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NICKELOCENE CHEMISTRY

I. REACTIONS OF METHYLENETRIPHENYLPHOSPHORANE WITH η^5 -CYCLOPENTADIENYLNICKEL COMPLEXES

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Summary

Nickelocene reacts with methylenetriphenylphosphorane with displacement of one of the cyclopentadienyl rings to give the cation $[\text{Ni}(\text{CH}_2\text{PPh}_3)_2(\eta^5\text{-C}_5\text{H}_5)]^+$ which can also be obtained by reaction of the cationic complexes $[\text{Ni}(\eta^5\text{-C}_5\text{H}_5)\text{L}_2]\text{X}$ ($\text{L} = \text{PPh}_3$ or P-n-Bu_3) with Ph_3PCH_2 . With $[\text{NiBr}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)]$ the ylide displaces Br^- to form $[\text{Ni}(\text{CH}_2\text{PPh}_3)(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)]\text{Br}$.

Introduction

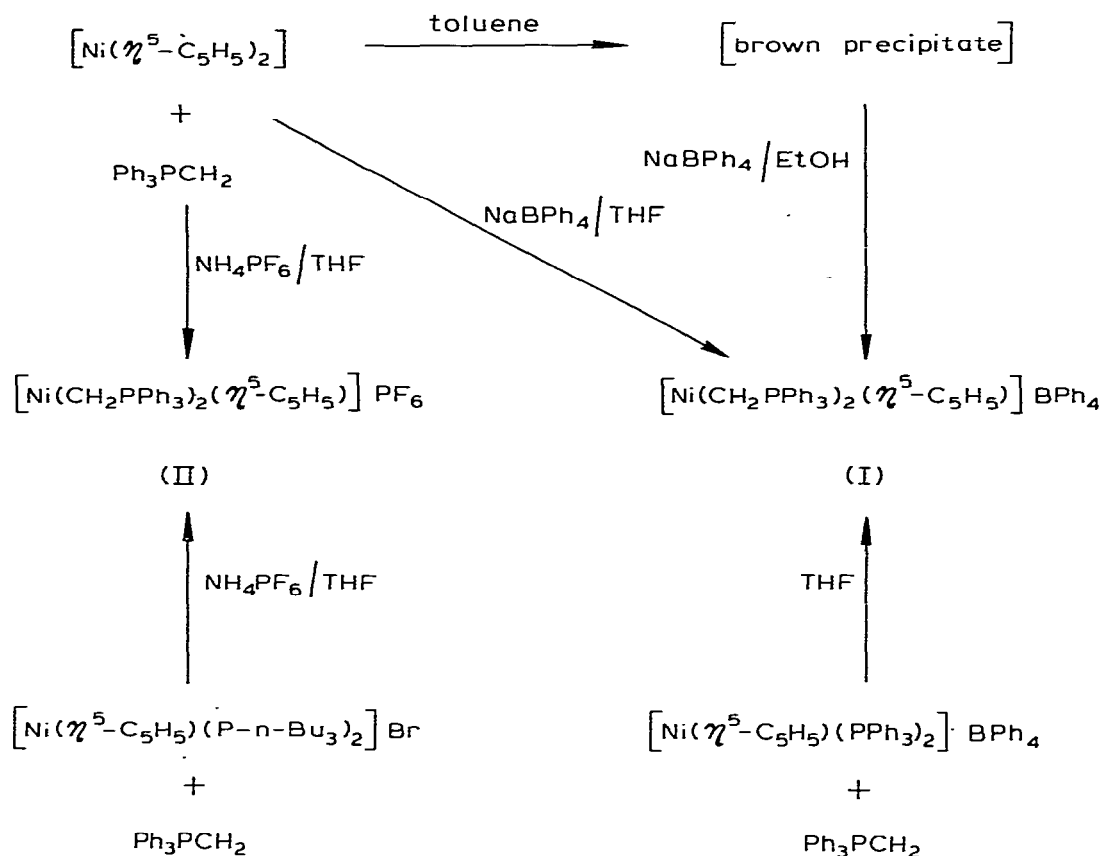
The interaction of ylides with transition metal complexes is a rapidly expanding field of study that is steadily gaining in popularity. With transition metal carbonyl compounds phosphonium ylides either attack the carbonyl ligand to give a Wittig-type reaction, or result in ligand displacement with the formation of a transition metal ylide complex [1–6]. Several transition metal ylide complexes containing resonance stabilised N, P, As and S keto-ylides have been reported [7–13], as have complexes of P, As and S cyclopentadienylylides [14–17]. However, non-stabilised ylides have received rather less attention, apart from reports of complexes of non-stabilised S ylides [18,19], the bulk of the work reported in this area has been carried out by Schmidbaur and his co-workers [20] mainly on Ni, Pd or Pt and the coinage metals.

A recent report [21] of the indirect synthesis of the nickel nitrogen ylide complex, $[\text{Ni}(\text{CH}_2\text{NMe}_3)(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)]\text{I}$, by reaction of $[\text{Ni}(\text{CH}_2\text{NMe}_2)(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)]$ with iodomethane, has prompted us to describe the facile preparation of similar nickel complexes by the direct reaction of methylenetriphenylphosphorane with either nickelocene, $[\text{Ni}(\eta^5\text{-C}_5\text{H}_5)\text{L}_2]\text{X}$ ($\text{L} = \text{phosphine}$) or $[\text{NiBr}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)]$.

Results and discussion

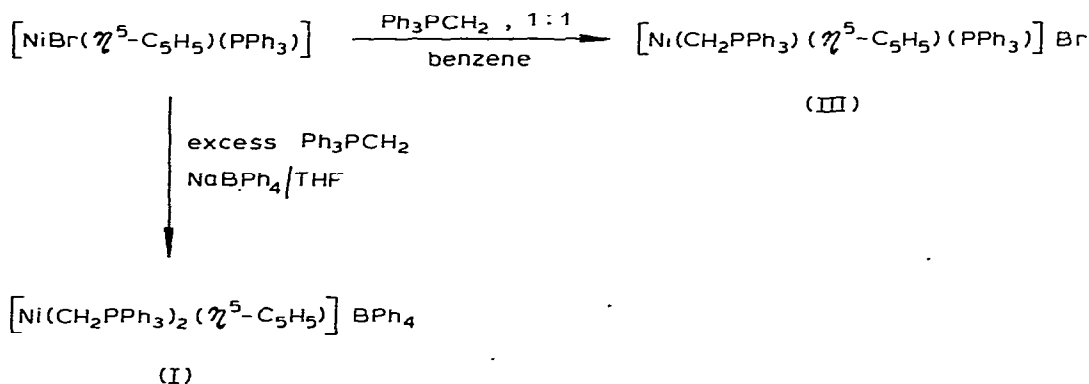
Reaction of a 2/1 excess of Ph_3PCH_2 with nickelocene in toluene solvent under mild conditions gave an air-sensitive brown precipitate, which on treatment with NaBPh_4 in ethanol gave air-stable dark brown needle crystals of stoichiometry $[\text{Ni}(\text{CH}_2\text{PPh}_3)_2(\eta^5\text{-C}_5\text{H}_5)]\text{BPh}_4$ (I). The same product was obtained either by direct reaction of the ylide with nickelocene in THF in the presence of NaBPh_4 or by reaction of the phosphine complex $[\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2]\text{BPh}_4$ with an excess of PPh_3CH_2 . The analogous PF_6^- salt (II) was obtained either from nickelocene or $[\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{P-n-Bu}_3)_2]\text{Br}$ by reaction of the ylide in the presence of NH_4PF_6^- (see Scheme 1).

SCHEME 1



The nature of the product from the reaction of Ph_3PCH_2 with the complex $[\text{NiBr}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)]$ depends upon the reaction conditions. In benzene solution with the reactants in a 1/1 molar ratio, nucleophilic displacement of bromide ion occurs to give the mono-ylide complex $[\text{Ni}(\text{CH}_2\text{PPh}_3)(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)]\text{Br}$ (III), characterised as its BPh_4^- and PF_6^- derivatives, IV and V, respectively. In THF solution with an excess of the ylide both Br^- and PPh_3 are displaced to give the bis-ylide complex I (see Scheme 2).

SCHEME 2



It has been reported previously that methylenetriphenylphosphorane causes displacement of phosphine and/or chloride ligand from $[\text{NiR}^1\text{R}^2(\text{PMe}_3)_2]$ ($\text{R}^1 = \text{R}^2 = \text{Cl}$; $\text{R}^1 = \text{Me}$, $\text{R}^2 = \text{Cl}$) or $[\text{NiMe}_2(\text{PMe}_3)_2]$ to give products in which the ylide ligand is coordinated to the nickel atom by a Ni-C σ -bond [22]. Alkylidenetriarylphosphoranes have similarly been found to yield the expected C-bonded ylide derivatives with tetracarbonylnickel [23]. However, it has been clearly demonstrated that in certain cases reaction of the methylenetriphenylphosphorane, Ph_3PCH_2 , results in a Steven's rearrangement to benzyldiphenylphosphine [23]. So, for example, reaction between Ph_3PCH_2 and $[\text{Ni}(\text{COD})_2]$ affords $[\text{Ni}(\text{PPh}_2\text{Bz})_4]$ and not the expected ylide complex. Furthermore, a number of nickel(0) complexes have been found to catalyse this rearrangement [23].

Confirmation that the cyclopentadienylnickel complexes prepared in this present work contain ylide rather than benzyldiphenylphosphine ligands comes from a comparison of their IR, ^1H and ^{31}P NMR spectra with those of authentic samples of the compounds $[\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_2\text{Bz})_2]\text{BPh}_4$ (VI) and $[\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{PPh}_2\text{Bz})]\text{BPh}_4$ (VII) synthesised as air-stable, green crystalline solids by reaction of either nickelocene or $[\text{NiBr}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)]$ respectively with benzyldiphenylphosphine and NaBPh_4 .

The ^1H NMR spectra of the ylide complexes II and V (Table 1) show a band in the region of τ 9.0 to 9.8 for the methylene protons of the ylide ligand and

TABLE 1
 ^1H NMR SPECTROSCOPIC DATA ^a

Compound	C_5H_5	CH_2	C_6H_5	BPh_4
$[\text{Ni}(\text{CH}_2\text{PPh}_3)_2(\eta^5\text{-C}_5\text{H}_5)]\text{PF}_6$ ^b (II)	5.53 (s)	9.75 (d) ^c	2.25 (m)	
$[\text{Ni}(\text{CH}_2\text{PPh}_3)(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)]\text{Br}$ (III)	5.04 (s)	—	2.50 (m)	
$[\text{Ni}(\text{CH}_2\text{PPh}_3)(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)]\text{PF}_6$ (V)	5.04 (s)	9.02 (dd) ^d	2.53 (m)	
$[\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_2\text{Bz})_2]\text{BPh}_4$ (VI)	4.36 (s)	6.54 (br)	2.70 (m)	3.16 (m)
$[\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_2\text{Bz})(\text{PPh}_3)]\text{BPh}_4$ (VII)	4.67 (s)	6.51 (br)	2.67 (m)	3.18 (m)

^a All spectra were recorded in acetone- d_6 and chemical shifts are reported as τ values (TMS internal reference except where stated); s singlet, d doublet, dd doublet of doublets, br broad, m multiplet. ^b Reference $p\text{-C}_6\text{H}_4\text{Cl}_2$ (τ 2.73). ^c $J(\text{P}-\text{CH}_2)$ 13.0 Hz. ^d $J(\text{P}-\text{CH}_2)$ 13.5 Hz; $J(\text{P}-\text{Ni}-\text{CH}_2)$ 7.0 Hz.

this is quite distinct from the chemical shift (τ 6.5 to 6.6) of the benzylic hydrogens of the coordinated PPh_2Bz ligand in compounds VI and VII. The resonance of the methylene hydrogens of the mono-ylide complex III was not observed due to the low solubility of this compound in $(\text{CD}_3)_2\text{CO}$. The chemical shift values for the ylide methylene protons in both II and V are to lower field than those in the free ylide (τ 9.87 in $\text{C}_6\text{D}_5\text{CD}_3$) [25]. Wilke et al. [23] reported a similar observation for the complex $[\text{Ni}(\text{CH}_2\text{PPh}_3)(\text{CO})_3]$ in which the methylene protons (τ 8.82; $J(\text{P}-\text{CH}_2)$ 12.5 Hz) are shifted downfield relative to the free ligand. This downfield shift has been attributed to the transfer of charge from the methylene group to the nickel atom presumably caused by the strong acceptor properties of the carbonyl ligands. The downfield shifts observed for II and V ($\Delta\tau$ 0.12 and 0.85 ppm, respectively) appear to be less than that observed for $[\text{Ni}(\text{CH}_2\text{PPh}_3)(\text{CO})_3]$ ($\Delta\tau$ 1.05 ppm) although an absolute comparison cannot be made since the spectrum of the latter was recorded in a different solvent, however, this is unlikely to affect the value of $\Delta\tau$ to any significant extent. It is not unreasonable, as suggested by the values of $\Delta\tau$, that transfer of charge from the methylene groups to the nickel atom will be diminished when it is coordinated to good electron donor ligands such as η^5 -cyclopentadienyl and triphenylphosphine ligands. This implies that despite the cationic nature of these η^5 -cyclopentadienylnickel-ylide complexes the ylide ligand should have more carbanion character than the corresponding ligand in $[\text{Ni}(\text{CH}_2\text{PPh}_3)(\text{CO})_3]$. It is interesting also that the sharp singlet observed for the cyclopentadienyl protons in the ylide complexes II, III and V occurs at relatively high field in comparison with the phosphine complexes of type $[\text{Ni}(\eta^5\text{-C}_5\text{H}_5)\text{L}_2]\text{X}$, which all have values in the range τ 4.18–4.95 [24]. This suggests [26] an increased electron density at the nickel atom of the ylide complexes when compared with the corresponding phosphine complexes.

A noteworthy feature of the ^1H NMR spectra of compounds VI and VII is that the benzylic protons of the phosphine ligands appear as a broad, unresolved multiplet rather than the expected doublet. This is probably attributable to strong virtual coupling between the phosphorus atoms which would give rise to a $\text{X}_2\text{AA}'\text{X}'_2$ pattern as previously noted [27] for the complex $[\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PMe}_2\text{Bz})_2]\text{BPh}_4$ in which the benzylic hydrogens appear as an apparent triplet.

The ^{31}P NMR spectra of compounds I, III, VI and VIII are given in Table 2. The bis-ylide complex I shows the expected single resonance for the equivalent P atoms. Coordination of the ylide ligand results in a considerable downfield shift when compared to the chemical shift of -20.30 ppm relative to external

TABLE 2
 ^{31}P NMR SPECTROSCOPIC DATA ^a

Compound	CH_2PPh_3	$\text{PPh}_2\text{CH}_2\text{Ph}$	PPh_3
I	-34.6		
III	-37.5		-40.9
VI		-32.0	
VII		-32.1	-36.6

^a All spectra were recorded in CH_2Cl_2 solution and chemical shifts are reported in ppm from external 85% aq. H_3PO_4 . $^1\text{H}-^{31}\text{P}$ coupling was eliminated by broadband ^1H noise decoupling.

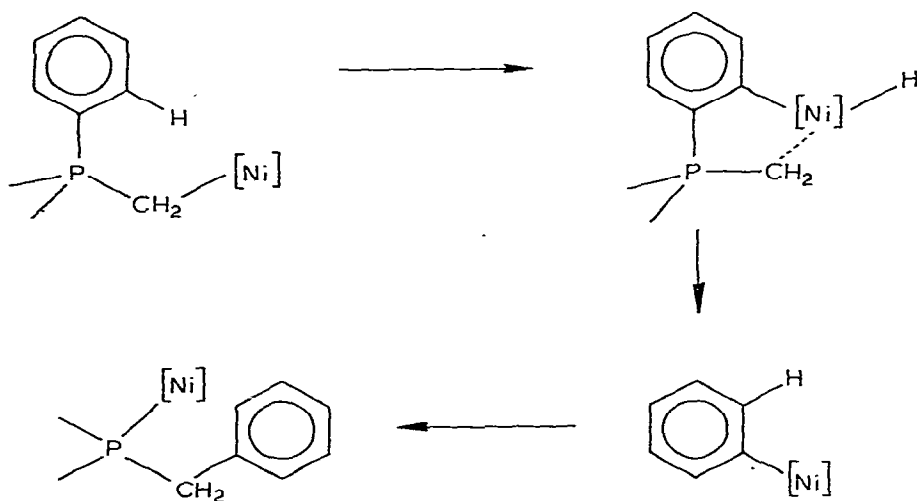
H_3PO_4 for the free ylide [28]. An even greater downfield shift is observed for the ylide P atom in the mono-ylide complex III. The chemical shift difference between an ylide and a phosphine P atom is not large and there is considerable overlap of the two chemical shift ranges.

The IR spectra of the ylide complexes I–V all show a strong absorption at ca. 1115 cm^{-1} , which is in the region of $1100\text{--}1125\text{ cm}^{-1}$ normally associated with phenylphosphonium salts [29]. In contrast, the phosphine complexes VI and VII show no band in this region.

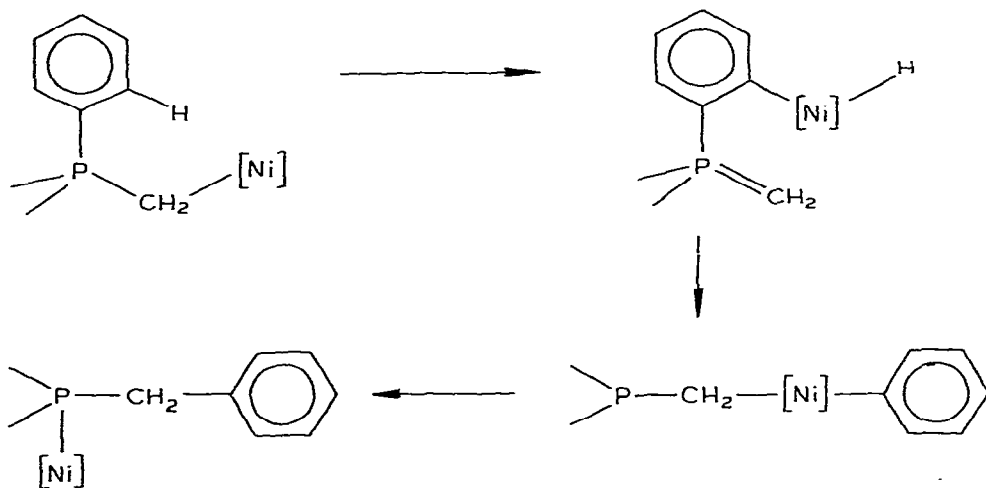
With the exception of $[\text{Ni}(\eta^3\text{-C}_3\text{H}_5)\text{Cl}]_2$, the compounds known to cause

SCHEME 3

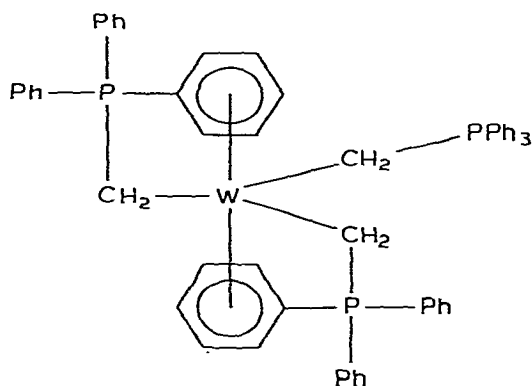
(a)



(b)



Stevens rearrangement of methylenetriphenylphosphorane are all nickel(0) complexes of the type $[\text{NiL}_n]$ ($\text{L} = \text{triaryl- or tricyclohexyl-phosphine or COD}$; $n = 2$ or 4) or $[\text{Ni}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2]$. Nickel(II) salts do not catalyse rearrangement and $[\text{Ni}(\text{CO})_4]$ affords the ylide complex $[\text{Ni}(\text{CH}_2\text{PPh}_3)(\text{CO})_3]$ [23]. Two mechanisms (see Scheme 3), both involving an initial *ortho*-metallation step, have been suggested for this rearrangement reaction [23,30], but both suffer from the disadvantage that it is necessary to postulate an unlikely carbon-phosphorus bond cleavage reaction in order to form the rearranged product. Also, these mechanisms do not explain why rearrangement is observed in some cases but not in others. In a recent paper [31] it is suggested that the absence of any Stevens rearrangement product during the synthesis of the compound $[\text{W}(\text{CH}_2\text{PPh}_3)_3]$ from Ph_3PCH_2 and tris(methyl vinylketone)tungsten may be explained by interaction of the benzene rings of the ylide ligand with the tungsten atom as in VIII.



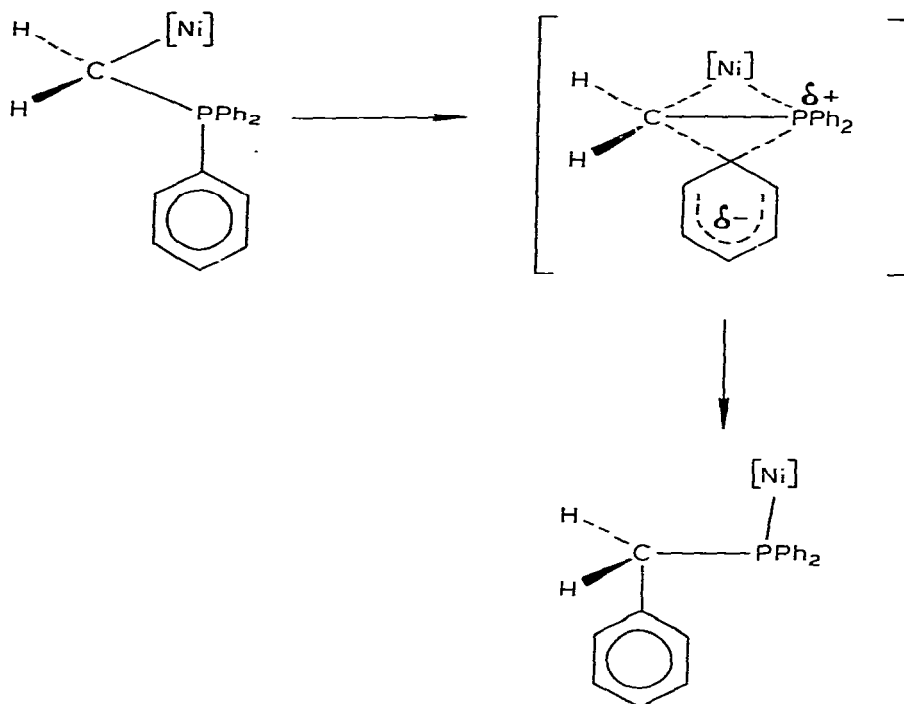
(VIII)

While this may be a valid explanation for the lack of rearrangement of the tungsten complex, the same argument cannot be applied to the cyclopentadienyl-nickel complexes described above.

It is apparent from ^1H NMR chemical shift data and the fact that several transition metal ylide complexes act as Wittig reagents to give olefins on reaction with ketones [32], that the carbon atom of a coordinated ylide ligand still retains some carbanion character. The nucleophilicity of this carbon atom will depend upon the oxidation state of the metal atom and upon the nature of the other ligands coordinated to the metal. Making the basic assumption that rearrangement only occurs after the ylide has become coordinated to the metal atom, the known data can be explained by the mechanism outlined in Scheme 4, in which internal nucleophilic attack of the ylide on the phenyl ring leads to the polar transition state shown. Only when the metal atom is in a low oxidation state and is coordinated to good donor ligands will the ylide carbon atom be sufficiently nucleophilic to undergo this $S_{\text{N}}\text{i}$ reaction. This would explain the lack of reactivity observed for the nickel(II) complexes prepared in this work and the nickel(0) complexes $[\text{Ni}(\text{R}^1\text{R}^2\text{PAr}_3)(\text{CO})_3]$ described by Wilke et al. [23].

We have also prepared a number of related cyclopentadienylnickel complexes which incorporate a variety of substituted ylides and bidentate ylides. The preparation and reactions of these compounds will be reported in due course.

SCHEME 4



Experimental

Unless otherwise stated all reactions were conducted at room temperature under an atmosphere of dry nitrogen. Benzene and toluene were 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 [33], $[\text{NiBr}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)]$ [34], $[\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2]\text{BPh}_4$ [35], $[\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{P-n-Bu}_3)_2]\text{Br}$ [36], methylenetriphenylphosphorane [37] and benzyldiphenylphosphine [38].

IR spectra were recorded as mulls on a Perkin-Elmer 621 spectrophotometer. ^1H NMR spectra were recorded on a Varian HA100 spectrometer operating at 100 MHz and ^{31}P NMR spectra were recorded on a JEOL FX60 spectrometer operating at 24.15 MHz.

Reaction between nickelocene and Ph_3PCH_2 in toluene

A solution of methylenetriphenylphosphorane (2.30 g, 8.32 mmol) in toluene (65 ml) was added dropwise, with stirring, to a solution of nickelocene (0.81 g, 4.29 mmol) in toluene (20 ml). Immediate precipitation occurred to give a dark brown, air-sensitive solid. The precipitate was taken up in ethanol (30 ml), filtered and treated with a solution of sodium tetraphenylboron (1.50 g, 4.37 mmol) in water (25 ml) to give a dark brown precipitate, which was recrystallised from an acetone/water mixture to give dark brown, air-stable needle crystals.

tals of I (1.77 g, 1.77 mmol, 41%), m.p. 163–165°C (dec.). Anal: Found: C, 80.8; H, 6.0; Ni, 5.7; P, 6.0. $C_{67}H_{59}BNiP_2$ calcd.: C, 81.1; H, 6.0; Ni, 5.9, P, 6.2%.

Reaction between nickelocene and Ph_3PCH_2 in THF

A solution of methylenetriphenylphosphorane (4.98 g, 18.02 mmol) in THF (40 ml) was added dropwise with stirring to a solution of nickelocene (1.38 g, 7.30 mmol) and sodium tetraphenylboron (2.10 g, 6.14 mmol) in THF (30 ml) at 0°C. The mixture was stirred for 0.5 h at 0°C and for a further 1 h at room temperature. Water (75 ml) was added to the dark brown solution to give an orange-brown precipitate, which was recrystallised from an acetone/water mixture to give dark brown needles of I (2.73 g, 2.73 mmol, 38%), m.p. 164–165°C (dec.). Anal.: Found: C, 80.4; H, 5.9; Ni, 5.7; P, 6.1. $C_{67}H_{59}BNiP_2$ calcd.: C, 81.1; H, 6.0; Ni, 5.9; P, 6.2%.

The IR spectrum was identical to that of the product of the reaction between nickelocene and Ph_3PCH_2 in toluene.

In a similar experiment using ammonium hexafluorophosphate in place of sodium tetraphenylboron the PF_6^- analogue was obtained as dark brown needles of II (1.08 g, 1.31 mmol, 18%), m.p. 186–188°C (dec.). Anal.: Found: C, 62.1; H, 4.7; F, 13.3; Ni, 6.6. $C_{43}H_{39}F_6NiP_3$ calcd.: C, 62.9; H, 4.8; F, 13.9; Ni, 7.1%.

Reaction between $[Ni(\eta^5-C_5H_5)(P-n-Bu_3)_2]Br$ and Ph_3PCH_2

A solution of $[Ni(\eta^5-C_5H_5)(P-n-Bu_3)_2]Br$ (1.30 g, 2.14 mmol) and methylenetriphenylphosphorane (1.20 g, 4.34 mmol) in THF (75 ml) was stirred for 16 h. Diethyl ether (75 ml) was added to give a brown precipitate, which was taken up in acetone (40 ml), filtered and treated with a solution of ammonium hexafluorophosphate (0.40 g, 2.45 mmol) in water (40 ml) to give an orange-brown precipitate, which was recrystallised from an acetone/water mixture to give dark brown needles of II (1.00 g, 1.22 mmol, 57%), m.p. 186–188°C (dec.). Anal.: Found: C, 62.4; H, 5.1; F, 13.1. $C_{43}H_{39}F_6NiP_3$ calcd.: C, 62.9; H, 4.8; F, 13.9%.

Reaction between $[Ni(\eta^5-C_5H_5)(PPh_3)_2]BPh_4$ and Ph_3PCH_2

A solution of $[Ni(\eta^5-C_5H_5)(PPh_3)_2]BPh_4$ (2.73 g, 2.82 mmol) in THF (50 ml) was added to a solution of methylenetriphenylphosphorane prepared in situ [39] from methyltriphenylphosphonium bromide (7.00 g, 19.59 mmol) and phenyllithium (19.36 mmol) in THF (40 ml). The dark brown solution was stirred for 1 h and diethyl ether (100 ml) was added to give an orange-brown precipitate, which was recrystallised from an acetone/water mixture to give dark brown needles of I (1.51 g, 1.52 mmol, 54%), m.p. 164–166°C (dec.). Anal.: Found: C, 80.5; H, 6.2; P, 6.1. $C_{67}H_{59}BNiP_2$ calcd.: C, 81.1; H, 6.0; P, 6.2%.

Reaction between $[NiBr(\eta^5-C_5H_5)(PPh_3)]$ and Ph_3PCH_2 in benzene

A solution of methylenetriphenylphosphorane (2.91 g, 10.53 mmol) in benzene (80 ml) was added dropwise, with stirring, to a solution of $[NiBr(\eta^5-C_5H_5)(PPh_3)]$ (4.43 g, 9.51 mmol) in benzene (60 ml). Immediate precipitation occurred to give a yellow-green solid, which was collected, washed with benzene and diethyl ether and dried in vacuo to give III (4.35 g, 5.86 mmol, 62%), m.p.

110–113°C (dec.). Anal.: Found: C, 67.9; H, 5.2; Br, 10.6; P, 7.9. $C_{42}H_{37}BrNiP_2$ calcd.: C, 68.0; H, 5.0; Br, 10.8; P, 8.3%.

A sample of the product was taken up in ethanol and treated with sodium tetraphenylboron to give the BPh_4^- salt (IV) as green crystals, m.p. 89–90°C (dec.). Anal.: Found: C, 79.9; H, 6.1; P, 6.1. $C_{66}H_{57}BNiP_2$ calcd.: C, 80.7; H, 5.8; P, 6.3%.

Similar treatment with ammonium hexafluorophosphate gave the PF_6^- derivative as dark green needles of V, m.p. 179–181°C (dec.). Anal.: Found: C, 62.2; H, 4.5; F, 13.8; P, 11.1. $C_{42}H_{37}F_6NiP_3$ calcd.: C, 62.5; H, 4.6; F, 14.1; P, 11.5%.

Reaction between $[NiBr(\eta^5-C_5H_5)(PPh_3)]$ and Ph_3PCH_2 in THF

A solution of $[NiBr(\eta^5-C_5H_5)(PPh_3)]$ (2.50 g, 5.36 mmol) in THF (30 ml) was added to a solution of methylenetriphenylphosphorane prepared in situ [39] from methyltriphenylphosphonium bromide (5.00 g, 14.00 mmol) and phenyllithium (13.92 mmol) in THF (40 ml). After stirring for 1 h the dark brown mixture was treated with diethyl ether (100 ml) to give a brown precipitate. The precipitate was taken up in ethanol (30 ml) and treated with a solution of sodium tetraphenylboron (1.90 g, 5.55 mmol) in water (30 ml) to give a dark brown precipitate, which was recrystallised from an acetone/water mixture to give dark brown needles of I (2.68 g, 2.69 mmol, 50%), m.p. 163–166°C (dec.). Anal.: Found: C, 80.4; H, 6.1; P, 6.2. $C_{67}H_{59}BNiP_2$ calcd.: C, 81.1; H, 6.0; P, 6.2%.

Preparation of $[Ni(\eta^5-C_5H_5)(PPh_2Bz)_2]BPh_4$

The method described by Bennett, Bruce and Stone for the synthesis of $[Ni(\eta^5-C_5H_5)(PMe_2Bz)_2]BPh_4$ [27] was adopted for the preparation of this complex.

A solution of nickelocene (0.85 g, 4.50 mmol) and benzyldiphenylphosphine (1.20 g, 4.34 mmol) in chloroform (45 ml) was refluxed for 2 h. The dark red oil remaining after removal of solvent (in vacuo) was taken up in ethanol (50 ml), filtered and treated with a solution of sodium tetraphenylboron (1.50 g, 4.38 mmol) in ethanol (40 ml). The mixture was stirred for 0.5 h to give green-yellow crystals of VI (0.96 g, 0.96 mmol, 21%), m.p. 140–142°C (dec.). Anal.: Found: C, 81.1; H, 6.0; P, 6.1. $C_{67}H_{59}BNiP_2$ calcd.: C, 81.1; H, 6.0; P, 6.2%.

Preparation of $[Ni(\eta^5-C_5H_5)(PPh_2Bz)(PPh_3)]BPh_4$

A similar method to the one used by Treichel and Shubkin for the preparation of $[Ni(\eta^5-C_5H_5)(PPh_3)_2]BPh_4$ [35] was employed to prepare this complex.

A solution of sodium tetraphenylboron (1.50 g, 4.38 mmol) in ethanol (50 ml) was added dropwise, with stirring, to a solution of $[NiBr(\eta^5-C_5H_5)(PPh_3)]$ (2.00 g, 4.29 mmol) and benzyldiphenylphosphine (1.20 g, 4.34 mmol) in benzene (50 ml) to give a green precipitate, which was collected, washed with ethanol and diethyl ether and dried in vacuo to yield VII (3.13 g, 3.19 mmol, 74%), m.p. 129–131°C (dec.). Anal.: Found: C, 80.1; H, 6.0; P, 6.1. $C_{66}H_{57}BNiP_2$ calcd.: C, 80.7; H, 5.9; P, 6.3%.

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