

CYCLOPENTADIENYLNICKEL COMPLEXES

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Summary

The neutral complexes $(\eta^5\text{-C}_5\text{H}_5)\text{NiXL}$ ($X = \text{Cl}$, $L = \text{PPh}_3$ (I); $L = \text{PCy}_3$ (II); $X = \text{Br}$, $L = \text{PPh}_3$ (III); $L = \text{PCy}_3$ (IV); $X = \text{I}$, $L = \text{PPh}_3$ (V); $L = \text{PCy}_3$ (VI)) have been obtained by treating NiX_2L_2 with thallium cyclopentadienide. The same reaction in the presence of TIBF_4 gives cationic derivatives $[(\eta^5\text{-C}_5\text{H}_5)\text{NiL}_2]\text{BF}_4$ ($L = 2\text{PPh}_2\text{Me}$ (VII); $L = \text{dppe}$ (VIII)), whereas mononuclear complexes containing two different ligands ($L_2 = \text{PPh}_3 + \text{PCy}_3$ (IX)) or dinuclear $\{[(\eta^5\text{-C}_5\text{H}_5)\text{Ni}(\text{PPh}_3)]_2\text{dppe}\}(\text{BF}_4)_2$ (X) are obtained from the reaction of III with TIBF_4 in the presence of a different ligand. Reduction of cationic complexes with Na/Hg gives very unstable nickel(I) derivatives $(\eta^5\text{-C}_5\text{H}_5)\text{NiL}_2$, which could not be isolated purely. Similar reduction of neutral complexes under CO gives a mixture of decomposition products containing $[(\eta^5\text{-C}_5\text{H}_5)\text{Ni}(\text{CO})]_2$ and nickel(0) carbonyls, whereas in the presence of acetylenes, dinuclear $[(\eta^5\text{-C}_5\text{H}_5)\text{Ni}]_2(\text{RC}\equiv\text{CR}')$ ($R = R' = \text{Ph}$; $R = \text{Ph}$, $R' = \text{H}$) are obtained.

Introduction

Many neutral and cationic η^5 -cyclopentadienylnickel(II) complexes are known [1] and these have been prepared from nickelocene by reactions with NiX_2L_2 [2] or halogenating agents [3] and from $[(\eta^5\text{-C}_5\text{H}_5)\text{Ni}(\text{CO})]_2$ by oxidative cleavage of the Ni-Ni bond [4]. Many other anion or ligand substitution reactions have been described [5]. Few η^5 -cyclopentadienylnickel(I) complexes have been reported, although their involvement in several reactions has been demonstrated [6]. We report a new route to neutral and cationic η^5 -cyclopentadienylnickel(II) complexes, and present the results of a study of their reduction with Na/Hg under various conditions.

Results and discussion

The direct reaction between NiX_2 and TiCp in the presence of appropriate ligands takes place with very low yields, probably because both the nickel and

TABLE 1
 ANALYSES, COLOURS, AND YIELDS OF CYCLOPENTADIENYLNICKEL COMPLEXES

Complex	Analysis (Found) (Calcd.) (%)		Colour	Yield (%)
	C	H		
	$(\eta^5\text{-C}_5\text{H}_5)\text{NiCl}(\text{PPh}_3)$ (I)	66.06 (65.50)		
$(\eta^5\text{-C}_5\text{H}_5)\text{NiCl}(\text{PCy}_3)$ (II)	63.92 (62.78)	9.11 (8.64)	fuchsia	80
$(\eta^5\text{-C}_5\text{H}_5)\text{NiBr}(\text{PPh}_3)$ (III)	61.36 (59.25)	4.34 (4.29)	pink	55
$(\eta^5\text{-C}_5\text{H}_5)\text{NiBr}(\text{PCy}_3)$ (IV)	57.99 (57.01)	9.12 (7.85)		
$(\eta^5\text{-C}_5\text{H}_5)\text{Ni}(\text{PPh}_3)$ (V)	54.27 (53.84)	4.16 (3.93)	red brown	60
$(\eta^5\text{-C}_5\text{H}_5)\text{Ni}(\text{PCy}_3)$ (VI)	52.90 (51.97)	7.87 (7.16)		
$[(\eta^5\text{-C}_5\text{H}_5)\text{Ni}(\text{PPh}_2\text{Me})_2]\text{BF}_4$ (VII)	61.80 (60.95)	5.20 (5.08)	green	50
$[(\eta^5\text{-C}_5\text{H}_5)\text{Ni}(\text{dppe})]\text{BF}_4$ (VIII)	61.02 (61.09)	5.52 (4.76)		
$[(\eta^5\text{-C}_5\text{H}_5)\text{Ni}(\text{PPh}_3)(\text{PCy}_3)]\text{BF}_4$ (IX)	65.74 (65.32)	6.04 (5.97)	yellow	70
$\{[(\eta^5\text{-C}_5\text{H}_5)\text{Ni}(\text{PPh}_3)]_2(\mu\text{-dppe})\}(\text{BF}_4)_2$ (X)	65.79 (64.32)	5.06 (4.76)		
$(\eta^5\text{-C}_5\text{H}_5)\text{Ni}(\text{PPh}_2\text{Me})_2$ (XI)	69.18 (71.03)	6.24 (5.91)	brown violet	70

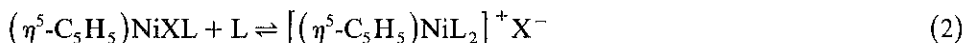
thallium reagents are scarcely soluble. However, when the reaction is carried out by stirring a THF suspension of the previously isolated halo complex NiX_2L_2 and TICp substitution does take place, and after 10 h at room temperature TIX can be filtered off to leave a solution containing the nickel complex along with the eliminated free ligands.



(X = Cl, Br, I; L = PPh_3 , PCy_3)

The evaporation of the solvent gives acceptable yields of red crystalline complexes which analyze as the neutral species $(\eta^5\text{-C}_5\text{H}_5)\text{NiXL}$, as shown in Table 1. Complexes I–VI are soluble in warm cyclohexane, from which they were recrystallized. When the complex is very soluble its extraction from the solution containing free ligand is difficult, and the yield is very low, as observed for VI; this is better made from II by treatment with KI in acetone.

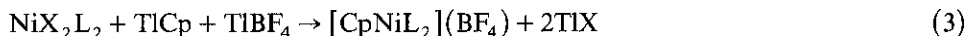
As the product solutions contain an excess of the ligand, the equilibrium shown in eq. 2 is always present [7].



The neutral species is favored under these conditions for PPh_3 and PCy_3 , but the cationic complex is the main product when PPh_2Me is used. Thus the reaction of $\text{NiBr}_2(\text{PPh}_2\text{Me})_2$ with TICp in THF gives a solution containing the neutral red

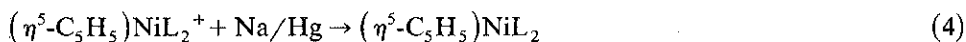
complex and a yellow precipitate of the cationic derivative, which is obtained in high yield if additional amounts of the phosphine are present.

The cationic complexes are easily obtained by the direct reaction of the halonickel complex with an equimolar mixture of TICp and TIBF₄, according to eq. 3.



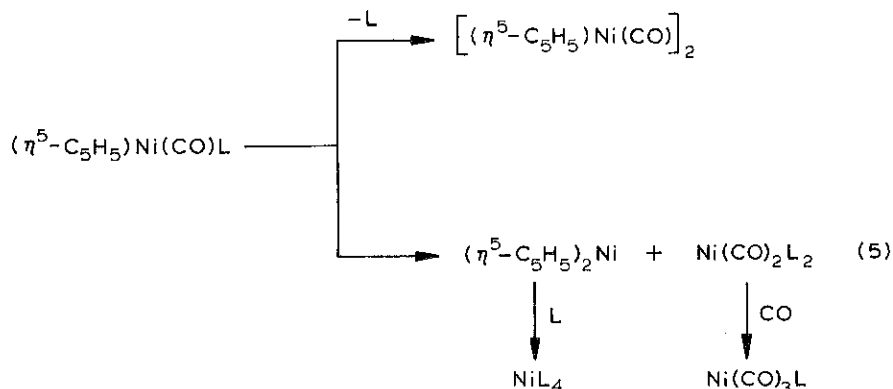
This was the method used for complexes VII–VIII containing PPh₂Me and dppe, as shown in Table 1. If the same reaction with TIBF₄ is carried out with the neutral complex previously isolated, species containing two different ligands can be obtained. Thus complex III reacts with TIBF₄ in the presence of PCy₃ or dppe to give the mononuclear complex IX and the dinuclear cationic derivative X, respectively. Analytical data are shown in Table 1.

The behaviour of some of the nickel(II) complexes described above in reductions with sodium amalgam has been studied under various conditions. The reduction with one equivalent of Na/Hg of THF solutions of the cationic complexes VII–IX gave red brown or dark green (dppe) solutions, and evaporation to dryness and recrystallization from hexane or petroleum ether gave crystalline solids which were identified as ($\eta^5\text{-C}_5\text{H}_5$)NiL₂, (L₂ = 2PPh₂Me (XI), L₂ = PPh₃PCy₃ (XII); L₂ = dppe (XIII)).



These products are very air sensitive (as reported for similar derivatives [6]) and difficult to isolate because of their marked tendency to decompose to Cp₂Ni and NiL₄. The analytical data for apparently pure crystalline solids showed variations (6% lower in C) probably because of decomposition induced by the manipulation of samples in air. Thus only XI gave a satisfactory analysis but all the compounds were characterized as nickel(I) complexes from structural studies and their chemical behaviour.

The reduction of neutral complexes must be carried out in the presence of ligands. Thus, the reduction of III with one equivalent of Na/Hg in toluene gave an intractable residue containing only decomposition products, which were not further investigated. The reduction of THF solutions of I–IV under CO gives solutions from which the expected carbonyl complex could not be isolated, and instead a mixture of compounds was produced, probably by decomposition according to eq. 5.



When L = PCy₃, the dimer [($\eta^5\text{-C}_5\text{H}_5$)Ni(CO)]₂ [8] was recovered as the main

product along with a much smaller amount of $\text{Ni}(\text{CO})_2(\text{PCy}_3)_2$. The dimer is probably formed by elimination of the phosphine, whereas a simultaneous disproportionation leads to formation of the nickel(0) carbonyl. When $\text{L} = \text{PPh}_3$ similar behaviour was observed, but a small amount of $\text{Ni}(\text{PPh}_3)_4$ was also obtained, probably by the reaction of nickelocene with the excess of free ligand dissociated in the first reaction.

The same reductions of I–IV in the presence of acetylenes give green solutions; evaporation of these and recrystallization of the residue from toluene/pentane afforded crystals of the previously reported dimers $[(\eta^5\text{-C}_5\text{H}_5)\text{Ni}]_2 (\mu\text{-RC}\equiv\text{CR}')$, with $\text{R} = \text{R}' = \text{Ph}$ and $\text{R} = \text{Ph}$, $\text{R}' = \text{H}$ [9].

Structural study

All the neutral complexes are non-conducting in solution, whereas VII–IX have conductivities between 100 and 140 $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ in acetone corresponding to their formulation as 1/1 electrolytes. Complex X shows a higher conductivity (190 $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$), in agreement with its formulation as a 1/2 electrolyte.

All the nickel(II) derivatives I–X are diamagnetic at room temperature. The nickel(I) complexes XI–XII are paramagnetic, with a μ_{eff} between 1.64 and 1.85 BM at room temperature; this confirms their formulation as mononuclear species. The carbonyl and acetylene complexes are dimeric diamagnetic compounds containing a nickel–nickel bond, as previously described.

The IR spectra of complexes I–XIII show absorptions due to the different phosphines and the expected bands due to the $(\eta^5\text{-C}_5\text{H}_5)$ ring [10]. The characteristic absorption at 780–790 cm^{-1} is particularly evident from PCy_3 complexes as the ligand does not absorb in this region, in which PPh_3 and PPh_2Me derivatives show intense absorptions. The chloro complexes I, II show the stretching vibration $\nu(\text{Ni}-\text{Cl})$ at 390 cm^{-1} . All the cationic complexes VII–X show the BF_4^- characteristic broad absorption between 1000 and 1150 cm^{-1} . The spectroscopic features of carbonyl and acetylene complexes have been reported previously [8,9].

The ^1H NMR spectra of complexes I–X show a singlet due to the $(\eta^5\text{-C}_5\text{H}_5)$ ring between δ 4.93 and 5.23 ppm as shown in Table 2. This singlet is displaced to lower

TABLE 2
 ^1H NMR DATA FOR $\eta^5\text{-CYCLOPENTADIENYLNICKEL}$ COMPLEXES

Complex	Solvent	δ (ppm), multiplicity, J in Hz, assignment
I	CDCl_3	5.03 s ^a Cp; 7.73 m Ph
II	C_6D_6	5.12 s Cp; 1.63 m Cy
III	CDCl_3	5.08 s Cp; 7.72 m Ph
IV	C_6D_6	5.15 s Cp; 1.63 m Cy
V	CDCl_3	5.16 s Cp; 7.71 m Ph
VI	C_6D_6	5.22 s Cp; 1.65 m Cy
VII	CDCl_3	5.18 s Cp; 7.38 m Ph; 1.74 d $J(\text{P}-\text{H})$ 10.3 Me
VIII	CDCl_3	5.20 s Cp; 7.40 m Ph; 2.51 d $J(\text{P}-\text{H})$ 21.0 CH_2
IX	CDCl_3	5.23 s Cp; 7.30 m Ph; 1.59 m Cy
X	CDCl_3	5.13 s Cp; 7.40 m Ph; 2.51 d $J(\text{P}-\text{H})$ 21.0 CH_2

^a s, singlet; d, doublet; m, multiplet.

field as the basicity of the phosphine is increased and the electronegativity of the anion decreased, and is lower for cationic than for neutral complexes.

Experimental

All operations were carried out under vacuum or in an inert atmosphere using Schlenk-type glassware. Solvents were dried, distilled and deoxygenated before use. NiX_2L_2 were prepared as previously described [11] and TiCp as in ref. 12. C and H analyses were performed with a Perkin-Elmer 240B microanalyzer. Conductivities were measured in acetone with a LF-42 conductimeter. Magnetic measurements were carried out by the Faraday method at room temperature with a Bruker magnet system. IR spectra were recorded as KBr or Nujol mulls between CsI plates using a Perkin-Elmer 457 spectrophotometer. ^1H NMR spectra were recorded on a Varian FT-80A instrument.

$(\eta^5\text{-C}_5\text{H}_5)\text{NiXL}$ (I-VI). Solid TiCp (1.00 mmol) was added to a suspension of NiX_2L_2 (1.00 mmol) in THF (40 ml) and the mixture was stirred at room temperature for 10 h. After filtration the solution was evaporated to dryness and the residue is extracted with 100 ml of warm cyclohexane. Evaporation of the solvent and cooling gave crystals of I-VI. Yields 55-80%.

Complex VI was best prepared by treating a solution of IV (1.00 mmol) in acetone (30 ml) with KI (1.00 mmol). After stirring for 3 h at room temperature the insoluble solid was filtered off and the solvent evaporated under reduced pressure to give garnet crystals of VI. Yield 90%.

$[(\eta^5\text{-C}_5\text{H}_5)\text{NiL}_2]\text{BF}_4$ (VII, VIII). A mixture of NiX_2L_2 (1.00 mmol) and TiCp (1.00 mmol) was stirred in THF (25 ml) for 1 h and then treated with solid TiBF_4 (1.00 mmol). After stirring at room temperature for 12 h the solution was filtered and evaporated to dryness. The residue was repeatedly washed with pentane and recrystallized from dichloromethane/hexane to give green crystals of VII (VIII). Yield 50-75%.

$[(\eta^5\text{-C}_5\text{H}_5)\text{Ni}(\text{PPh}_3)\text{L}]\text{BF}_4$ (IX, X). Addition of solid TiBF_4 (1.00 mmol) to a stirred solution containing III (1.00 mmol) and PCy_3 (1.00 mmol) in 20 ml of dichloromethane was followed by stirring at room temperature for 5 h. The solution was then filtered and evaporated to dryness and the residue was washed with pentane and recrystallized from dichloromethane/hexane, to give yellow crystals of IX. Yield 58%. Complex X was similarly obtained from V by addition of *dppe*. Yield 45%.

$(\eta^5\text{-C}_5\text{H}_5)\text{NiL}_2$ (XI-XIII). A solution of VII (1.00 mmol) in 35 ml of THF was added to one equivalent of Na/Hg (10%) and the mixture was stirred for 2-3 h at -5°C . After filtration and evaporation to dryness, the residue was recrystallized from petroleum ether or hexane to give crystals of XI. Complexes XII and XIII are prepared similarly from VIII and IX, respectively. Yields 50-65%.

Reduction of neutral complexes in the presence of acetylenes and CO

A solution containing III (1.00 mmol) and $\text{RC}\equiv\text{CR}'$ (0.50 mmol) ($\text{R} = \text{R}' = \text{Ph}$; $\text{R} = \text{Ph}$, $\text{R}' = \text{H}$) in 50 ml of toluene was added to one equivalent of Na/Hg (10%). The mixture was stirred at room temperature for 10 h, and the solution was then filtered and evaporated to dryness. The residue was extracted with pentane and crystallized by evaporation under reduced pressure with cooling to give green crystals of $[(\eta^5\text{-C}_5\text{H}_5)\text{Ni}]_2(\mu\text{-CR}\equiv\text{CR}')$.

Similar reduction of complex III under CO gave a residue containing a mixture of compounds from which $[(\eta^5\text{-C}_5\text{H}_5)\text{Ni}(\text{CO})]_2$ was easily separated. Work-up of the solution led to isolation of some other compounds, such as NiL_4 and $\text{Ni}(\text{CO})_2\text{L}_2$. Similar results were obtained with complexes, I, II and IV.

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