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NICKELOCENE CHEMISTRY

IV [*]. NEW NICKELACYLES $[Ni\{Ph_3PCH(CH_2)_nCHPPh_3\}(\eta\text{-}C_5H_5)]PF_6$ ($n = 1$—3) FROM REACTIONS OF NICKELOCENE AND $[NiBr(\eta\text{-}C_5H_5)(PPh_3)]$ WITH BIS-YLIDS

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Summary

Nickelocene reacts with the bis-ylids, $Ph_3PCH(CH_2)_nCHPPh_3$ ($n = 1$—3) to give the new chelate complexes $[Ni\{Ph_3PCH(CH_2)_nCHPPh_3\}(\eta\text{-}C_5H_5)]PF_6$. The same compounds are also formed on reaction of the bis-ylids with $[NiBr(\eta\text{-}C_5H_5)(PPh_3)]$. The compounds with ring size greater than 6 are unstable and could not be isolated. Reaction of nickelocene with the mono-ylids ethylidenetriphenylphosphorane and triphenylphosphoniumcyclopentadienylid afford the complexes $[Ni(CHMePPh_3)_2(\eta\text{-}C_5H_5)]X$ ($X = BPh_4, PF_6$) and the new sandwich complex $[Ni(\eta\text{-}C_5H_5PPh_3)_2]^{2+}(PF_6^-)_2$, respectively; the latter has also been synthesised by reaction of the ylid with $NiBr_2$. The similar reactions of the cyclopentadienylid with $[NiY_2(PPh_3)_2]$ ($Y = Br, I$) gave $[Ni(\eta\text{-}C_5H_4PPh_3)(PPh_3)_2](PF_6)_2$.

Introduction

We recently described the synthesis of new nickel ylid complexes of the type $[Ni(ylid)(\eta\text{-}C_5H_5)(PPh_3)]X$ ($X = Br, PF_6$) by nucleophilic displacement of bromide ion from $[NiBr(\eta\text{-}C_5H_5)(PPh_3)]$ by phosphorus, arsenic, and sulphur ylids [1]. In an earlier paper [2] we also described the synthesis of the complexes $[Ni(CH_2PPh_3)_2(\eta\text{-}C_5H_5)]X$ ($X = BPh_4, PF_6$) either by displacement of a cyclopentadienyl ligand from nickelocene, or displacement of two phosphine ligands from $[Ni(\eta\text{-}C_5H_5)L_2]X$ ($L = PPh_3, PBu^n_3$; $X = BPh_4, PF_6$). It seemed feasible that the use of a difunctional ylid, that is, either a bis-ylid or an ylid anion, could

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[*] For Part 3, see ref. 1.

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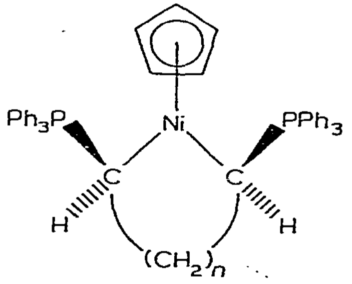
lead to new nickelacycles. A similar approach using ylid anions of the type $[R_2P(CH_2)_2]^-$, $[CH_2PMe_2NPMe_2CH_2]^-$, $[CH_2PMe_2CHPMe_2CH_2]^-$ and $[CH_2PMe_2BH_2PMe_2CH_2]^-$ with transition metal halides has been used to great effect by Schmidbaur and his coworkers [3—5] for the synthesis of a range of transition metal heterocycles. Surprisingly, however, the use of bis-ylids of the type $R_3\dot{P}CH(CH_2)_nCHPR_3$ for chelate formation has not, to our knowledge, been described previously, despite the ready availability of these compounds from the corresponding bis(triphenylphosphonio)alkane dibromides [6].

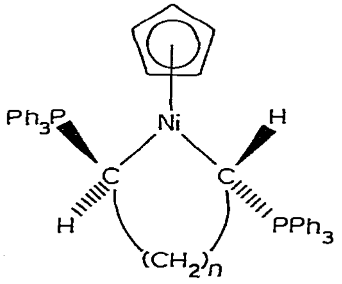
Results and discussion

An attempted reaction between nickelocene and the ylid anion $[Ph_2P(CH_2)_2]^-$, prepared in situ by the action of two equivalents of butyllithium on dimethylphosphonium iodide [7], gave only an air-sensitive brown oil after treatment with NH_4PF_6 and no pure product could be obtained. In contrast, the bis-ylid 1,3-bis(triphenylphosphorylidene)propane reacted readily at room temperature to give a 68% yield of the complex $[Ni(Ph_3PCHCH_2CHPPh_3)(\eta\text{-}C_5H_5)]PF_6$ as air-stable, green-brown needles. A repeat of this reaction with the addition of $NaBPh_4$ in place of NH_4PF_6 gave the corresponding tetraphenylboron derivative in 65% yield. The similar reactions of nickelocene with 1,4-bis(triphenylphosphorylidene)butane and 1,5-bis(triphenylphosphorylidene)pentane in the presence of NH_4PF_6 gave the chelate complexes $[Ni(Ph_3PCHCH_2CH_2CHPPh_3)(\eta\text{-}C_5H_5)]PF_6$ and $[Ni(Ph_3PCHCH_2CH_2CH_2CHPPh_3)(\eta\text{-}C_5H_5)]PF_6$ in 62% and 32% yields, respectively. Attempts to extend this reaction to prepare the 7-membered nickelacycle $[Ni\{Ph_3PCH(CH_2)_4CHPPh_3\}(\eta\text{-}C_5H_5)]PF_6$ by reaction of 1,6-bis(triphenylphosphorylidene)hexane gave a brown solid which rapidly darkened upon exposure to air, and an analytically pure sample could not be obtained.

These bis-ylid complexes are not very soluble in common organic solvents and meaningful ^1H NMR spectra could not be obtained. Evidence for the structures rests on elemental analysis and the fact that the IR and UV/visible spectra of the compounds closely resemble those of other compounds of the type $[Ni(ylid)_2(\eta\text{-}C_5H_5)]PF_6$. The ^{31}P NMR spectra are complicated by the fact that each of the compounds has two chiral carbon centres and can exist as two diastereoisomers I and II. The spectrum of compound $[Ni(Ph_3PCHCH_2CHPPh_3)(\eta\text{-}C_5H_5)]PF_6$ shows only a broad, unresolved signal at —35 ppm for the phos-



meso-(I)



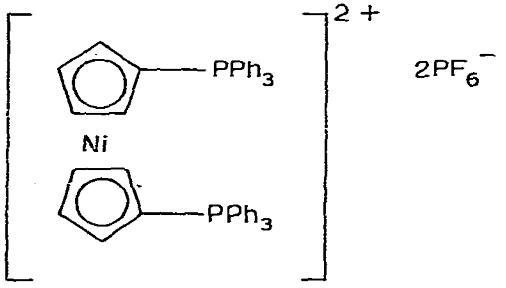
rac-(II)

phorus atoms of the ylid ligand, suggesting that it is a mixture of both diastereoisomers. In contrast, in the spectrum of $[Ni(Ph_3PCHCH_2CH_2CHPPh_3)(\eta\text{-}C_5H_5)]PF_6$ the ^{31}P atoms of the ylid ligand appear as a sharp singlet at —35.8 ppm, while that of the 6-membered nickelacycle $[Ni(Ph_3PCHCH_2CH_2CH_2CHPPh_3)(\eta\text{-}C_5H_5)]$ shows two distinct, sharp singlets at —37.8 and —36.8 ppm. The spectra also show the expected septet at +144.6 ppm (J(P—F) = 713 Hz) for the PF_6^- anion. It seems probable that all three compounds are mixtures of diastereoisomers, and that in the 5-membered ring nickelacycle the signals for the ^{31}P atoms of the ylid ligands are accidentally coincident, but a more detailed spectroscopic study is necessary before this can be confirmed.

In an effort to synthesise ylid-bridged complexes of the type $[(\eta\text{-}C_5H_5)(PPh_3)Ni\{\mu\text{-}Ph_3PCH(CH_2)_nCHPPh_3\}Ni(PPh_3)(\eta\text{-}C_5H_5)](X)_2$ (X = Br or PF_6), a solution of the bis-ylid, $Ph_3PCHCH_2CHPPh_3$, was added dropwise to 2 : 1 molar excess of $[NiBr(\eta\text{-}C_5H_5)(PPh_3)]$ in tetrahydrofuran at room temperature, but the only product, isolated in 29% yield, was the chelate complex $[Ni(Ph_3PCHCH_2PPh_3)(\eta\text{-}C_5H_5)]PF_6$. The yield of this product increased to 58% when equimolar amounts of the reactants were used. Similar results were also obtained on dropwise addition of solutions of the bis-ylids, $Ph_3PCH(CH_2)_nCHPPh_3$, (n = 2, 3) to an equimolar amount of $[NiBr(\eta\text{-}C_5H_5)(PPh_3)]$ in tetrahydrofuran, and the only products were the chelate complexes $[Ni(Ph_3PCH(CH_2)_nCHPPh_3)(\eta\text{-}C_5H_5)]PF_6$. Even reactions in which the chelate effect of the bis-ylid should be less dominant, as with $Ph_3PCH(CH_2)_nCHPPh_3$ (n = 5 or 8), gave no evidence for stable ylid-bridged complexes, and it appears that loss of the PPh_3 ligand from the intermediates $[Ni(Ph_3PCH(CH_2)_nCHPPh_3)(\eta\text{-}C_5H_5)(PPh_3)]Br$ by nucleophilic attack of the uncoordinated ylid group is a particularly facile reaction.

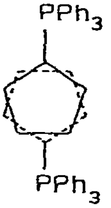
Ethylidenetriphenylphosphorane reacts smoothly with nickelocene at room temperature in diethyl ether to give the expected complex $[Ni(CHMePPh_3)_2(\eta^5\text{-}C_5H_5)]BPh_4$ in 46% yield after addition of $NaBPh_4$. The use of NH_4PF_6 in this reaction gave the corresponding PF_6^- salt in 40% yield. This compound, like the bis-ylid complexes, has two chiral carbon centres and can exist in diastereomeric forms. The ^{31}P NMR spectrum of the PF_6^- salt shows two signals at —38.8 and —36.2 ppm for the ^{31}P atoms of the ylid ligands in addition to the septet at +144.6 ppm (J(P—F) = 713 Hz) for the PF_6 group. This indicates that both isomers are present. Attempted reactions of nickelocene with other nonstabilised ylids, including $CHEtPPh_3$, $CHPr^nPPh_3$, CMe_2PPh_3, CH_2AsPh_3, CH_2SMe_2, and $CH_2S(O)Me_2$ gave either brown oils or tarry solids from which no pure products could be isolated. In all cases these products had similar IR spectra to those of other $[Ni(ylid)_2(\eta\text{-}C_5H_5)]PF_6$ complexes, but satisfactory analytical data could not be obtained. The weakly nucleophilic keto-stabilised ylides $Ph_3PCHCOPh$ and Ph_3PCHCO_2Me failed to react with nickelocene even after several hours at the reflux temperature of tetrahydrofuran.

When nickelocene and triphenylphosphoniumcyclopentadienylid (1 : 1 molar ratio) were heated at the reflux temperature of chloroform before addition of NH_4PF_6 the product was the nickelocene analogue III obtained in 37% yield as a violet solid. The yield of compound III increased to 86% with a 2 : 1 molar ratio of ylid to nickelocene in this reaction. The same compound was also isolated in 86% yield from the reaction between the ylid and anhydrous nickel bromide. The ^1H NMR spectrum (acetone-d_6) of III showed only a

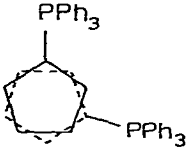


(III)

multiplet centred at δ 7.72 ppm, and it is possible that the aromatic protons and cyclopentadienyl protons overlap; in the ^{1}H NMR spectrum of the palladium complexes [(diene)Pd$C_5H_4PPh_3$]$(BF_4)_2$ (diene = nbd, cod) the cyclopentadienyl ring protons are reported to be at δ 7.18 and 6.92 ppm, and these protons may be even further downfield in the nickel complex. However, in view of the low solubility of the complex in acetone we cannot exclude the possibility that the cyclopentadienyl signals are too weak to observe. The ^{31}P NMR spectrum of III showed an intense signal at −15.6 ppm and a weak signal at 11.7 ppm in addition to the septet at +144.7 ppm for the PF_6^- anion. The compound appears to be analytically pure, and the presence of two signals for the ylid ^{31}P atoms may indicate the presence of rotomers, e.g. IV and V; a third rotomer (VI) is also possible but less likely.



(IV)



(V)

The phosphine complexes $[NiX_2(PPh_3)_2]$ (X = Br, I) also reacted rapidly with triphenylphosphoniumcyclopentadienylid in chloroform at room temperature producing deep violet solutions, which, on treatment with NH_4PF_6, give deep violet microcrystals which analyse for [Ni(η-$C_5H_4PPh_3$)$(PPh_3)_2$]2 PF_6. The ^{1}H NMR spectrum again showed only a multiplet centred at δ 7.44 ppm. It is more than 20 years since Wilkinson prepared the first transition metal complexes having an η^5-$C_5H_4\overset{+}{P}Ph_3$ ligand [9], and since that time there have been several reports of other transition metal complexes containing this ligand, including [M(η-$C_5H_4PPh_3$)$(CO)_3$] (M = Cr, Mo, W) [9–11], [M(η-$C_5H_4PPh_3$)$(CO)_3$]PF_6 (M = Mn, Re) [12,13], [$TiCl_3$(η-$C_5H_4PPh_3$)] · 4 H_2O, [MCl_4(η-$C_5H_4PPh_3$)$_2$] (M = Ti, Zr, Hf) [14], [$MoCl_3(OH)_2$(η-$C_5H_4PPh_3$)] [15], [(diene)Pd(η-$C_5H_4PPh_3$)]-2 BF_4 [8] and the compound [Pd{$C_4(CO_2Me)_4$}(η^3-$C_5H_4PPh_3$)] [16]. The complexes described in this present work represent the first examples of nickel complexes of the cyclopentadienylid ligand.

Experimental

Unless otherwise stated all reactions were conducted at room temperature under an atmosphere of dry nitrogen. Toluene was dried over sodium wire and THF was distilled from lithium aluminium hydride immediately before use.

The following compounds were prepared and purified by literature methods: nickelocene [17], $[NiBr(\eta\text{-}C_5H_5)(PPh_3)]$ [18], ethylidenetriphenylphosphorane [19], triphenylphosphoniumcyclopentadienylid [20], 1,3-bis(triphenylphosphonio)propane dibromide, 1,4-bis(triphenylphosphonio)butane dibromide, 1,5-bis(triphenylphosphonio)pentane dibromide, and 1,6-bis(triphenylphosphonio)hexane dibromide [21].

IR spectra were recorded as Nujol mulls on a Perkin-Elmer 621 spectrophotometer. UV/vis spectra were recorded on a Beckmann Acta Mark IV spectrometer using 10^{-3} to 10^{-5} *M* solutions in dichloromethane and cells of 1 cm pathlength. ^{31}P NMR spectra were determined on solutions in dichloromethane using a JEOL FX60 spectrometer operating at 24.15 MHz. Chemical shifts are referenced to external 85% aqueous phosphoric acid. ^1H NMR spectra were recorded on a Varian HA 100 spectrometer.

Reaction between nickelocene and Ph_3PCHMe

A solution of ethylidenetriphenylphosphorane [prepared in situ from ethyltriphenylphosphonium iodide (7.60 g, 18.17 mmol) and phenyllithium (18.06 mmol)] in diethyl ether (100 cm^3) was added dropwise, with stirring, to a solution of nickelocene (1.70 g, 9.00 mmol) in diethylether (25 cm^2). After stirring for 1 h the mixture was allowed to stand overnight before decanting off the solvent and treatment of the brown tarry residue with acetone (150 cm^3) containing sodium tetraphenylboron (3.00 g, 8.77 mmol). After filtration, water was added to the filtrate to give a brown precipitate, which was recrystallised from an acetone/water mixture to give dark brown needles of $[Ni(CHMePPh_3)_2(\eta\text{-}C_5H_5)]BPh_4$ (4.20 g, 4.10 mmol, 46%), m.p. 141—143°C with decomp. (Found: C, 80.0, H, 6.2; P, 5.9. $C_{69}H_{63}BNiP_2$ calcd.: C, 80.9; H, 6.2; P, 6.0%).

The use of ammonium hexafluorophosphate in place of sodium tetraphenylboron under similar conditions gave dark brown crystals of the corresponding PF_6^- salt (3.45 g, 4.06 mmol, 40%), m.p. 153—156°C with decomp. (Found: C, 63.7; H, 5.4; F, 12.8; P, 10.0. $C_{45}H_{43}F_6NiP_3$ calcd.: C, 63.6; H, 5.1; F, 13.4; P, 10.9%). IR: 3050w, 2965w, 2855w, 1584w, 1570w, 1476s, 1438s, 1410w, 1374w, 1354w, 1312w, 1189w, 1162w, 1117(sh), 1103vs, 1050w, 1030w, 1016w, 998m, 980w, 928w, 875m, 856(sh), 840vs, 792m, 757m, 747m, 731s, 717vs, 693vs, 663m, 560vs, 536s, 504s, 478m, 464m, 387w, 335w, 299w, 272w, 250w, 241 cm^{-1}.

Preparation of $[Ni(\eta\text{-}C_5H_4PPh_3)_2]_2PF_6$

a) From nickelocene. When a solution of triphenylphosphoniumcyclopentadienylid (1.70 g, 5.21 mmol) and nickelocene (1.00 g, 5.29 mmol) in chloroform (50 cm^3) was heated under reflux the mixture became brown and then deep violet. After 2 h the mixture was filtered and the solvent was removed from the filtrate to give a violet oil, which was taken up in ethanol (50 cm^3) and treated with NH_4PF_6 (0.85 g, 5.21 mmol) in ethanol (15 cm^3) to give an amorphous violet precipitate. This was chromatographed (Florisil, CH_2Cl_2 eluent) to give deep violet microcrystals of $[Ni(\eta\text{-}C_5H_4PPh_3)_2]2\,PF_6$ (1.98 g, 1.98 mmol, 37%), m.p. 162—165°C with decomp. (Found: C, 55.9; H, 4.2. $C_{46}H_{38}F_{12}NiP_4$ calcd.: C, 55.2; H, 3.8%). IR: 3060w, 2950w, 2860w, 1590w, 1562w, 1480s, 1362m, 1340m, 1308w, 1291w, 1188w, 1160w, 1142w, 1108s, 1070w, 1025w, 990w, 972w, 863(sh), 835vs(br), 745m, 716s, 684s, 550s, 522m, 506m, 480w cm^{-1}..

A repeat of the above reaction using triphenylphosphoniumcyclopentadienylid (3.40 g, 10.42 mmol) and nickelocene (1.00 g, 5.29 mmol) at the reflux temperature of chloroform (50 cm^3) for 3 h, after treatment with NH_4PF_6 (1.70 g, 10.42 mmol) and chromatography, gave $[Ni(\eta\text{-}C_5H_4PPh_3)_2]2\,PF_6$ (4.59 g, 4.58 mmol, 86%).

b) From nickel bromide. Bromine (3.10 g, 38.80 mmol) was added to a slurry of nickel powder (0.50 g, 8.52 g atom) in 1,2-dimethoxyethane (30 cm^3), and after stirring the mixture for 3 h the solvent was removed to give a yellow brown residue of anhydrous nickel bromide. This was taken up in chloroform (50 cm^3) and a solution of triphenylphosphoniumcyclopentadienylid (5.60 g, 17.16 mmol) in chloroform (40 cm^3) was added. After stirring at room temperature for 20 h the mixture had become deep violet. The solvent was removed and the residue was dissolved in ethanol (60 cm^3), filtered, and treated with an aqueous solution of NH_4PF_6 (2.80 g, 17.18 mmol) to give violet microcrystals of $[Ni(\eta\text{-}C_5H_4PPh_3)_2]2\,PF_6$ (7.31 g, 7.30 mmol, 86%), which were recrystallised from an acetone/water mixture.

Preparation of $[Ni(\eta\text{-}C_5H_4PPh_3)(PPh_3)_2]2\,PF_6$

a) From $[NiBr_2(PPh_3)_2]$. A green solution of the ylid (2.64 g, 8.07 mmol) and $[NiBr_2(PPh_3)_2]$ (6.00 g, 8.07 mmol) in chloroform (50 cm^3) on stirring at room temperature for 3 h rapidly became dark red and then violet. Removal of the solvent and treatment of an ethanol solution of the residue with NH_4PF_6 (1.32 g, 8.07 mmol) in ethanol (15 cm^3) gave violet microcrystals of $[Ni(\eta\text{-}C_5H_4PPh_3)(PPh_3)_2]2\,PF_6$ (2.90 g, 2.42 mmol, 30%), m.p. 175—178°C with decomp. (Found: C, 59.5; H, 4.3; F, 18.4; P, 11.9. $C_{59}H_{49}FNiP_5$ calcd.: C, 59.0; H, 4.1; F, 19.0; P, 12.8%). IR: 3060w, 2960w, 2930w, 2890w, 2690w, 2580w, 1587w, 1567w, 1484s, 1433s, 1400m, 1362m, 1350s, 1335m, 1312w, 1258w, 1240w, 1190w, 1164w, 1110s(br), 1090(sh), 1028w, 1020w, 1009m, 998s, 974m, 956m, 930w, 918m, 877(sh), 859s, 835vs(br), 750s, 724s, 690s, 618w, 556s, 528s, 510s, 466w cm^{-1}.

b) From $[NiI_2(PPh_3)_2]$. A solution of $[NiI_2(PPh_3)_2]$ (2.00 g, 2.39 mmol) and the ylid (0.78 g, 2.39 mmol) in chloroform (50 cm^3) was stirred for 2 h, and after treatment with an ethanol solution of NH_4PF_6 (0.39 g, 2.39 mmol) gave $[Ni(\eta\text{-}C_5H_4PPh_3)(PPh_3)_2]2\,PF_6$ (0.66 g, 0.55 mmol, 23%).

Preparation of $[Ni(Ph_3PCHCH_2CHPPh_3)(\eta\text{-}C_5H_5)]PF_6$

a) From nickelocene. A solution of nickelocene (1.50 g, 7.94 mmol) in tetrahydrofuran (35 cm^3) was added dropwise with stirring to a suspension of 1,3-bis(triphenylphosphorylidene)propane prepared in situ from 1,3-bis(triphenylphosphonio)propane dibromide (6.00 g, 8.26 mmol) and n-butyllithium (17.55 mmol) in tetrahydrofuran (50 cm^3). The mixture was stirred for 16 h before removing the solvent to give a brown solid residue, which was treated with a solution of NH_4PF_6 (1.20 g, 7.36 mmol) in acetone (130 cm^3) and filtered. Addition of water to the filtrate gave a brown precipitate which was recrystallised from an acetonitrile/diethyl ether mixture to give green-brown needles of $[Ni(Ph_3PCHCH_2CHPPh_3)(\eta\text{-}C_5H_5)]PF_6$ (4.50 g, 5.40 mmol, 68%) m.p. 133—135°C with decomp. (Found: C, 63.4; H, 4.5; F, 13.4; Ni, 6.3; P, 10.6. $C_{44}H_{39}F_6NiP_3$ calcd. C, 63.4; H, 4.7; F, 13.7; Ni, 7.0; P, 11.1%). IR: 3060w, 2960w, 2930w, 2890w, 1590w, 1486s, 1440s, 1409m, 1352w, 1315w, 1222w, 1188w, 1164w, 1115s, 1101s, 1073w, 1051w, 1029w, 1017w, 999s, 960w, 925w, 840vs(br), 787m, 735s, 720s, 692s, 600w, 559s, 539s, 528m, 512w, 502w, 373w, 342w, 271w cm^{-1}. UV/vis: $\lambda_{max}(\epsilon)$ 309 (10211), 457 (967), 665 nm (82).

When the brown solid residue from a reaction carried out under similar conditions was treated with sodium tetraphenylboron it gave $[Ni(Ph_3PCHCH_2CHPPh_3)(\eta\text{-}C_5H_5)]BPh_4$ (65%), m.p. 109—112°C with decomp. (Found: C, 79.9; H, 5.9; P, 5.7. $C_{68}H_{59}BNiP_2$ calcd.: C, 81.0; H, 5.9; P, 6.1%).

b) From $[NiBr(\eta\text{-}C_5H_5)(PPh_3)]$. A solution of $[NiBr(\eta\text{-}C_5H_5)(PPh_3)]$ (3.80 g, 8.15 mmol) in tetrahydrofuran (40 cm^3) was added dropwise to a suspension of 1,3-bis(triphenylphosphorylidene)propane [from 1,3-bis(triphenylphosphonio)propane dibromide (6.00 g, 8.26 mmol) and n-butyllithium (17.55 mmol)] in tetrahydrofuran (50 cm^3). The mixture was stirred for 2 h, and the solvent was removed to give a dark brown oil, which on treatment with a solution of NH_4PF_6 (1.30 g, 9.79 mmol) in acetone (100 cm^3) gave $[Ni(Ph_3PCHCH_2CHPPh_3)(\eta\text{-}C_5H_5)]PF_6$ (3.96 g, 4.75 mmol, 58%).

When this reaction was repeated by adding the suspension of the bis-ylid (4.13 mmol) in diethyl ether dropwise with stirring to a solution of $[NiBr(\eta\text{-}C_5H_5)(PPh_3)]$ (3.90 g, 8.37 mmol) in diethyl ether (60 cm^3) a similar work-up procedure to that described above gave $[Ni(Ph_3PCHCH_2CHPPh_3)(\eta\text{-}C_5H_5)]PF_6$ (1.72 g, 2.06 mmol, 25%).

Preparation of $[Ni(Ph_3PCHCH_2CH_2CHPPh_3)(\eta\text{-}C_5H_5)]PF_6$

a) From nickelocene. Dropwise addition of a solution of nickelocene (1.50 g, 7.94 mmol) in tetrahydrofuran (40 cm^3) to a stirred suspension of 1,4-bis(triphenylphosphorylidene)butane [from 1,4-bis(triphenylphosphonio)butane dibromide (6.10 g, 8.24 mmol) and n-butyllithium (17.55 mmol)] in tetrahydrofuran (75 cm^3) at room temperature gave a dark brown solution. This was allowed to stand overnight, before removal of the solvent, and addition of NH_4PF_6 (1.30 g, 7.97 mmol) in acetone (120 cm^3) to the residue. The resulting solution was filtered and some of the acetone was removed under reduced pressure before addition of light petroleum to give orange-brown crystals of $[Ni(Ph_3PCH(CH_2)_2CHPPh_3)(\eta\text{-}C_5H_5)]PF_6$ containing one mole of acetone of crystallisation, (4.43 g, 4.89 mmol, 62%), m.p. 165—169°C with decomp. (Found: C, 63.1; H, 5.1; F, 12.7; Ni, 6.6; P, 10.2. $C_{45}H_{41}F_6NiP_3 \cdot C_3H_6O$ calcd.: C, 63.7; H, 5.2; F, 12.6; Ni, 6.5; P, 10.3%). IR: 3060w, 2920w, 2850w, 1705w, 1588w, 1483s, 1458w, 1440s, 1407w, 1365w, 1351w, 1312w, 1220w, 1185m, 1160w, 1113s(br), 1070w, 1048w, 1017w, 999m, 980w, 926w, 835vs(br), 778s, 743s, 719(sh), 711s, 690s, 560s, 547(sh), 537s, 516m, 269w cm^{-1}. UV/vis: $\lambda_{max}(\epsilon)$ 309 (10211), 457 (697), 665 nm (82).

b) From [NiBr(η-C_5H_5)(PPh_3)]. A solution of 1,4-bis(triphenylphosphorylidene)butane, from 1,4-bis(triphenylphosphonio)butane dibromide (3.10 g, 4.19 mmol) and phenyllithium (8.70 mmol), in diethyl ether (40 cm^3) was added dropwise with stirring to a solution of [NiBr(η-C_5H_5)(PPh_3)] (3.80 g, 8.15 mmol) in tetrahydrofuran (40 cm^3), and the mixture was stirred for 2 h. Removal of the solvent gave a brown solid, which was washed with diethyl ether and recrystallised from an acetone/water mixture to give brown crystals of impure [Ni{$Ph_3PCH(CH_2)_2CHPPh_3$}(η-C_5H_5)]Br (2.65 g, 3.39 mmol, 41%), m.p. 141—145°C with decomp. (Found: C, 65.3; H, 5.2; Br, 9.6, P, 7.3. $C_{45}H_{41}BrNiP_2$ calcd.: C, 69.1; H, 5.3; Br, 10.2; P, 7.9%). This was dissolved in acetone (70 cm^3), filtered, and treated with an aqueous solution of NH_4PF_6 (0.60 g, 3.68 mmol) to give [Ni{$Ph_3PCH(CH_2)_2CHPPh_3$}(η-C_5H_5)]PF_6. $(CH_3)_2CO$ (2.62 g, 2.89 mmol, 35%).

Preparation of [Ni($Ph_3PCHCH_2CH_2CH_2CHPPh_3$)(η-$C_5H_5$)]$PF_6$

a) From nickelocene. Following the same procedure as described above nickelocene (1.50 g, 7.94 mmol) in tetrahydrofuran (40 cm^3) was added to a suspension of 1,5-bis(triphenylphosphorylidene)pentane (8.22 mmol) in the same solvent to give, after stirring for 17 h, a dark brown solution. Removal of the solvent, and addition of an acetone solution of NH_4PF_6 (1.30 g, 7.97 mmol) followed by filtration, and addition of water, gave a brown solid, which was recrystallised from acetone/diethyl ether to give dark brown needles of [Ni{$Ph_3PCH(CH_2)_3CHPPh_3$}(η-C_5H_5)]PF_6. $(CH_3)_2CO$ (2.33 g, 2.53 mmol, 32%), m.p. 127—129°C with decomp. (Found: C, 63.5; H, 5.3; F, 12.1; Ni, 6.7; P, 9.9. $C_{46}H_{43}F_6NiP_3$. C_3H_6O calcd.: C, 64.0; H, 5.4; F, 12.4; Ni, 6.4; P, 10.1%). Recrystallisation from acetonitrile/diethyl ether gave a product free from acetone of crystallisation (Found: C, 63.7; H, 5.0; F, 13.6; P, 11.2. $C_{46}H_{43}F_6NiP_3$ calcd.: C, 64.1; H, 5.0; F, 13.2; P, 10.8%). IR: 3060w, 2960w, 2840w, 1705m, 1584w, 1564w, 1485s, 1440s, 1405m, 1380w, 1360w, 1321w, 1220w, 1188w, 1115s, 1100s, 1072w, 1044w, 1017w, 1000s, 964w, 915w, 840vs(br), 780w, 741s, 719s, 695s, 560s, 536s, 513w, 368w, 272w cm^{-1}. UV/vis: $\lambda_{max}(\epsilon)$ 308 (7982), 480 (656), 714 nm (96).

b) From [NiBr(η-C_5H_5)(PPh_3)]. A solution of 1,4-bis(triphenylphosphorylidene)pentane [from 1,4-bis(triphenylphosphonio)pentane dibromide (3.10 g, 4.11 mmol) and phenyllithium (8.70 mmol)] in diethyl ether (40 cm^3) added dropwise to a stirred solution of [NiBr(η-C_5H_5)(PPh_3)] (3.75 g, 8.05 mmol) in ether (90 cm^3) gave, after 3 h, a brown precipitate. This was filtered off, dissolved in acetone (90 cm^3) and treated with an aqueous solution of ammonium hexafluorophosphate (1.30 g, 7.97 mmol) to give a solid, which was recrystallised from acetone/diethyl ether to afford [Ni{$Ph_3PCH(CH_2)_3CHPPh_3$}(η-C_5H_5)]PF_6. $(CH_3)_2CO$ (2.21 g, 2.40 mmol, 30%).

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