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III *. REACTIONS OF BROMO(η^5-CYCLOPENTADIENYL)TRIPHENYLPHOSPHINENICKEL WITH PHOSPHORUS, ARSENIC AND SULPHUR YLIDS

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Summary

The phosphorus ylids Ph_3PCHR (R = Me, Et, Pr^n, Pr^i, Bu^n, Cl, and OMe), and the ylids Ph_3AsCH_2, Me_2SCH_2, and $Me_2S(O)CH_2$ react with $[Ni(\eta^5\text{-}C_5H_5)Br(PPh_3)]$ at room temperature to give the complexes $[Ni(Ph_3PCHR)(\eta^5\text{-}C_5H_5)(PPh_3)]Br$, $[Ni(Ph_3AsCH_2)(\eta^5\text{-}C_5H_5)(PPh_3)]Br$, $[Ni(Me_2SCH_2)(\eta^5\text{-}C_5H_5)(PPh_3)]Br$ and $[Ni\{Me_2S(O)CH_2\}(\eta^5\text{-}C_5H_5)(PPh_3)]Br$, respectively. These are readily converted into the corresponding hexafluorophosphate salts on reaction with ammonium hexafluorophosphate. Under more forcing conditions the stabilised ylid $Ph_3PCHCOPh$ gives a product believed to be the complex $[Ni(Ph_3PCHCOPh)_2(\eta^5\text{-}C_5H_5)]Br$, isolated and characterised as its PF_6^- salt.

Introduction

We have described recently [1] the synthesis of the mono-ylid complex $[Ni(CH_2PPh_3)(\eta^5\text{-}C_5H_5)(PPh_3)]Br$, and its BPh_4^- and PF_6^- derivatives, by direct reaction between methylenetriphenylphosphorane and $[NiBr(\eta^5\text{-}C_5H_5)(PPh_3)]$ in a 1 : 1 molar ratio. We now describe the extension of this reaction to other ylids containing phosphorus, arsenic and sulphur, and discuss some of the limitations found for this preparative route.

Results and discussion

The non-stabilised alkylidenephosphoranes, $Ph_3PCR^1R^2$ (R_1 = H, R^2 = Me, Et, Pr^n and Bu^n), conveniently generated in situ by treatment of the corresponding

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phosphonium bromides with phenyllithium in diethyl ether, react rapidly upon dropwise addition to a solution of $[NiBr(\eta^5\text{-}C_5H_5)(PPh_3)]$ in toluene to give green to orange-brown precipitates of the complexes $[Ni(CR^1R^2PPh_3)(\eta^5\text{-}C_5H_5)(PPh_3)]Br$ in 62—74% yields. These were readily converted to the corresponding hexafluorophosphate salts by reaction with NH_4PF_6 in ethanol. The ylids $Ph_3PCR^1R^2$ (R^1 = H, R^2 = OMe, Cl; $R^1 = R^2$ = Me), which were obtained from the corresponding phosphonium chlorides (R^1 = H, R^2 = OMe, Cl) or iodide ($R^1 = R^2$ = Me) also reacted at room temperature to give the expected complexes $[Ni(CR^1R^2PPh_3)(\eta^5\text{-}C_5H_5)(PPh_3)]Br$, but these were contaminated by chloride or iodide ions and could not be obtained in a pure state. Analytically pure samples of the corresponding hexafluorophosphate salts were obtained, however, by anion exchange.

The sterically-hindered ylid, cyclohexylidenetriphenylphosphorane, and the resonance-stabilised ylids benzylidenetriphenylphosphorane and triphenylphosphoniumcyclopentadienylid failed to react with $[NiBr(\eta^5\text{-}C_5H_5)(PPh_3)]$ at room temperature. When the reaction with benzylidenetriphenylphosphorane was attempted in tetrahydrofuran solvent the only product isolated in 33% yield was $[Ni(\eta^5\text{-}C_5H_5)(PPh_3)_2]Br$, characterised as the PF_6^- salt. The same product was also formed in 37% yield in the attempted reaction between $[NiBr(\eta^5\text{-}C_5H_5)(PPh_3)]$ and $Bu^n{}_3PCH_2$ generated from $[Bu^n{}_3PCH_3]I$ by treatment with sodamide at the reflux temperature of tetrayhdrofuran. It is possible that these bis(triphenylphosphine)nickel salts arise by disproportionation of $[NiBr(\eta^5\text{-}C_5H_5)(PPh_3)]$; a reaction noted previously during treatment of $[NiCl(\eta^5\text{-}C_5H_5)(PPh_3)]$ with $NaBPh_4$ [2] or $SnCl_2$ [3] to give $[Ni(\eta^5\text{-}C_5H_5)(PPh_3)_2]X$ (X = BPh_4 or $SnCl_3$).

As might be expected, the less nucleophilic carbonyl-stabilised ylids carbomethoxymethylenetriphenylphosphorane and phenacylidenetriphenylphosphorane, did not react with $[NiBr(\eta^5\text{-}C_5H_5)(PPh_3)]$ even after a prolonged period in refluxing benzene. Surprisingly, however, phenacylidenetriphenylphosphorane did react in chloroform to give a product believed to be $[Ni(Ph_3PCHCOPh)_2(\eta^5\text{-}C_5H_5)]Br$, isolated in 21% yield as its PF_6^- derivative. The yield could be improved to 47% by using a 2 : 1 molar excess of the ylid in this reaction. The product could not be obtained analytically pure, and evidence for the structure rests on the ^{31}P NMR spectrum of the PF_6^- salt, which shows a singlet at —22.2 ppm for ylid ligand and a septet centred at 144.6 ppm (J(P—F) = 713 Hz) for PF_6^-. There was no evidence for a triphenylphosphine ligand, which usually appears in the region of —36.δ to —40.9 ppm (see Table 1). The IR spectrum showed a strong carbonyl absorption at 1578 cm^{-1}, which represents a shift of 54 cm^{-1} from the frequency of the free ylid (ν(CO) = 1524 cm^{-1}). A similar shift has been observed for other transition metal complexes of phenacylidenetriphenylphosphorane and has been attributed to transfer of charge from the ylid carbon atom to the metal atom [4,5].

Methylenetriphenylarsenane reacts readily with $[NiBr(\eta^5\text{-}C_5H_5)(PPh_3)]$ in toluene at room temperature to give $[Ni(CH_2AsPh_3)(\eta^5\text{-}C_5H_5)(PPh_3)]Br$ as a green solid isolated in 52% yield. This complex, and the corresponding PF_6^- derivative, appear to be the first examples of compounds having an arsenic ylid ligand coordinated to nickel. Extension of the reaction to the sulphur ylids, dimethylsulphoniummethylid and dimethylsulphoxoniummethylid,

gave, after treatment of the solution with NH_4PF_6, green crystals of the complexes $[Ni(CH_2SMe_2)(\eta^5\text{-}C_5H_5)(PPh_3)]PF_6$ and $[Ni\{CH_2S(O)Me_2\}(\eta^5\text{-}C_5H_5)(PPh_3)]PF_6$ isolated in 23% and 12% yields, respectively. The low yields can be attributed in part to the thermal instabiiity of the sulphur ylids.

Spectroscopic data

^1H NMR spectroscopic data for the ylid complexes are displayed in Table 1. The complexes all show a sharp singlet in the range δ 4.78—4.96 ppm for the cyclopentadiene protons, but the resonance for the methine proton of the ylid ligands of type $CHRPPh_3$ was not observed, due to the low solubility of the complexes and the unfavourable ratio of intensities of the methine: aromatic protons. ^{31}P NMR spectroscopic data are also shown in Table 1. In the case of the phosphorus ylids two peaks are observed, corresponding to the phosphorus atoms of the coordinated ylid and the triphenylphosphine ligand, in addition to the septet for the PF_6^- anion. For the compounds $[Ni(CR^1R^2PPh_3)(\eta^5\text{-}C_5H_5)(PPh_3)]PF_6$ (R^1 = H, R^2 = Et, Pr^n, Bu^n) the chemical shifts of the ^{31}P atom in the ylid ligand lie in the range of 37.6 to 37.8 ppm downfield from phosphoric acid. The ethylidenetriphenylphosphorane complex is anomalous and the ^{31}P signal is shifted approximately 1.0 ppm downfield. A similar anomalous downfield shift has been noted previously [6,7] for ethyltriphenylphosphonium bromide when compared with the ^{31}P chemical shifts of other alkyltriphenylphosphonium salts, but we can offer no explanation for this effect.

There is also an interesting trend in the ^{31}P chemical shifts of the Ph_3P ligands. As the length of the alkyl substituent in the ylid ligand increases according to R^1 = Me < Et < Pr^n < Bu^n, then the ^{31}P chemical shift of the Ph_3P ligand shifts upfield. This effect possibly reflects an increased steric interaction between the ylid ligand and the PPh_3 ligand in these five-coordinate nickel complexes. As the bulk of the ylid ligand increases this may cause a decrease in the cone angle of the adjacent phosphine ligand resulting in increased *s* character, and hence increased shielding [8] of the phosphorus atom. Some evidence for the steric origin of this effect is that replacement of the C—H of the ylid ligand in $[Ni(CHMePPh_3)(\eta^5\text{-}C_5H_5)(PPh_3)]PF_6$ by a CH_3 group as in $[Ni(CMe_2PPh_3)(\eta^5\text{-}C_5H_5)(PPh_3)]PF_6$ causes a significant shift of the ^{31}P signal of the PPh_3 ligand to high field. Also, when the methylenephosphorane ligand in $[Ni(CH_2PPh_3)(\eta^5\text{-}C_5H_5)(PPh_3)]Br$ is replaced by the less bulky methylenetriphenylarsanane ligand [9] the value of $\delta(PPh_3)$ is shifted downfield.

A similar steric effect may have been noted previously by Thomson and Baird [10,11] in their examination of the ^{31}P NMR spectra of a series of compounds of the type $[NiR(\eta^5\text{-}C_5H_5)(PPh_3)]$ (R = alkyl, aryl, or halogen). The attempted correlation of $\delta(PPh_3)$ with the electronegativity of the group R was unsatisfactory, suggesting that inductive effects are not important; If their results are reinterpreted on the basis of a steric argument it can be seen from Table 2 that there is a reasonable correlation between the increasing cone angle of R with the downfield shift of $\delta(PPh_3)$.

All the nickel ylid complexes show a characteristic high energy band in the UV/visible spectra in the region of λ_{max} 297—312 nm with extinction coefficient 4776 to 13934, and two lower energy bands in the regions λ_{max} 434—481 nm and 560—728 nm (see Table 3). Similar spectra have been reported for the

TABLE 1

^1H AND ^{31}P NMR DATA FOR [Ni(ylid)(η^5-C_5H_5)(PPh_3)]X COMPLEXES

Ylid ligand	^1H NMR data [a]				^{31}P NMR data [b]		
	X	C_6H_5	C_5H_5	aliphatic protons	$CR^1R^2PPh_3$	PPh_3	PF_6 [d]
	Br				−38.7	−40.2	
$CHMePPh_3$							
	PF_6 [c]	7.44m	4.78s	1.2m (CH_3)	−39.0	−40.2	+144.6
	Br				−37.7	−37.4	
$CHEtPPh_3$							
	PF_6	7.49m	4.89s	1.03m (CH_3); 1.48m (CH_2)	−37.8	−37.4	+144.6
	Br				−37.5	−37.0	
CH-n-$PrPPh_3$							
	PF_6 [c]	7.68m	4.82s	0.86t [J(H—H) = 7.0 Hz, CH_3], 1.22m (CH_2), 1.54m (CH_2)	−37.6	−36.9	+144.6
	Br				−37.7	−36.8	
CH-n-$BuPPh_3$							
	PF_6 [c]	7.65	4.82s	0.75t [J(H—H) = 7.0 Hz, CH_3], 1.22m (CH_2CH_2), 1.50 (CH_2)	−37.7	−36.8	+144.6
$CHClPPh_3$	PF_6 [c]	7.49m	4.86s		−33.6	−41.2	+144.6
$CHOMePPh_3$	PF_6	7.77m	4.92s	4.57s (OCH_3)			
CMe_2PPh_3	PF_6	7.50m	4.95s	1.10br (2 CH_3)	−36.8	−37.6	+144.6
CH_2AsPh_3	Br	7.32m	4.86s	1.21s (CH_2)		−41.7	
CH_2SMe_2	PF_6	7.42m	5.36s	2.86s (2 CH_3), 2.45s (CH_2)			
$CH_2S(O)Me_2$	PF_6 [c]	7.36m	5.12s	2.10s (2 CH_3), 1.51s (CH_2)			

[a] Except where stated spectra were recorded on a Varian Associates HA 100 spectrometer operating at 100 MHz, and obtained on solutions in $(CD_3)_2CO$ with Me_4Si as internal reference. Chemical shifts are reported as δ values; br = broad, m = unresolved multiplet, s = singlet, t = triplet, dd = double doublet. [b] Recorded on solutions in dichloromethane in 10 mm tubes incorporating a coaxial tube containing D_2O, using a JEOL FX 60 spectrometer operating at 24.15 MHz. Chemical shifts are in ppm relative to external 85% aqueous phosphoric acid. [c] ^1H NMR spectrum recorded in $CDCl_3$. [d] Septet, J(P—F) = 713 Hz.

TABLE 2

^{31}P NMR AND CONE ANGLE DATA FOR [NiR(η^5-C_5H_5)(PPh_3)] COMPLEXES

R	θ(R) (°) [a]	δ(PPh_3) (ppm) [b]
Me	90	—49.5
Et	102	—49.0
Pr^i	114	—47.6
CH_2CMe_3	120	—46.1
CH_2SiMe_3	120	—45.9

[a] Cone angle data taken from ref. 9. [b] ^{31}P NMR data taken from ref. 10.

TABLE 3

UV/VIS SPECTRA OF THE COMPLEXES [Ni(YLID)(η^5-C_5H_5)(PPh_3)]PF_6 [a]

Ylid ligand	λ_{max} (nm) [ϵ]		
$CHMePPh_3$	304 [9193]	452 [1489]	643 [133]
$CHEtPPh_3$	308 [13934]	457 [1090]	588 [104]
$CHClPPh_3$	301 [11680]	443 [1286]	634 [84]
CH_2AsPh_3	297 [9900]	435 [981]	550 [124]
CH_2SOMe_2	330 [4776]	434 [1120]	560 [168]

[a] 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 pathlengths.

related five-coordinate complexes [NiR(η^5-C_5H_5)(PPh_3)] (R = alkyl, aryl or halogen) and the high energy band has been attributed to a charge transfer transition associated with aromatic ligands [10]. The two low energy bands have been assigned to transitions between orbitals which are essentially nickel *d* orbitals in character.

Experimental

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

Bromo(η^5-cyclopentadienyl)triphenylphosphinenickel was prepared and purified according to a previously reported procedure [12], and the following phosphonium salts were prepared by quaterisation of triphenylphosphine with the appropriate alkyl halide following established procedure [13]; ethyltriphenylphosphonium bromide [14], n-propyltriphenylphosphonium bromide [15], isopropyltriphenylphosphonium iodide [16], n-butyltriphenylphosphonium bromide [17], n-pentyltriphenylphosphonium bromide [18].

Preparation of [Ni(CHMePPh$_3$)(η^5-C$_5$H$_5$)(PPh$_3$)]Br and PF$_6^-$ salt

A solution of ethylidenetriphenylphosphorane prepared in situ from ethyltriphenylphosphonium bromide (3.40 g, 9.15 mmol) and phenyllithium (9.00 mmol) in diethyl ether (70 cm^3) was added dropwise to a solution of [NiBr(η^5-C_5H_5)(PPh_3)] (4.20 g, 9.01 mmol) in toluene (40 cm^3). The mixture was

stirred for 1 h and filtered to yield a khaki solid, which was recrystallised from aqueous ethanol to give green crystals of $[Ni(CHMePPh_3)(\eta^5\text{-}C_5H_5)(PPh_3)]Br$ (4.72 g, 6.24 mmol, 69%) m.p. 112—115°C with decomposition (Found: C, 68.1; H, 5.2; Br, 10.6; Ni, 7.4; P, 7.9. $C_{43}H_{39}BrNiP_2$ calcd.: C, 68.3; H, 5.2; Br, 10.5; Ni, 7.8; P, 8.2%).

Treatment of a sample of the product with ammonium hexafluorophosphate in ethanol gave dark green crystals of $[Ni(CHMePPh_3)(\eta^5\text{-}C_5H_5)(PPh_3)]PF_6$, m.p. 130—132°C with decomp. (Found: C, 62.6; H, 5.1; F, 14.4; Ni, 6.6; P, 10.8. $C_{43}H_{39}F_6NiP_3$ calcd.: C, 62.9; H, 4.8; F, 13.9; Ni, 7.1; P, 11.3%).

Preparation of $[Ni(CHEtPPh_3)(\eta^5\text{-}C_5H_5)(PPh_3)]Br$ and PF_6^- salt

Propylidenetriphenylphosphorane prepared in situ from n-propyltriphenylphosphonium bromide (3.5 g, 9.08 mmol) and phenyllithium (9.00 mmol) in diethyl ether (90 cm^3) was added dropwise with stirring to a solution of $[NiBr(\eta^5\text{-}C_5H_5)(PPh_3)]$ (4.15 g, 8.91 mmol) in toluene (60 cm^3). The mixture was stirred for 1.5 h and filtered to give a yellow-brown solid, which on recrystallisation from ethanol gave brown microcrystals of $[Ni(CHEtPPh_3)(\eta^5\text{-}C_5H_5)(PPh_3)]Br$ (4.21 g, 5.46 mmol, 61%), m.p. 132—135°C with decomp. (Found: C, 67.6; H, 5.4; Br, 9.9. $C_{44}H_{41}BrNiP_2$ calcd.: C, 68.6; H, 5.4; Br, 10.4%).

Treatment of this with ammonium hexafluorophosphate in ethanol gave orange-brown crystals of $[Ni(CHEtPPh_3)(\eta^5\text{-}C_5H_5)(PPh_3)]PF_6$, m.p. 127—129°C with decomp. (Found: C, 63.0; H, 4.9; F, 13.6; Ni, 7.0; P, 10.8. $C_{44}H_{41}F_6NiP_3$ calcd.: C, 63.3; H, 4.9; F, 13.6; Ni, 7.0; P, 11.1%).

Preparation of $[Ni(CMe_2PPh_3)(\eta^5\text{-}C_5H_5)(PPh_3)]PF_6$

Dropwise addition of isopropylidenetriphenylphosphorane [from isopropyltriphenylphosphonium iodide (2.80 g, 6.48 mmol) and phenyllithium (6.50 mmol)] in diethyl ether (50 cm^3) to a stirred solution of $[NiBr(\eta^5\text{-}C_5H_5)(PPh_3)]$ (3.00 g, 6.44 mmol) in toluene (40 cm^3), gave, after 1 h at room temperature, a light brown solid which contained both Br^- and I^- ions. Treatment of a solution of this solid in ethanol (50 cm^3) with ammonium hexafluorophosphate (1.00 g, 6.13 mmol) in ethanol (20 cm^3) gave green crystals of $[Ni(CMe_2PPh_3)(\eta^5\text{-}C_5H_5)(PPh_3)]PF_6$ (2.71 g, 3.24 mmol, 50%), m.p. 101—104°C with decomp. (Found: C, 63.0; H, 4.8; F, 13.6; P, 11.0. $C_{44}H_{41}F_6NiP_3$ calcd.: C, 63.3; H, 4.9; F, 13.6; P, 11.1%).

Preparation of $[Ni(CHPr^nPPh_3)(\eta^5\text{-}C_5H_5)(PPh_3)]Br$ and PF_6^- salt

Reaction between $[NiBr(\eta^5\text{-}C_5H_5)(PPh_3)]$ (4.10 g, 8.80 mmol) in toluene (30 cm^3) and a solution of butylidenetriphenylphosphorane [from n-butyltriphenylphosphonium bromide (3.60 g, 9.04 mmol) and phenyllithium (9.00 mmol)] in diethyl ether (90 cm^3) at room temperature for 1 h gave a pale brown solid, which, on recrystallisation from aqueous ethanol, gave orange-brown microcrystals of $[Ni(CHPr^nPPh_3)(\eta^5\text{-}C_5H_5)(PPh_3)]Br$ (5.05 g, 6.44 mmol, 73%), m.p. 138—141°C with decomp. (Found: C, 65.8; H, 5.7; Br, 9.7; Ni, 7.0; P, 7.7. $C_{45}H_{43}BrNiP_2$ calcd.: C, 68.9; H, 5.5; Br, 10.2; Ni, 7.5; P, 7.9%).

Treatment with a solution of NH_4PF_6 in ethanol gave dark brown crystals of the PF_6^- salt, m.p. 63.5°C with decomposition (Found: C, 63.3; H, 5.1; F, 13.0; Ni, 6.9; P, 11.3. $C_{45}H_{43}F_6NiP_3$ calcd.: C, 63.6; H, 5.1; F, 13.4; Ni, 6.9; P, 10.9%).

Preparation of [Ni(CHBu^{n}PPh$_3$)(η^5-C$_5$H$_5$)(PPh$_3$)]Br and PF$_6^-$ salt

Addition of pentylidenetriphenylphosphorane [from n-pentyltriphenylphosphonium bromide (3.37 g, 8.15 mmol) and phenyllithium (8.11 mmol)] in diethyl ether (70 cm^3) to a stirred solution of [NiBr(η^5-C$_5$H$_5$)(PPh$_3$)] in toluene (50 cm^3) gave, after 1.5 h at room temperature, a yellow brown solid. This was recrystallised from aqueous methanol to give orange-brown microcrystals of [Ni(CHBu^{n}PPh$_3$)(η^5-C$_5$H$_5$)(PPh$_3$)]Br (4.79 g, 6.00 mmol, 74%) m.p. 126—129°C with decomposition (Found: C, 67.1; H, 5.6; Br, 9.6. C$_{46}$H$_{45}$BrNiP$_2$ calcd.: C, 69.2; H, 5.7; Br, 10.0%). On treatment with NH_4PF_6 this gave dark brown crystals of the corresponding PF_6^- salt, m.p. 104—108°C (Found: C, 64.3; H, 5.6; F, 12.7; Ni, 6.4. C$_{46}$H$_{45}$F$_6$NiP$_3$ calcd.: C, 64.0; H, 5.3; F, 13.2; Ni, 6.8%).

Preparation of [Ni(CHClPPh$_3$)(η^5-C$_5$H$_5$)(PPh$_3$)]PF$_6$

When a solution of chloromethylenetriphenylphosphorane [from chloromethyltriphenylphosphonium chloride (2.85 g, 8.21 mmol) and phenyllithium (8.11 mmol)] in diethyl ether (80 cm^3) was added to a solution of [NiBr(η^5-C$_5$H$_5$)(PPh$_3$)] (3.80 g, 8.15 mmol) in toluene (40 cm^3), after 4 h at room temperature an oily khaki solid (1.44 g) had formed. This was dissolved in ethanol (30 cm^3), filtered, and treated with a solution of ammonium hexafluorophosphate (0.50 g, 3.01 mmol) in ethanol (25 cm^3) to give yellow-green microcrystals of [Ni(CHClPPh$_3$)(η^5-C$_5$H$_5$)(PPh$_3$)]PF$_6$ (1.47 g, 1.75 mmol, 21%), m.p. 103—108°C with decomp. (Found: C, 59.6; H, 4.1; Cl, 4.3; F, 14.0; Ni, 6.6; P, 10.7. C$_{42}$H$_{36}$ClF$_6$NiP$_3$ calcd.: C, 59.9; H, 4.3; Cl, 4.2; F, 13.5; Ni, 7.0; P, 11.0%).

Preparation of [Ni(CHOMePPh$_3$)(η^5-C$_5$H$_5$)(PPh$_3$)]PF$_6$

Reaction between methoxymethylenetriphenylphosphorane [19] [from methoxymethyltriphenylphosphonium chloride (2.30 g, 6.71 mmol) and phenyllithium (6.76 mmol) in diethyl ether (50 cm^3)] and [NiBr(η^5-C$_5$H$_5$)(PPh$_3$)] (3.00 g, 6.44 mmol) in toluene (35 cm^3) gave, after 2.5 h at room temperature, a brown tar (1.78 g). A solution of this tar in ethanol (40 cm^3), filtered and treated with NH_4PF_6 (0.60 g, 3.61 mmol) in ethanol (20 cm^3) gave brown crystals of [Ni(CHOMePPh$_3$)(η^5-C$_5$H$_5$)(PPh$_3$)]PF$_6$ (1.63 g, 1.95 mmol, 30%), m.p. 169—173°C with decomp. (Found: C, 61.2; H, 4.8; F, 13.3; P, 11.0. C$_{43}$H$_{39}$F$_6$NiOP$_3$ calcd.: C, 61.7; H, 4.7; F, 13.6; P, 11.1%).

Reaction between [NiBr(η^5-C$_5$H$_5$)(PPh$_3$)] and phenacylidenetriphenylphosphorane

A solution of the nickel salt (2.00 g, 4.29 mmol) and phenacylidenetriphenylphosphorane (1.65 g, 4.33 mmol) in chloroform (40 cm^3) was heated at reflux temperature for 3 h during which time the violet solution became deep brown. Removal of the solvent under vacuum gave a brown residue, which was dissolved in ethanol (50 cm^3) and treated with a solution of NH_4PF_4 (0.70 g, 4.29 mmol) in ethanol (20 cm^3) to give a white precipitate (0.55 g) and an orange solution. Careful addition of water to the solution gave impure orange-brown crystals believed to be [Ni(PhCOCHPPh$_3$)$_2$(η^5-C$_5$H$_5$)]PF$_6$ (0.92 g, 0.89 mmol, 21%) m.p. 128—131°C with decomp. (Found: C, 60.9; H, 4.2. C$_{57}$H$_{47}$F$_6$NiO$_2$P calcd.: C, 66.5; H, 4.6%).

The same product was also obtained in 47% yield when this reaction was repeated using a 2 : 1 molar ratio of phenacylidenetriphenylphosphorane to nickel salt.

Preparation of [Ni(CH_2AsPh_3)(η^5-C_5H_5)(PPh_3)]Br and PF_6^- salt

A solution of methylenetriphenylarsenane [20] from methyltriphenylarsonium iodide (4.10 g, 9.15 mmol) and phenyllithium (9.00 mmol)] in diethyl ether (40 cm^3) added dropwise to a stirred solution of [NiBr(η^5-C_5H_5)(PPh_3)] (4.00 g, 8.58 mmol) in toluene (80 cm^3) gave an immediate green precipitate. This was recrystallised from aqueous methanol to give green crystals of [Ni(CH_2AsPh_3)(η^5-C_5H_5)(PPh_3)]Br (3.49 g, 4.44 mmol, 52%), m.p. 135—136°C with decomp. (Found: C, 64.0; H, 4.8; Br, 9.8; Ni, 7.4; P, 3.5. $C_{42}H_{37}AsBrNiP$ calcd.: C, 64.1; H, 4.7; Br, 10.2; Ni, 7.5; P, 3.9%).

Treatment of an ethanol solution of this solid with a solution of NH_4PF_6 in ethanol gave dark green crystals of [Ni(CH_2AsPh_3)(η^5-C_5H_5)(PPh_3)]PF_6, m.p. 168—172°C (Found: C, 59.0; H, 4.5; F, 13.4; Ni, 6.7; P, 7.2. $C_{42}H_{37}AsFNiP_2$ calcd.: C, 59.3; H, 4.4; F, 13.4; Ni, 6.9; P, 7.3%).

Preparation of [Ni(CH_2SMe_2)(η^5-C_5H_5)(PPh_3)]PF_6

A suspension of dimethylsulphoniummethylid, prepared in situ from trimethylsulphonium iodide (1.50 g, 7.35 mmol), sodium hydride (0.2 g, 8.33 mmol) and dimethylsulphoxide (15 cm^3) in tetrahydrofuran (25 cm^3) at 0°C, was added dropwise to a stirred solution of [NiBr(η^5-C_5H_5)(PPh_3)] (3.30 g, 7.08 mmol) in diethyl ether (90 cm^3) at 0°C. The mixture was stirred for 2 h at 0°C to give a brown solution. Removal of the diethyl ether and after filtration, treatment of the filtrate with NH_4PF_6 (1.20 g, 7.23 mmol) in water (15 cm^3) gave a pale green precipitate, which was recrystallized from aqueous ethanol to give [Ni(CH_2SMe_2)(η^5-C_5H_5)(PPh_3)]PF_6 (0.97 g, 1.60 mmol, 23%) as light green crystals, m.p. 176—180°C with decomp. (Found: C, 50.8; H, 4.7; S, 5.6. $C_{26}H_{28}F_6NiP_2S$ calcd.: C, 51.4; H, 4.6; S, 5.3%).

Preparation of [Ni{$CH_2S(O)Me_2$}(η^5-C_5H_5)(PPh_3)]Br and PF_6^- salt

Dropwise addition of dimethylsulphoxoniummethylid [from trimethylsulphoxonium iodide (1.50 g, 6.81 mmol) and sodium hydride (0.20 g, 8.33 mmol)] in dimethyl sulphoxide (10 cm^3) to a stirred solution of [NiBr(η^5-C_5H_5)(PPh_3)] (3.10 g, 6.65 mmol) in tetrahydrofuran (35 cm^3) at 0°C, gave a dark brown solution. After 16 h at room temperature, diethyl ether (50 cm^3) was added to give a brown precipitate, which was recrystallised from aqueous acetone to give pale green crystals of [Ni{$CH_2S(O)Me_2$}(η^5-C_5H_5)(PPh_3)]Br (0.43 g, 0.77 mmol, 12%), m.p. 139—144°C with decomp. (Found: C, 54.9; H, 5.0; S, 5.6. $C_{26}H_{28}BrNiOPS$ calcd.: C, 55.9; H, 5.1; S, 5.7%.)

A sample of this product treated with a solution of NH_4PF_6 in ethanol gave green crystals of [Ni{$CH_2S(O)Me_2$}(η^5-C_5H_5)(PPh_3)]PF_6, m.p. 186—190°C with decomp. (Found: C, 50.5; H, 4.6; F, 17.9; S, 5.0. $C_{26}H_{28}F_6NiOP_2S$ calcd.: C, 50.1; H, 4.5; F, 18.3; S, 5.1%).

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