Binuclear σ- and η^3-Benzylic Derivatives of Nickel†

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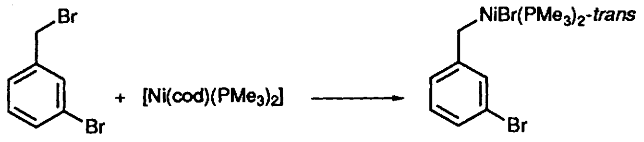
The stepwise reaction of the dibromides *m*- and *p*-$BrCH_2C_6H_4Br$ with $[Ni(cod)(PMe_3)_2]$ (cod = cycloocta-1,5-diene) affords the σ-benzylic derivatives *trans*-$[Ni(CH_2C_6H_4Br)Br(PMe_3)_2]$ **1a** (*meta*) or **1b** (*para*) and the binuclear species *trans,trans*-$[(Me_3P)_2BrNi(\mu\text{-}\sigma{:}\sigma\text{-}CH_2C_6H_4)NiBr(PMe_3)_2]$ **2a** (*meta*) or **2b** (*para*). If the second oxidative addition is carried out using equimolar amounts of $[Ni(cod)_2]$ and PMe_3 the pseudo-allyl complexes *trans*-$[(Me_3P)BrNi(\mu\text{-}\eta^3{:}\sigma\text{-}CH_2C_6H_4)NiBr(PMe_3)_2]$ **5a** (*meta*) or **5b** (*para*) are obtained instead. Carbonylation of the binuclear compounds **2** yields the stable bis(acyl) derivatives *trans,trans*-$[(Me_3P)_2BrNi(\mu\text{-}COCH_2C_6H_4CO)NiBr(PMe_3)_2]$ **3a** (*meta*) or **3b** (*para*) while excess of PMe_3 induces a reductive elimination process that furnishes the bis(aryl) species *trans,trans*-$[(Me_3P)_2BrNi(\mu\text{-}C_6H_4CH_2CH_2C_6H_4)NiBr(PMe_3)_2]$ **4a** (*meta*) or **4b** (*para*). A crystal structure determination of complex **2b** has been undertaken: monoclinic, space group $P2_1/c$, with cell dimensions $a = 11.241(1)$, $b = 8.866(2)$, $c = 29.323(8)$ Å, $\beta = 90.22(1)°$ and $Z = 4$. The geometry around both nickel atoms is distorted square planar, with a dihedral angle between the two co-ordination planes of 103.77(9)°.

Bimetallic transition-metal complexes in which the two metal centres are bridged by hydrocarbon ligands have become prominent in the last decade.[1] These complexes may display unusual chemistry and reactivity by means of the co-operative effects between the two potentially reactive metal units. Additional interest arises, not only because of the often peculiar structural and bonding characteristics, but also due to the information their study may provide on important topics such as organometallic mechanisms, fluxionality of ligand exchange and catalysis.[1] The possibility of these complexes being used as models for hydrocarbon groups bonded to metal surfaces is actively being explored and it is hoped that a smooth transition from the chemistry of mononuclear compounds to that of metal surfaces, through bi- and poly-nuclear clusters,[2] can be found.

Recent work from our laboratory has dealt with the formation of binuclear complexes of nickel in which the two metal centres are firmly held together in close contact by the *o*-$CH_2C_6H_4$ bridging ligand.[3] As a natural extension of this work we have now investigated the chemistry of the closely related *m*- and *p*-$CH_2C_6H_4$ biradicals. In this contribution we present the results of this study, which include an X-ray crystal structure determination of the compound *trans,trans*-$[(Me_3P)_2BrNi(\mu\text{-}\sigma{:}\sigma\text{-}p\text{-}CH_2C_6H_4)NiBr(PMe_3)_2]$ **2b**. The formation of some of these complexes has been briefly mentioned in a preliminary communication.[4]

Results and Discussion

Mononuclear Complexes trans-$[Ni(\sigma\text{-}CH_2C_6H_4Br)Br(PMe_3)_2]$ **1a** *and* **1b**.—Alkyl and aryl complexes of Ni^{II} containing phosphine ligands can be conveniently prepared by the oxidative addition of the corresponding organic halides to suitable nickel(0) complexes.[5] For PMe_3-containing organometallics several nickel compounds, including $[Ni(PMe_3)_4]$[6] and $[Ni(cod)_2]$ (cod = cycloocta-1,5-diene)[7] can be used as precursors. However, for the large majority of the preparations reported herein, which involve oxidative addition of the *m*- and *p*-bromobenzyl bromides, $BrCH_2C_6H_4Br$, a more convenient route is the use of freshly prepared solutions of $[Ni(cod)(PMe_3)_2]$, made *in situ* by the room-temperature reaction of $[Ni(cod)_2]$ with 2 equivalents of PMe_3. The use of this starting material avoids, to a large extent, uncontrolled bromination of the nickel(0) precursor to give blue $[NiBr_2(PMe_3)_3]$.



1a

Scheme 1

Upon addition of equimolar amounts of *m*- or *p*-$BrCH_2C_6H_4Br$ to $[Ni(cod)(PMe_3)_2]$ a smooth oxidative-addition reaction, involving the more labile benzylic C–Br bond, takes place with formation of complexes **1** (*m*-Br **1a**, *p*-Br **1b**) as depicted in Scheme 1. Compounds **1** are highly crystalline, air-sensitive materials, moderately soluble in common organic solvents. The NMR studies are in agreement with the proposed formulation and indicate in addition fluxional behaviour in solution. This is clearly evidenced by $^{13}C\text{-}\{^1H\}$ NMR spectroscopy which shows the methylene carbon resonance as a broad singlet at δ 10–15 (see Experimental section). The relatively high-field shift of this signal indicates the CH_2 is bonded to nickel. In addition the PMe_3 ligands give rise to broad ^1H and $^{13}C\text{-}\{^1H\}$ singlets, although at low temperatures (−70 °C) these are converted into virtually coupled triplets, in accord with the proposed *trans* stereochemistry.[8] As no coupling between the CH_2 nuclei and the phosphine ligands is observed in the fast-exchange regime, the fluxional process must be intermolecular in nature. By similarity with other benzylic complexes of nickel containing PMe_3 as co-ligand, it is likely that the fluxionality is

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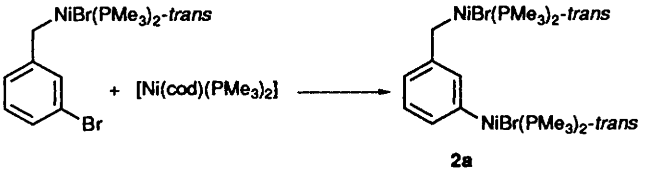
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

Non-SI unit employed: atm = 101 325 Pa.

Table 1 Bond distances (Å) and angles (°) for compound **2b**

Ni(1)–Br(1)	2.361(3)	Ni(2)–C(1)	1.951(12)	P(2)–C(23)	1.789(14)	C(1)–C(2)	1.484(16)
Ni(1)–P(1)	2.183(4)	Ni(2)–C(2)	2.590(11)	P(3)–C(31)	1.816(14)	C(2)–C(3)	1.396(17)
Ni(1)–P(2)	2.202(4)	P(1)–C(11)	1.731(19)	P(3)–C(32)	1.811(13)	C(2)–C(7)	1.396(16)
Ni(1)–C(5)	1.881(12)	P(1)–C(12)	1.715(19)	P(3)–C(33)	1.832(13)	C(3)–C(4)	1.401(18)
Ni(2)–Br(2)	2.407(2)	P(1)–C(13)	1.754(20)	P(4)–C(41)	1.840(13)	C(4)–C(5)	1.390(16)
Ni(2)–P(3)	2.202(4)	P(2)–C(11)	1.799(15)	P(4)–C(42)	1.835(14)	C(5)–C(6)	1.407(17)
Ni(2)–P(4)	2.218(4)	P(2)–C(22)	1.768(15)	P(4)–C(43)	1.813(16)	C(6)–C(7)	1.397(17)
P(2)–Ni(1)–C(5)	86.3(4)	Ni(1)–P(1)–C(13)	115.5(7)	C(41)–P(4)–C(42)	100.8(7)	C(21)–P(2)–C(23)	104.5(7)
P(1)–Ni(1)–C(5)	89.0(4)	Ni(1)–P(1)–C(12)	112.5(7)	Ni(2)–C(1)–C(2)	96.9(8)	C(21)–P(2)–C(22)	102.3(8)
P(1)–Ni(1)–P(2)	175.2(2)	Ni(2)–P(3)–C(32)	116.9(5)	C(1)–C(2)–C(7)	121.2(10)	Ni(2)–P(3)–C(33)	110.9(5)
Br(1)–Ni(1)–C(5)	169.8(4)	Ni(2)–P(3)–C(31)	122.0(5)	C(1)–C(2)–C(3)	122.4(10)	C(3)–C(2)–C(7)	116.4(10)
Br(1)–Ni(1)–P(2)	92.3(1)	C(32)–P(3)–C(33)	101.9(6)	Ni(1)–P(1)–C(11)	119.5(7)	C(2)–C(3)–C(4)	122.2(10)
Br(1)–Ni(1)–P(1)	92.4(1)	C(31)–P(3)–C(33)	101.2(7)	C(12)–P(1)–C(13)	101.3(9)	C(3)–C(4)–C(5)	120.8(11)
P(4)–Ni(2)–C(1)	94.5(4)	C(31)–P(3)–C(32)	101.2(6)	C(11)–P(1)–C(13)	97.3(9)	Ni(1)–C(5)–C(4)	117.2(9)
P(3)–Ni(2)–C(1)	93.9(4)	Ni(2)–P(4)–C(43)	114.4(5)	C(11)–P(1)–C(12)	108.5(9)	C(4)–C(5)–C(6)	117.5(11)
P(3)–Ni(2)–P(4)	159.2(2)	Ni(2)–P(4)–C(42)	110.8(5)	Ni(1)–P(2)–C(23)	117.1(5)	Ni(1)–C(5)–C(6)	125.3(9)
Br(2)–Ni(2)–C(1)	163.6(4)	Ni(2)–P(4)–C(41)	123.9(5)	Ni(1)–P(2)–C(22)	120.6(6)	C(5)–C(6)–C(7)	120.8(10)
Br(2)–Ni(2)–P(4)	88.5(1)	C(42)–P(4)–C(43)	103.8(7)	Ni(1)–P(2)–C(21)	109.5(5)	C(2)–C(7)–C(6)	122.0(11)
Br(2)–Ni(2)–P(3)	88.8(1)	C(41)–P(4)–C(43)	100.8(7)	C(22)–P(2)–C(23)	100.8(7)		



2a

Scheme 2

due to phosphine dissociation and reassociation through the intermediacy of the corresponding η^3-pseudo-allylic species.[9]

Binuclear, Monohapto Benzylic Complexes, trans,trans-[(Me$_3$P)$_2$BrNi)(μ-σ:σ-CH$_2$C$_6$H$_4$)NiBr(PMe$_3$)$_2$] **2a** (meta) *and* **2b** (para).—Compounds **1** contain a C–Br bond susceptible to further oxidative addition. Indeed, treatment of complexes **1** with another equivalent of [Ni(cod)(PMe$_3$)$_2$] affords the binuclear species **2a** and **2b** (Scheme 2). Not unexpectedly, these compounds can be obtained by direct reaction of [Ni(cod)-(PMe$_3$)$_2$] and the dibromides (2:1 molar ratio) without isolation of the mononuclear intermediates.

In solution compounds **2** are also fluxional and as a result of an intermolecular phosphine-exchange process the room-temperature ^{31}P-{^{1}H} NMR spectrum consists of a broad signal which in the case of **2b** splits, upon cooling at -70 °C, into the two singlets expected for the proposed *trans* stereochemistry, with the assumption of rapid rotation around the Ni–CH$_2$ bond. On the other hand, the gated ^{13}C NMR spectrum of complex **2a** recorded at room temperature reveals the methylene carbon at δ 23.2 as a triplet with ^1J(CH) 142 Hz. Large values of ^1J(CH) (>130 Hz) for the CH$_2$ group have been found in distorted benzyl structures resulting from interactions of the π system of the phenyl ring with the metal[10] but the situation is not clear-cut and in fact there are well authenticated nickel[3] and cobalt[11] σ-benzylic derivatives for which ^1J(CH) values of *ca.* 135 Hz have been found. For complex **2a**, however, the observed value is somewhat higher than expected and this, coupled with the fact that one of the aromatic carbons resonates at the high-field value of δ 110.5, seems to indicate that a rapid equilibrium with important amounts of the pseudo-allylic derivative **5a** (see below) is established under these conditions. A similar process may be responsible for the fluxionality of **2b** but in this case the equilibrium seems to be much more displaced toward the σ-benzylic side.

The *para* binuclear derivative **2b** has been additionally characterized by X-ray crystallography. Fig. 1 shows a perspective view of the molecules of this complex, including the atom numbering scheme. Table 1 contains bond distances and angles. As can be seen the co-ordination geometry around each nickel centre is distorted square planar, with the co-ordination plane around Ni(2), *i.e.* that comprising the benzylic moiety, showing the largest deviation from planarity. For this entity, the average deviation with respect to the least-squares plane is 0.30 Å with the benzylic carbon C(1) showing the largest deviation (0.75 Å). Conversely, the nickel–arylic unit exhibits almost regular square-planar geometry, the average deviation from the mean co-ordination plane being 0.065 Å, and the largest, due to the arylic carbon C(5), being only 0.29 Å.

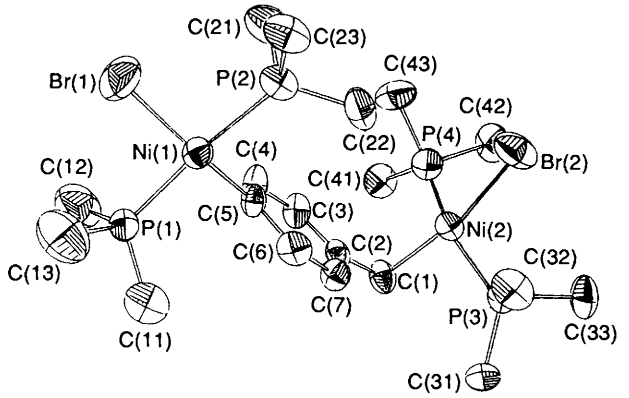
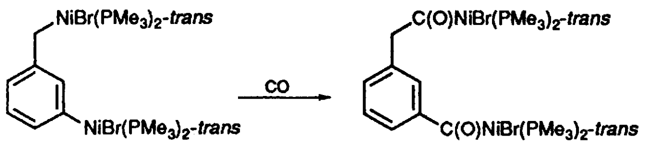


Fig. 1 Molecular structure of compound **2b**

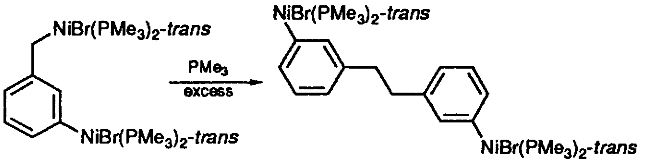
As expected the aromatic ring is perpendicularly oriented with respect to the co-ordination plane around Ni(1), and the Ni(1)–C(5) distance of 1.881(12) Å compares well with literature values for other aryl complexes of nickel.[12] As shown in Fig. 1 the benzylic part of the hydrocarbon ligand is bonded to Ni(2) only through the methylene carbon atom, no interaction with the *ipso*- or *ortho*-carbons being observed. The Ni(2)–C(1) separation of 1.951(12) Å is also normal, and similar to corresponding distances in other monohapto nickel-benzylic complexes, *e.g.* 1.95(1) Å (average) in [Ni$_3$(σ-CH$_2$C$_6$H$_4$Me-*o*)$_4$-(PMe$_3$)$_2$(μ_3-OH)$_2$][7] and 1.946(7) Å in [{Ni(σ-CH$_2$C$_6$H$_4$-Me-*o*)(PMe$_3$)(μ-OH)}$_2$]·2.5L (L = 2,5-dimethylpyrrole).[13] Finally it is worth mentioning that in order to minimize the steric pressure of the ligands in the co-ordination spheres of Ni(1) and Ni(2) both co-ordination planes are almost perpendicular [dihedral angle 103.77(9)°].

Compounds **2a** and **2b** react readily with CO (20 °C, 1 atm), with formation of the corresponding bis(acyl) derivatives, **3a** and **3b** (Scheme 3). Both are orange air-sensitive crystalline



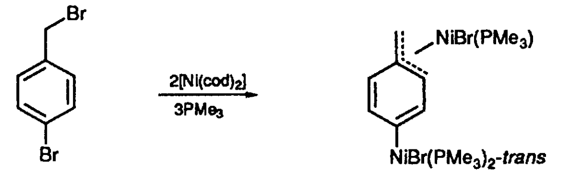
2a **3a**

Scheme 3



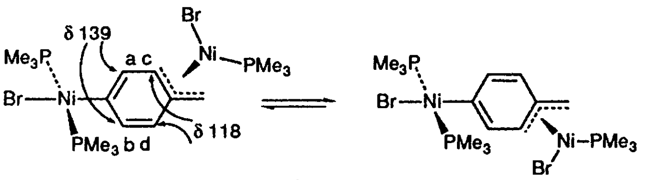
2a **4a**

Scheme 4



5b

Scheme 5



A

Scheme 6

solids with good solubility properties in common organic solvents. The acyl functionalities in these complexes are characterized by IR absorptions in the range 1640–1570 cm^{-1}, *i.e.* characteristic of σ co-ordination, and by two ^{13}C NMR resonances in the vicinity of δ 250 (see Experimental section). Interestingly both compounds are fluxional in solution but, rather intriguingly, the intermolecular phosphine-exchange process responsible for the observed changes in the NMR spectra with temperature affects only the benzoylic moiety. In the room-temperature ^{13}C-{^{1}H} NMR spectrum of **3a** and **3b** a broad singlet is observed for the carbonyl group adjacent to the benzylic carbon while the aroyl functionality Ni–C(O) gives rise to a triplet at δ *ca.* 252 [^2J(CP) $\approx$ 25 Hz]. As *trans*-[Ni(COCH$_2$R)Cl(PMe$_3$)$_2$][7] and *trans*-[Ni(COR)Cl(PMe$_3$)$_2$][9] (R = aryl) are respectively fluxional and non-fluxional species under the same experimental conditions, it is clear that the acyl functionalities in compounds **3a** and **3b** behave as if they were completely independent.

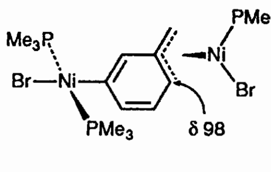
As found for the related *ortho* derivative,[3] the use of a slight excess of PMe$_3$ in the reactions leading to the binuclear complexes **2a** and **2b** induces formation of small amounts of the binuclear arylic derivatives *trans,trans*-[(Me$_3$P)$_2$BrNi(μ-σ:σ-C$_6$H$_4$CH$_2$CH$_2$C$_6$H$_4$)NiBr(PMe$_3$)$_2$] **4a** (*meta*) and **4b** (*para*). These compounds are best obtained by treatment of **2** with an excess of PMe$_3$ (Scheme 4). This is an interesting reaction which may prove synthetically useful for the preparation of aryl complexes of Ni that cannot be obtained by more direct pathways. Both the nature of the resulting products and a possible route explaining their formation have already been advanced[3,7] and will not be further discussed.

Binuclear η^3:σ-*Benzylic Complexes, trans*-[(Me$_3$P)BrNi(μ-η^3:σ-CH$_2$C$_6$H$_4$)NiBr(PMe$_3$)$_2$] **5a** (meta) *and* **5b** (para).—If the reaction of *m*- and *p*-bromobenzyl bromides with [Ni(cod)$_2$] is carried out in the presence of 3 molar equivalents of PMe$_3$ the new compounds **5a** and **5b** containing an arylic and a pseudo-allylic functionality are obtained (Scheme 5). For the *para* derivative **5b** there is only one possible ground-state structure and this has been represented by **A** in Scheme 6. The pseudo-allylic unit is characterized by (*i*) a methylenic carbon resonance at δ 23.4, exhibiting a small cisoid coupling to the ^{31}P nucleus [^2J(CP) 8 Hz], (*ii*) a large ^1J(CH) coupling constant of 152 Hz for this group in accord with the sp^2 hybridization of the methylene carbon and (*iii*) a unique resonance for the aromatic carbons c and d, at δ *ca.* 118 (see below).

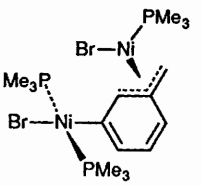
An interesting structural feature of this compound is the positioning of the NiBr(PMe$_3$) unit of the pseudo-allylic functionality on one of the faces of the aromatic ring. This clearly introduces asymmetry in the molecule and results in the observation at low temperatures (−70 °C) of separate ^{31}P NMR resonances for the two mutually *trans*-PMe$_3$ groups of the arylic unit. In accord with this distribution, these ^{31}P nuclei are strongly coupled [^2J(PP) 322 Hz], and curiously exhibit long-range coupling (six bonds) with the PMe$_3$ group of the pseudo-allylic entity [^6J(PP) 8 Hz, average]. This indicates a very effective coupling transmission through the π system of the *para*-substituted aromatic ring. The ^{13}C-{^{1}H} NMR spectrum of compound **5b** in the aromatic region is simpler than expected and displays, even at low temperatures, only two signals for the four aromatic methinic carbons. As for other related complexes[9,14] this is indicative of a fast suprafacial shift of the NiBr(PMe$_3$) group which interchanges the two degenerate ground-state structures shown in Scheme 6. In addition to the above fluxionality,^{31}P NMR studies reveal that at temperatures near ambient the two *trans*-phosphine ligands become equivalent on the NMR time-scale. This exchange takes place without loss of the long-range ^6J(PP) coupling and must therefore be intramolecular. A possible mechanism that fulfils this condition is rotation around the Ni–C(aryl) bond while an antarafacial shift of the NiBr(PMe$_3$) unit through the intermediacy of a σ-benzyl species, formed by traces of PMe$_3$, can be ruled out since it would imply cancellation of ^6J(PP) and also of ^2J(CP) between the benzyl carbon and the unique ^{31}P nucleus.

A somewhat more complicated structural problem arises for the *meta* derivative **5a** for which, at variance with the situation found for **5b**, two isomeric structures are in principle possible (**B** and **C**). The NMR data for compound **5a** indicate the existence of only one species which has a rigid structure at room temperature. Structure **B** should be preferred on steric grounds and although a definite distinction between the two isomeric formulations is not possible on the basis of the available data the following qualitative arguments seem to favour the above proposal.

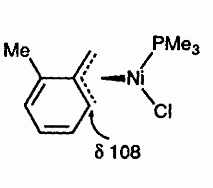
The ^{13}C-{^{1}H} spectrum of compound **5a** shows an aromatic resonance at the distinctively high-field value of δ 98 [doublet, ^2J(CP) 11 Hz], clearly corresponding to the CH carbon of the aromatic ring involved in the pseudo-allylic interaction. For the related complexes **D** and **E** the analogous resonance appears at δ 108 (complex **D**; in ref. 7 this resonance was typographically mistakenly given as δ 128) and 117 (**E**, ref. 9). Since for the latter compound the observed value is the average of the pseudo-allylic aromatic resonance and a normal aromatic resonance, it can be concluded that a chemical shift of *ca.* δ 110 is a reasonable value for the aromatic pseudo-allylic CH carbon, in the absence of suprafacial shift. The formal incorporation of an electron-rich NiBr(PMe$_3$)$_2$ fragment at the 3-position of the aromatic ring in structure **E** should induce a small shift to lower field at the adjacent carbons[15] (namely 2 and 4) and a paramagnetic (that is, high-field shift) at the most remote carbon[15] (2′, *i.e.* the pseudo-allylic aromatic carbon). These expectations are indeed fulfilled in the model compound *trans*-[NiPh(Br)(PMe$_3$)$_2$][9] and operate both in favour of structure **B** and against **C**.



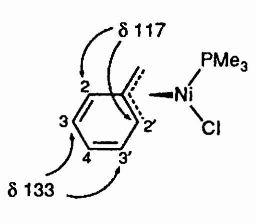
B



C



D



E

Irrespective of the true identity of the species existing in solutions of compound **5a**, it is evident that **5a** and **5b** are less prone than related mononuclear η^3-pseudo-allyls to undergo exchange between the η^3 and the σ forms. This is possibly a consequence of the electron-rich nature of the arylic NiBr$(PMe_3)_2$ substituent which results in a decreased electrophilicity of the pseudo-allylic moiety and hence in a reduced tendency to form reversibly, on the NMR time-scale, a σ-benzylic species by incorporation of a second molecule of the strongly basic PMe_3.

Experimental

Microanalyses were by Pascher Microanalytical Laboratory, Remagen, Germany and the Microanalytical Service of the University of Sevilla. Perkin-Elmer model 577 and 684 spectrometers were used for IR spectra and a Varian XL-200 instrument for NMR studies. The ^{13}C NMR resonance of the solvent was used as internal standard, but chemical shifts are reported with respect to $SiMe_4$. The ^{31}P NMR shifts are relative to external 85% H_3PO_4. All preparations and other operations were carried out under oxygen-free nitrogen, by conventional Schlenk techniques. Solvents were dried and degassed before use. The compounds $[Ni(cod)_2]$ [16] and PMe_3 [17] were prepared by published methods.

trans-$[Ni(CH_2C_6H_4Br$-*m*$)Br(PMe_3)_2]$ **1a**.—To a stirred suspension of $[Ni(cod)_2]$ (0.55 g, 2 mmol) in diethyl ether (70 cm^3) was added trimethylphosphine (0.4 cm^3, 4 mmol). After 2–3 h of stirring at room temperature the resulting yellow solution was cooled at -80 °C and a toluene solution of $BrCH_2C_6H_4Br$-*m* (2.0 cm^3, *ca.* 1 mol dm^{-3}) was introduced dropwise into the reaction flask by means of a syringe. The cooling bath was removed and after warming at room temperature the reaction mixture was filtered, the filtrate concentrated under vacuum and cooled at -30 °C. Complex **1a** was isolated as a brown crystalline material in 70% yield (Found: C, 33.2; H, 5.4. $C_{13}H_{24}Br_2NiP_2$ requires C, 33.9; H, 5.2%). NMR (CD_2Cl_2): ^1H, δ 1.34 (br s, 18 H, 2 PMe_3), 1.83 (br s, 2 H, CH_2) and 7.13–7.39 (m, 4 H, aromatics); ^{31}P-$\{^1H\}$, δ -12.7 (br s); ^{13}C-$\{^1H\}$, δ 14.7 (br s, PMe_3), 15.8 (br s, CH_2), 124.5, 127.1, 128.7 and 129.9 (s, aromatic CH). Quaternary carbons were not located.

Following an essentially identical procedure, complex **1b** was obtained as dark red needles in 60% yield (Found: C, 33.8; H, 5.1%). NMR: ^1H (CD_2Cl_2), δ 1.32 (br s, 18 H, 2 PMe_3), 1.86 (br s, 2 H, CH_2), 7.04 and 7.31 [d and d, 2 H and 2 H, $^3J(HH)$ 8.4 Hz, aromatics]; ^{31}P-$\{^1H\}$ (CD_2Cl_2), δ -14.6 (br s); ^{13}C-$\{^1H\}$ (C_6D_6), δ 10.3 (br s, CH_2), 13.4 (br s, PMe_3), 129.7 and 130.5 (s, 1 : 1 ratio, aromatic CH).

trans,trans-$[(Me_3P)_2BrNi(\mu$-$\sigma:\sigma$-*m*-$CH_2C_6H_4)NiBr(PMe_3)_2]$ **2a**.—A tetrahydrofuran (thf) solution of $[Ni(cod)(PMe_3)_2]$ was prepared as above from $[Ni(cod)_2]$ (0.30 g, 1.1 mmol) and trimethylphosphine (2.2 cm^3, *ca.* 1 mol dm^{-3} solution in diethyl ether). After cooling at -80 °C this was added to a cooled, stirred solution of complex **1a** (0.51 g, 1.1 mmol) in thf. After warming at room temperature the resulting red mixture was stirred for 2 h, the solvent evaporated and the residue extracted with Et_2O. Filtration, concentration and cooling at -30 °C furnished the desired complex **2a** as red crystals in 65% yield (Found: C, 34.1; H, 6.4. $C_{19}H_{42}Br_2Ni_2P_4$ requires C, 34.0; H, 6.3%). NMR: ^1H (CD_3COCD_3), δ 1.31 (br s, 36 H, 4 PMe_3), 1.67 (br s, 2 H, CH_2) and 6.31–7.33 (m, 4 H, aromatics); ^{31}P-$\{^1H\}$ (CD_3COCD_3), δ -11.8 (br s); ^{13}C-$\{^1H\}$ (CD_2Cl_2), δ 15.0 (br s, PMe_3), 23.2 [s, $^1J(CH)$ 142 Hz, CH_2], 110.5, 129.0, 134.2, 135.0 [s (the first being somewhat broad), aromatic CH], 129.5 and 159.5 (s, quaternary aromatics).

Complex **2b** is a dark red crystalline solid that can be obtained by the same method in 75% yield. In addition, it was prepared from $[Ni(cod)_2]$ and $BrCH_2C_6H_4Br$-*p*, in a one-pot reaction, without isolating the intermediate species **1b**. Yield 60% (Found: C, 33.5; H, 6.0%). NMR: ^1H (CD_3COCD_3), δ 1.24 (br s, 36 H, 4 PMe_3), 1.59 (br s, 2 H, CH_2), 6.87 and 7.24 [d and d, 2 H and 2 H, $^3J(HH)$ 7.6, aromatics]; $(CD_2Cl_2$, -70 °C), δ 1.07 [pseudo-triplet, 18 H, $J(HP)_{ap}$ 3.8, 2 PMe_3], 1.32 [pseudo-triplet, 18 H, $J(HP)_{ap}$ 3.4, 2 PMe_3] and 1.61 [t, 2 H, $^3J(HP)$ 13.0 Hz, CH_2]; ^{31}P-$\{^1H\}$ $(CD_3COCD_3$, -70 °C), δ -13.0 (s, 2 PMe_3) and -9.9 (s, 2 PMe_3); ^{13}C-$\{^1H\}$ (thf–C_6D_6), δ 14.1 (br s, PMe_3), 14.8 (br s, CH_2), 126.9 and 136.0 (s, 1 : 1 ratio, aromatic CH). Quaternary carbons were not located.

trans,trans-$[(Me_3P)_2BrNi(\mu$-*m*-$COCH_2C_6H_4CO)NiBr(PMe_3)_2]$ **3a**.—Complex **5a** (0.60 g, 1 mmol) was dissolved in thf (50 cm^3) and, with stirring, 1 equivalent of PMe_3 (1 cm^3 of a 1 mol dm^{-3} solution in Et_2O) was added. The resulting mixture was cooled at -60 °C and CO was bubbled through it for a few minutes. The cooling bath was removed and the orange solution taken to dryness. The residue was treated with Et_2O and the resulting yellow microcrystalline precipitate filtered off and dried *in vacuo* (50% yield). The analytical sample was recrystallized from Et_2O–acetone (Found: C, 34.1; H, 5.6. $C_{21}H_{42}Br_2Ni_2O_2P_4$ requires C, 34.6; H, 5.8%). IR (Nujol) $\nu(C=O)$ 1630, 1600 and 1570 cm^{-1}. NMR (CD_2Cl_2): ^1H, δ 1.13 (br, 36 H, 4 PMe_3), 4.08 (s, 2 H, CH_2) and 7.45–8.39 (m, 4 H, aromatics); ^{31}P-$\{^1H\}$, δ -14.4 (s, 2 PMe_3) and -14.0 (br s, 2 PMe_3); ^{13}C-$\{^1H\}$, δ 13.5 [pseudo-triplet, $J(CP)_{ap}$ 14, 2 PMe_3], 14.0 (br s, 2 PMe_3), 55.6 (s, CH_2), 126.6, 127.0, 128.4, 132.5 (s, aromatic CH), 134.3, 140.8 (s, quaternary aromatics), 253.0 (br s, $COCH_2$) and 253.2 [t, $^2J(CP)$ 25 Hz, COC_6H_4].

Compound **3b** was prepared from a solution of **2b** (0.40 g, 0.6 mmol) in Et_2O (60 cm^3). Carbon monoxide was bubbled through it at room temperature and the bis(acyl) complex crystallized from Et_2O in 95% yield (Found: C, 34.4; H, 5.8%). IR (Nujol) $\nu(C=O)$ 1640, 1625 and 1590 cm^{-1}. NMR: ^1H (CD_3COCD_3), δ 1.21 (br s, 36 H, 4 PMe_3), 3.96 (s, 2 H, CH_2), 7.74 and 8.32 [d and d, 2 H and 2 H, $^3J(HH)$ 8.0, aromatics]; ^{31}P-$\{^1H\}$ (CD_2Cl_2), δ -11.7 (s, 2 PMe_3) and -11.3 (s, 2 PMe_3); ^{13}C-$\{^1H\}$ (CD_2Cl_2), δ 13.4 [pseudo-triplet, $J(CP)_{ap}$ 15, 2 PMe_3], 13.7 (br s, 2 PMe_3), 56.0 (s, CH_2), 127.3, 129.4 (s, 1 : 1 ratio, aromatic CH), 137.6, 139.2 (s, quaternary aromatics), 252.0 (br s, $COCH_2$) and 252.5 [t, $^2J(CP)$ 24 Hz, COC_6H_4].

trans,trans-$[(Me_3P)_2BrNi(\mu$-*m*-$C_6H_4CH_2CH_2C_6H_4$-*m*$)NiBr(PMe_3)_2]$ **4a**.—To a solution of complex **5a** (0.20 g, 0.3 mmol) in the minimum volume of thf (1 cm^3) was added an excess (*ca.* 10 mmol) of neat PMe_3. The resulting solution was stirred at room temperature for 1 h and the volatiles removed *in vacuo*. The residue was extracted several times with methanol to dissolve all the blue $[NiBr_2(PMe_3)_3]$ present. The remaining yellow microcrystalline product (80% yield) was recrystallized from Et_2O–acetone (Found: C, 40.4; H, 6.2. $C_{26}H_{48}Br_2Ni_2P_4$ requires C, 40.9; H, 6.3%). NMR (CD_2Cl_2): ^1H, δ 1.05 [pseudo-triplet, 18 H, $J(HP)_{ap}$ 3.8, 2 PMe_3], 2.69 (s, 2 H, CH_2) and 6.58–

Table 2 Crystal and refinement data for compound **2b**

Formula	$C_{19}H_{42}Br_2Ni_2P_4$
M	671.2
Crystal system	Monoclinic
Space group	$P2_1/c$
a/Å	11.241(1)
b/Å	8.866(2)
c/Å	29.323(8)
β/°	90.22(1)
U/Å^3	2922(1)
F(000)	1368
Z	4
D_c/g cm^{-3}	1.53
T/°C	22
μ/cm^{-1}	42.2
Scan technique	ω–2θ
hkl ranges	−13 to 13, 0–10, 0–36
Reflections collected	6439
Unique data	5720
Observed data [$I \geqslant 2\sigma(I)$]	2462
R(int)	0.039
Standard reflections	3 every 135
Decay	⩽3% variation
R	0.057
R'	0.063 (unit weight)
$\Delta\rho$/e Å^{-3}	2.3
Average shift/error	0.023
Average absorption correction	0.971

Table 3 Atomic coordinates for compound **2b**

Atom	X/a	Y/b	Z/c
Ni(1)	0.778 71(14)	0.105 29(19)	−0.020 29(5)
Ni(2)	0.689 91(14)	0.332 39(19)	0.190 09(5)
Br(1)	0.790 59(19)	−0.074 17(22)	−0.079 58(6)
Br(2)	0.772 11(14)	0.105 11(20)	0.222 22(7)
P(1)	0.753 53(33)	0.291 20(43)	−0.068 23(12)
P(2)	0.801 23(31)	−0.068 69(43)	0.032 60(13)
P(3)	0.853 51(30)	0.452 04(43)	0.210 31(12)
P(4)	0.510 58(30)	0.229 73(43)	0.195 92(12)
C(1)	0.638 85(110)	0.490 28(144)	0.147 99(38)
C(2)	0.671 47(105)	0.410 90(134)	0.105 33(37)
C(3)	0.590 14(105)	0.324 07(157)	0.080 65(41)
C(4)	0.623 43(107)	0.240 32(164)	0.042 15(41)
C(5)	0.741 04(98)	0.237 54(144)	0.027 68(37)
C(6)	0.822 76(99)	0.330 18(157)	0.050 92(42)
C(7)	0.787 51(100)	0.415 69(146)	0.088 51(38)
C(11)	0.792 46(184)	0.472 43(210)	−0.052 00(64)
C(12)	0.612 54(165)	0.295 62(228)	−0.090 75(66)
C(13)	0.839 98(173)	0.282 65(251)	−0.117 77(67)
C(21)	0.664 18(127)	−0.171 08(190)	0.039 28(62)
C(22)	0.836 08(155)	−0.017 92(186)	0.089 38(50)
C(23)	0.910 36(110)	−0.211 45(158)	0.022 38(53)
C(31)	0.876 49(125)	0.650 23(156)	0.197 37(48)
C(32)	0.993 02(106)	0.371 28(166)	0.191 55(48)
C(33)	0.871 65(124)	0.451 58(187)	0.272 37(42)
C(41)	0.372 26(103)	0.325 11(171)	0.178 52(48)
C(42)	0.476 77(133)	0.184 33(194)	0.255 45(46)
C(43)	0.494 43(136)	0.050 81(170)	0.166 58(55)

7.20 (m, 4 H, aromatics); ^{31}P-{^{1}H}, δ −10.5 (s); ^{13}C-{^{1}H}, δ 12.9 [pseudo-triplet, J(CP)$_{ap}$ 14 Hz, 2 PMe$_3$], 38.1 (s, CH$_2$), 124.4, 126.0, 132.8, 135.1 (s, aromatic CH) and 139.3 (s, quaternary aromatic). The nickel-bonded carbon nucleus was not located.

Following a similar procedure, the *para*, *para* **4b** isomer was obtained as a yellow crystalline solid in 60% yield (Found: C, 40.2; H, 6.1%). NMR (CD$_2$Cl$_2$): ^{1}H, δ 1.15 [pseudo-triplet, 18 H, J(HP)$_{ap}$ 3.5, 2 PMe$_3$], 2.60 (s, 2 H, CH$_2$), 6.65 and 7.19 [d and d, 2 H and 2 H, ^3J(HH) 6.0, aromatics]; ^{31}P-{^{1}H}, δ −10.9 (s); ^{13}C-{^{1}H}, δ 13.0 [pseudo-triplet, J(CP)$_{ap}$ 14, 2 PMe$_3$], 37.5 (s, CH$_2$), 127.2, 134.6 (s, 1:1 ratio, aromatic CH), 134.6 (quaternary aromatic) and 150.1 [t, ^2J(CP) 36 Hz, Ni–C$_q$].

trans-[(Me$_3$P)BrNi(μ-η^3:σ-*m*-CH$_2$C$_6$H$_4$)NiBr(PMe$_3$)$_2$] **5a**.—A mixture of [Ni(cod)$_2$] (1.1 g, 4 mmol) and PMe$_3$ (0.6 cm^3, 6 mmol) was stirred in Et$_2$O (80 cm^3) for 2–3 h at room temperature. After cooling at −80 °C, 2 cm^3 of a 1 mol dm^{-3} solution of BrCH$_2$C$_6$H$_4$Br-*m* in toluene was added dropwise. The resulting mixture was stirred at that temperature for 2 h and the precipitate formed was filtered off, washed with Et$_2$O–light petroleum (1:1) and dried *in vacuo* (95% yield). This pink material could be recrystallized from Et$_2$O–CH$_2$Cl$_2$ mixtures (Found: C, 31.4; H, 5.6. C$_{16}$H$_{33}$Br$_2$Ni$_2$P$_3$ requires C, 32.3; H, 5.5%). NMR (CD$_2$Cl$_2$): ^{1}H, δ 1.17 (br s, 18 H, 2 PMe$_3$), 1.33 [d, 9 H, ^2J(HP) 9.9, 1 PMe$_3$], 5.66–7.74 (m, 4 H, aromatics); ^{31}P-{^{1}H}, δ −11.9, −11.0 (central peaks of the AB quartet; the smaller, outer absorptions could not be observed, 2 PMe$_3$) and −2.5 (s, 1 PMe$_3$); ^{13}C-{^{1}H}, δ 13.7 [broad pseudo-triplet, J(CP)$_{ap}$ 13, 2 PMe$_3$], 15.7 [d, ^1J(CP) 29, 1 PMe$_3$], 27.1 [d, ^2J(CP) 10, ^1J(CH) 153, CH$_2$], 97.6, 132.2, 132.6, 136.4 [d, s, t, d, respectively, J(CP) 11, 4, 4 Hz, aromatic CH] and 113.4 (s, quaternary aromatic).

Complex **5b** was similarly obtained, as dark red needles, in 60% yield (Found: C, 32.0; H, 5.7%). NMR: ^{1}H (CD$_3$COCD$_3$), δ 1.14 [pseudo-triplet, 18 H, J(HP)$_{ap}$ 3.9, 2 PMe$_3$], 1.37 [d, 9 H, ^2J(HP) 10, 1 PMe$_3$], 2.85 (br s, 2 H, CH$_2$), 6.70 and 7.47 [d and d, 2 H and 2 H, ^3J(HH) 7.9, aromatics]; ^{31}P-{^{1}H} (CD$_2$Cl$_2$, −70 °C), ABX spin system, δ$_A$ −12.5, δ$_B$ −9.7, δ$_X$ −0.4, J(AB) 322, J(AX) 7, J(BX) 9; ^{13}C-{^{1}H} (CD$_2$Cl$_2$), δ 13.3 [pseudo-triplet, J(CP)$_{ap}$ 14, 2 PMe$_3$], 15.7 [d, ^1J(CP) 29, 1 PMe$_3$], 23.4 [d, ^2J(CP) 8, ^1J(CH) 152, CH$_2$], 118.2, 139.4 (s, 1:1 ratio, aromatic CH), 107.4 (s, quarternary aromatic), 163.8 [t, ^2J(CP) 37 Hz, Ni–C$_q$].

X-Ray Structure Determination of Compound **2b**.—An air-sensitive single crystal of compound **2b** (0.40 × 0.34 × 0.20 mm) was sealed in a glass capillary under N$_2$ and mounted in the goniometer of an Enraf-Nonius CAD-4 diffractometer. Graphite-monochromated Mo-Kα radiation (λ = 0.710 69 Å) was used. The cell dimensions were refined by least-squares fitting the values of 25 reflections. A summary of the crystal and refinement data is given in Table 2. The intensities were corrected for Lorentz and polarization effects. Scattering factors for neutral atoms and anomalous dispersion corrections for Ni, Br and P were taken from ref. 18. The structure was solved by Patterson and Fourier methods. An empirical absorption correction[19] was applied at the end of the isotropic refinement. Final refinement with fixed isotropic factors and coordinates for H atoms. Most of the calculations were carried out with the X-RAY 80 system.[20] Fig. 1 was produced by ORTEP.[21] Atomic coordinates are given in Table 3.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates and thermal parameters.

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