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Journal of Organometallic Chemistry 667 (2003) 8–15

Journal of Organo metallic Chemistry

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Generation of nickel(0)–aryne and nickel(II)–biphenyldiyl complexes via in situ dehydrohalogenation of arenes. Molecular structures of [Ni(2,2′-$C_6H_4C_6H_4$)(dcpe)] and C_2-hexabenzotriphenylene

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Received 30 April 2002; received in revised form 28 June 2002; accepted 28 June 2002

Abstract

Reactions of the aromatic halides chlorobenzene, 9-bromophenanthrene and chloro-*p*-xylene with lithium 2,2,6,6-tetramethylpiperidide (LiTMP) in the presence of [Ni(η^2-C_2H_4)(dcpe)] (**1**) generated the corresponding η^2-aryne complexes [Ni(η^2-aryne)(dcpe)] [aryne = C_6H_4 (**2**), 9,10η-$C_{14}H_8$ (**4**) and 2,3η-1,4-$Me_2C_6H_2$ (**9**)], which could not be isolated as pure compounds but were identified tentatively on the basis of spectroscopic data. In the case of **2**, further insertion of free benzyne formed the biphenyldiyl complex [Ni(2,2′-$C_6H_4C_6H_4$)(dcpe)] (**3**). In addition to forming **4**, 9,10-phenanthryne also underwent cyclotrimerisation under the reaction conditions to give hexabenzotriphenylene (**6**), having C_2-symmetry. Compounds **3** and **6** were structurally characterised by X-ray diffraction analyses.

Keywords: Aryne complex; Nickel; Cyclotrimerisation; Insertion reaction; Dehydrohalogenation

1. Introduction

Although benzyne (and, more generally, arynes) are transient species [1], the aryne or arylene-1,2-diyl fragment can be employed as a ligand in a variety of mononuclear [2] and polynuclear [3] complexes of the d-block elements. With few exceptions, the aryne fragment in these complexes is generated within the coordination sphere of a suitable precursor, not from the free aryne. The ability of simple molecules to insert into the metal–aryne bond offers possibilities for organic synthesis, exemplified by the reactions of the transient zirconocene–benzyne complex [$ZrCp_2$(η^2-C_6H_4)], which can be generated in situ by thermal decomposition of [$ZrCp_2$(Ph)(R)] (R = Me, Ph) and stored as its PMe_3 adduct [4]. We [5–10] have shown that naphthalenes can be produced with fair to excellent regioselectivity by double insertion of alkynes into aryne–nickel(0) complexes such as [Ni(η^2-C_6H_4)(PEt_3)$_2$] (Scheme 1). It would be desirable to develop catalytic procedures based on this type of reaction, but because the preparation of the complexes requires the alkali metal reduction of a nickel(II) precursor, the reactions have to be carried out stoichiometrically, the alkynes being added after the reducing agent has been removed.

Recently, some palladium-catalysed reactions of arynes have been reported. The arynes were generated in situ by treatment of the appropriate *o*-trimethylsilylaryl triflate with CsF and led to cyclotrimers [11,12] or, in the presence of alkynes, to polyaromatic compounds such as phenanthrenes, naphthalenes and indenes (Scheme 2) [13–17]. Depending on conditions (catalyst, solvent), free benzyne is supposed either to undergo catalysed co-cyclisation with one or two molecules of alkyne, or to insert into an aryl–palladium(II) bond

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Abbreviations: LiTMP, lithium 2,2,6,6-tetramethylpiperidide; LDA, lithium diisopropylamide; DMAD, dimethyl acetylenedicarboxylate; dcpe, 1,2-bis(dicyclohexylphosphino)ethane, $Cy_2PCH_2CH_2PCy_2$; dippe, 1,2-bis(diisopropylphosphino)ethane, $^iPr_2PCH_2CH_2P^iPr_2$; dppe, 1,2-bis(diphenylphosphino)ethane, $Ph_2PCH_2CH_2PPh_2$; depe, 1,2-bis(diethylphosphino)ethane, $Et_2PCH_2CH_2PEt_2$.

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[1] Single crystal X-ray diffraction unit.

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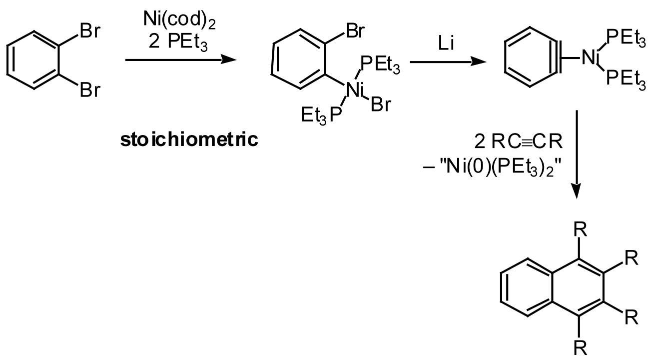
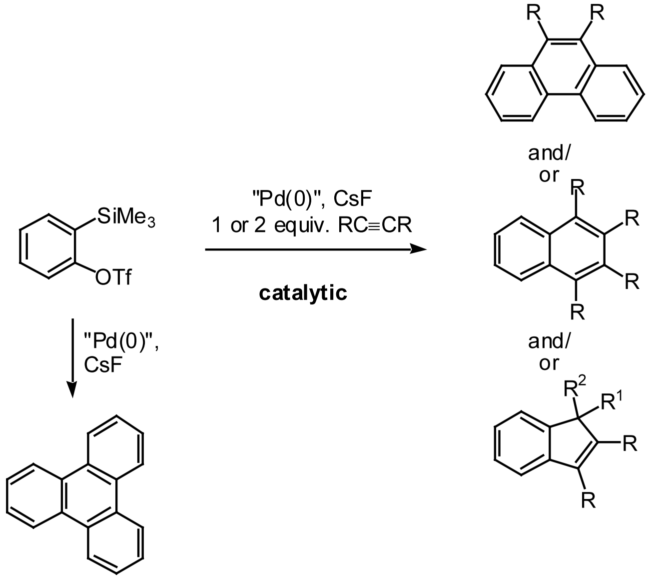
doi:10.1016/S0022-328X(02)01667-4



Scheme 1.



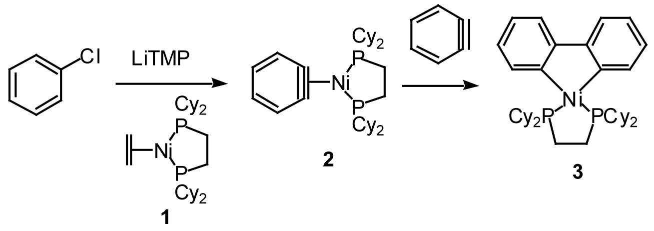
Scheme 2.

generated by oxidative addition of the aryl triflate to palladium(0).

We wondered whether an approach based on intermolecular capture of free benzyne could be used to generate known benzyne–nickel(0) complexes. Such a procedure, if successful, might be adapted to catalytic applications. However, since the aryl triflates used in the case of palladium would be likely to undergo oxidative addition with nickel(0) species, other aryl precursors have been investigated. Arynes can be generated readily by reaction of aromatic halides with a strong base such as lithium 2,2,6,6-tetramethylpiperidide (LiTMP) or LDA [18], and such halides, especially the chloro derivatives, would not be expected to oxidatively add rapidly to zerovalent nickel below room temperature. Furthermore, this procedure has already been applied successfully to the preparation of several cyclic alkyne complexes of Group 10 metals. For example, a 1,4-benzdiyne complex, [(dcpe)Ni(μ-1,2η:4,5η-C_6H_2)Ni(dcpe)], was prepared by LiTMP-promoted dehydrohalogenation of the fluoro precursor [Ni(1,2η-4-FC_6H_3)(dcpe)] in the presence of [Ni(η^2-C_2H_4)(dcpe)] [19]. Treatment of a mixture of 1-, 2-, and 3-bromocycloheptatrienes with LDA in the presence of [Pt(PPh_3)$_3$] gave a mixture of the Pt(PPh_3)$_2$ complexes of cyclohepta-3,5-dien-1-yne and cyclohepta-3,6-dien-1-yne, which could be converted into the tropyne–platinum(0) complex [Pt(η^2-C_7H_5)(PPh_3)$_2$]BF_4 by treatment with [Ph_3C]BF_4. The related complexes of cyclohexyne and cycloheptyne could be obtained similarly from the corresponding bromoalkene precursors [20–22]. The benzyne–platinum(0) complex [Pt(η^2-C_6H_4)(PPh_3)$_2$] has been identified tentatively, on the basis of its $^{31}P\{^1H\}$-NMR spectrum, as the initial product of reaction of chlorobenzene, [Pt(η^2-C_2H_4)(PPh_3)$_2$] and LiTMP. It could not be isolated because, under the reaction conditions, it underwent rapid insertion of free benzyne to give the (2,2′-biphenyldiyl)platinum(II) complex [Pt(η^1:η^1-$C_6H_4C_6H_4$)(PPh_3)$_2$] and also isomerised to the *ortho*-metalated complex [Pt(2-$C_6H_4PPh_2$-κ*C*,*P*)(η^1-C_6H_5)(PPh_3)$_2$] [23]. In this paper, the results from dehydrohalogenation of several chloro- or bromoarenes and their reactions with the nickel(0) precursor [Ni(η^2-C_2H_4)(dcpe)] (**1**) are presented.

2. Results

Slow addition of LiTMP to a THF solution containing an excess of chlorobenzene and [Ni(η^2-C_2H_4)(dcpe)] (**1**) at 0 °C caused the appearance of a singlet at δ_P 78.4 in the ^{31}P-NMR spectrum, in addition to the main signal at δ_P 63.5 due to **1**. The chemical shift of the new species corresponds with that reported for [Ni(η^2-C_6H_4)(dcpe)] (**2**) [24]. However, addition of one mol equivalent of base (with respect to **1**) gave less than 20% of **2** as estimated from the ^{31}P-NMR spectrum. Further addition of LiTMP led to a decrease of the amount of **1**, but a second complex (**3**) showing a singlet at δ_P 62.6 appeared almost immediately. After complete disappearance of **1**, the intensity ratio of the peaks due to the benzyne complex **2** and compound **3** ranged typically from 2:1 to 1:2; the faster the addition of LiTMP the more **3** was formed. This reaction proved very sensitive to the rate of addition of the base and the conditions were difficult to control. The highest proportion of **2** was obtained by employing the reactants **1**, LiTMP and chlorobenzene in a ratio of 1:6:10, and adding dilute base solution very slowly (typically one mol equivalent/30 min). The temperature range in which **2** (and **3**) were formed was also very narrow. Below −10 °C, no reaction was observed presumably because the C_2H_4 fragment was not displaced from **1**, and at room temperature the reaction mixture decomposed to unidentified products. Oxidative addition of chlorobenzene to the nickel(0) centre was not observed under these reaction conditions.

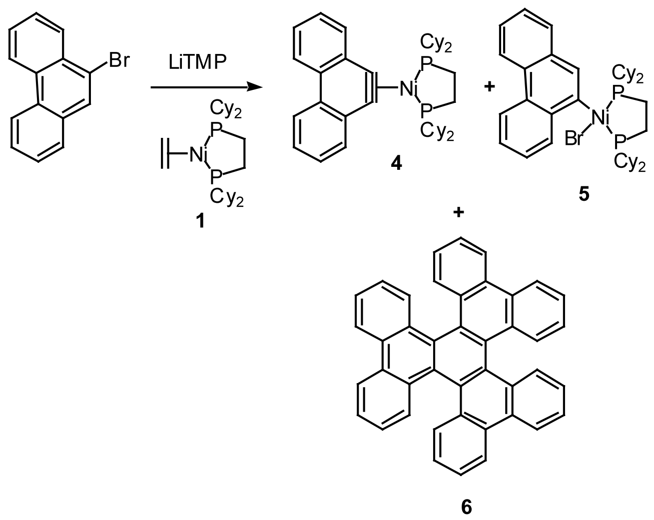


Scheme 3.

Complex **3** could be isolated from the reaction mixture as an air-stable solid. Its fast-atom bombardment (FAB)-mass spectrum (MS) showed the highest mass peak corresponding to [Ni($C_{12}H_8$)(dcpe)] and its ^1H and ^{13}C-NMR spectra showed four different signals for the aromatic CH groups; the aromatic peaks and the peak due to the CH_2 resonance of dcpe were in an intensity ratio of 2:1. Hence, this species was identified as the biphenyldiyl complex [Ni(2,2′-$C_6H_4C_6H_4$)(dcpe)] (**3**) and its structure was confirmed by X-ray analysis (see below).

The formation of **3** can be accounted for by insertion of free benzyne into the Ni–C bond of the benzyne complex **2** (Scheme 3). Unfortunately, an excess of base, hence of free benzyne, is always required to bring the reaction to completion and no suitable reaction conditions for the exclusive formation of the benzyne complex **2** have been found.

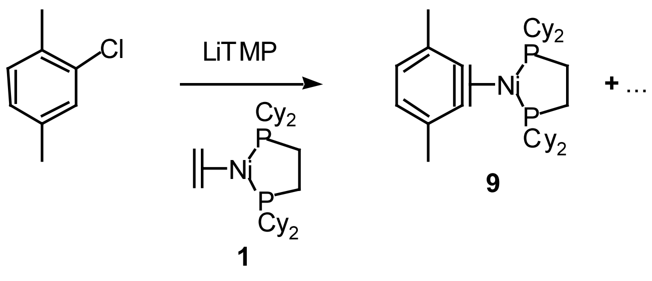
In an attempt to slow down the insertion reaction relative to the formation of the aryne complex, substituents that would sterically clash during the insertion step were introduced in the 3 and 6 positions of the arene. Thus, reaction of 9-bromophenanthene with LiTMP in the presence of **1**, under the same conditions as those described above, led to the formation of a compound believed to be the 9,10-phenanthryne complex [Ni(η^2-$C_{14}H_8$)(dcpe)] (**4**), which showed a ^{31}P-NMR singlet at δ_P 81.9 (Scheme 4). Yields estimated from ^{31}P-NMR spectra ranged from 5 to 50%. The main side-product in these reactions was an unsymmetrical nickel(II) complex characterised by two doublets in the ^{31}P-NMR spectrum at δ_P 62.6 and 66.7 ($J_{PP} = 20.1$ Hz) similar to the values reported for [NiBr(aryl)(dcpe)] complexes [25]; presumably oxidative addition of the bromoarene to **1** had taken place to give the 9-phenanthryl complex **5**. Attempted extraction of complex **4** from the reaction mixture, which also contained several organic phenanthrene-based species, proved impossible because the compound was poorly soluble and decomposed on chromatography. However, the FABMS of the crude solid containing **4** showed a molecular ion consistent with the presence of the 9,10-phenanthryne complex [Ni(η^2-$C_{14}H_8$)(dcpe)].



Scheme 4.

One organic species, which was extracted with benzene from the reaction mixture and separated by crystallisation, proved interesting in its own right. The molecular structure solved by X-ray analysis showed the compound to be hexabenzotriphenylene (**6**) (see below). A crystal structure of an isomer of **6**, having D_3 symmetry, has already been reported [26], but our structure differs in that the compound displays a lower symmetry, C_2. Such a conformation has been proposed recently for the kinetic product of the palladium-catalysed cyclotrimerisation of 9,10-phenanthryne [12,27], whereas the compound with D_3 symmetry was obtained under thermodynamic conditions (vacuum pyrolysis of phenanthrene-9,10-dicarboxylic anhydride at 550–700 °C). The interconversion between the two conformations has been studied by variable temperature NMR spectroscopy as well as ab initio and DFT calculations [27]; the C_2 structure computed for **6** is in good agreement with the present experimental one.

The reaction of chloro-*p*-xylene with LiTMP in the presence of **1** proved to be much cleaner than those described above: only one phosphorus-containing complex, showing a ^{31}P-NMR singlet at δ_P 79.1, was formed. The formulation as the *p*-xylyne complex [Ni(2,3η-1,4-$Me_2C_6H_2$)(dcpe)] (**9**) (Scheme 5) was supported by the presence, in the ^{13}C-NMR spectrum of the reaction mixture, of a characteristic symmetrical five-line multiplet at δ_C 144.10 (the second and fourth lines being more intense than the other three) assigned to the



Scheme 5.

directly bound aryne carbon atoms. This signal, analogous to that reported for the benzyne complex [Ni(η^2-C_6H_4)(dcpe)] (**2**) [24], is typical of one half of an AA′XX′ pattern, the sum of the two P–C coupling constants being 51.8 Hz (separations of lines 1–2 and 4–5 = 10.5 Hz, lines 2–3 and 3–4 = 15.4 Hz). Unfortunately, once again, complex **9** could not be separated from other unidentified organic side-products.

As the 9,10-phenanthryne and *p*-xylyne complexes could not be isolated, we attempted to trap them by reaction with CO or DMAD to give more stable nickel(II) insertion products, this behaviour being well established for the corresponding complexes of benzyne, 4,5-difluorobenzyne and 2,3η-naphthalyne [5,28,29]. Surprisingly, solutions containing both complexes failed to react with these unsaturated molecules even at 50 °C; heating to higher temperature led to complete decomposition.

3. Molecular structures of [Ni(2,2′-$C_6H_4C_6H_4$)(dcpe)] (3) and $(C_{14}H_8)_3$ (6)

The molecular structure of the biphenyldiyl complex **3** is shown in Fig. 1 and selected values of bond lengths and angles are given in Table 1. The nickel centre has a slightly distorted square-planar coordination, the two carbon atoms C1 and C12 of the biphenyldiyl unit lying −0.177 and 0.298 Å, respectively, from the plane defined by Ni and the two phosphorus atoms. This deviation results in a dihedral angle between the two aromatic rings of the biphenyldiyl unit of 5.44°. The Ni–C and Ni–P distances are comparable with those of the structure reported for the bis(diisopropylphosphino) analogue [Ni(2,2′-$C_6H_4C_6H_4$)(dippe)] [30]; several other biphenyldiyl complexes of Group 10 metals displaying similar structures are known: [Pd(2,2′-C_6H_4-C_6H_4)(dppe)] [31], [Pd(2,2′-$C_6H_4C_6H_4$)(depe)] [32] and [Pt(2,2′-$C_6H_4C_6H_4$)$(PPh_3)_2$] [23].

Table 1
Selected bond lengths (Å) and angles (°) for [Ni(2,2′-$C_6H_4C_6H_4$)(dcpe)] (**3**)

Bond lengths	
Ni1–P1	2.199(4)
Ni1–C1	1.92(1)
P1–C25	1.84(1)
C1–C2	1.38(2)
C1–C6	1.44(2)
C6–C7	1.46(2)
Ni1–P2	2.207(4)
Ni1–C12	1.97(1)
P2–C26	1.82(1)
C11–C12	1.39(2)
C7–C12	1.40(2)
Bond angles	
P1–Ni1–P2	86.7(2)
Ni1–P1–C25	107.4(4)
Ni1–C1–C6	115(1)
C6–C7–C12	114(1)
C1–Ni1–C12	83.5(6)
Ni1–P2–C26	108.0(5)
Ni1–C12–C7	114(1)
C1–C6–C7	112(1)

The structure of the hexabenzotriphenylene **6** is shown in Figs. 2 and 3, and selected values of bond lengths and angles are given in Table 2. The molecule is highly distorted but displays an approximate C_2 symmetry with the axis bisecting the C2–C3, C5–C6 and

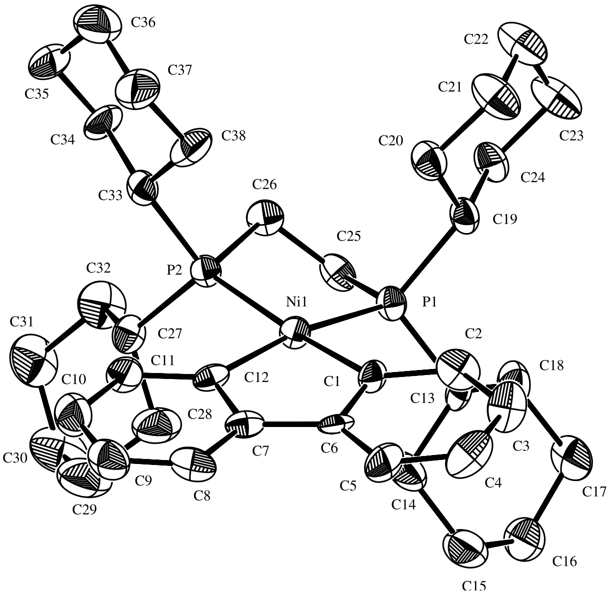


Fig. 1. Molecular structure of [Ni(2,2′-$C_6H_4C_6H_4$)(dcpe)] (**3**) with selected atom labelling. Displacement ellipsoids show 30% probability levels; hydrogen atoms have been omitted for clarity.

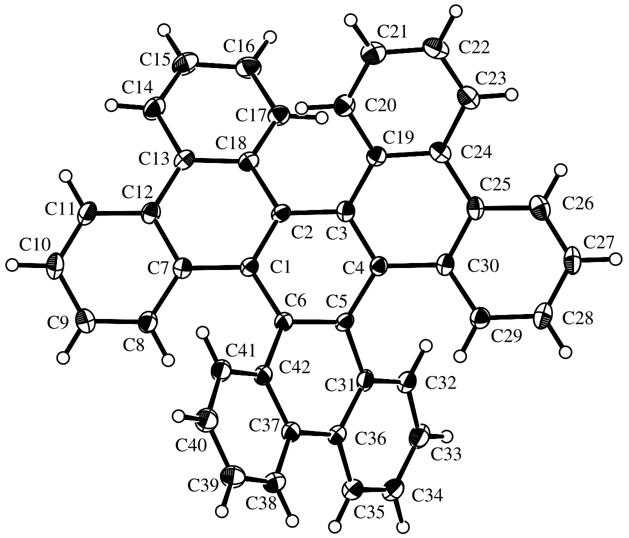


Fig. 2. Molecular structure of the C_2 conformation of hexabenzotriphenylene (**6**) with selected atom labelling. Displacement ellipsoids show 30% probability levels; hydrogen atoms are drawn as circles with small radii.

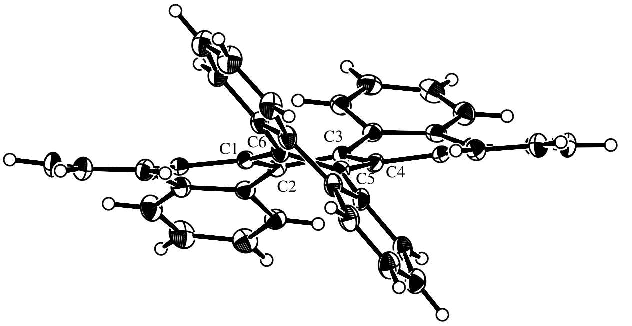


Fig. 3. Side-on view of **6**. Displacement ellipsoids show 30% probability levels; hydrogen atoms are drawn as circles with small radii.

Table 2
Selected bond lengths (Å) and angles (°) for C_2-hexabenzotriphenylene (**6**)

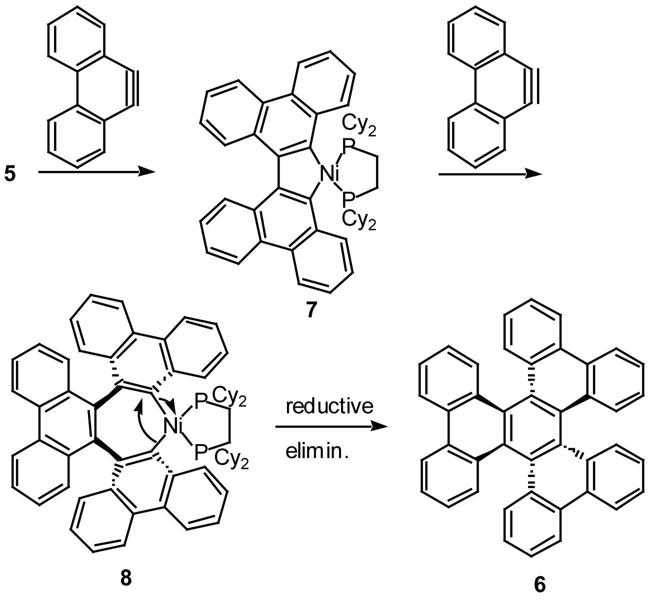
Bond lengths	
C1–C2	1.394(4)
C3–C4	1.410(4)
C5–C6	1.400(4)
C1–C7	1.477(4)
C3–C19	1.450(4)
C5–C31	1.463(5)
C2–C3	1.449(4)
C4–C5	1.444(4)
C1–C6	1.445(4)
C2–C18	1.461(4)
C4–C30	1.474(4)
C6–C42	1.454(4)
Bond angles	
C1–C2–C18	119.2(3)
C3–C4–C30	119.0(3)
C5–C6–C42	116.3(3)
C7–C1–C2–C18	−8.7(5)
C31–C5–C6–C42	41.8(4)
C2–C3–C19	122.5(3)
C4–C5–C31	127.4(3)
C6–C1–C7	121.8(3)
C19–C3–C4–C30	−6.9(5)

C36–C37 bonds. The central phenyl ring is best described as having a twist–boat conformation; the double bonds in the C1 to C6 core are mainly localised within the three phenanthrene units as shown by the shorter distances of C1–C2, C3–C4, C5–C6 (1.394(4), 1.410(4) and 1.400(4) Å (compared with those of C2–C3, C4–C5 and C1–C6 (1.449(4), 1.444(4) and 1.445(4) Å, respectively). These values, and those of the remaining C–C bonds, are similar to those reported for the conformer having D_3 symmetry [26]. They are also very close to the values computed for the C_2 isomer (average values of 1.382 Å for the short distance and 1.449 Å for the long one) [27], although the computations seem to overestimate slightly the localisation of the double bonds. The main difference between the C_2 isomer **6** and the reported structure of the D_3 isomer is the disposition of the outer C_6H_4 fragments. In the propeller-like D_3 species, the C_6H_4 units are located alternately above and below the plane of the central C1–C6 core. In the structure of **6**, one phenanthrene unit has its two C_6H_4 fragments above the plane defined by C1–C6, those of the second one are located below the plane, while the third phenanthrene is highly tilted and bisects the plane with one C_6H_4 below and one above. The dihedral angle between the plane of this phenanthrene unit and the C1–C6 plane is 45.7°, which is much larger than the three dihedral angles of 28.5, 30.0 and 29.7° measured in the D_3 isomer [26]. The corresponding torsion angle C31–C5–C6–C42 of **6** (41.8(4)°) is very close to the corresponding computed angle (40.5°) [27].

4. Discussion

An aryne that has been generated from haloarene and strong base can be trapped by coordination to the nickel(0) fragment Ni(dcpe) to form the corresponding η^2-aryne–nickel(0) complex. Unfortunately, in the case of benzyne (C_6H_4), the rate of formation of the benzyne complex **2**, by displacement of the C_2H_4 fragment from the nickel(0) precursor [Ni(η^2-C_2H_4)(dcpe)], and the rate of the insertion reaction between free benzyne and the aryne complex are comparable, and formation of the corresponding biphenyldiyl species **3** cannot be avoided. As mentioned in the Introduction, similar behaviour has already been observed in the analogous reaction of [Pt(η^2-C_2H_4)(PPh_3)$_2$] with benzyne [23].

It seems reasonable to assume that the palladium-catalysed reactions mentioned in the Introduction (Scheme 2) and the nickel-promoted reactions that lead to the biphenyldiyl complex **3** or to the cyclotrimer **6** proceed by similar mechanisms. The aryne-complex reacts initially with one molecule of free aryne to give a five-membered metallacycle such as the isolated compound **3**. A similar mechanism has been proposed for the insertion of alkynes into the benzyne–nickel(0) complexes [Ni(η^2-C_6H_4)(PR_3)$_2$] ($2PR_3 = 2PEt_3$, dcpe) [2b,5,6,9], and stable, five-membered nickelacycles were isolated after reaction of **2** with DMAD [24], C_2F_4 [33] or C_2H_4 [24]. Although we have been unable to detect it, the biphenanthrenyl-9,9′-diyl intermediate **7** is presumably generated similarly by the insertion reaction of complex **4** with free 9,10-phenanthryne (Scheme 6). Subsequent insertion of another molecule of free 9,10-phenanthryne into **7** would then lead to the formation of a seven-membered metallacycle, analogous to those isolated from consecutive reactions of aryne complexes with C_2F_4 and DMAD [28,33]. Such a compound would probably have a boat-shaped conformation with the phenanthrene units disposed above and below the median plane of the molecule, hence reductive elimination from an intermediate such as **8** (Scheme 6) would be expected to form the aromatic



Scheme 6.

product **6** having C_2 symmetry, as observed. In general, however, the presence of substituents at the 3- and 6-positions of benzyne seems to prevent or drastically slow subsequent stepwise insertion reactions of the resulting Ni(dcpe) complexes with unsaturated molecules.

In summary, the method to generate aryne complexes described in this paper has proved difficult to control because the unavoidable excess of free benzyne gives mixtures of products. To solve this problem, attachment of the aryl group to the nickel centre, e.g. by oxidative addition, before the benzyne complex is formed seems to be a prerequisite for any catalytic preparation of polyaromatic compounds to be achieved. This methodology would maintain an equimolar ratio between benzyne and metal, thus avoiding the problem of undesired insertion reactions. In order to achieve this goal, new ways of preparing benzyne complexes from aryl–nickel(II) and -palladium(II) precursors are currently under investigation [31].

5. Experimental

5.1. General procedures

All experiments were carried out under nitrogen. All solvents were dried and degassed prior to use. NMR spectra were recorded on a Varian XL-200E (^{1}H at 200 MHz, ^{13}C at 50.3 MHz, ^{31}P at 81.0 MHz) instrument. The chemical shifts (δ) for ^{1}H and ^{13}C are given in ppm relative to residual signals of the solvent and to external 85% H_3PO_4 for ^{31}P. The spectra of all nuclei (except ^{1}H) were ^{1}H-decoupled. The coupling constants (J) are given in Hz with an estimated error of ±0.2 Hz. Mass spectra of the complexes were obtained on a ZAB-SEQ4F spectrometer by the FAB technique using matrices of (3-nitrophenyl)octyl ether (NOPE). The microanalyses were done in-house.

5.2. Starting materials

The complex [Ni(η^2-C_2H_4)(dcpe)] was prepared following a published procedure [24].

5.3. Typical procedure

The base (LiTMP) was prepared by addition of *n*BuLi (1.37 N, 0.44 ml, 0.6 mmol) to a solution of tetramethylpiperidine (0.12 ml, 0.7 mmol) in THF (5 ml) at −78 °C, followed by stirring at 0 °C for 1 h. The LiTMP was then added dropwise (time varying from 15 min to 1 h) to a mixture of [Ni(η^2-C_2H_4)(dcpe)] (**1**) (50 mg, 0.1 mmol) and chlorobenzene (0.1 ml, 1 mmol) in THF (10 ml) at 0 °C. The reaction was monitored by ^{31}P-NMR spectroscopy (see text). The same procedure was used with 9-bromophenanthrene and chloro-*p*-xylene.

5.4. [Ni(2,2′-$C_6H_4C_6H_4$)(dcpe)] (**3**)

One reaction mixture, prepared as described above, containing the benzyne complex **2** and **3** in a 1:2 ratio was evaporated to dryness and the residue washed with hexane. The residue was redissolved in CH_2Cl_2, filtered through silica gel and single crystals of **3** were obtained by slow evaporation of the solvent.

^{1}H-NMR (200 MHz, CD_2Cl_2) δ 1.05–2.50 (m, 48H, CH_2 and CH of dcpe), 6.73 (t, 2H, $J = 7.5$, $H^{4\text{ or }5}$), 6.87 (t, 2H, $J = 7.5$, $H^{5\text{ or }4}$), 7.15–7.28 (m, 4H, $H^{3,6}$).

$^{13}C\{^1H\}$-NMR (50.3 MHz, CD_2Cl_2) δ 19.02 (t, $J_{PC} = 20.0$, PCH_2), 26.27–28.37 (m, CH_2), 30.13 (t, $J_{PC} = 3.0$, CH_2), 32.86 (t, $J_{PC} = 3.8$, CH_2), 36.68–37.08 (m, PCH), 118.66 (s, CH), 124.22 (s, CH), 124.77 (t, $J_{PC} = 4.4$, CH), 140.29 (t, $J_{PC} = 7.6$, CH); the quaternary carbons C–Ni and C^2–$C^{2'}$ were not located.

$^{31}P\{^1H\}$-NMR (81.0 MHz, CD_2Cl_2) δ 62.6.

FABMS ($C_{38}H_{56}NiP_2$, NOPE): 633 [MH^+].

Anal. Calc. for $C_{38}H_{56}NiP_2 \cdot CH_2Cl_2$: C, 65.20; H, 8.14. Found: C, 65.72; H, 8.14%.

5.5. X-ray crystallography of **3** and **6**·$2C_6H_6$

Crystal data, details of data collection, data processing, structure analyses and structure refinements are given in Table 3.

A fragment of an orange crystal of **3** was attached to a glass capillary and data were recorded at 293 K on a Philips 1100/20 diffractometer with graphite monochromated Mo–K_α δ ($\lambda = 0.71073$ Å) by use of the ω–2θ scan technique, the resulting data being quite weak due

Table 3
Crystal and structure refinement data for **3** and **6**·**2C$_6$H$_6$**

Molecular compound	**3**	**6**
(a) Crystal data		
Chemical formula	$C_{38}H_{56}NiP_2$	$C_{42}H_{24}\cdot 2C_6H_6$
Formula weight	633.51	684.88
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)
a (Å)	14.00(2)	15.6222(5)
b (Å)	17.33(2)	12.4569(4)
c (Å)	14.73(2)	18.8509(6)
α (°)		
β (°)	99.6(1)	104.367(2)
γ (°)		
V (Å^3)	3525(6)	3553.7(2)
D_{calc} (g cm^{-3})	1.193	1.280
Z	4	4
μ (mm^{-1})	0.665 (Mo–K$_\alpha$)	0.072 (Mo–K$_\alpha$)
(b) Data collection, processing and refinement		
2θ max (°)	40.1	55.0
Data collected (h, k, l)	($-hh$, $-kk$, $-ll$) to (hh, kk, ll)	($-hh$, $-kk$, $-ll$) to (hh, kk, ll)
Total reflections	3610	15 314
Unique reflections [R_{int}] (%)	3451 (8.4)	8075 (6.7)
Observed reflections	1375 [$I > 3\sigma(I)$]	3020 [$I > 3\sigma(I)$]
Absorption corrections	Empirical	None
Transmission factors	0.7073–1.0000	
Number of parameters	370	487
R	0.047	0.052
R_w	0.043	0.050
Decay (%)	4.0	Nil

to the poor quality of the crystals. The structure was solved by the Patterson method (PATTY) [34] and expanded using Fourier techniques [35]. The absorption, mainly due to the capillary and the grease holding the crystal, was corrected empirically by use of the program DIFABS [36]. Hydrogen atoms were included at geometrically determined positions (C–H 0.95 Å) and periodically recalculated, but they were not refined. The maximum and minimum peaks in the final difference Fourier map were 0.27 and −0.27 e Å^{-3}, respectively.

A yellow flake crystal of **6**·2C$_6$H$_6$ was mounted on a glass fibre and data were collected at 200 K on a Nonius Kappa CCD diffractometer equipped with a 95 mm camera and graphite-monochromated Mo–K$_\alpha$ δ ($\lambda =$ 0.71073 Å) by use of COLLECT [37]; the intensities of the reflections were processed and the data reduced by use of the computer programs Denzo and Scalepak [38]. The structure was solved by direct methods by use of SIR92 [39]. The structure of **6**·2C$_6$H$_6$ consists of one molecule of hexabenzotriphenylene with two well-ordered benzene molecules. Hydrogen atoms were included at geometrically determined positions (C–H 0.95 Å) and periodically recalculated, but they were not refined. The maximum and minimum peaks in the final difference Fourier map were 0.19 and −0.25 e Å^{-3}, respectively.

The calculations were performed by use of the crystallographic software packages TEXSAN [40], MAXUS [41] and XTAL [42]. The neutral atom scattering factors were taken from ref. [43]. Mass attenuation coefficients used were those implemented in MAXUS for **6** [41], and those from ref. [44] for **3**.

6. Supplementary material

Crystallographic data for the structure determinations of compounds **3** and 6·2C$_6$H$_6$ have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 184365 and 184366, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

E.W. thanks the Australian Research Council for the award of a QEII Fellowship and M.R.K. is grateful to the Alexander von Humboldt Foundation for a Feodor von Lynen Fellowship.

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