The Reactivity of Complexes of Nickel(0) and Platinum(0) Containing Benzyne and Related Small-Ring Alkynes☆

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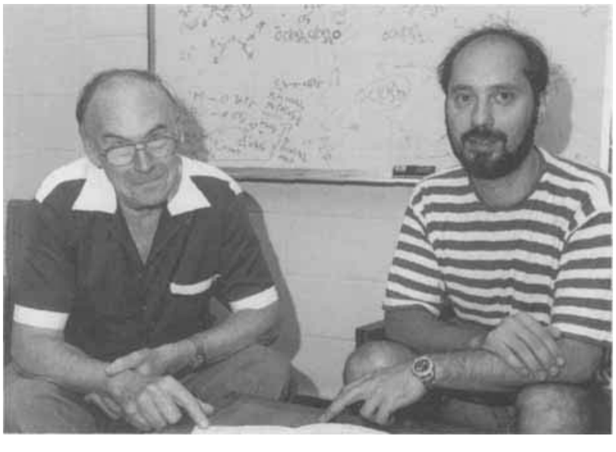
The preparation and reactivities of cyclohexyne and aryne complexes of platinum(0) and nickel(0) are reviewed. These complexes undergo insertions with unsaturated molecules such as alkenes, alkynes, isocyanides, CO and CO_2. In the case of the nickel–benzyne complexes, consecutive insertions are observed with alkynes, leading to substituted naphthalenes with good regioselectivities. A possible mechanism for these double insertions, based on a combination of steric and electronic factors, is discussed in detail.

1. Introduction

Transient unsaturated organic compounds can often be stabilized by coordination to a transition metal centre and their reactivity is thereby dramatically altered. One of the earliest and most elegant examples is the anti-aromatic hydrocarbon cyclobutadiene, which can be conveniently generated by oxidative degradation of its $Fe(CO)_3$ complex. In contrast to the free hydrocarbon, the complex is so stable that it will undergo typical aromatic substitution reactions[1]. The general principle has been applied to obtain transition metal complexes of short-lived, strained cyclic alkynes, such as cycloheptyne, cyclohexyne, and benzyne; detailed reviews have appeared[2–4]. In this account, we dis-

Martin Bennett (left) was born in Harrow, near London, England in August 1935. He graduated from Imperial College of Science, London in 1957 and obtained his PhD from the same institution in 1960 under the direction of the late Professor Sir Geoffrey Wilkinson. After postdoctoral studies at the University of Southern California with Professor Arthur Adamson and at University College London with the late Professor Sir Ronald Nyholm in the period 1960–1963, he was appointed Lecturer in Chemistry at University College London. In 1967 he moved to the Research School of Chemistry, Australian National University, where he is now Professor of Inorganic Chemistry. His research interests lie mainly in organo-transition metal chemistry and the activation of organic and inorganic molecules by transition metal compounds. Jointly with Professor Helmut Werner (University of Würzburg) he received a Max-Planck prize in 1994 and was elected Fellow of the Royal Society, London in 1995.



Eric Wenger (right) was born in Geneva, Switzerland in September 1961. He received his PhD from the University of Geneva in 1990 under the supervision of Professor E. Peter Kündig and joined the group of Professor Martin Bennett for postdoctoral work with a grant from the Swiss National Science Foundation in 1991. He became Research Fellow at the Research School of Chemistry in 1995 and, in 1997, was awarded a Queen Elizabeth II Fellowship by the Australian Research Council.

MICROREVIEWS: This feature introduces Berichte's readers to the authors' research through a concise overview of the selected topic. Reference to important work from others in the field is included.

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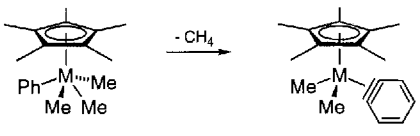
cuss recent work on the chemistry of such species with nickel(0) and platinum(0), and compare it where appropriate with that of the corresponding compounds with early transition metal fragments, especially bis(cyclopentadienyl)zirconium(II) (zirconocene).

2. Aryne and Strained Alkyne Complexes of the Early Transition Metals

Benzyne complexes were first implicated as transient intermediates in the thermal decomposition of bis(phenyl) derivatives of titanocene and zirconocene[2,4]. The first isolable η^2-benzyne complexes $[M(\eta^5\text{-}C_5Me_5)(\eta^2\text{-}C_6H_4)Me_2]$ (M = Ta, Nb) (**1**) were obtained by thermolysis of the organotantalum or organoniobium complexes $[M(\eta^5\text{-}C_5Me_5)PhMe_3]$ (Scheme 1)[5,6].

Scheme 1

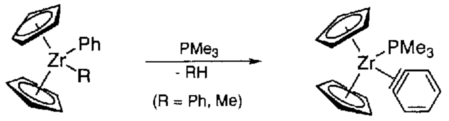


1

M = Ta, Nb

The elimination of benzene from a bis(phenyl) derivative, or of methane from a (methyl)(phenyl) derivative, has proved to be a general route to η^2-benzyne complexes of most of the early transition elements, i.e. titanium[7], zirconium[8], vanadium[9], niobium[10,11], tantalum[10,12,13], molybdenum[14], tungsten[14] and rhenium[15,16], and also ruthenium[17]. Common co-ligands are η^5-cyclopentadienyl, tertiary phosphanes, and η^1-alkyl or η^1-aryl groups; in the case of niobium or tantalum, 1,3-butadiene[12], alkylimido[11] and the *nido*-carborane anion $Et_2C_2B_4H_4$[13] have also been employed. Some examples of η^2-benzyne (or aryne) complexes, **2**–**5**, formed by the thermal β-hydrogen elimination procedure, are shown in Schemes 2–5.

Scheme 2



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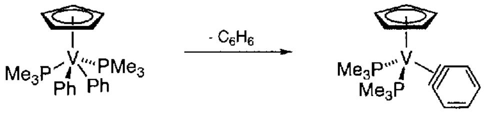
Scheme 3



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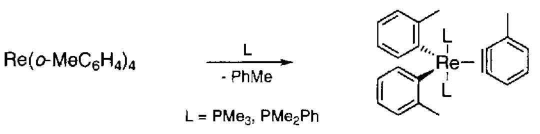
Scheme 4



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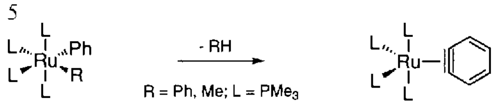
Scheme 5



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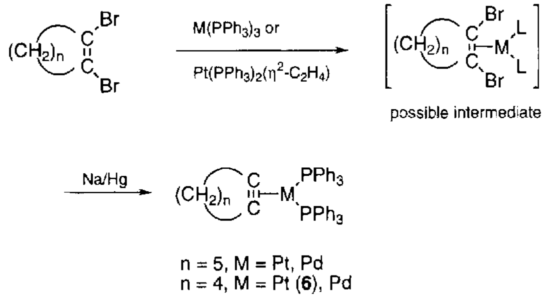
Zirconocene complexes of cyclohexyne[18], 3,3-dimethylcyclopentyne[19], and [2.2]-paracyclophane-1-yne[20] have been made similarly.

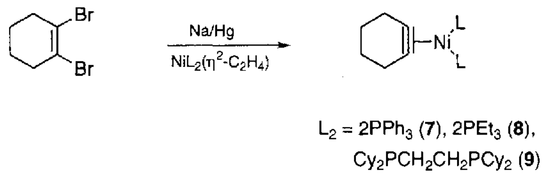
3. Aryne and Cyclic Alkyne Complexes of Nickel(0), Palladium(0), and Platinum(0)

Unfortunately these complexes cannot be made by the methods employed for the early transition metals because bis(phenyl) or (methyl)(phenyl) derivatives of Ni^{II}, Pd^{II}, and Pt^{II} do not eliminate benzene or methane, respectively, on heating. Cycloheptyne complexes $[M(PPh_3)_2(\eta^2\text{-}C_7H_{10})]$ (M = Pt, Pd)[21] and cyclohexyne complexes $[ML_2(\eta^2\text{-}C_6H_8)]$ [M = Pt (**6**), Pd, 2 L = 2 PPh_3[21]; M = Pt, 2 L = 2 $P\mathit{t}BuPh_2$, 2 $P\mathit{t}Bu_2Ph$[22]; M = Ni, 2 L = 2 PPh_3 (**7**), 2 PEt_3 (**8**), $Cy_2PCH_2CH_2PCy_2$ (**9**)[23]) are obtained by reduction of the appropriate 1,2-dibromocycloalkene with 1% sodium amalgam in the presence of a zerovalent metal complex (Schemes 6 and 7); the procedure has been applied also to the preparation of the $Pt(PPh_3)_2$ complexes of 4-homoadamantyne[24] and [2.2]-paracyclophane-1-yne[25].

Scheme 6



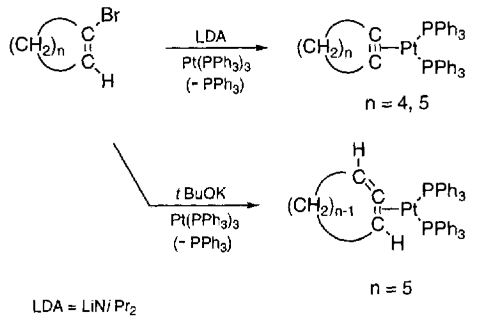
Scheme 7



In the case of 4-homoadamantyne, the authors suggest that the free alkyne is generated and trapped by Pt^0. For the cyclohexyne complexes, a more plausible alternative is that a zerovalent metal complex of 1,2-dibromocyclohexene, $[ML_2(\eta^2\text{-}1,2\text{-}Br_2C_6H_8)]$, is generated transiently and reduced rapidly. The corresponding sequence involving $[Pt(PPh_3)_2(\eta^2\text{-}1,2\text{-}Br_2C_5H_6)]$ has been established for the formation of the cyclopentyne complex $[Pt(PPh_3)_2(\eta^2\text{-}C_5H_6)]$[26].

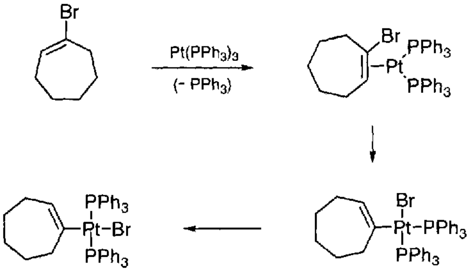
An alternative, high-yield route to the $Pt(PPh_3)_2$ complexes of cyclohexyne and cycloheptyne is to treat a mixture of the appropriate 1-bromocycloalkene and $[Pt(PPh_3)_3]$ with lithium diisopropylamide (LDA) (Scheme 8)[27]; use of *t*BuOK instead of LDA gives mainly the $Pt(PPh_3)_2$ complex of the isomeric cyclic allene, cyclohepta-1,2-diene, in the case of the seven-membered ring, and fails in the case of the six-membered ring. The reasons for these differences are unknown.

Scheme 8



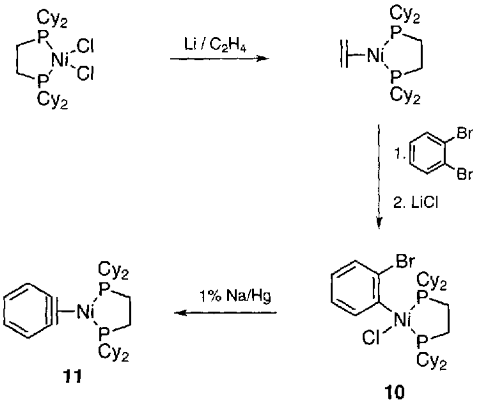
The LDA reaction probably proceeds by base-promoted elimination of HBr from a transient intermediate $Pt(PPh_3)_2$ complex of the 1-bromocycloalkene. Such a species could be detected in the reaction of $[Pt(PPh_3)_3]$ with 1-bromocycloheptene in the absence of LDA (Scheme 9). In the absence of base, it isomerizes first to the *cis*- and then to the *trans*-(1-cycloheptenyl)platinum(II) complexes, which are unaffected by base. The $Pt(PPh_3)_2$ complex of 1,2-dibromocyclopentene isomerizes similarly to *cis*- then *trans*-(1-bromocyclopentenyl)platinum(II) complexes[26].

Scheme 9



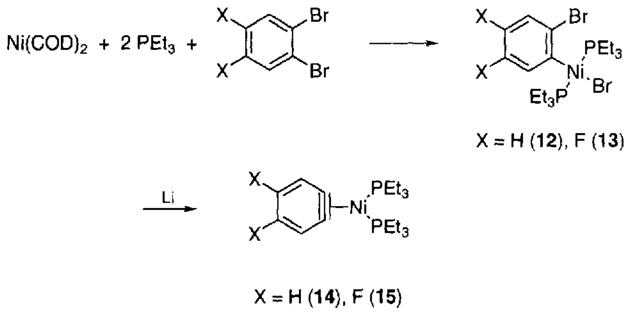
Although nickel(0)–benzyne complexes should in principle be accessible from Na/Hg reduction of a mixture of a 1,2-dibromoarene and a nickel(0)–phosphane complex, in practice it is more satisfactory to reduce a pre-formed (2-halogenoaryl)nickel(II) halide complex. Thus, the first nickel(0)–benzyne complex was made in two steps (Scheme 10): reaction of *o*-dibromobenzene with the ethylene complex $[Ni(dcpe)(\eta^2\text{-}C_2H_4)]$ (dcpe = $Cy_2PCH_2CH_2PCy_2$) gave, after treatment with Cl^-, the 2-bromophenylnickel(II) chloride $[NiCl(2\text{-}BrC_6H_4)(dcpe)]$ (**10**), which was reduced with 1% sodium-amalgam to give $[Ni(dcpe)(\eta^2\text{-}C_6H_4)]$ (**11**)[28].

Scheme 10



A more convenient route to nickel(II) precursors analogous to **10** is to reduce a mixture of the 1,2-dibromoarene and $[NiBr_2(PPh_3)_2]$ with zinc dust, giving $[NiBr(2\text{-bromoaryl})(PPh_3)_2]$, and then to replace the triphenylphosphane ligands by heating with dcpe. Reaction of the 1,2-dibromoarene $4,5\text{-}X_2C_6H_2Br_2$ with $[Ni(COD)_2]$ in the presence of 2.5 equivalents of triethylphosphane gives the nickel(II) complexes $[NiBr(2\text{-Br-}3,4\text{-}X_2C_6H_2)(PEt_3)_2]$ [X = H (**12**), F (**13**)], which are reduced by lithium to the corresponding nickel(0)–aryne complexes $[Ni(PEt_3)_2(1,2\eta\text{-}4,5\text{-}X_2C_6H_2)]$ [X = H (**14**), F (**15**)] (Scheme 11)[29].

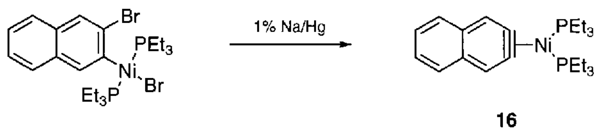
Scheme 11



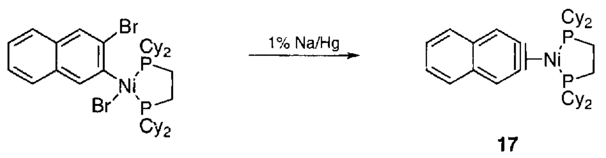
These bis(triethylphosphane) complexes are low melting solids that are much more sensitive to heat, air, and moisture than the corresponding dcpe complexes. They have been characterized by NMR (^1H, ^{13}C, ^{31}P) spectroscopy and are monomeric as shown by FAB mass spectrometry. The low-melting solid obtained in 1971 by lithium reduction of $[NiCl(2\text{-}BrC_6H_4)(PEt_3)_2]$, which was formulated as a dimeric μ-*o*-phenylenenickel(II) complex $[Ni_2(PEt_3)_2(\mu\text{-}o\text{-}C_6H_4)_2]$[30], is probably the monomeric benzyne complex $[Ni(PEt_3)_2(\eta^2\text{-}C_6H_4)]$ (**14**), although the reason for the high molecular weight values in the early report remains unclear.

The η^2-naphthalyne complexes $[NiL_2(2,3\eta\text{-}C_{10}H_6)$ [L_2 = 2 PEt_3 (**16**), dcpe (**17**)] are prepared by similar routes from 2,3-dibromonaphthalene, but in this case it is necessary to use the stronger reducing agent 1% sodium amalgam instead of lithium for the reduction step (Schemes 12 and 13)[31].

Scheme 12



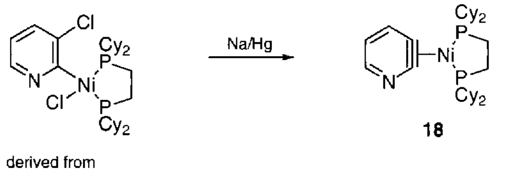
Scheme 13



Reduction of 2-chlorophenylnickel(II) halides [NiX(2-ClC_6H_4)L_2] (X = Cl, Br; L_2 = 2 PEt_3, dcpe) also requires 1% Na/Hg, indicating that the first step of the reduction occurs at the C−X bond. Attempts to prepare nickel(0)−benzyne complexes containing strongly electron-donating substituents such as OMe in the aromatic ring have failed owing to the instability of the nickel(II) precursors.

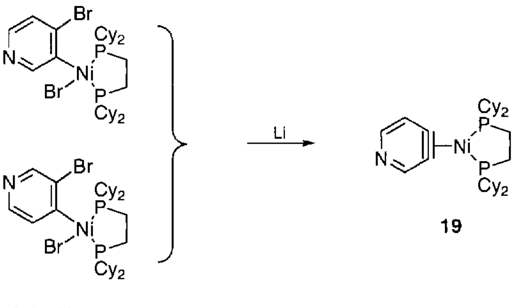
Alkali metal reduction of the appropriate *o*-halogenopyridylnickel(II) halide complexes gives species that have been identified tentatively on the basis of their ^{31}P-NMR spectra as nickel(0) complexes of 2,3- and 3,4-pyridyne, **18** and **19** respectively (Scheme 14 and 15), but these were too unstable thermally to be isolated or further characterized[32].

Scheme 14



derived from
2,3-dichloropyridine

Scheme 15

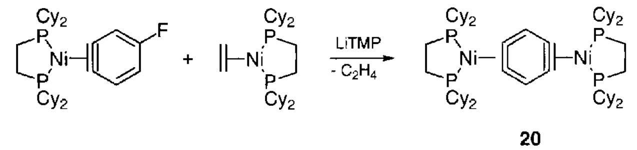


derived from
3,4-dibromopyridine

Platinum(0)−benzyne complexes [$PtL_2(\eta^2\text{-}C_6H_4)$] ($L_2$ = 2 PEt_3, 2 $PiPr_3$, 2 PCy_3, dcpe) can be made by reduction of (2-halogenophenyl)platinum(II) complexes with 43% sodium amalgam (both the 1% amalgam and lithium are ineffective), but their chemistry has not been studied in detail[33]. All attempts to prepare bis(triphenylphosphane) benzyne complexes of nickel(0) or platinum(0), [$M(PPh_3)_2(\eta^2\text{-}C_6H_4)$] (M = Ni, Pt), by the reductive procedure have been unsuccessful.

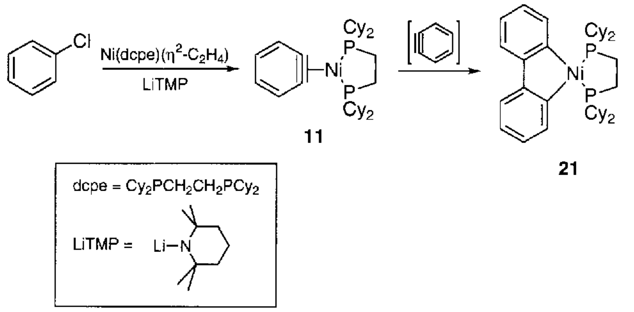
The high-yield preparation of the $Pt(PPh_3)_2$ complexes of cyclohexyne and cycloheptyne from [$Pt(PPh_3)_3$], LDA, and the appropriate 1-bromocycloalkene raises the question whether a similar route could be used to generate benzyne complexes from aromatic halides. Benzyne itself is formed by deprotonation of aromatic halides[34−36] and, if a non-nucleophilic base such as lithium 2,2,6,6-tetramethylpiperidide (LiTMP) is used, the benzyne can be trapped either with typical Diels-Alder reagents such as 1,3-diphenylisobenzofuran[37] or with an added nucleophile such as LiSPh[38]. The idea of trapping an aryne with a metal complex has already been employed in the high yield preparation of the dinickel(0) complex of 1,4-benzdiyne (1,2,4,5-tetradehydrobenzene) (**20**) shown in Scheme 16[39].

Scheme 16



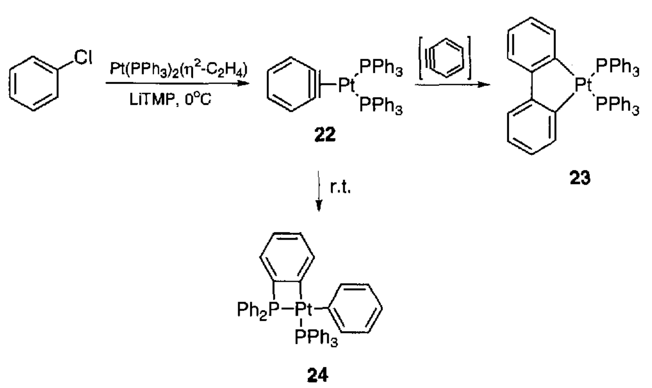
Indeed, slow treatment of an excess of chlorobenzene with LiTMP in the presence of [$Ni(dcpe)(\eta^2\text{-}C_2H_4)$] does form the benzyne complex [$Ni(dcpe)(\eta^2\text{-}C_6H_4)$] (**11**), as shown by ^{31}P-NMR spectroscopy. The problem is that free benzyne also inserts rapidly into the nickel−benzyne bond to form the 2,2′-biphenylylnickel(II) complex **21** (Scheme 17), which is the main product isolated if an excess of LiTMP is used[40]. We have been unable to control the reaction conditions to make **11** the main product, since it is not formed completely in the presence of ≤1 equivalent of LiTMP.

Scheme 17



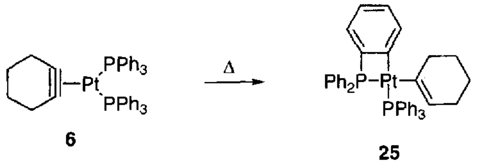
Similarly, the reaction of chlorobenzene with LiTMP and [$Pt(PPh_3)_2(\eta^2\text{-}C_2H_4)$] at 0°C generates successively the η^2-benzyne complex [$Pt(PPh_3)_2(\eta^2\text{-}C_6H_4)$] (**22**), and the 2,2′-biphenylylplatinum(II) complex **23** (Scheme 18).

Scheme 18



The benzyne complex has been identified on the basis of the similarity of its ^{31}P-NMR spectroscopic parameters to those of the cyclohexyne complex $[Pt(PPh_3)_2(\eta^2\text{-}C_6H_8)]$ (**6**). It isomerizes over a period of hours at room temperature by an intramolecular hydride migration to the cycloplatinated η^1-phenyl complex **24** (Scheme 18)[40]. A similar process occurs for **6**, though much more slowly (refluxing toluene for several days); the product is the η^1-cyclohexenyl complex **25** (Scheme 19)[41].

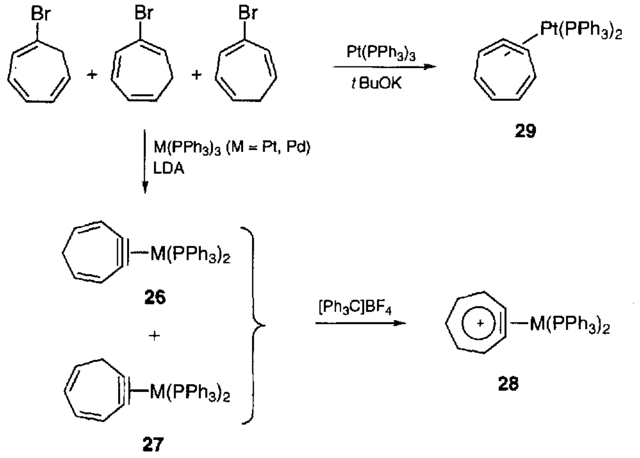
Scheme 19



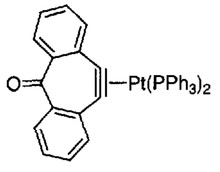
A general conclusion from all the preparative work is that the benzyne complexes are less easily formed and less stable than their cyclohexyne or cycloheptyne analogues. The success of the base-promoted reactions in forming the $Pt(PPh_3)_2$ complexes of cyclohexyne and cycloheptyne can be traced to the facts that much of the 1-bromocycloalkene coordinates through the double bond to $Pt(PPh_3)_2$ and that the resulting complex is rapidly deprotonated by LDA. In contrast, the aromatic halides coordinate only weakly and deprotonation therefore gives mostly free benzyne. Although the latter can be intercepted by the metal complex, it also inserts rapidly into the metal–benzyne bond of the resulting adduct.

The same methodology has been used to prepare the first tropyne complexes of d^{10} metals, $[M(PPh_3)_2(\eta^2\text{-}C_7H_5)]^+$ (M = Pt[27,42], Pd[43]). Reaction of a mixture of isomeric bromocycloheptatrienes with LDA in the presence of $[M(PPh_3)_3]$ gives a mixture of the two possible cycloheptadienyne complexes **26** and **27**, which are aromatized to the corresponding tropyne complex **28** by hydride abstraction with $[Ph_3C]BF_4$ (Scheme 20).

Scheme 20



In accordance with the usual trend, the platinum complex is stable up to 70°C, whereas the palladium analogue decomposes even at −35°C. In the case of platinum, use of *t*BuOK as base instead of LDA leads to the isomeric η^2-allene complex **29** (Scheme 20, see also Scheme 8)[27,44]. However, *t*BuOK has been used successfully to prepare dibenzannelated didehydrotropone (**30**), didehydrooxepin (**31**) and didehydrocycloheptatriene (**32**).



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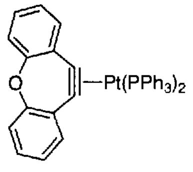

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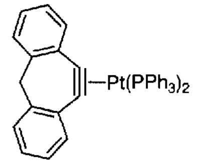

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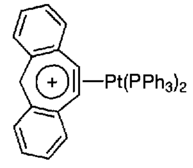


33

Complex **32** is converted into the dibenzannelated tropyne complex **33** on treatment with $[Ph_3C]BF_4$, but **32** is re-formed when $K[Et_3BH]$ is added to **33**[45]. Analogues of **26**–**28** containing a $Mo(CO)_3$ group bound to the π-electrons of the seven-membered rings have also been prepared[46].

4. Insertion Reactions into the Metal–Alkyne or Metal–Aryne Bond

4.1. General Remarks

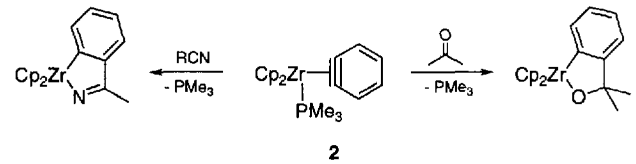
The reactivity of cyclic alkyne and aryne complexes of transition elements is dominated by two characteristic features:

(i) cleavage of the metal−alkyne or metal−aryne bond by electrophiles, especially acids (sometimes even weak acids such as water and methanol)[4,21];

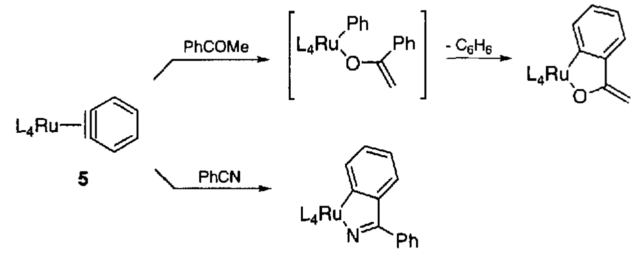
(ii) insertion of molecules containing multiple bonds, such as alkenes, alkynes, nitriles, aldehydes, ketones, CO, CO_2, and CS_2, into the metal−alkyne or metal−aryne bond.

The reactivity of a particular system depends strongly on the nature of the metal atom (early or late; first-, second- or third-row) and on the accompanying ligands. The zirconocene−benzyne and −cyclohexyne complexes seem to be the most reactive towards insertion, whereas the later transition metal complexes often undergo protonation in preference to insertion. The similarities and differences are exemplified in the reactions of **2** and **5** with methyl ketones and nitriles (Schemes 21 and 22).

Scheme 21



Scheme 22



The rhenium-*o*-methylbenzyne complexes (Scheme 4) and the tantalum−benzyne complexes containing the *nido*-carborane anion are remarkably inert towards insertion reactions.

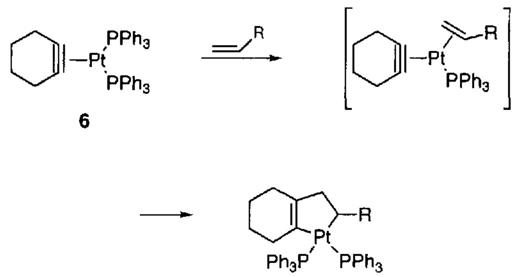
4.2. Cyclic Alkyne Complexes of Platinum(0) and Nickel(0)

In general, the platinum(0)−cyclohexyne complexes are less reactive than zirconocene−cyclohexyne towards the insertion of alkenes and alkynes. Thus, $[Pt(PPh_3)_2(\eta^2\text{-}C_6H_8)]$ reacts slowly on heating with the electrophilic olefins methyl vinyl ketone, acrolein, methyl acrylate, and acrylonitrile to give the corresponding platinacyclopentenes **34**−**37** (Scheme 23)[41].

In contrast, the disubstituted alkenes RCH=CR′R″ (R = H, R′ = Me, R″ = CHO, CO_2Me; R = Me, R′ = H, R″ = CHO, CO_2Me) give $[Pt(PPh_3)_2(\eta^2\text{-alkene})]$ as the only identifiable organometallic product; the fate of the cyclohexyne has not been determined. A similar reaction occurs slowly with a large excess of styrene.

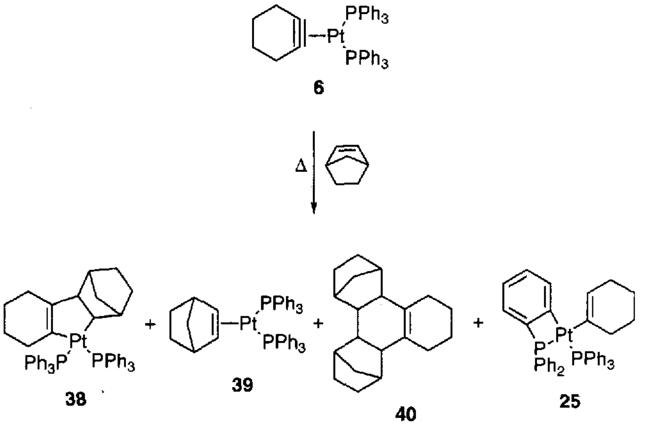
The strained alkene norbornene gives mainly the insertion product **38**, in addition to small amounts of $[Pt(PPh_3)_2(\eta^2\text{-norbornene})]$ (**39**), the cycloplatinated complex **25** and a mixture of isomers of organic compound **40** probably derived from coupling of cyclohexyne with two molecules of norbornene (Scheme 24). Dimethyl maleate and dimethyl fumarate also give mixtures of the corresponding isomeric insertion products with the $[Pt(PPh_3)_2(\eta^2\text{-olefin})]$ complexes[41].

Scheme 23



R = COMe (**34**), CHO (**35**), CO_2Me (**36**), CN (**37**)

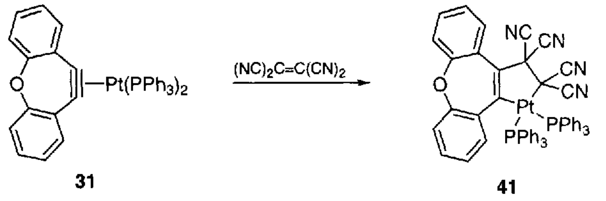
Scheme 24



The regioselectivity observed in the formation of the platinacyclopentenes (Scheme 23) is consistent with attack of the electron-rich coordinated cyclic alkyne on the electron-deficient carbon atom of the alkene. The reactions are inhibited by free PPh_3, so they probably proceed by initial dissociation of one PPh_3 ligand and formation of a cyclic alkyne−alkene intermediate (Scheme 23). In agreement, the alkenes do not undergo insertion reactions with $[Pt(R_2PCH_2CH_2PR_2)(\eta^2\text{-}C_6H_8)]$ (R = Ph, Cy), although the corresponding insertion products can be obtained by displacement of PPh_3 from **34** with the chelate ligand. Treatment of **34** with the chiral ditertiary phosphane (*S*,*S*)-*o*-$C_6H_4(PMePh)_2$ immediately gives a 2:1 mixture of the two possible diastereomers. This observation shows that the (*R*)- and (*S*)-configurations of the carbon atom bearing the acyl group in **34** are in rapid equilibrium, probably owing to keto−enol tautomerism[41].

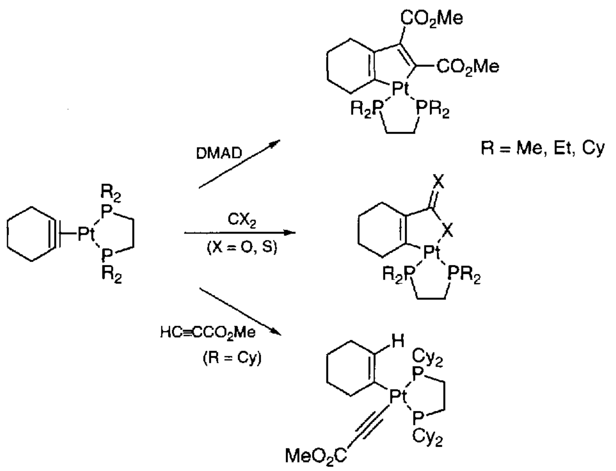
The cyclohexyne and dibenzannelated didehydrotropone complexes, $[Pt(PPh_3)_2(\eta^2\text{-}C_6H_8)]$ (**6**) and $[Pt(PPh_3)_2\{\eta^2\text{-}C_2(C_6H_4)_2CO\}]$ (**30**), react with TCNE to give $[Pt(PPh_3)_2(\eta^2\text{-TCNE})]$; in the latter case the acetylene is released and isolated in the form of an aromatic cyclotrimer. Surprisingly, treatment of $[Pt(PPh_3)_2\{\eta^2\text{-}C_2(C_6H_4)_2O\}]$ (**31**) with TCNE gives a mono-insertion product **41** (Scheme 25)[45].

Scheme 25



The complexes [$PtL_2(\eta^2-C_6H_8)$] (L_2 = 2 PPh_3 (**6**), dppe)[21], and the dibenzannelated cycloheptadieneyne complexes **30**–**33**[45] do not react with diphenylacetylene, but in view of the result with activated olefins, it is surprising that **6** reacts neither with electrophilic alkynes such as methyl propiolate and dimethyl acetylenedicarboxylate (DMAD) nor with CS_2, all of which could have been expected to displace PPh_3 from platinum(0). Complexes [$PtL_2(\eta^2-C_6H_8)$] containing more strongly basic bidentate ditertiary phosphanes [L_2 = $Me_2PCH_2CH_2PMe_2$ (dmpe), $Et_2PCH_2CH_2PEt_2$ (depe), $Cy_2PCH_2CH_2PCy_2$ (dcpe)], do however, give the expected insertion products with DMAD, CS_2, and CO_2 (Scheme 26). In contrast to the reactions of olefins with **6**, these insertions evidently do not require prior dissociation of tertiary phoshane; they may proceed through highly polar intermediates or transition states.

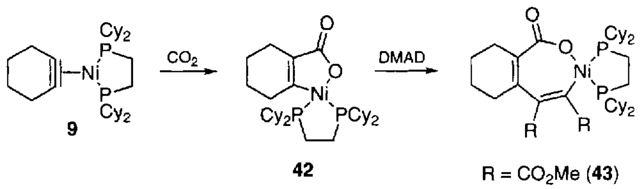
Scheme 26



Alkynes such as but-2-yne, 1-phenylprop-1-yne, bis(trimethylsilyl)acetylene, or di-*tert*-butylacetylene do not react with [$PtL_2(\eta^2-C_6H_8)$][47]. The complex [$Pt(dcpe)(\eta^2-C_6H_8)$] is protonated by methyl propiolate to give an acetylide complex, [$Pt(\eta^1-C_6H_9)(\eta^1-C{\equiv}CCO_2Me)(dcpe)$] (Scheme 26), rather than giving the expected insertion product[48].

The cyclohexyne-nickel(0) complexes [$NiL_2(\eta^2-C_6H_8)$] [L_2 = 2 PPh_3 (**7**), 2 PEt_3 (**8**), dcpe (**9**)] are much more reactive than the platinum(0) complexes towards unsaturated molecules[23]. They react readily with ethylene to give [$NiL_2(\eta^2-C_2H_4)$] and with alkynes (hex-3-yne, DMAD) to give the corresponding alkyne complexes. These reactions may be double or multiple insertions similar to those of [$Pt(PPh_3)_2(\eta^2-C_6H_8)$] with norbornene and of the benzyne–nickel(0) complexes with acetylenes (see below), but the organic products have not been identified. Insertion products also could not be isolated from the rapid reactions of **7** and **8** with CO_2 and CS_2, although it was established that cyclohexyne was not released. In contrast, **9** reacts with CO_2 to give the expected insertion product **42**, the nickel–aryl bond of which undergoes insertion with DMAD to give **43** containing a seven-membered chelate ring (Scheme 27).

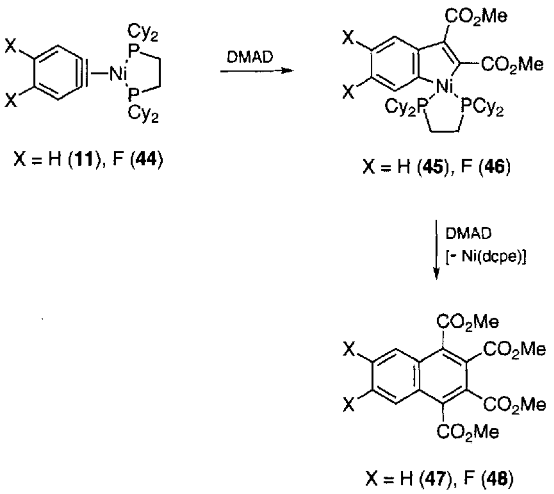
Scheme 27



4.3. Aryne Complexes of Nickel(0)

The nickel(0) complexes of benzynes and 2,3-naphthalyne are much more reactive than the platinum(0) complexes of cyclohexyne towards alkenes and alkynes, and show a more marked tendency to undergo sequential insertions. For example, slow addition of DMAD to the benzyne complex [$Ni(dcpe)(\eta^2-C_6H_4)$] (**11**) gives the isolable nickelaindene complex **45**[28], which readily reacts with more DMAD to give, after reductive elimination of Ni(dcpe), the tetrasubstituted naphthalene 1,2,3,4-$(CO_2Me)_4C_{10}H_4$ (**47**) (Scheme 28).

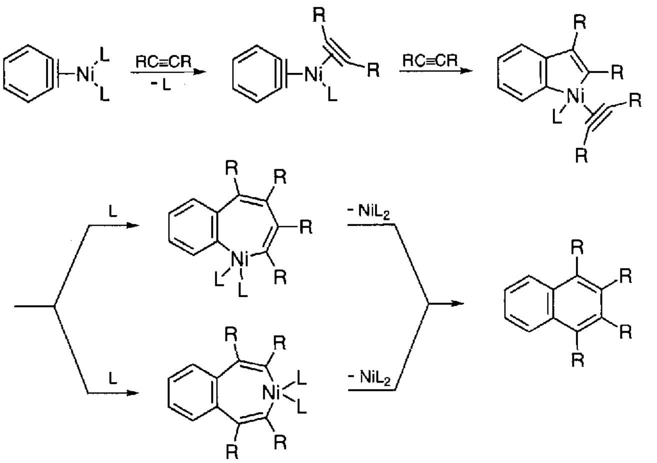
Scheme 28



A similar sequence takes place with the 4,5-difluorobenzyne complex [$Ni(dcpe)(1,2\eta-C_6H_2F_2)$] (**44**); in this case, the intermediate nickelaindene **46** can only be detected spectroscopically[29]. In general, the PEt_3 complexes are more reactive than their dcpe analogues, which suggests that one PEt_3 ligand must dissociate before the acetylene coordinates. Thus, the 2,3η-naphthalyne complex [$Ni(PEt_3)_2(\eta^2-C_{10}H_6)$] (**16**) reacts with diphenylacetylene to give 1,2,3,4-tetraphenylanthracene, whereas the dcpe analogue **17** fails to react[31]. The bis(triethylphosphane) complex [Ni(PEt$_3$)$_2$(1,2η-4,5-F$_2$C$_6$H$_2$)] (**15**) reacts with hex-3-yne at −25°C to give 1,2,3,4-tetraethyl-6,7-difluoronaphthalene in good yield, whereas the dcpe analogue **44** requires 16 h at room temperature[29].

As illustrated for benzyne complexes in Scheme 29, these insertions are supposed to proceed by reversible dissociation of one phosphane ligand and formation of a nickelaindene (observed only for **45** and its difluoro analogue **46**).

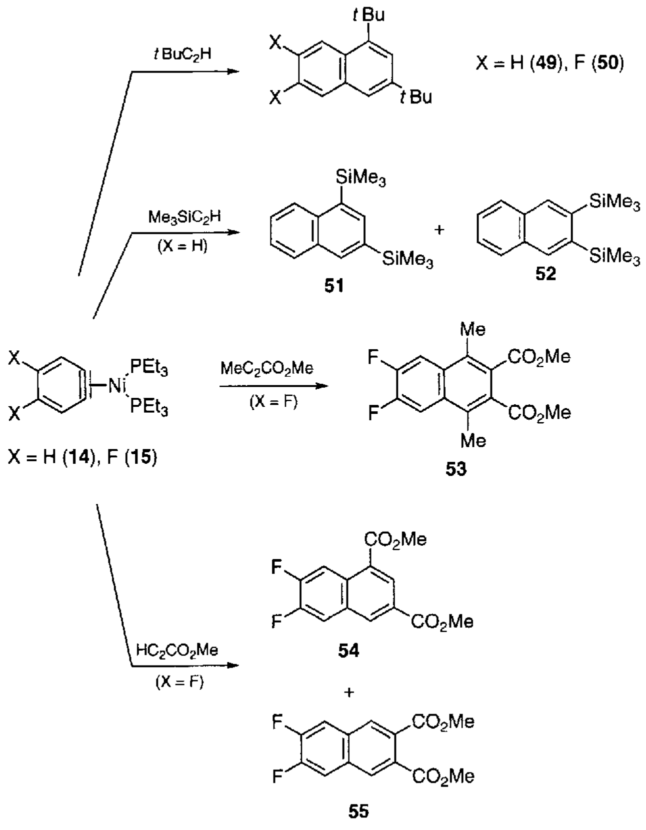
Scheme 29



In principle, the second molecule of acetylene could insert either into the nickel−vinyl bond or the nickel−aryl bond of this intermediate, leading to isomeric benzonickelacycloheptatrienes. Finally, reductive elimination of NiL$_2$ from either of these compounds gives the tetrasubstituted naphthalene.

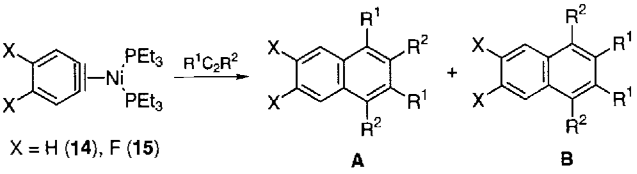
Double insertions of this type occur also with unsymmetrical acetylenes, often with surprisingly good regioselectivities (Scheme 30).

Scheme 30



We have studied these reactions in some detail because of their obvious relationship to the well-known but still poorly understood oligomerisation (especially cyclotrimerisation) of acetylenes catalysed by a variety of transition metal-based systems[49−52]. The results are summarised in Table 1. Thus, *tert*-butylacetylene reacts with the benzyne−nickel(0) complexes **14** and **15** to give exclusively the 1,3-disubstituted naphthalenes **49** and **50**.

Table 1. Isomer distributions for the reaction of **14** and **15** with unsymmetrical acetylenes

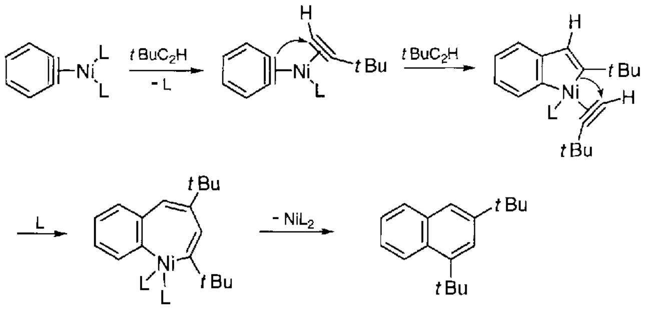


Entry	Complex	Added PR$_3$	R1	R2	Isomeric Ratio (%) A	B	Yield
1	**14**	no	*t*Bu	H	100	0	56%
2	**15**	no	*t*Bu	H	100	0	45%
3	**14**	no	SiMe$_3$	H	86	14	50%
4	**14**	PPh$_3$	SiMe$_3$	H	85	15	55%
5	**15**	no	CO$_2$Me	Me	0	100	57%
6	**15**	no	CO$_2$Me	H	39	61	33%
7	**15**	PEt$_3$	CO$_2$Me	H	26	74	56%
8	**15**	PPh$_3$	CO$_2$Me	H	20	80	66%
9	**14**	PPh$_3$	CO$_2$Me	H	23	77	81%
10	**14**	PPh$_3$	CO$_2$*t*Bu	H	62	38	73%

Trimethylsilylacetylene behaves similarly to *tert*-butylacetylene with **14**, giving a 6:1 mixture of the 1,3- and 2,3-bis(trimethylsilyl)naphthalenes **51** and **52**. In contrast, double insertion of methyl 2-butynoate with **15** gives dimethyl 1,4-dimethyl-6,7-difluoronaphthalene-2,3-dicarboxylate (**53**) in 57% yield as the only naphthalene-containing product. Reaction of methyl propiolate with **15** gives the 1,3- and 2,3-dicarboxylates 1,3-(CO$_2$Me)$_2$-6,7-F$_2$C$_{10}$H$_4$ (**54**) and 2,3-(CO$_2$Me)$_2$-6,7-F$_2$C$_{10}$H$_4$ (**55**) in a ratio of ca. 1 to 1.5, although in this case the yield was only 33% owing to fast competing cyclotrimerisation of the alkyne catalysed by the NiL$_2$ fragment formed by reductive elimination. This process, which is always a problem with the activated acetylenes, can be largely though not completely suppressed by addition of free tertiary phosphane to trap NiL$_2$. A similar observation was made by Carmona et al.[53] in their study of the insertion of acetylenes into the nickelaindane complex [$\overline{\text{Ni(CH}_2\text{CMe}_2\text{-}o\text{-C}}_6H_4$)(PMe$_3$)$_2$] to give 1,2-dihydronaphthalenes. Thus, reaction of methyl propiolate with **15** in the presence of PEt_3 (2 equivalents) at −30°C gave a 1:2.8 mixture of **54** and **55** in 56% yield; under the same conditions, use of two equivalents of PPh_3 instead of PEt_3 gave a 1:4 ratio of **54** and **55** in 66% yield. Similarly, methyl propiolate reacted with **14** in the presence of PPh_3 (two equivalents) to give the dimethyl 1,3- and 2,3-naphthalenedicarboxylates, in a 1 to 3.3 ratio and 81% yield. The corresponding reaction of *tert*-butyl propiolate with **14** under the same conditions also gave a high yield of the di-*tert*-butyl compounds 1,3- and 2,3-$(CO_2\text{-}t\text{Bu})_2C_{10}H_6$, but the proportion of 1,3-isomer had increased markedly (mol ratio 1.6:1). In all cases, some aromatic cyclotrimer was also formed (3 to 20% based on the acetylenes)[54].

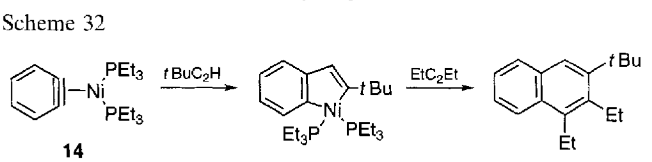
In the case of unsymmetrical acetylenes, the substitution pattern of the final napththalene is determined by the regioselectivity of the successive insertions. Two arguments lead us to believe that, in the first step of insertion of *tert*-butylacetylene, the Ni−C bond of **14** and **15** initially attacks the sterically less hindered carbon atom of the coordinated acetylene to give a metallaindene in which the *tert*-butyl substituent is adjacent to nickel (Scheme 31).

Scheme 31



First, we studied the reaction of **14** with a mixture of *tert*-butylacetylene and hex-3-yne in a 1:3 ratio, the former being known to react faster with a nickel−benzyne complex than the latter[29]. The product is a mixture of 1,2,3,4-tetramethylnaphthalene, formed by double insertion of hex-3-yne, and 1,2-diethyl-3-*tert*-butylnaphthalene, formed by sequential insertion of *tert*-butylacetylene and hex-3-yne (Scheme 32); the large excess of hex-3-yne suppresses the formation of 1,3-di-*tert*-butylnaphthalene.

Scheme 32



Second, the same regioselectivity is observed in the insertion of phenylpropyne and other unsymmetrical acetylenes into the nickel−methyl bonds of $[NiMe(acac)(PPh_3)]$[55] and $[NiClMe(PMe_3)_2]$[56], in which the methyl group attacks the less hindered carbon atom of the acetylene to give a η^1-vinyl complex having the more bulky substituent next to the metal.

The insertion of the second molecule of *tert*-butylacetylene could occur either into the nickel−vinyl or the nickel−aryl bond. Since the regioselectivity of this step is likely to be the same as that of the first, the exclusive formation of 1,3-di-*tert*-butylnaphthalene is best explained if the acetylene inserts into the nickel−vinyl bond (Scheme 31).

For the first insertion of methyl propiolate, *tert*-butylpropiolate or methyl 2-butynoate, the same direction of addition as postulated for *tert*-butylacetylene could result from electronic as well as steric control, i.e. the Ni−C bond of **14** and **15** could preferentially attack the electron-poor β-carbon atom of the acetylenic ester. The second insertion in the case of methyl 2-butynoate may proceed under electronic control by attack on the electrophilic carbon atom of the nickelaindene by the coordinated alkyne in its allenol resonance form (analogous to the one drawn for methyl propiolate in Scheme 33). The resulting benzonickelacycloheptatriene contains adjacent ester groups, hence reductive elimination of NiL_2 leads to the naphthalene-2,3-dicarboxylate.

Presumably, for methyl and *tert*-butyl propiolates, both steric and electronic effects operate in the second insertion step, hence both 2,3- and 1,3-isomers are formed. The former is favoured for methyl propiolate, the latter for *tert*-butyl propiolate. This trend is likely to occur as a result of steric repulsion between the *tert*-butyl groups in the pathway leading to the 2,3-isomer. The competing electronically and sterically controlled pathways are illustrated for the reaction of methyl propiolate with **15** in Scheme 33.

The increase in proportion of the 2,3-isomer in the presence of PPh_3 (entries 8 and 9 of Table 1) may be a consequence of steric hindrance between the more bulky ligand (which can exchange with the coordinated PEt_3) and the ester group of the incoming acetylene, thus favouring the pathway leading to the 2,3-isomer.

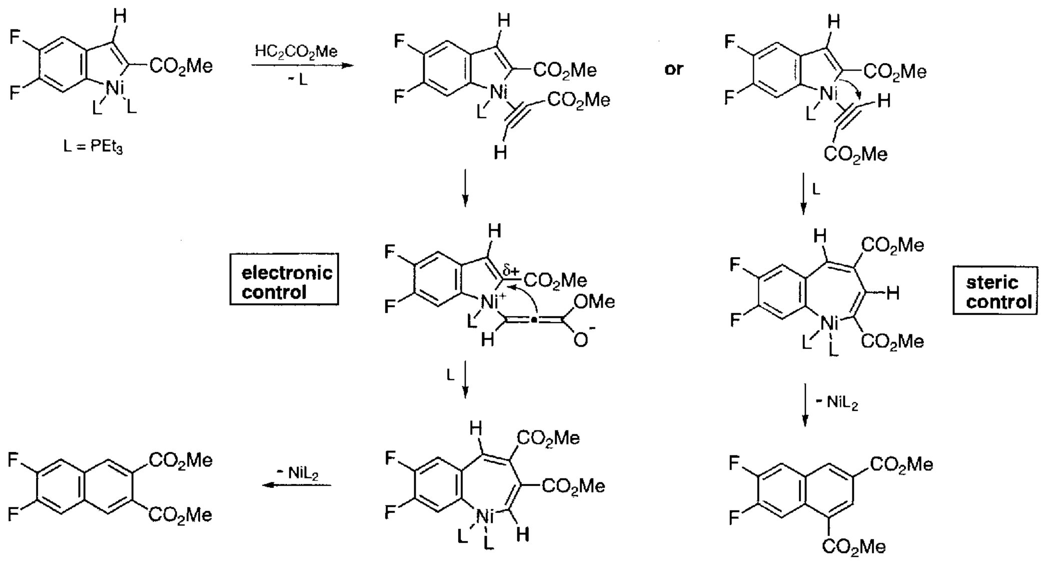
A case in which the second alkyne insertion is under purely electronic control is that of the reaction of the nickelaindene **45** with methyl propiolate, which gives trimethyl 1,2,3-naphthalenetricarboxylate but none of the 1,2,4-isomer (Scheme 34). Presumably the two ester groups in **45** make the nickel-bound carbon atom highly electrophilic, thus driving the reaction along the electronically controlled pathway (Scheme 33).

It is of interest that an excess of octa-1,7-diyne reacts with **14** to give 1,2,3,4-tetrahydroanthracene, isolated in 48% yield, as the only product of double insertion[54]. This observation can be accounted for as shown in Scheme 35.

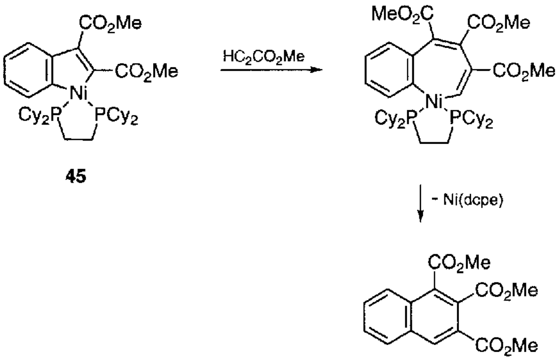
The first insertion, as usual, forms the nickelaindene **56** in which the substituted carbon is attached to the metal. The carbon chain carrying the second triple bond is too short to allow insertion into the nickel−aryl bond; hence, in this case, the alkyne has no alternative but to insert into the nickel−vinyl bond, forming the observed product via the benzonickelacycloheptatriene **57**. The direction of this second insertion, however, is opposite to that occuring with *tert*-butylacetylene, since the length of the carbon chain does not allow the substituted carbon to be adjacent to nickel.

The regioselectivity of the acetylene insertions into the metal−benzyne bonds of **14** and **15** can be compared with that of the corresponding reactions with the nickelaindane

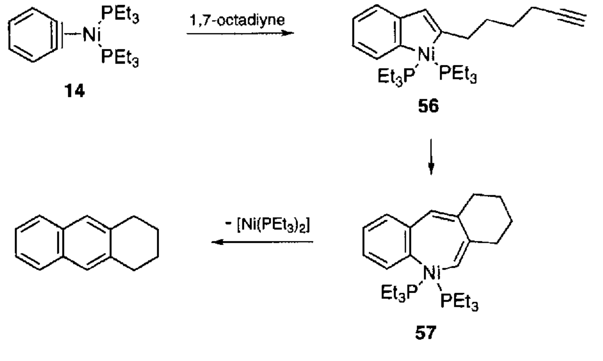
Scheme 33



Scheme 34

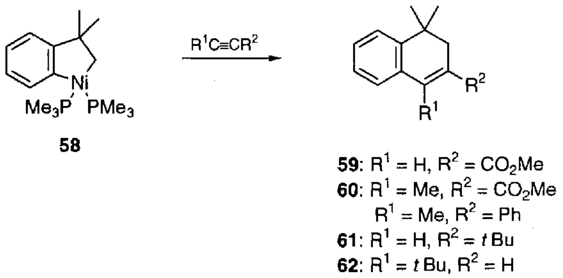


Scheme 35



$[\overline{Ni(CH_2CMe_2\text{-}o\text{-}C_6H_4)}(PMe_3)_2]$ (**58**), which give dihydronaphthalenes after reductive elimination of the Ni(PMe$_3$)$_2$ fragment (Scheme 36)[53,57].

Scheme 36

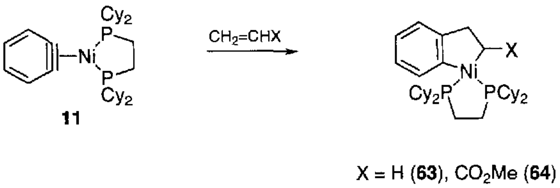


In this case, the alkyne inserts exclusively into the nickel−phenyl bond, apparently because the PMe$_3$ ligand trans to the Ni−C(sp^3) bond is more labile than that trans to the Ni−C(sp^2) bond, hence the alkyne enters the coordination sphere cis to the nickel−phenyl bond. The stereospecificity of the reactions with methyl propiolate and methyl but-2-ynoate to give **59** and **60**, respectively, are the same as those of **14** and **15** with the latter acetylene, and presumably both reactions are under electronic control. On the other hand, *tert*-butylacetylene gives a 2.2 to 1 mixture of **61** and **62**. In this case, the preference for the nickel−phenyl bond to attack the sterically less hindered alkyne carbon atom seems less marked than in the case of **14** and **15**, although an alternative pathway where *tert*-butylacetylene, for steric reasons, also inserts with the expected regioselectivity into the Ni−CH$_2$ bond cannot be ruled out; such insertions have been observed for formaldehyde[57] or CO[58].

Dihapto-benzyne complexes of earlier transition elements, either isolated or generated in situ, generally undergo mono-insertion of disubstituted alkynes to give isolable metallaindenes, but these apparently resist further insertion, presumably because there is no readily available coordination site for an additional acetylene molecule. A possible exception is provided by the reactions of triphenylchromium(III) with but-2-yne or tolane, which give 1,2,3,4-tetramethylnaphthalene or 1,2,3,4-tetraphenylnaphthalene, respectively, in addition to the cyclotrimer of the acetylene[59–62]. These products have been suggested to arise by reaction of the acetylene with an intermediate benzyne–chromium species formed from triphenylchromium, although alternative mechanisms have been proposed[63].

In contrast with acetylenes, olefins do not appear to undergo sequential insertions into nickel–benzyne complexes. Thus, [Ni(dcpe)(η^2-C_6H_4)] (**11**) reacts with ethylene (3 bar)[28] and with methyl acrylate[64] to give the nickelaindane complexes **63** and **64** (Scheme 37), the regiospecificity in the latter case being the same as that of the reaction with [Pt(PPh_3)$_2$(η^2-C_6H_8)] (Scheme 23).

Scheme 37

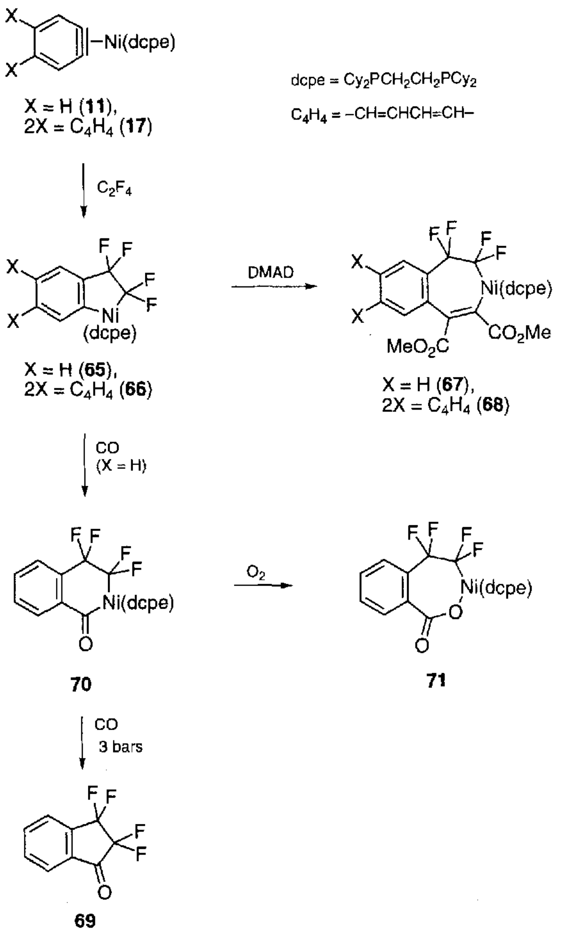


Similarly, the more electrophilic olefin tetrafluoroethylene reacts readily with **11** and with its 2,3η-naphthalyne analogue [Ni(dcpe)(η^2-$C_{10}H_6$)] (**17**) to form the very stable tetrafluoronickelaindanes **65** and **66** (Scheme 38)[65].

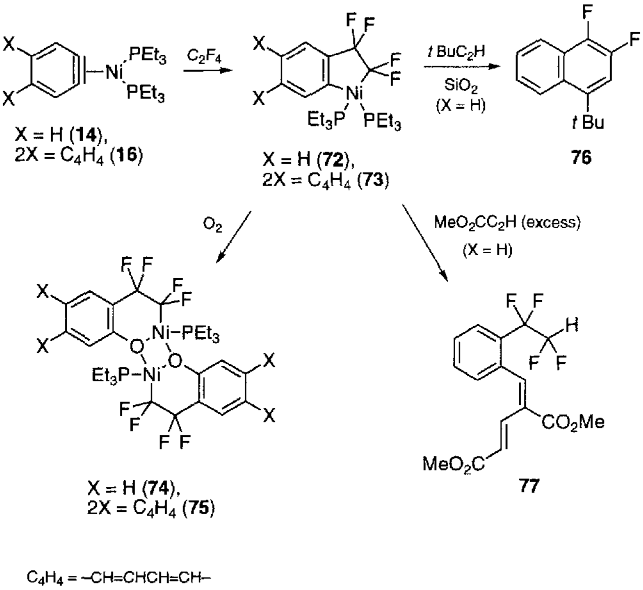
These compounds are unreactive towards alkenes and most alkynes, although DMAD inserts slowly into the nickel–aryl bonds (not the Ni–CF_2 bonds) to give the seven-membered nickelacycles **67** and **68**. Complex **65** also reacts slowly with CO to form 2,2,3,3-tetrafluoroindanone (**69**). This reaction occurs by CO insertion into the nickel–aryl bond of **65** to give a spectroscopically detectable intermediate acyl complex **70** which, under CO, undergoes reductive elimination of the Ni(dcpe) fragment with formation of **69**. In the presence of oxygen, **70** forms the stable carboxylato complex **71**. The preference of CO and DMAD to insert into the Ni–aryl rather than the Ni–CF_2 bond is in accord with the well-known reluctance of fluoroalkyl (and, more generally, electron-withdrawing alkyl) groups attached to transition metals to undergo insertion of CO[66].

The triethylphosphane complexes [Ni(PEt_3)$_2$(η^2-C_6H_4)] (**14**) and [Ni(PEt_3)$_2$(2,3η-$C_{10}H_6$)] (**16**) also insert C_2F_4, but the resulting nickelaindanes **72** and **73** are much more reactive than their dcpe analogues owing to the tendency of PEt_3 to dissociate (Scheme 39)[65]. Thus, in the presence of oxygen, one PEt_3 ligand is removed irreversibly in the form of triethylphosphane oxide and an oxygen atom inserts into the nickel–aryl bond to form the dimeric μ-aryloxonickel complexes **74** and **75**. Structurally similar μ-alkoxo compounds have been obtained by Carmona and coworkers[57] from the insertion of formaldehyde into the Ni–CH_2 bond of [Ni(CH_2CMe_2-o-C_6H_4)(PMe_3)$_2$] (**58**).

Scheme 38



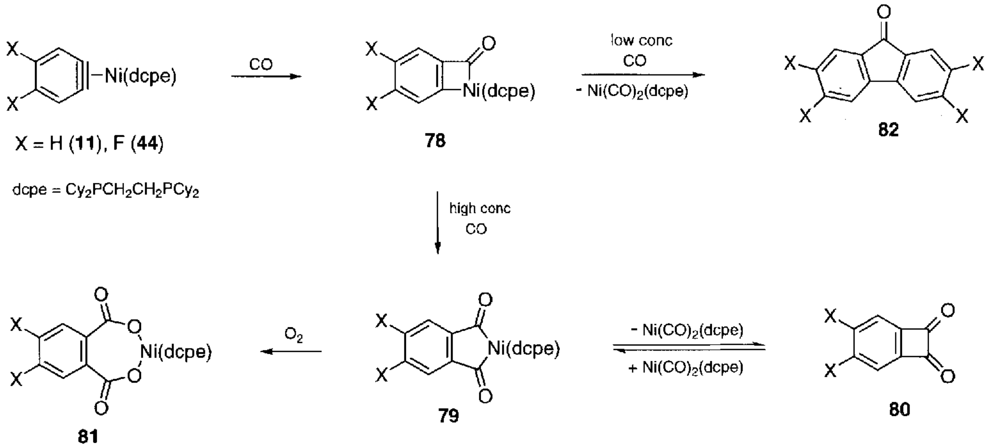
Scheme 39



Complexes **72** and **73** also react with acetylenes. For example, *tert*-butylacetylene with **72** gives, after chromatography on silica gel, 1,2-difluoro-4-*tert*-butylnaphthalene (**76**), which presumably arises by insertion of the acetylene and subsequent aromatisation on work-up (Scheme 39). It should be pointed out that, if the acetylene insertion occurs at the nickel–aryl bond rather than the Ni–CF_2 bond (which seems likely but is not proven), then the regioselectivity is opposite to that found in the sequential acetylene insertions discussed previously. The reasons for this reversal are not known at present. An excess of methyl propiolate apparently undergoes double insertion into the nickel−aryl bond of **72**. The product isolated is the 1,2-disubstituted aromatic compound **77**, which presumably arises by protonation of the intermediate insertion product.

The nickel(0) complexes of benzyne and 4,5-difluorobenzyne, [Ni(dcpe)(1,2η-4,5-$X_2C_6H_2$)] [X = H (**11**), F (**42**)] react readily with CO, but the nature of the products depends on conditions, especially the concentration of CO[67]. The only organometallic product that has been isolated under all conditions is [$Ni(CO)_2$(dcpe)]. As shown in Scheme 40, the first step is believed to be insertion of one CO, giving a highly reactive and so far unobserved benzonickelacyclobutenone **78**. A second molecule of CO inserts into the nickel−aryl bond of **78** to give a phthaloylnickel(II) complex **79**, which has been detected by ^{31}P- and ^{19}F-NMR spectroscopy for X = F. Complex **79** reversibly eliminates [$Ni(CO)_2$(dcpe)] to form the benzocyclobutene-1,2-dione **80** and is oxidized irreversibly in the presence of air to give the phthalatonickel(II) complex **81**. Under low CO concentrations, the second insertion of CO is very slow, so **78** reacts with its precursor to form the fluorenone **82**, again with elimination of [$Ni(CO)_2$(dcpe)].

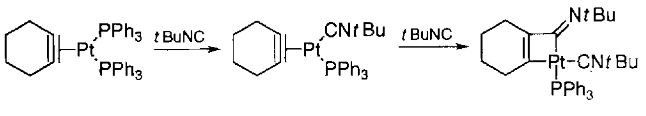
Scheme 40



Although mono-carboxylato complexes can be made by direct insertion of CO_2 into the nickel−benzyne and −naphthalyne bonds of cmplexes **11** and **17**, insertion of a second molecule of CO_2 to form complexes analogous to **81** does not occur[28,31].

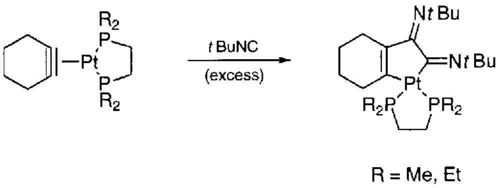
Support for the proposed benzonickelacyclobutenone **78** as an intermediate in Scheme 40 is provided by the isolation of an analogous complex containing a four-membered ring from the reaction of *tert*-butyl isocyanide with [$Pt(PPh_3)_2(\eta^2-C_6H_8)$] (**6**) (Scheme 41)[21].

Scheme 41

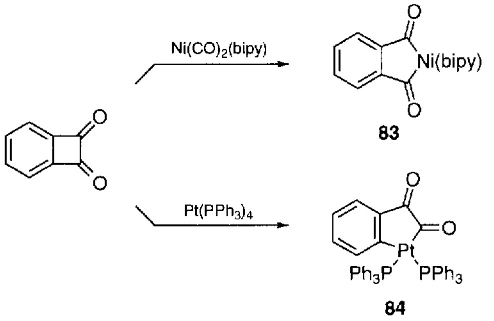


However, the regioselectivity for the insertion of a second *t*BuNC molecule in the Pt−C_6H_8 system differs from that of a second CO molecule in the Ni−C_6H_4 system, as is clear from Scheme 42[47].

Scheme 42



Scheme 43



A closely related difference, which is probably thermodynamic in origin, is evident from a comparison of the behaviour of benzocyclobutene-1,2-dione with the nickel(0) complex [$Ni(CO)_2$(bipy)] and with the platinum(0) complex [$Pt(PPh_3)_4$] (Scheme 43). In the first case, the CO−CO bond is cleaved, giving the phthaloylnickel(II) complex **83**[68], whereas in the second case a phenyl−CO bond is cleaved giving the α-ketoacyl complex **84**[69].

5. Conclusions

Free benzyne and cyclohexyne behave as strongly electrophilic alkynes, which characteristically undergo nucleophilic additions, Diels-Alder reactions with dienes, and [2 + 2]-cycloaddition reactions[34−36]. The formation of stable benzyne- and cyclohexyne-complexes with low-valent, electron-rich metal systems can be regarded as a particular example of the electrophilicity of these strained alkynes. The reactivity of the nickel(0) and platinum(0) complexes is, therefore, very different from that of the free alkynes, but their nucleophilic behaviour is characteristic of σ-bonded complexes of nickel(II) and platinum(II) in which the metal−carbon σ-bonds are highly strained. In many respects, therefore, a benzyne complex is best regarded as a benzometallacyclopropene. The sequential insertion of acetylenes into the nickel−benzyne bond to give substituted naphthalenes is closely related to the well-known metal-catalysed cyclotrimerisation of acetylenes to arenes, its regioselectivity being governed by a delicate combination of steric and electronic effects. The step that controls the regioselectivity of these processes seems to be the second insertion into the nickelaindene or nickelaindane resulting from the first insertion of an alkyne or alkene, respectively. The nature of the different nickel−carbon bonds present in the five-membered nickelacycles is also crucial. From our observations, together with those of Carmona et al.[53], the relative reactivities of $Ni^{II}-C$ bonds towards insertion of an alkyne seem to follow the order Ni−vinyl > Ni−aryl > $Ni-CH_2$ > $Ni-CF_2$. Preliminary calculations on the model complexes $[Ni(PH_3)_2(CH_3)R]$ and $Ni(PH_3)(C_2H_2)(CH_3)R$ ($R = CH_3, CF_3, C_2H_3$) suggest that the ordering of the Ni−R bond strengths ($CF_3 \approx C_2H_3 > CH_3$) alone is not responsible for the regioselectivity of the insertions. However, computation of the energies released upon C_2H_2 insertion into the Ni−R bonds (energy for $R = C_2H_3 > CH_3 > CF_3$) reveals a trend consistent with the observed reactivities[70].

The nickel−benzyne complexes are in some respects less reactive than the zirconocene analogues, e.g. they do not undergo insertion with nitriles or ketones, probably because nickel is less electrophilic than zirconium, and they are less reactive towards olefins, possibly because of steric hindrance by the coordinated tertiary phosphanes. However, the presence of a tertiary phosphane, which could be chiral, could be turned to advantage in controlling the stereoselectivity of insertions of substituted alkenes. It is important for further development of this fascinating class of compounds that more versatile syntheses be developed, starting from monohalogenoarenes or even arenes rather than the relatively inaccessible 1,2-dihalogenoarenes, so that a wider range of functionality can be introduced into the aromatic ring.

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