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Functionally substituted monocyclopentadienyl compounds. Formation of $[\text{Ni}(\eta\text{-CH}_3\text{C}_5\text{H}_4)(\text{X})(\text{PPh}_3)]$ and derivatives with other phosphines. X-Ray crystal structure of $[\text{Ni}(\eta\text{-CH}_3\text{C}_5\text{H}_4)(\text{I})(\text{PPh}_3)]$

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Abstract

$[\text{Ni}(\eta\text{-CH}_3\text{C}_5\text{H}_4)_2]$ reacts with $[\text{NiX}_2(\text{PPh}_3)_2]$ ($\text{X} = \text{Cl, Br, I, CN, SCN}$) to give monocyclopentadienyl complexes. The reactions of these complexes with tertiary phosphines or carbon monoxide are described. The crystal structure of $[\text{Ni}(\eta\text{-CH}_3\text{C}_5\text{H}_4)(\text{I})(\text{PPh}_3)]$ has been determined, and shows the nickel atom to be in a pseudo-pentacoordinate environment.

Introduction

The chemistry of nickelocene and ring-substituted derivatives is dominated by displacement reactions of one or both cyclopentadienyl rings [1]. A variety of reactions lead to the formation of $[\text{Ni}(\eta\text{-C}_5\text{H}_5)(\text{X})(\text{PR}_3)]$ ($\text{X} = \text{anionic ligand}$), the main preparative routes being those in which the chloro ligand is displaced by other anionic ligands [2], the substitution reactions in these complexes have been extensively studied by Kuhn et al. [3]. The compounds can also be obtained by reaction of nickelocene with $[\text{NiX}_2(\text{PR}_3)_2]$ or, alternatively, by use of thallium cyclopentadienide [4].

The reactivity of nickelocene towards the formation of 18-electron species is enhanced in the 1,1'-bisdimethylnickelocene owing to the presence of electron-donating groups in the aromatic ring. We have attempted to make methylcyclopentadienyl derivatives by reaction of $[\text{Ni}(\eta\text{-CH}_3\text{C}_5\text{H}_4)_2]$ and $[\text{NiX}_2(\text{PPh}_3)_2]$. Functionally-monosubstituted cyclopentadienyl compounds of other transition metals have been extensively studied, especially in order to elucidate conformational

preferences [5]. In the case of nickel, Salzer et al. [6] have described anionic $[\text{Ni}(\eta\text{-RC}_5\text{H}_4)(\text{diene})](\text{BF}_4)$ ($\text{R} = \text{H}, \text{CH}_3, \text{t-C}_4\text{H}_9$) complexes.

We now report the synthesis of $[\text{Ni}(\eta\text{-CH}_3\text{C}_5\text{H}_4)(\text{X})(\text{PPh}_3)]$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{CN}, \text{SCN}$) and their reactivity towards dppe ($\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$), tcep ($\text{P}\{\text{CH}_2\text{CH}_2\text{CN}\}_3$), and CO.

In previously described studies reductive carbonylation processes were observed only at high pressures (80 atm) [7] and the analogous complexes $[\text{Ni}(\eta\text{-C}_5\text{H}_5)(\text{CO})(\text{PR}_3)](\text{BF}_4)$ were only obtained when bulky phosphines were used [8].

Results and discussion

Table 1 lists the new compounds and some of their properties. All compounds are diamagnetic and stable under nitrogen. Their solutions are very air-sensitive, and have lower stabilities than those of corresponding unsubstituted cyclopentadienyl derivatives.

The complexes $[\text{Ni}(\eta\text{-CH}_3\text{C}_5\text{H}_4)(\text{X})(\text{PPh}_3)]$ (I–V) were obtained by refluxing a THF solution of $[\text{Ni}(\eta\text{-CH}_3\text{C}_5\text{H}_4)_2]$ and $[\text{NiX}_2(\text{PPh}_3)_2]$. The same reaction in the case of the unsubstituted nickelocene when $\text{X} = \text{CN}, \text{SCN}$ gives better yields than the methods previously used [2].

The reaction of I, III and IV with dppe results in the substitution of phosphine and anionic ligand and formation of $[\text{Ni}(\eta\text{-CH}_3\text{C}_5\text{H}_4)(\text{dppe})\text{X}]$ (VI–VIII) by chelation of the diphosphine. The ionic character of these complexes is unambiguously shown by the conductivity data for their acetone solutions (Table 1). The low values for the chloro and iodo derivatives are presumably due to ion pairing and solvent association. Complex V reacts with dppe to give a neutral complex of formula $[\text{Ni}(\eta\text{-CH}_3\text{C}_5\text{H}_4)(\text{CN})_2(\mu\text{-dppe})]$ (IX). The low conductivity shown by this complex is attributed to dissociation in solution.

The reaction of complexes IV and V with the less basic tcep also occurs with phosphine exchange and the neutral complexes $[\text{Ni}(\eta\text{-CH}_3\text{C}_5\text{H}_4)(\text{X})(\text{tcep})]$ ($\text{X} = \text{CN}$ (X), SCN (XI)) can be obtained. Complex VIII also reacts with tcep to give the derivative $[\text{Ni}(\eta\text{-CH}_3\text{C}_5\text{H}_4)(\text{dppe})(\text{tcep})](\text{NCS})$ (XII), with the dppe acting as monodentate in the ionic complex.

The IR spectra of these complexes (Table 2) show the presence of a strong band in the $798\text{--}810\text{ cm}^{-1}$ region, characteristic of a pentahapto cyclopentadienyl ring. The frequency of this band can be related to the electron density on the cyclopentadienyl ring. In our complexes this band is shifted between 5 and 20 cm^{-1} to higher frequencies relative to those for analogues with unsubstituted rings as a consequence of the electron-donating character of the methyl group. It is also notable that this band appears at higher values for the ionic complexes than for the neutral ones.

Complexes IV, V, IX, X and XI show strong $\nu(\text{CN})$ bands in the $2100\text{--}2120\text{ cm}^{-1}$ region for terminal cyano and thiocyanate ligands. These bands are shifted by ca 60 cm^{-1} to lower frequencies in complexes VIII and XII, indicating the ionic character of the thiocyanate in these compounds. Complexes IV and XI also show a band at $835\text{--}860\text{ cm}^{-1}$ characteristic of an *N*-bonded isothiocyanate.

The ^1H NMR data for these complexes are listed in Table 3. The cyclopentadienyl protons appear as two pseudo singlets for the 2,5 and 3,4 protons, the former appearing at lower fields. The difference between the chemical shifts of these

Table 1
Analytical and physical data for the new complexes

Compound	Colour	Yield (%)	Elemental analysis (Found (calc.) (%))			M.p. (°C)	Λ^a
			C	H	N		
I [Ni(η -CH ₃ C ₅ H ₄ XCl)(PPh ₃)]	red	85	66.7 (66.1)	5.2 (5.1)		123	
II [Ni(η -CH ₃ C ₅ H ₄ XBr)(PPh ₃)]	red	88	60.5 (60.0)	4.4 (4.6)		126	
III [Ni(η -CH ₃ C ₅ H ₄ XI)(PPh ₃)]	red	85	55.2 (54.7)	4.2 (4.2)		107	
IV [Ni(η -CH ₃ C ₅ H ₄ XNCS)(PPh ₃)]	purple	83	65.8 (65.5)	5.1 (4.8)	3.0 (3.0)	151	
V [Ni(η -CH ₃ C ₅ H ₄ XCN)(PPh ₃)]	brown	82	70.0 (70.4)	5.1 (5.2)	3.1 (3.3)	120	
VI [Ni(η -CH ₃ C ₅ H ₄ X(dppe))Cl]	green	60	66.7 (67.2)	5.2 (5.5)		195	51
VII [Ni(η -CH ₃ C ₅ H ₄ X(dppe))I]	green	92	57.3 (57.9)	4.6 (4.7)		112	72.5
VIII [Ni(η -CH ₃ C ₅ H ₄ X(dppe))NCS]	green	78	66.3 (66.6)	5.1 (5.2)	2.1 (2.4)	78	144
IX [Ni(η -CH ₃ C ₅ H ₄ XCN)] ₂ (μ -dppe)	green	45	65.5 (66.1)	5.0 (5.3)	3.9 (3.8)	198	26.6 ^b
X [Ni(η -CH ₃ C ₅ H ₄ XCN)(tcep)]	green	51	53.2 (53.8)	4.9 (5.3)	15.3 (15.7)	122	
XI [Ni(η -CH ₃ C ₅ H ₄ XNCS)(tcep)]	brown	65	48.6 (49.3)	4.7 (4.9)	13.9 (14.4)	160	
XII [Ni(η -CH ₃ C ₅ H ₄ X(dppe)(tcep))(NCS)]	green	84	63.7 (64.0)	5.3 (5.5)	6.8 (7.1)	55	120

^a In 10⁻³ M acetone solutions (ohm⁻¹ cm² mol⁻¹). ^b In dichloromethane.

Table 2

Infrared spectral data (cm⁻¹)

Compound	$\nu(\text{CN})_{\text{NCS,CN}}$	$\nu(\text{CS})_{\text{NCS}}$	$\gamma_{\text{oop}}(\text{CH})$	Others
I			798s (783) ^a	339w $\nu(\text{Ni-Cl})$
II			803s	
III			808s	
IV	2113vs	835s	808s (790) ^a	
V	2107vs		805 (800) ^a	
VI			810s	
VII			810s	
VIII	2060vs		813m	
IX	2104vs		790s	
X	2112vs	860s	812m	2242s $\nu(\text{CN})_{\text{tcep}}$
XI	2104vs		810s	2240s $\nu(\text{CN})_{\text{tcep}}$
XII	2050vs		840m	2242s $\nu(\text{CN})_{\text{tcep}}$

^a Values for unsubstituted cyclopentadienyls.

two signals (Δ) is related to the electron affinity of the pseudohalogen attached to the metal (Table 4). Thus for complexes I, II, III and V we obtained the regression line shown in Fig. 1 ($r = 0.995$), from which we can estimate the electron affinity of the isothiocyanate group as 3.68 eV, significantly higher than the value reported for the thiocyanate group (2.17 eV) [9]. The Δ value is almost unaltered in complex IX relative to that for complex V, suggesting that the basicity of the phosphine does not affect the difference of electronic density between the cyclopentadienyl protons in the neutral complexes. For the ionic VI–VIII and XII the two signals are very close, and as expected, neither the Δ values nor the chemical shifts are affected by the change of the counterion.

In some of the derivatives, the methyl protons are coupled to phosphorus. This

Table 3

¹H NMR data for the complexes (δ (ppm))^a

Compound	Ph	C_5H_5			Me	P-CH ₃
		H _{2,5}	H _{3,4}	Δ^b		
I	8.0–7.2m	5.65s	4.13s	1.52	1.44d $J = 4.5$ Hz	
II	8.0–7.2m	5.48s	4.26s	1.22	1.61d $J = 4.5$ Hz	
III	7.86, 7.52m	5.52s	4.62s	0.90	2.04s	
		5.35 ^c	4.36 ^c		1.97 ^c	
IV	7.67, 7.46m	5.67s	4.07	1.60	1.46d $J = 4$ Hz	
		5.48 ^c	3.82 ^c		1.40s ^c	
V	7.67, 7.42m	5.46s	4.50	0.96	1.85s	
VI	7.7–7.6m	5.30s	5.21s	0.09	1.26t $J = 6$ Hz	2.88d $J = 18$ Hz
VII	7.66m	5.29s	5.17s	0.12	..26s	2.71br
VIII	7.7–7.4m	5.36s	5.24s	0.12	1.33t $J = 6$ Hz	2.73s, 2.36s
IX	7.6–7.3m	5.38s	4.44s	0.94	1.76d $J = 4$ Hz	2.75br
		5.32s	4.41s	0.91	1.74d $J = 3$ Hz	
XII	7.4m	5.23s	5.03	0.20	1.82s	2.8–2.5m

^a In CDCl₃. ^b $\Delta = \delta(\text{H}_{2,5}) - \delta(\text{H}_{3,4})$. ^c In C₆D₆.

Table 4

 Δ and electron affinity values for the complexes I–V

Group	Δ (ppm)	EA (eV) ^a
Cl	1.52	3.617
Br	1.22	3.363
I	0.90	3.059
CN	0.96	3.17
NCS	1.60	–

^a Data taken from ref. 9.

coupling seems to be through space, since there is no appreciable coupling between the phosphine and the cyclopentadienyl protons.

The ¹³C NMR spectra of III and IV (Table 5) also show all the cyclopentadienyl and methyl signals as singlets, with no appreciable coupling to phosphorus. In the cyclopentadienyl carbon signals a split in two signals is also observed. As for the proton spectra, the difference $\delta(C_{2,5}) - \delta(C_{3,4})$ is higher for the isothiocyanate than for the iodide complex.

Crystal structure of $[Ni(\eta\text{-}CH_3C_5H_4)(I)(PPh_3)]$, III

Figure 2 shows a view of the molecule and the atom numbering. Tables 6 and 7 give the main bond lengths and angles. The overall geometry around the nickel is similar to that previously found in the analogous $[Ni(\eta\text{-}C_5H_5)(R)(PPh_3)]$ ($R = C_6H_5, C_6F_5$) [10]. The molecule is a discrete unit with Ni–P and Ni–I distances in the range reported for other nickel complexes [11]. The carbon–carbon ring distances are also in the expected range for cyclopentadienyl complexes.

The nickel–cyclopentadienyl carbon distances vary from 2.058 Å for Ni–C(3) to

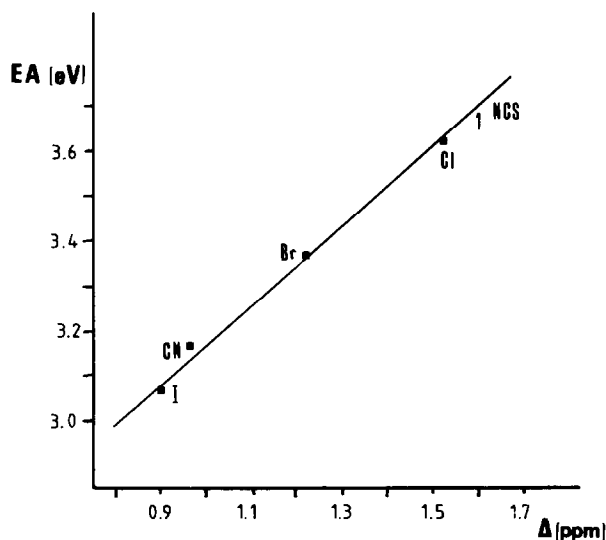


Fig. 1. Plot of the value of Δ ($\Delta = \delta(H_{2,5}) - \delta(H_{3,4})$) against the electron affinity of X in $[Ni(\eta\text{-}CH_3C_5H_4)(X)(PPh_3)]$ (I–V).

Table 5

 ^{13}C NMR data for III and IV in CDCl_3

	III	IV
NCS		172.1s
Ph(2,6)	134.79d $J = 10$ Hz	133.48d $J = 12$ Hz
Ph(1)	134.20d $J = 18$ Hz	131.62d $J = 20$ Hz
Ph(4)	130.29s	130.74d $J = 1$ Hz
Ph(3,5)	128.21d $J = 8$ Hz	128.65d $J = 10$ Hz
$\text{CH}_3\text{C}_5\text{H}_4(1)$	101.90s	87.81s
$\text{CH}_3\text{C}_5\text{H}_4(2,5)$	97.60s	99.90s
$\text{CH}_3\text{C}_5\text{H}_4(3,4)$	90.05s	85.64s
Me	15.74s	13.67s

2.168 Å for Ni–C(1). The longest distance reflects a small ring bending opposite to that observed in $[\text{Ni}(\eta\text{-CH}_3\text{C}_5\text{H}_4)(\mu\text{-CO})_2]$, where C(1) is bent towards the nickel atom [12]. This bending was attributed to a stronger than expected interaction of C(1) with the metal, which can be attributed, at least in part, to the electron releasing ability of the methyl group. In our case the effect produced has the opposite sign [13].

The shortest Ni–C distance Ni–C(3), is found for the carbon that lies over the phosphine, although there is no appreciable interaction C(3)–P through space as shown by the NMR spectra. The dihedral angle between the cyclopentadienyl and the I–Ni–P plane of 84.1° shows a contraction relative to the observed value of 90.4° for the analogous $[\text{Ni}(\eta\text{-C}_5\text{H}_5)(\text{C}_6\text{H}_5)(\text{PPh}_3)]$ [10].

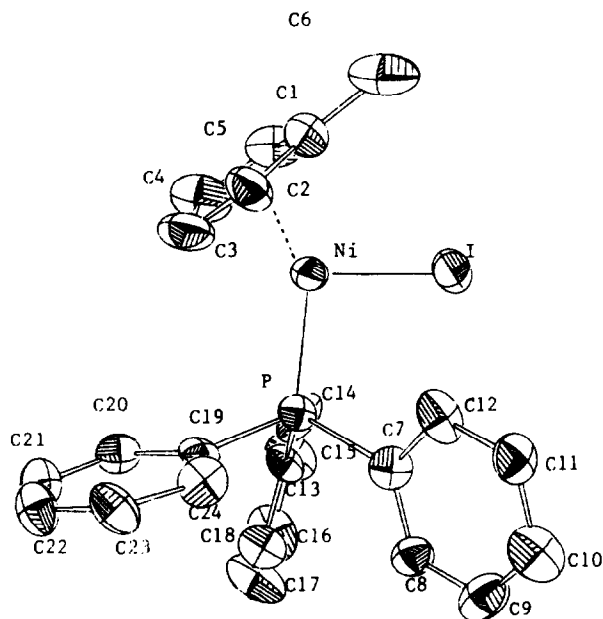


Fig. 2. ORTEP view of complex III.

Table 6

Bond distances (Å) and angles (°) for complex III with esd's in parentheses

I–Ni	2.500(2)	C1–C6	1.482(19)	C13–C18	1.401(15)
Ni–P	2.159(3)	C2–C3	1.431(26)	C14–C15	1.401(16)
Ni–C1	2.169(12)	C3–C4	1.394(25)	C15–C16	1.379(21)
Ni–C2	2.138(14)	C4–C5	1.360(20)	C16–C17	1.367(19)
Ni–C3	2.058(12)	C7–C8	1.396(15)	C17–C18	1.382(16)
Ni–C4	2.121(16)	C7–C12	1.406(16)	C19–C20	1.406(17)
Ni–C5	2.112(12)	C8–C9	1.379(18)	C19–C24	1.391(16)
P–C7	1.830(12)	C9–C10	1.371(20)	C20–C21	1.403(15)
P–C13	1.806(11)	C10–C11	1.380(17)	C21–C22	1.349(18)
P–C19	1.832(10)	C11–C12	1.384(16)	C22–C23	1.373(16)
C1–C2	1.389(18)	C13–C14	1.396(15)	C23–C24	1.392(16)
C1–C5	1.452(18)				
I–Ni–P	97.93(9)	C11–C12–C7	120.0(1)		
Ni–P–C7	114.7(4)	P–C13–C14	118.9(8)		
Ni–P–C13	114.2(4)	P–C13–C18	122.2(8)		
Ni–P–C19	115.4(3)	C14–C13–C18	118.9(10)		
C7–P–C13	106.7(5)	C13–C14–C15	119.0(1)		
C7–P–C19	101.9(5)	C14–C15–C16	120.0(1)		
C13–P–C19	102.4(5)	C15–C16–C17	120.0(1)		
C2–C1–C5	106.0(1)	C16–C17–C18	120.0(1)		
C2–C1–C6	128.0(1)	C17–C18–C13	121.0(1)		
C5–C1–C6	126.0(1)	P–C19–C20	118.6(9)		
C1–C2–C3	109.0(1)	P–C19–C24	121.8(9)		
C2–C3–C4	107.0(1)	C20–C19–C24	119.5(9)		
C3–C4–C5	109.0(1)	C19–C20–C21	119.0(1)		
C4–C5–C1	109.0(1)	C20–C21–C22	122.0(1)		
C8–C9–C10	121.0(1)	C21–C22–C23	119.0(1)		
C9–C10–C11	121.0(1)	C22–C23–C24	122.0(1)		
C10–C11–C12	120.0(1)	C23–C24–C19	119.1(10)		

Reactions with CO

Complex I reacts with CO at atmospheric pressure with displacement of the anionic ligands and reduction to the complexes $[\text{Ni}(\text{CO})_x(\text{PPh}_3)_{4-x}]$ ($x = 2, 3$). This reaction is favoured by the presence of additional phosphine, and $[\text{Ni}(\text{CO})_2(\text{PPh}_3)_2]$ is also obtained when $[\text{Ni}(\eta\text{-C}_5\text{H}_5)(\text{PPh}_3)_2]\text{Cl}$ reacts with CO in the presence of a 4-fold excess of PPh_3 .

In the presence of an halogen trap, like AgBF_4 , I reacts with CO to give $[\text{Ni}(\eta\text{-CH}_3\text{C}_5\text{H}_4)(\text{CO})(\text{PPh}_3)_2]\text{BF}_4$. A similar reaction was observed by Kuhn et al.

Table 7

Bond distances (Å) and angles (°) for the hydrogen atoms in complex III with esd's in parentheses

H21–C2	0.92(13)	H41–C4	0.75(14)
H31–C3	1.06(12)	H51–C5	0.97(13)
H21–C2–C1	128.0(8)	H41–C4–C3	123.0(10)
H21–C2–C3	124.0(8)	H41–C4–C5	125.0(10)
H31–C3–C2	128.0(8)	H51–C5–C1	116.0(8)
H31–C3–C4	125.0(8)	H51–C5–C4	134.0(8)

[3] in an attempt to obtain the 16-electron species $[\text{Ni}(\eta\text{-C}_5\text{H}_5)(\text{PR}_3)]^+$. This reaction can be considered as a simple halogen substitution, whereas the reductive carbonylation reactions probably proceed through interaction of the starting nickel(II) complex with CO followed by a $\pi\sigma$ rearrangement of the cyclopentadienyl ring in the 20-electron intermediate, and finally elimination of the ring to form the reduced product.

Experimental

All reactions were carried out under oxygen-free nitrogen. $[\text{Ni}(\eta\text{-CH}_3\text{C}_5\text{H}_4)_2]$ and $[\text{NiX}_2(\text{PPh}_3)_2]$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{CN}, \text{SCN}$) were prepared as previously reported [14].

Analyses were by Elemental Microanalysis Ltd., Devon. Conductance measurements were performed at room temperature with a Philips conductivity bridge PW9506120 and a conductivity cell PW9510160. IR spectra were recorded with KBr disks on a Perkin-Elmer 325 spectrophotometer. NMR spectra were recorded at room temperature on a Varian EM-90 or a Varian VXR-300 spectrometer with the residual solvent as reference.

$[\text{Ni}(\eta\text{-CH}_3\text{C}_5\text{H}_4)(\text{X})(\text{PPh}_3)]$ (I-V)

Solid $[\text{NiX}_2(\text{PPh}_3)_2]$ (10 mmol) was added to a solution of $[\text{Ni}(\eta\text{-CH}_3\text{C}_5\text{H}_4)_2]$ (10 mmol) in 150 mL of THF and the mixture was refluxed for 4 h. The $[\text{NiX}_2(\text{PPh}_3)_2]$ slowly dissolved with formation of a brownish solution. This solution was filtered and the solvent removed in vacuo. The residue was extracted with benzene (2×20 mL), hexane (25 mL) was added, and the solutions kept at -20°C for two days to give red crystals of the product.

$[\text{Ni}(\eta\text{-CH}_3\text{C}_5\text{H}_4)(\text{dppe})\text{X}]$ (VI-VIII)

A solution of dppe (1.15 mmol) in 25 mL of acetone was added to a stirred solution of I, II or III (1 mmol) in 30 mL of acetone. Stirring was maintained for 24 h and the colour changed slowly to green. After removal of the solvent, the residue was repeatedly washed with Et_2O and then extracted with acetone (15 mL). Addition of hexane to the acetone extract followed by cooling afforded the desired products as green solids. The same reaction takes place in benzene as solvent; in this case the product can be purified directly by recrystallization from acetone.

$[\text{Ni}(\eta\text{-CH}_3\text{C}_5\text{H}_4)(\text{CN})]_2(\mu\text{-dppe})$ (IX)

The reaction of V and dppe was carried out as above and the product was recrystallized from chloroform/hexane as green crystals.

$[\text{Ni}(\eta\text{-CH}_3\text{C}_5\text{H}_4)(\text{X})(\text{tcep})]$ (X-XI)

A solution of tcep (0.5 mmol) in acetone was added to a stirred solution of IV or V in 30 mL of acetone. After 4 h stirring the solution was concentrated to 10 mL and 15 mL of hexane were added. The solid that separated was filtered off and washed with Et_2O .

$[\text{Ni}(\eta\text{-CH}_3\text{C}_5\text{H}_4)(\text{dppe})(\text{tcep})](\text{NCS})$ (XII)

This complex was made as described for X-XI from tcep and VIII.

Reactions of [Ni(η -CH₃C₅H₄)(X)(PR₃)] with CO

(a) *In dichloromethane.* Carbon monoxide was bubbled through dichloromethane solutions of [Ni(η -CH₃C₅H₄)(Cl)(PPh₃)] or [Ni(η -CH₃C₅H₄)(PPh₃)₂]Cl in the presence of excess of PPh₃. After 3 h the solution was filtered and the solvent removed *in vacuo*. Addition of ethanol gave a yellow-white precipitate which was recrystallized from acetone with addition of charcoal. The product was identified as [Ni(CO)₂(PPh₃)₂]. Yield 50–60%.

(b) *In ethanol.* Carbon monoxide was bubbled for 5 h through an ethanolic solution of [Ni(η -CH₃C₅H₄)(Cl)(PPh₃)]. Addition of hexane, filtration and removal of solvent gave crude [Ni(CO)₃(PPh₃)] that can be recrystallized from acetone to white crystals obtained in 53% yield.

(c) [Ni(η -CH₃C₅H₄)(CO)(PPh₃)₂]BF₄. This complex can be obtained, as previously reported for the unsubstituted cyclopentadienyl [3] by bubbling CO through a nitromethane solution in the presence of AgBF₄.

X-Ray study of [Ni(η -CH₃C₅H₄)(I)(PPh₃)]

A brown prismatic crystal of size 0.09 × 0.06 × 0.05 mm was mounted on a Enraf Nonius CAD4-F diffractometer. The cell dimensions were refined by least-squares fitting of the θ values for 25 reflections. The intensities of 3851 unique reflections with $1 < \theta < 25^\circ$ were measured at 295 K with monochromatic Mo-K α radiation ($\lambda = 0.71069 \text{ \AA}$) and $\omega/2\theta$ scan techniques. There was no appreciable variation in intensity of three standard reflections, checked every hour. The intensities were corrected for Lorentz and polarization effects and 1349 of these were considered as observed by the criterion $I \geq 2\sigma(I)$.

Scattering factors for neutral atoms and the anomalous dispersion corrections for Ni, P, and I atoms were taken from *International Tables for X-Ray Crystallography* [15].

The structure was solved by three dimensional Patterson and Fourier syntheses which allowed location of all non-hydrogen atoms.

An empirical absorption correction [16] was applied at the end of the isotropic refinement. Anisotropic full matrix least-squares refinement with unit weights led to $R = 0.038$. No trend in F vs F_0 or $\sin(\theta/\lambda)$ was observed. Hydrogen atoms of the methyl and phenyl groups were fixed at calculated positions. Only the cyclopentadienyl hydrogen atoms were located in a difference synthesis calculated with reflections having $\sin(\theta/\lambda) < 0.5 \text{ \AA}^{-1}$. Final refinement with fixed isotropic temperature factors and coordinates for H atoms gave $R = 0.032$. Maximum and average shift/error were 0.06 and 0.02 respectively. A final difference synthesis showed no significant electron density. Most of the calculations were carried out with XRAY80 [17]. Table 8 shows the final atomic parameters.

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References

- 1 P.W. Jolly and G. Wilke, *The Organic Chemistry of Nickel*, Vol. 1, Academic Press, New York, 1974, p. 21.

- 2 (a) J. Thomson and M.C. Baird, *Can. J. Chem.*, 51 (1973) 1179; (b) M. van der Akker and F. Jellinek, *Recl. Trav. Chim. Pays Bas*, 86 (1967) 897.
- 3 N. Kuhn and M. Winter, *J. Organomet. Chem.*, 301 (1986) C9 and references cited.
- 4 (a) E. Hernández and P. Royo, *J. Organomet. Chem.*, 291 (1985) 387; (b) J.W. Faller and B.V. Johnson, *ibid.*, 96 (1975) 99.
- 5 D.W. Macomber, W.P. Hart and M.D. Rausch, *Adv. Organomet. Chem.*, 21 (1982) 1.
- 6 A. Salzer, T.L. Court and H. Werner, *J. Organomet. Chem.*, 54 (1973) 325.
- 7 H. Yamazaki, T. Nishido, Y. Matsumoto, S. Sumida and N. Hagiara, *J. Organomet. Chem.*, 6 (1966) 86.
- 8 N. Kuhn, N. Heuser and M. Winter, *J. Organomet. Chem.*, 267 (1984) 221.
- 9 Data taken from R.C. Weast (Ed.), *Handbook of Chemistry and Physics*, 58th ed., CRC Press, Boca Raton, Florida, 1977–78.
- 10 M.R. Churchill and T.A. O'Brien, *J. Chem. Soc. (A)*, (1970) 161.
- 11 (a) J.M. Coleman and L.F. Dahl, *J. Am. Chem. Soc.*, 89 (1967) 542; (b) W. Klani, K. Schmidt, A. Bockmann, D.J. Brauer, J. Wilke, H. Lueken and U. Elserhans, *Inorg. Chem.*, 25 (1986) 4125.
- 12 N. Kuhn, N. Henser and M. Winter, *J. Organomet. Chem.*, 267 (1984) 221.
- 13 L.R. Byers and L.F. Dahl, *Inorg. Chem.*, 19 (1980) 680.
- 14 (a) L.T. Reynolds and G. Wilkinson, *J. Inorg. Nucl. Chem.*, 9 (1959) 86; (b) L.M. Venanzi, *J. Chem. Soc.*, (1958) 719.
- 15 *International Tables for X-Ray Crystallography*, Vol. IV, Kynoch Press, Birmingham, 1974, p. 72–98.
- 16 N. Walter and D. Stuart, *Acta Crystallogr., Sect. A* 39 (1983) 158.
- 17 M. Martínez-Ripoll and F.H. Cano, PESOS program, Instituto Rocasolano, C.S.I.C., Madrid, Spain.