélanger-Gariépy, D. Zargarian, Organometallics 14 (1995) 4997;
(b) R. Vollmerhaus, F. Bélanger-Gariépy, D. Zargarian, Organometallics 16 (1997) 4762;
(c) T.A Huber, M. Bayrakdarian, S. Dion, I. Dubuc, F. Bélanger-Gariépy, D. Zargarian, Organometallics 16 (1997) 5811;
(d) L.F. Groux, F. Bélanger-Gariépy, D. Zargarian, R. Vollmerhaus, Organometallics 19 (2000) 1507.

[18] R.T. Baker, T.H. Tulip, Organometallics 5 (1986) 839.

[19] M.J. Calhorda, L.F. Veiros, Coord. Chem. Rev. 185-186 (1999) 37.

[20] H. Friebolin, Basic One- and Two-dimensional NMR Spectroscopy, VCH, New York, 1991 (pp. 267–274).

[21] (a) R.D. Barr, M. Green, T.B. Marder, F.G.A. Stone, J. Chem. Soc. Dalton Trans. (1984) 1261;
(b) T.B. Marder, J.C. Calabrese, D.C. Roe, T.H. Tulip, Organometallics 6 (1987) 2012.

[22] L.M. Venanzi, J. Chem. Soc. (1958) 719.

[23] (a) I.E. Nifant'ev, P.V. Ivchenko, M.V. Borzov, J. Chem. Res. (S) (1992) 162;
(b) I.E. Nifant'ev, P.V. Ivchenko, L.G. Kuz'mina, Y.N. Luzikov, A.A. Sitnikov, O.E. Sizan, Synthesis (1997) 468.

[24] (a) G.M. Sheldrick, SHELXS-97 Crystallographic Calculation Program, University of Göttingen, Göttingen, 1997; see also Acta Crystallogr. (1993) D49;
(b) G.M. Sheldrick, SHELXL-97, A Computer Program for Refinement of Crystal Structures, University of Göttingen, Göttingen, 1997;
(c) M.N. Burnett, C.K. Johnson, ORTEPIII: Oak Ridge Thermal Ellipsoid Plot Program for Crystal Structural Illustrations, Oak Ridge National Laboratory Report ORNL 6895, 1996;
(d) P. McArdle, J. Appl. Crystallogr. 28 (1995) 65.