Insertions of Unsymmetric Alkynes into the Metal–Carbon Bonds of Nickelacycles: What Determines the Regiochemistry?

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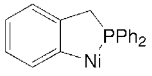
In memoriam Professor *Luigi M. Venanzi*, who contributed so much to coordination and organometallic chemistry

Although the insertion of alkynes into transition-metal–carbon bonds plays an important role in synthesis, the regioselectivities observed with unsymmetric alkynes have usually been interpreted on the basis of steric effects. In this perspective paper, we review the available data for such reactions with nickelacycles and present the results of some preliminary theoretical (DFT) calculations. These suggest that, even for unactivated alkynes, the regiochemistry may also be controlled by electronic factors such as frontier-orbital interactions between the triple-bond of the alkyne and the polarized metal–carbon bond.

1. Introduction. – The insertion of an unsaturated molecule into a metal–carbon (M–C) bond is a fundamental reaction in organometallic chemistry that has been exploited in both organic syntheses and industrial processes. Detailed experimental studies have been carried out on alkene and CO insertions [1][2], and these have been underpinned by extensive theoretical investigations [3]. Alkyne insertion reactions have also received considerable attention, especially in the context of transition-metal-catalysed cyclotrimerization and oligomerization reactions [4–8]. The insertion of an alkyne into the M–C σ-bond of a metallacycle provides a synthetically useful process, because cyclometallated compounds can often be prepared directly by cleavage of a C–H bond close to a suitable donor atom [9–11]. In particular, alkyne reactions with palladacycles have found wide application in the synthesis of important polycyclic and heterocyclic molecules [12–18]; a stoichiometric process based on cyclomanganated complexes derived from aromatic ketones [19][20] and a process based on α-tetralone catalysed by $[\mathrm{RuH_2(CO)(PPh_3)_3}]$ [21] have also been reported.

If unsymmetric alkynes are to be used in such reactions, good regioselectivity or even complete regiocontrol is essential. Although several mechanistic studies of the insertions of alkynes into Ni–C and Pd–C bonds have been reported [22–27], little is known about the factors governing the regiochemistry of alkyne insertions into M–C bonds. Both electronic and steric effects have been invoked to explain the regioselectivities observed for the insertions of alkynes into Pd–aryl bonds, but, although the latter argument is generally preferred, neither could satisfactorily be applied in all cases [16][17][28]. For example, two investigations of the insertions of $^{t}\mathrm{BuC{\equiv}CMe}$ into Ni–C and Pd–C bonds have led to the conclusion that these reactions were under steric control [24][29], whereas the regioselectivities of the reactions of ester-activated alkynes with nickelaindenes are better accounted for by invoking electronic factors [30]. Studies over the last ten years have revealed the existence of a series of nickelacycles, containing the units shown in **1**–**5**, which readily undergo insertions with a range of alkynes. In this paper we review what is known about the behaviour of unsymmetric alkynes with these systems in an attempt to illustrate the main trends and differences observed experimentally. We discuss the observed regioselectivities in the light both of recent experimental results obtained in our laboratories and of DFT calculations that provide additional insight into the problem.



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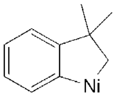

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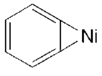

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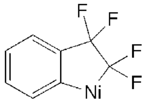

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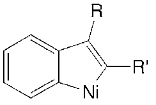

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Relevant background material dealing with metallacycles of the Group-10 elements [31][32], oxa- and aza-nickelacycles [33], the chemistry of 3,3-dimethylnickelaindane (**2**) [34], and benzyne and related small-ring acetylenes [35–37] has been published.

2. Insertion Reactions of Phosphanickelacycles Containing the Unit Ni(*o*-$C_6H_4CH_2PPh_2$-*κC,P*) (1). – The starting compounds are obtained by oxidative addition of (2-halogenobenzyl)diphenylphosphines, *o*-$XC_6H_4CH_2PPh_2$ (X = Cl, Br), to [Ni(cod)$_2$]¹) and are isolated either as halogen-bridged dimers, [NiX(*o*-$C_6H_4CH_2PPh_2$-*κC,P*)]$_2$ or as monomeric tertiary phosphine adducts [NiX(*o*-$C_6H_4CH_2PPh_2$-*κC,P*)(PR_3)] [22][38]. These complexes react readily with alkynes to form seven-membered rings, as shown in *Scheme 1*. Data for the regiochemistry of insertion of unsymmetrical alkynes are listed in *Table 1*, together with corresponding information for some simple, nonmetallacyclic $Ni^{II}-C$ σ-bonded complexes. Kinetic studies of the reaction of alkynes with [NiCl(*o*-$C_6H_4CH_2PPh_2$-*κC,P*)(PR_3)] ($PR_3 = PBz_3$ (**6a**), PMe_2Ph) or [NiCl(*o*-$C_6H_4CH_2PPh_2$-*κC,P*)]$_2$ suggest that the insertion into the Ni–C bond is preceded by alkyne coordination in a five-coordinate intermediate [22]. This conclusion is supported by studies of the reaction of $HC\equiv CCO_2R$ (R = Me, ^{t}Bu) with [NiBr(*o*-$C_6H_4CH_2PPh_2$-*κC,P*)(L)] (L = PEt_3 (**6b**), PBz_2Ph (**6c**)) [39]. Insertions of both alkynes into the Ni–C bond give preferentially the seven-membered nickelacycles **9** and **10**, respectively, having the carboxylate groups adjacent to the metal, *i.e.*, close to the bulky auxiliary phosphine ligand (*Table 1*, *Entries 5*, *6*; *Scheme 1*).

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[1] *Abbreviations:* cod = 1,5-cyclooctadiene; dcpe = bis(dicyclohexylphosphino)ethane, $Cy_2PCH_2CH_2PCy_2$; DMAD = dimethyl acetylenedicarboxylate, $MeO_2CC\equiv CCO_2Me$; DFT = density-functional theory; HMBC = heteronuclear multiple-bond correlation; GOESY = field-gradient *Overhauser*-effect spectroscopy.

Scheme 1

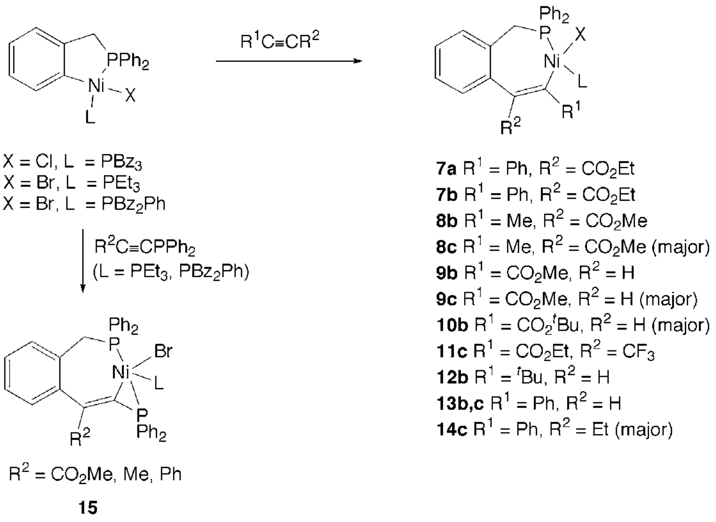
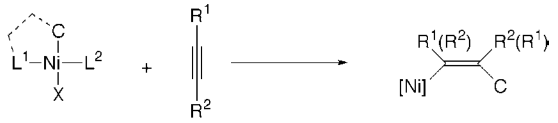


Table 1. *Selected Examples of Insertions of Unsymmetric Alkynes with Phosphanickelacycles or Related Complexes*[a])



Entry	X	C	L¹	L²	R¹	R²	Ratio	Ref.
1	Cl	$C_6H_4CH_2PPh_2$[b]) (**6a**)		PR_3	Ph	CO_2Et	100	[22, 38]
2	Br	$C_6H_4CH_2PPh_2$[b]) (**6b**)		PEt_3	Ph	CO_2Et	100	[39]
3	Br	$C_6H_4CH_2PPh_2$[b]) (**6b**)		PEt_3	Me	CO_2Me	100	[39]
4	Br	$C_6H_4CH_2PPh_2$[b]) (**6c**)		PBz_2Ph	Me	CO_2Me	88(12)	[39]
5	Br	$C_6H_4CH_2PPh_2$[b]) (**6b**)		PEt_3	CO_2Me	H	95(5)	[39]
6	Br	$C_6H_4CH_2PPh_2$[b]) (**6b**)		PEt_3	$CO_2{}^tBu$	H	83(17)	[39]
7	Br	$C_6H_4CH_2PPh_2$[b]) (**6c**)		PBz_2Ph	CO_2Et	CF_3	100	[39]
8	Br	$C_6H_4CH_2PPh_2$[b]) (**6b**)		PEt_3	Ph	H	100	[39]
9	Br	$C_6H_4CH_2PPh_2$[b]) (**6b**)		PEt_3	^tBu	H	100	[39]
10	Br	$C_6H_4CH_2PPh_2$[b]) (**6c**)		PBz_2Ph	Ph	Et	92(8)	[39]
11	acac	Me	acac	PPh_3	Ph	Me	100	[24]
12	acac	Me	acac	PPh_3	^tBu	H	100	[24]
13	acac	Ph	acac	PPh_3	^tBu	Me	100	[24]
14	Cl	Me	PMe_3	PMe_3	Ph	H	100	[44]
15	Cl	Me	PMe_3	PMe_3	Ph	Me	100	[44]
16	Cl	C(O)R	PMe_3	PMe_3	Ph	H	100	[45]

[a]) Insertions *via* four- or five-coordinate pathways. [b]) Metallacycle ($C \cap L^1$) (L^1 included in fragment formula).

However, the steric interaction between these two groups affects the isomer ratio. The reaction of $HC{\equiv}CCO_2Me$ with **6b** is almost regiospecific, whereas the same reaction carried out with **6c** forms some of the opposite regioisomer, which has the carboxylate group adjacent to the Ph ring of the nickelacycle. As the size of the ester group increases, *e.g.*, by use of $HC{\equiv}CCO_2{}^tBu$, the amount of the second isomer increases correspondingly. That these insertion reactions are sensitive to the size of both the carboxylate group and the auxiliary phosphine ligand suggests that both are present in the coordination sphere of the metal during the transition state (TS), in agreement with a five-coordinate associative mechanism.

A five-coordinate pathway has also been found by DFT calculations to be favored in the case of the reaction of $HC{\equiv}CH$ with the model complex $[NiBr(CH{=}CHCH_2PH_2\text{-}\kappa C,P)(PH_3)]$ (**16**) (see *Fig. 1*). Addition of $HC{\equiv}CH$ leads initially to two possible five-coordinate trigonal bipyramidal isomers: that computed with Br *trans* to the Ni–CH bond is –11.7 kJ/mol more stable relative to the total

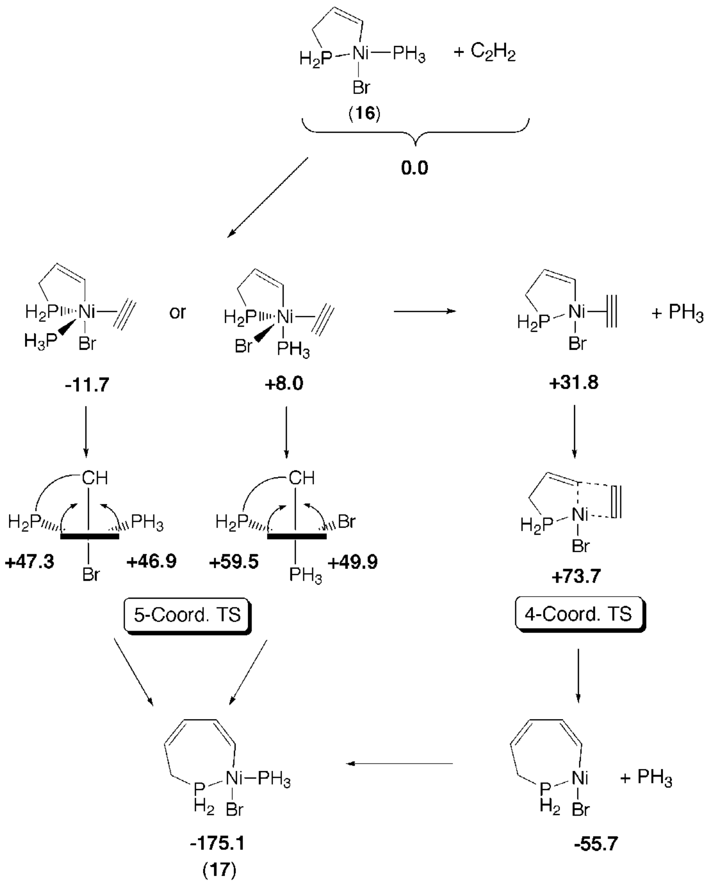


Fig. 1. *DFT Profiles for the insertion reaction of C_2H_2 with $[NiBr(CH{=}CHCH_2PH_2)(PH_3)]$)* (**16**). Energies in kJ/mol.

energy of the starting constituents, whereas that having a trans $H_3P-Ni-CH$ bond is slightly less stable (+ 8.0 kJ/mol). Two transition states (TS) can arise from each isomer because the alkyne can rotate either clockwise (viewed down the $(HC{\equiv}CH)-Ni$ coordination axis) before inserting into the Ni–C bond to give the seven-membered nickelacycle **17**, or anticlockwise as shown in *Fig. 1*; the computed energy barriers range from + 46.9 to 59.5 kJ/mol. The pathway to the model insertion product **17** is unlikely to be dissociative, as both intermediate four-coordinate species and the corresponding TS for the insertion into the Ni–C bond are much too high in energy (+ 31.8 and + 73.7 kJ/mol, resp.) [40].

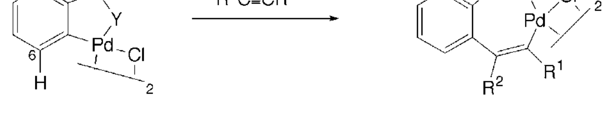
In contrast to this behaviour, kinetic studies show that insertion of $PhC{\equiv}CPh$ into the Ni–Me bond of $[NiMe(PPh_3)(acac)]$ is preceded by reversible replacement of PPh_3 by the alkyne [24], *i.e.*, a dissociative mechanism. In the case of Ni^{II}, the choice between associative and dissociative mechanisms is probably sensitive to the nature of the auxiliary ligands.

The insertion reactions of $PhC{\equiv}CCO_2Et$ with the phosphanickelacycles **6a**,**b** give exclusively seven-membered nickelacycles in which the carboxylate groups are adjacent to the aromatic ring of the nickelacycle (**7a**,**b**) (*Scheme 1*, *Table 1*, *Entries 1* and *2*) [38][39]. The same regioselectivity has also been observed frequently with various palladacycles [16], one example with $[PdCl(o\text{-}C_6H_4CH_2Y\text{-}\kappa C,Y)]_2$ (Y = NMe_2, SMe, S^tBu) [14][41–43] being illustrated in *Scheme 2*. The predominant regioisomers (**8b**,**c**) from the reactions of $MeC{\equiv}CCO_2Me$ with **6b**,**c** have the same substitution pattern, *i.e.*, replacement of the Ph by Me does not alter the regiochemistry of the reaction [39]. However, in the case of **6c**, the opposite isomer is also produced, probably due to steric interactions (*Entry 4*). The latter has the same regiochemistry as the preferred products obtained with $HC{\equiv}CCO_2R$ (R = Me, ^tBu) (**9b**,**c** and **10b**, respectively, see above and *Table 1*, *Entries 5* and *6*).

The reaction of **6c** with $CF_3C{\equiv}CCO_2Et$ gives exclusively the regioisomer in which the carboxylate group is adjacent to the metal (**11c**) (*Table 1*, *Entry 7*). The complete reversal of regioselectivity compared with that for $MeC{\equiv}CCO_2Me$ suggests that electronic factors must play a contributing role in determining the regiochemistry of alkyne insertions (see below).

The phosphanickelacycles **6b**,**c** also undergo insertion with $^tBuC{\equiv}CH$, $PhC{\equiv}CH$ and $PhC{\equiv}CEt$ to give unstable seven-membered nickelacycles (**12**–**14**, respectively) having the ^tBu or Ph groups adjacent to Ni (*Scheme 1*; *Table 1*, *Entries 8–10*) [39]; this sense of addition is also commonly observed for such alkynes in other systems and has usually been explained as an attack of the metal–C bond on the less hindered C-atom of the alkyne. For example, reaction of $PhC{\equiv}CMe$ with $[NiMe(acac)(PPh_3)]$ gives

Scheme 2



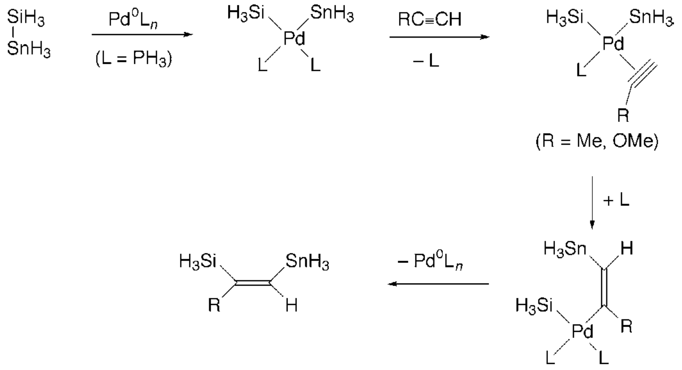
Y = NMe_2, SMe, S^tBu

R^1 = Ph; R^2 = CO_2R'
R^1 = ^tBu, Ph; R^2 = Me

exclusively [Ni{C(Ph)=CMe$_2$}(acac)(PPh$_3$)], and the insertion products from ^{t}BuC≡CR (R = H, Me) have the ^{t}Bu group adjacent to nickel (*Table 1*, *Entries 11–13*) [24]. The same regiospecificity is observed for the insertions of PhC≡CR (R = H, Me) into the Ni–Me bond of [NiCl(Me)(PMe$_3$)$_2$] (*Table 1*, *Entries 14* and *15*) [44] and for the insertion of PhC≡CH into Ni–acyl bonds (*Table 1*, *Entry 16*) [45]. It is interesting to note that, in a similar study of the insertion of ^{t}BuC≡CMe into various palladacycles [PdX(*o*-C$_6$H$_4$CH$_2$Y-κ*C*,*Y*)]$_2$ (X = Cl, I; Y = NMe$_2$, SMe, S^{t}Bu), the same regioselectivity prevailed [29]; steric interaction between the large ^{t}Bu group with the H–C(6) of the cyclometallated aromatic ring was thought to prevent the formation of the alternative isomer (see *Scheme 2*).

Apart from the results with activated alkynes discussed above, there are remarkably few unequivocal examples of electronic control of the regiochemistry of alkyne insertion into a M–C bond. It has been suggested [46] that the Pd^0-catalysed silastannation of alkynes proceeds by insertion of the alkynes into a Pd–Sn bond (*Scheme 3*). The main interaction responsible for the reactivity is electron donation from the HOMO of the Pd moiety (predominantly the Pd d orbital in bonding combination with a Sn p orbital), while the regiochemistry, *i.e.*, the orientation of the alkyne, is dictated mainly by an interaction of the alkyne HOMO ($\pi_\perp$), the one polarized by the substituent, with the LUMO of the Pd fragment, located primarily on the Sn-atom bonded to Pd.

Scheme 3



To see whether similar arguments can be applied to the alkyne insertions into the phosphanickelacycles **6b**,**c**, we have carried out DFT calculations [39] on the p-orbital contributions of the two C-atoms of various alkynes, both for the occupied (HOMO, $\pi_\perp$) and vacant (LUMO, π*) orbitals (*Table 2*). For the sake of simplicity, the esters RC≡CCO$_2$Me (R = H, Me, Ph) and CF$_3$C≡CCO$_2$Et have been modelled by the corresponding acids and ^{t}BuC≡CH has been modelled by CH$_3$C≡CH. For PhC≡CCO$_2$H or MeC≡CCO$_2$H, the p-orbital contribution for the HOMO ($\pi_\perp$) is higher for the C-atom bearing the carboxylate group (*Table 2*, *Entries 4* and *5*), hence interaction with the π* orbital located on the C-atom bonded to Ni will occur preferentially at this site; this should lead to seven-membered complexes in which the carboxylate group is remote from Ni and adjacent to the aromatic ring of the

Table 2. *Alkyne Carbon p-Orbital Contribution* [%] *Computed for the HOMO* ($\pi_\perp$) *and LUMO* (π^*) *of Several Alkynes* ($R^1C^1{\equiv}C^2R^2$)

			HOMO ($\pi_\perp$)		LUMO (π^*)	
Entry	R^1	R^2	C(1) (%)	C(2) (%)	C(1) (%)	C(2) (%)
1	H	Me	48.0	40.3	41.9	36.5
2	H	Ph	29.1	12.6	19.2	4.9
3	Me	Ph	27.5	16.5	17.0	3.6
4	CO_2H	Ph	25.9	8.5	12.2	14.3
5	CO_2H	Me	41.1	32.9	8.1	27.9
6	CO_2H	CF_3	29.5	32.5	14.2	28.0
7	CO_2H	H	38.2	38.6	9.9	31.0

nickelacycle. For $CF_3C{\equiv}CCO_2H$, the calculations suggest a reversal of polarity in the alkyne orbital (*Entry 6*), and, although the difference between the calculated contributions of C^1 and C^2 is small, it does correlate with the observed regioselectivity change. The regioselectivities observed for the insertions of HC≡CPh or MeC≡CPh (*Entries 2* and *3*) can also be explained as arising from a preferred electronic interaction of C^1 with the C-atom bonded to Ni in **6b**,**c**. This admittedly simple approach does suggest that frontier-orbital interactions play an important role in determining the regioselectivity of alkyne insertions into Ni–C bonds.

The few computational studies dealing with alkyne insertions into M–C bonds have been covered in recent reviews [47–49], but none discusses the problem of the regioselectivity. We have, therefore, carried out DFT calculations on the insertion of the model alkyne $MeC{\equiv}CCO_2H$ with the model complex $[NiBr(CH{=}CHCH_2PH_2\text{-}\kappa C,P)(PH_3)]$ (**16**); the transition states have been located only for the favored associative mechanism (see *Fig. 1*). The reaction profiles are shown in *Fig. 2*. Coordination of the alkyne to **16** leads to the formation of four five-coordinate intermediates (**18**–**21**); as in the case of C_2H_2, those having Br *trans* to CH are the most stable. Each intermediate gives rise to two transition states depending on whether the alkyne rotates clockwise or anticlockwise to reach the geometry suitable for insertion into the Ni–C bond. The lowest barrier computed for this system (+25.6 kJ/mol) results from a clockwise rotation of $MeC{\equiv}CCO_2H$ in intermediate **18**, which has Br *trans* to CH. This transition state leads to a product bearing the carboxylate on the β-C-atom, in agreement with experiment (**8**, *Scheme 1*). However, another transition state relatively close in energy that leads to an α-product has been located in the case of intermediate **20**. This small difference in energy may explain why regioisomeric mixtures are obtained when steric interactions become large.

A similar analysis was carried out for PhC≡CH; the results are shown in *Fig. 3*. In this case, the lowest-energy transition state results from clockwise rotation of the alkyne in intermediate **22**, leading to a seven-membered ring product in which the Ph group is located on the α-C-atom. This is in complete agreement with the experimental results discussed above and shows that steric effects do not need to be invoked to account for the regiochemistry. Similarly, the direction of insertion of MeC≡CH was computed correctly to give the product that has the alkyl group on the α-C-atom as observed experimentally for ^{t}BuC≡CH, while $PhC{\equiv}CCO_2H$ gave the product with the

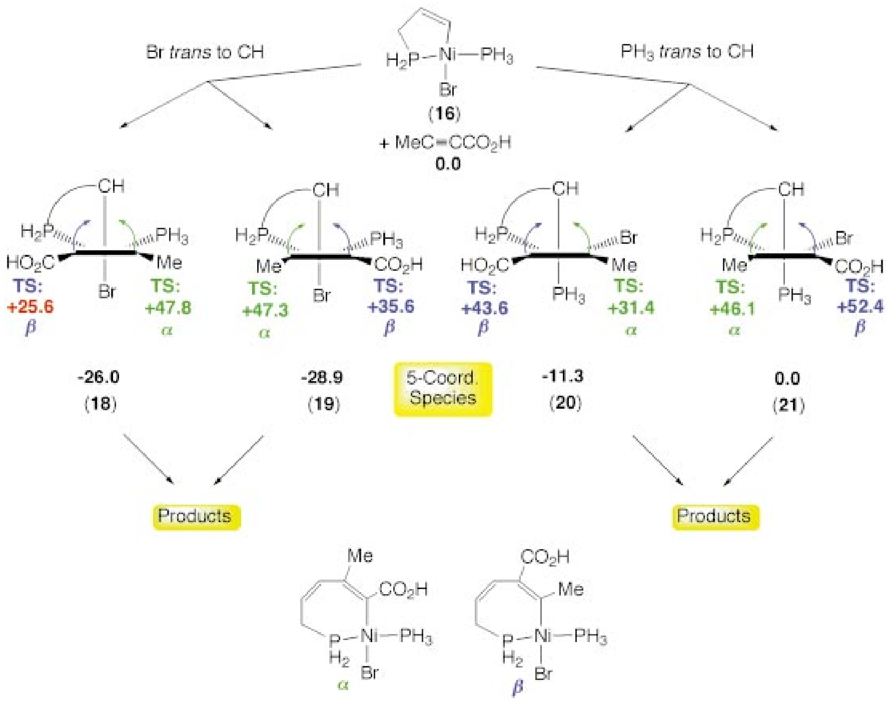


Fig. 2. *DFT Profile for the insertion reaction of* $MeC{\equiv}CCO_2H$ *with* $[NiBr(CH{=}CHCH_2PH_2)(PH_3)]$ (**16**). The five-coordinate intermediates (**18**–**21**) are viewed down the alkyne–Ni coordination axis, and the arrows indicate the rotations of the alkyne leading to the corresponding transition state (TS); energies in kJ/mol.

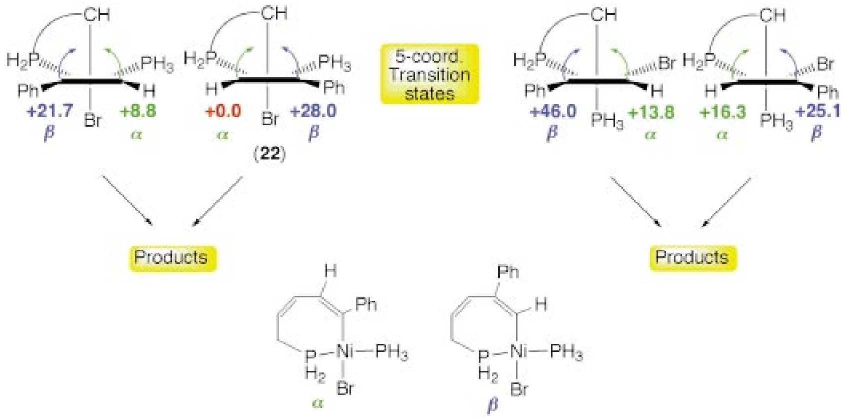


Fig. 3. *Five-coordinate intermediates formed by reaction of* $PhC{\equiv}CH$ *with* $[NiBr(CH{=}CHCH_2PH_2)(PH_3)]$ (**16**) *viewed down the alkyne–Ni coordination axis, and energies of the corresponding insertion transition states* (in kJ/mol, relative to favored TS)

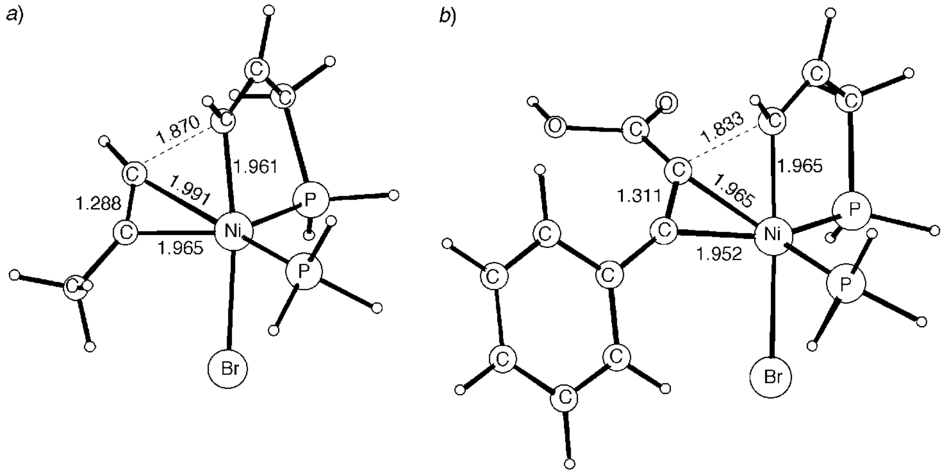
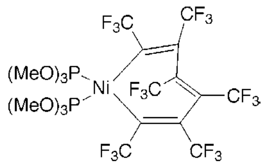


Fig. 4. *Preferred transition states for the insertion of various unsymmetric alkynes with [NiBr(CH=CHCH$_2$PH$_2$)(PH$_3$)]* (**16**). *a*) **16** + MeC≡CH (Me in α); *b*) **16** + PhC≡CCO$_2$H (CO$_2$H in β).

carboxylate on the β-C-atom. The preferred transition states for these insertions are given in *Fig. 4*. Unfortunately, the situation at this stage is not so clear for HC≡CCO$_2$H and CF$_3$C≡CCO$_2$H. The lowest transition states, computed for the simple nickelacycle model **16**, are very close in energy for the formation of both α- and the β-isomers. In these two cases, a more elaborate combined molecular-mechanics/quantum-mechanics method and introduction of more realistic phosphine ligands are clearly required.

3. Insertion Reactions of Nickelacycles Containing Two *cis*-Ni–C σ-Bonds (carbonickelacycles). Many compounds of the type [Ni(C∩C)L$_2$] are known, in most of which the Ni-atom is part of a five- or six-membered ring [8][31–33]. Larger metallacycles are generally difficult to isolate because the two M–C σ-bonds tend to undergo reductive elimination. One exception is complex **23**, which is formed by reaction of hexafluorobut-2-yne with [Ni{η^2-C$_6$(CF$_3$)$_6$}{P(OMe)$_3$}$_2$]; [50]; the three CF$_3$C$_2$CF$_3$ units adopt a *cis-trans-cis*-configuration.



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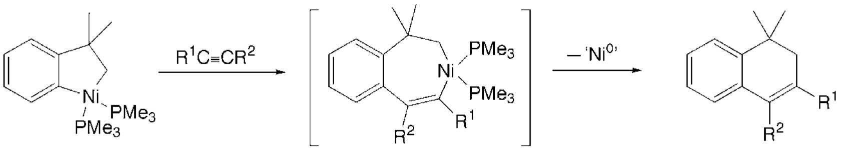
Available data for the regiochemistry of the insertion of unsymmetrical alkynes into the Ni–C σ-bonds of carbonickelacycles of the type **2**, **4**, and **5** are listed in *Table 3*. The nickelaindane complex [Ni(o-C$_6$H$_4$CMe$_2$CH$_2$-κC,C)(PMe$_3$)$_2$] (**24**), which is prepared by the treatment of [NiCl$_2$(PMe$_3$)$_2$] with two equivalents of ClMg(CH$_2$CMe$_2$Ph) [51][52], reacts with alkynes to give 1,2-dihydronaphthalenes. These are presumably formed by reductive elimination from unobserved intermediate seven-membered ring metallacycles (*Scheme 4*). Addition of excess PMe_3 inhibits the insertion of $PhC{\equiv}CPh$, suggesting that one of the PMe_3 ligands is displaced by the alkyne before insertion takes place [53]. The insertions of $HC{\equiv}CCO_2Me$ and $MeC{\equiv}CCO_2Me$ are regiospecific, giving 1,2-dihydronaphthalenes having the carboxylate substituents in the 3-position (**25** and **26**, respectively, *Table 3*, *Entries 10* and *11*; *Scheme 4*) [53]. Clearly, the

Scheme 4



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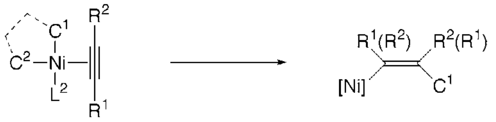
25 $R^1 = CO_2Me$, $R^2 = H$
26 $R^1 = CO_2Me$, $R^2 = Me$
27 $R^1 = Ph$, $R^2 = Me$
28 $R^1 = Ph$, $R^2 = H$ (major)
29 $R^1 = {}^tBu$, $R^2 = H$ (major)

Table 3. *Regioselectivity for the Insertion of Unsymmetric Alkynes with Carbonickelacycles*



Entry	Metallacycle	Insertion	L^2	R^1	R^2	Ratio	Ref.
1	$C_6H_4C(Me){=}C(CO_2Me)$ (**42**)[a]	Ni–aryl	PEt_3	CO_2Me	Me	100	[30]
2	$C_6F_2H_2CH{=}C(CO_2Me)$ (**44**)[a]	Ni–aryl	PEt_3	CO_2Me	H	74(26)	[60]
3	$C_6H_4CH{=}C(CO_2{}^tBu)$ (**45**)[a]	Ni–aryl	PEt_3/PPh_3	$CO_2{}^tBu$	H	38(62)	[60]
4	$C_6H_4C(Ph){=}C(CO_2Et)$ (**43**)[a]	Ni–vinyl	PEt_3	CO_2Et	Ph	100	this work
5	$C_6H_4C(CO_2Me){=}C(CO_2Me)$ (**30**)	Ni–aryl	η^1-dcpe	CO_2Me	H	100	[60]
6	$C_6H_4C(CO_2Me){=}C(CO_2Me)$ (**30**)	Ni–aryl	η^1-dcpe	CO_2Et	Ph	100	this work
7	$C_6H_4C(CO_2Me){=}C(CO_2Me)$ (**30**)	Ni–aryl	η^1-dcpe	CO_2Me	Me	100	this work
8	$C_6X_2H_2C(Me){=}C(PPh_2)$[a]	Ni–aryl	PEt_3	PPh_2	Me	100	[64] [65]
9	$C_6X_2H_2C(Ph){=}C(PPh_2)$[a]	Ni–aryl	PEt_3	PPh_2	Ph	100	[64] [65]
10	$C_6H_4CMe_2CH_2$ (**24**)	Ni–aryl	PMe_3	CO_2Me	H	100	[53]
11	$C_6H_4CMe_2CH_2$ (**24**)	Ni–aryl	PMe_3	CO_2Me	Me	100	[53]
12	$C_6H_4CF_2CF_2$ (**37**)	Ni–aryl	PEt_3	CO_2Me	H	100	[59]
13	$C_6H_4CH{=}C({}^tBu)$[a]	Ni–vinyl	PEt_3	${}^tBu$	H	100	[30]
14	$C_6H_4CH{=}C(SiMe_3)$[a]	Ni–vinyl	PEt_3	$SiMe_3$	H	86(14)	[60]
15	$C_6H_4CMe_2CH_2$ (**24**)	Ni–aryl	PMe_3	Ph	H	64(36)	[53]
16	$C_6H_4CMe_2CH_2$ (**24**)	Ni–aryl	PMe_3	${}^tBu$	H	69(31)	[53]
17	$C_6H_4CMe_2CH_2$ (**24**)	Ni–aryl	PMe_3	Ph	Me	100	[53]
18	$C_6H_4CMe_2CH_2$ (**24**)	Ni–aryl	PMe_3	CH_2OH	Me	75(25)	[53]
19	$C_6H_4CMe_2CH_2$ (**24**)	Ni–aryl	PMe_3	Ph	CH_2OH	100	[53]
20	$C_6H_4CMe_2CH_2$ (**24**)	Ni–aryl	PMe_3	CH_2Cl	H	100	[53]
21	$C_6H_4CMe_2CH_2$ (**24**)	Ni–aryl	PMe_3	Ph	Br	100	[53]
22	$C_6H_4CF_2CF_2$ (**37**)	Ni–aryl	PEt_3	H	${}^tBu$	100	[59]
23	$C(Ph){=}CHC_4O_2NR$	Ni–vinyl	PPh_3	Ph	H	100	[63]

[a] Nickelaindene intermediates (not observed) initially formed by reaction of $[Ni(\eta^2\text{-}C_6X_2H_2)(PEt_3)_2]$ ($X = H$ (**41a**) or F (**41b**) with 1 equiv. of the corresponding alkynes.

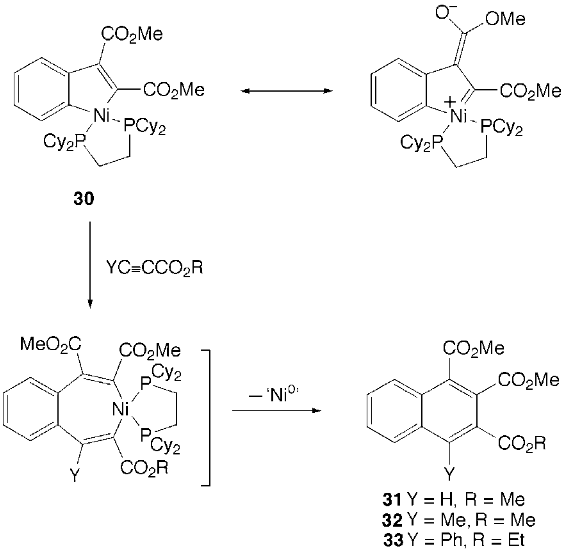
regioselectivity of the insertions can only be ascertained if the more reactive Ni–C bond can be identified. The available evidence [51][52][54–57] indicates that unsaturated molecules generally prefer to insert into the nickel–aryl rather than the nickel–alkyl bond, although there are exceptions, *e.g.*, formaldehyde inserts into the Ni–CH_2 bond. Insertion of $HC{\equiv}CCO_2Me$ and $MeC{\equiv}CCO_2Me$ into the Ni–C_6H_4 bond leads to intermediate seven-membered nickelacycles in which the carboxylate groups are adjacent to the metal atom.

Reaction of **24** with $PhC{\equiv}CMe$ gives the 3-phenyldihydronaphthalene **27**, presumably *via* a seven-membered nickelacycle having the Ph group close to the metal (*Scheme 4*) [53]. Both $PhC{\equiv}CH$ and $^tBuC{\equiv}CH$ give isomeric mixtures, although the 3-substituted dihydronaphthalenes (**28** and **29**, resp.) predominate (*Table 3, Entries 15–21*).

Stable nickelaindane complexes of general formula $[Ni(o\text{-}C_6H_4CX_2CX_2\text{-}\kappa C,C)L_2]$ (X = H, L_2 = dcpe; X = F, L_2 = 2 PEt_3, dcpe) have been obtained from insertion reactions of ethylene [58] or tetrafluoroethylene [59] with the benzyne complexes $[Ni(\eta^2\text{-}C_6H_4)L_2]$ (**3**). Similar nickelaindenes $[Ni(o\text{-}C_6H_4CX^1{=}CX^2\text{-}\kappa C,C)(PR_3)_2]$ are probably formed initially in a corresponding reaction with alkynes, but these compounds undergo alkyne insertion even more rapidly than the starting benzyne complex to give, after reductive elimination, substituted naphthalenes (*Schemes 5* and *9–11*; see below). Only in the reaction of DMAD with $[Ni(\eta^2\text{-}C_6H_4)(dcpe)]$ could the mono-insertion product $[Ni\{o\text{-}C_6H_4C(CO_2Me){=}C(CO_2Me)\text{-}\kappa C,C\}(dcpe)]$ (**30**) be isolated. Its relative stability may arise from electron delocalization into the carboxylate group on the β-C-atom, giving rise to a resonance contribution from a dipolar Ni–carbene structure [58][60], as illustrated in *Scheme 5*.

The second alkyne can insert into either the Ni–aryl bond, or, depending on the nickelacycle, the Ni–vinyl or –alkyl one. This reaction generates a seven-membered

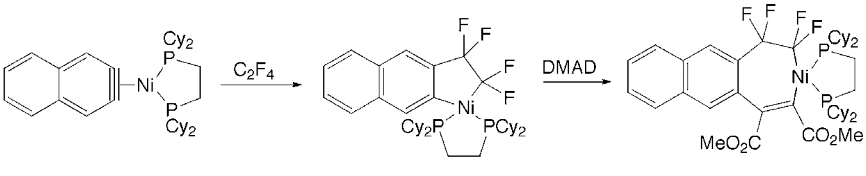
Scheme 5



metallacycle, but in only one case in this series has such a compound been isolated (*Scheme 6*). It arises from sequential insertion of C_2F_4 and DMAD into the 2,3η-naphthalyne complex [Ni(η^2-$C_{10}H_6$)(dcpe)]. The product, [Ni{C(CO_2Me)=C(CO_2Me)$C_{10}H_6CF_2CF_2$-$\kappa C,C$}(dcpe)] (**35**), results from insertion of the alkyne into the Ni–Ar bond of the first insertion product, [Ni(*o*-$C_{10}H_6CF_2CF_2$-$\kappa C,C$)(dcpe)] (**34**) [61]. The nickelaindene complex [Ni{*o*-C_6H_4C(CO_2Me)=C(CO_2Me)-$\kappa C,C$}(dcpe)] (**30**) reacts cleanly with the electrophilic alkynes Y$C\equiv CCO_2$R (Y = H, Me, R = Me; Y = Ph, R = Et) to give exclusively the naphthalene-1,2,3-triesters **31**–**33** (*Scheme 5*; *Table 3*, *Entries 5–7*) (see [60] and *Exper. Part*). The most likely pathway involves regiospecific insertion into the Ni–Ar bond to give a seven-membered metallacycle with the carboxylate group adjacent to the Ni-atom, and subsequent reductive elimination. It should be noted that the regioselectivity for $HC\equiv CCO_2Me$ and $MeC\equiv CCO_2Me$ is the same as that found for insertion into the carbonickelacycle **24**. A parallel can be found in related reactions with palladacycles, where the carbocyclic complex **36** reacts with $HC\equiv CCO_2Et$ and $PhC\equiv CCO_2Me$ to give predominantly intermediates in which the carboxylate groups are also adjacent to the metal (*Scheme 7*) [62]. The regioselectivity behaviour is, however, in marked contrast with that observed for insertion into the phosphanickelacycles **6a**,**b** (*Section 2*), where $PhC\equiv CCO_2Et$ (exclusively) and $MeC\equiv CCO_2Me$ (predominantly) insert to place the carboxylate group away from the metal atom and only $HC\equiv CCO_2Me$ inserts to give, predominantly, carboxylate adjacent to the metal atom.

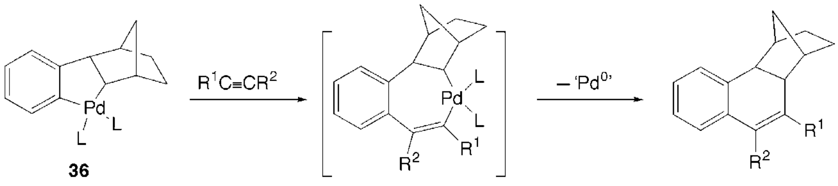
The nickelacycles [Ni(*o*-$C_6H_4CF_2CF_2$-$\kappa C,C$)(dcpe)] and [Ni(*o*-$C_{10}H_6CF_2CF_2$-$\kappa C,C$)(dcpe)] insert DMAD into the Ni–Ar bond to give stable seven-membered metallacycles (*Scheme 6*) [59][61]. The analogous complex [Ni(*o*-$C_6H_4CF_2CF_2$-$\kappa C,C$)(PEt_3)$_2$] (**37**) undergoes double insertion of $HC\equiv CCO_2Me$ into the Ni–Ar bond (*Scheme 8*; *Table 3*, *Entry 12*), the regiochemistry for each insertion placing the

Scheme 6



34 **35**

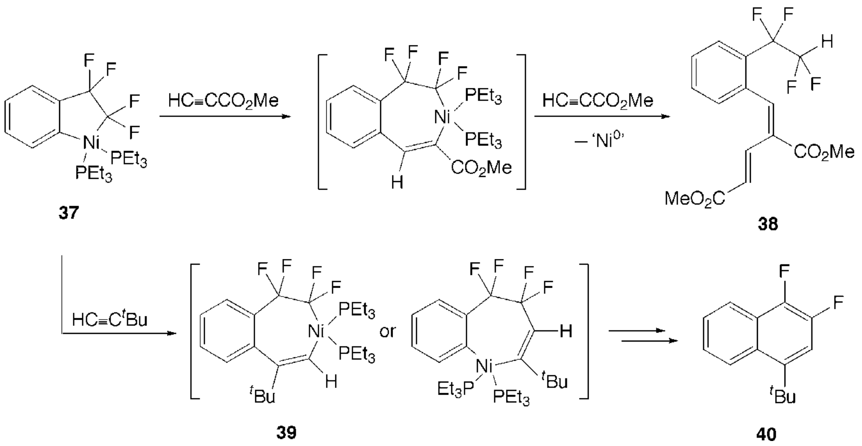
Scheme 7



36
L = $NC_5H_4CO_2Me$

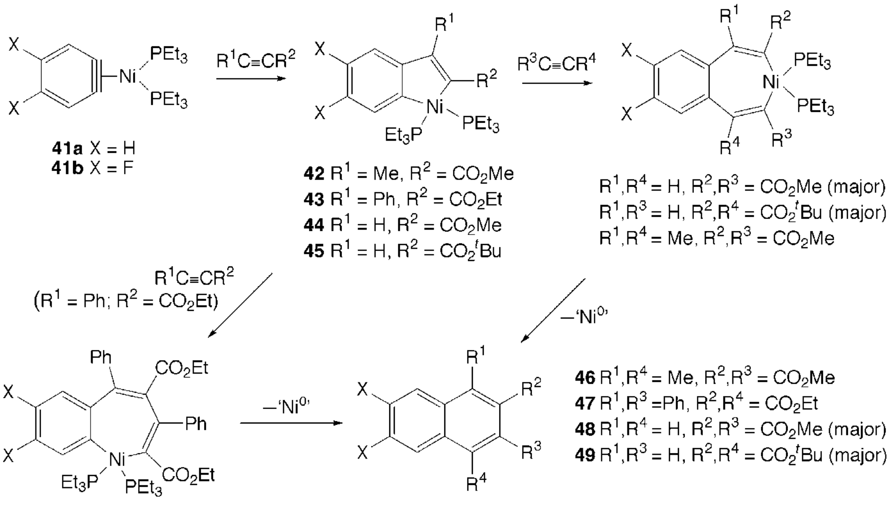
R^1 = CO_2Et, R^2 = H
R^1 = CO_2Me, R^2 = Ph (major)

Scheme 8



carboxylate group adjacent to the metal atom; however, the isolated organic product **38** is derived from protonation of the intermediate nickelacycle rather than reductive elimination. In this context, the double-insertion reactions of $HC\equiv CCO_2R$ (R = Me, ^{t}Bu), $MeC\equiv CCO_2Me$, or $PhC\equiv CCO_2Et$ with the benzyne complexes $[Ni(\eta^2\text{-}C_6H_2X_2)(PEt_3)_2]$ (X = H (**41a**), F (**41b**)) are of particular interest (*Scheme 9*) [30][60]. The initial insertions give the reactive five-membered intermediates **42**–**45** having the carboxylate group adjacent to Ni. These nickelaindenes undergo rapid insertion of a second molecule of alkyne, in either the Ni–vinyl or Ni–aryl bond, to give the corresponding substituted naphthalenes after reductive elimination. Although all four alkynes are expected, on the basis of the results described above, to insert with

Scheme 9

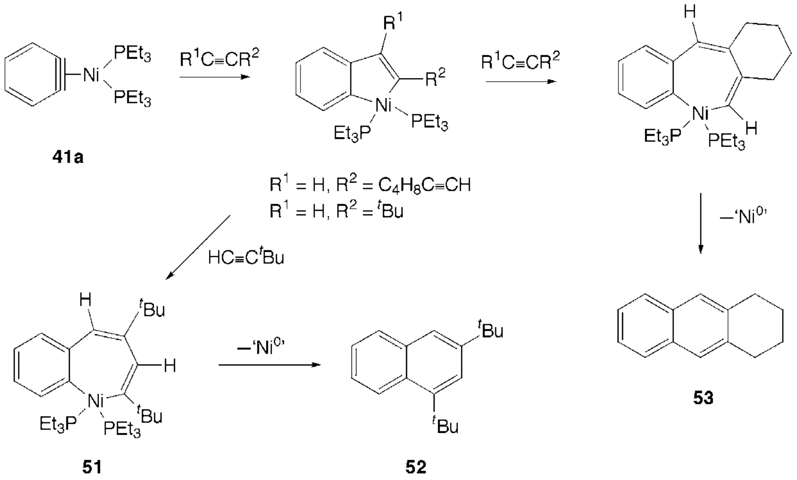


the same regiochemistry in these carbocyclic systems, the products do not all have the same substitution pattern: $MeC{\equiv}CCO_2Me$ forms exclusively the naphthalene bearing the carboxylate groups in the 2,3-positions (**46**) [30] while $PhC{\equiv}CCO_2Et$ gives only the 1,3-isomer (**47**) (see *Exper. Part*); $HC{\equiv}CCO_2Me$ forms a mixture of the two isomers but the 2,3-isomer (**48**) still predominates. In the latter case, steric influences on the regioselectivities can also be observed. If PPh_3 is added to the reaction mixture, the proportion of 1,3-isomer increases and this isomer becomes the major compound if $HC{\equiv}CCO_2{}^tBu$ is used (**49**) (*Table 3*, *Entries 2* and *3*). Hence, electronic control of the insertion of $HC{\equiv}CCO_2R$ seems to favour the 2,3-isomer, but steric repulsion between the ester group and the auxiliary phosphine ligand leads to the formation of the alternative product.

The regioselectivities of the insertions of $YC{\equiv}CCO_2H$ (Y = H, Me) have been investigated by DFT calculations with the model complex $[Ni(CH{=}CHCH{=}CH\text{-}\kappa C,C)(PH_3)_2]$ (**50**). Preliminary results indicate that the seven-membered nickelacycles having the carboxylate groups on the α-C-atom are the preferred products (see below). One possible explanation for the surprising difference in regiochemistry observed for the reactions of $MeC{\equiv}CCO_2Me$ and $PhC{\equiv}CCO_2Et$ with the benzyne complexes **41** is that, whereas $MeC{\equiv}CCO_2Me$ inserts into the Ni–aryl bond, $PhC{\equiv}CCO_2Et$ may react with the Ni–vinyl bond (*Scheme 9*, *Entries 1* and *4*). The latter may be destabilized by the tendency of the extra Ph group to increase the electron density on the α-C-atom of **43**, as in the case of styrene.

The exclusive formation of 1,3-di(*t*-butyl)naphthalene (**52**) (*Scheme 10*) from the reaction of $^tBuC{\equiv}CH$ with the benzyne complex **41** is most easily accounted for if the second molecule of the alkyne inserts into the Ni–vinyl bond of the initially formed nickelaindene to form the seven-membered nickelacycle **51**; in both insertion steps the ^tBu group is placed next to the metal atom (*Table 3*, *Entry 13*) [30]. This conclusion is supported by the observation that an excess of octa-1,7-diyne, $HC{\equiv}C(CH_2)_4C{\equiv}CH$,

Scheme 10



reacts with **41** to give only the tetrahydroanthracene **53** (*Scheme 10*), no disubstituted naphthalene of general formula $C_{10}H_6(C_4H_8C{\equiv}CH)_2$ being observed [60].

In the cocyclization of PhC≡CH with *N*-substituted maleimides, catalysed by $[Ni(CO)_2(PPh_3)_2]$, a nickelacyclopentene intermediate, $[Ni\{C(Ph){=}CHC_4O_2NR\text{-}\kappa C,C\}(PPh_3)_2]$, has been proposed, which undergoes insertion of a second molecule of PhC≡CH into the Ni–vinyl bond. In the resulting seven-membered nickelacycle, the Ph substituent is also located next to the metal and yields the observed cyclohexadiene after reductive elimination (*Table 3*, *Entry 23*). The observed regioselectivity was postulated to arise from minimization of the steric repulsion between the substituents [63].

In the light of these results, it is surprising that the nickelaindane complex $[Ni(o\text{-}C_6H_4CF_2CF_2\text{-}\kappa C,C)(PEt_3)_2]$ (**37**) reacts with ^{t}BuC≡CH to yield, after aromatization on a silica-gel column, 4-(*t*-butyl)-1,2-difluoronaphthalene (**40**) (*Table 3*, *Entry 22*; *Scheme 8*). All the available data suggest that the Ni–aryl bond should be more reactive to insertion than the $Ni{-}CF_2$ bond, implying the existence of the intermediate seven-membered nickelacycle (**39**) in which ^{t}Bu is remote from Ni; insertion of ^{t}BuC≡CH in the usual sense should have given 3-(*t*-butyl)-1,2-difluoronaphthalene. Insertion of ^{t}BuC≡CH into the $Ni{-}CF_2$ bond in the usual sense would also give the observed product. This reversal of regiochemistry deserves further investigation.

A trend that emerges clearly from the experimental results summarized above is that the regioselectivities for the reactions of activated alkynes, especially for $MeC{\equiv}CCO_2Me$ and $PhC{\equiv}CCO_2Et$, with carbonickelacycles are opposite to those with phosphanickelacycles. Moreover, the regiochemistry for the insertion of these two alkynes into the carbonickelacycles is the same as the predominant one found for $HC{\equiv}CCO_2Me$ in both phospha- and carbo-nickelacycles. A possible explanation for these results is that the Ni–C bond in a carbonickelacycle, which is *trans* to phosphine, is likely to be more electron-rich than that in a phosphanickelacycle, where it is *trans* to halide. Hence, the orientation of the alkyne during the insertion into the Ni–C bond may no longer be dictated by a HOMO(alkyne)–LUMO(Ni–C) interaction as for **6b**,**c** but by a HOMO(Ni–C)–LUMO(alkyne) interaction. This hypothesis is supported by the similar LUMO contributions of the alkyne C-atoms computed for all three alkynes $YC(1){\equiv}C(2)CO_2H$ (Y = H, Me, Ph) (*Table 2*, *Entries 4*, *5*, and *7*). An interaction between the π orbital of the C-atom bonded to Ni with C(1) could explain the formation of the observed products. Furthermore, one can also invoke a similar HOMO(Ni–C)–LUMO(alkyne) interaction to explain the insertions of the alkyl-substituted alkynes (*Table 2*, *Entries 1–3*).

DFT Calculations have confirmed that both $HC{\equiv}CCO_2H$ and $MeC{\equiv}CCO_2H$ do react with the model complex $[Ni(CH{=}CHCH{=}CH\text{-}\kappa C,C)(PH_3)_2]$ (**50**) to give preferentially seven-membered nickelacycles in which the carboxylate groups are adjacent to the Ni. The computed profiles for the insertion of $MeC{\equiv}CCO_2H$ with **50** are given in *Fig. 5*. The lowest-energy transition state (**55**) is derived from the tetrahedral four-coordinate $[Ni(CH{=}CHCH{=}CH\text{-}\kappa C,C)(PH_3)(\eta^2\text{-}MeC{\equiv}CCO_2H)]$ (**54**), in which one PH_3 has been replaced by the alkyne; the alkyne is located below the plane of the nickelacycle during the insertion step. The resulting seven-membered species **56** is rather unstable and readily undergoes reductive elimination to produce an η^2-arene complex **57**. These theoretical results are in agreement with the experiments,

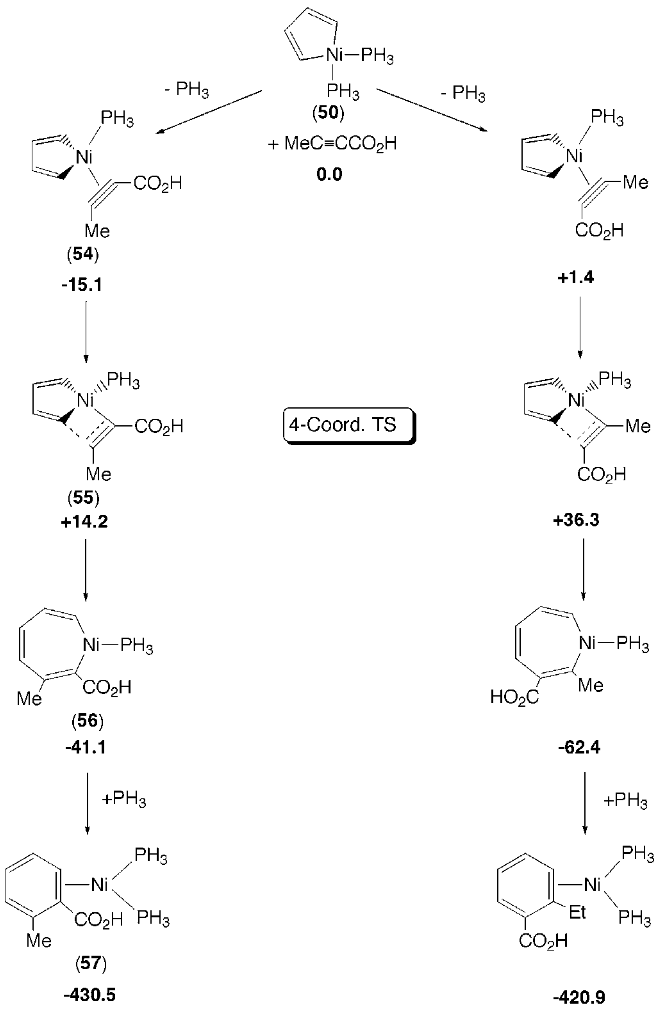


Fig. 5. *DFT Profiles for the insertion reaction of* $MeC{\equiv}CCO_2H$ *with* $[NiBr(CH{=}CHCH{=}CH)(PH_3)_2]$ (**50**). Energies in kJ/mol.

and suggest that the insertion reaction between an electron-rich nickelaindene complex and a polarized alkyne is electronically controlled.

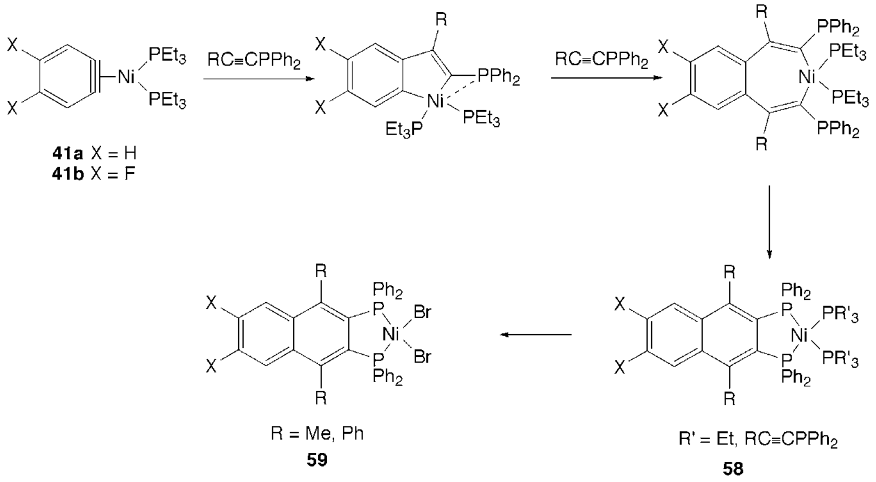
4. Insertion Reactions of Nickelacycles with Alkynyl Phosphines. – Alkynylphosphines such as $Ph_2PC{\equiv}CR$ ($R = Me$, Ph, CO_2Me) react regiospecifically with the phosphanickelacycles **6b**,**c** to yield unstable bicyclic complexes that contain a phosphanickelacyclopropane fragment (**15**) (*Scheme 1*) [39]. In these cases, the regioselectivity can be best rationalized by coordination of the phosphine group to the metal during the insertion. The strain of the three-membered nickelacycles causes these complexes to rearrange, either by internal migration of the substituent on the vinylic β-C-atom (R^2 in **15**), or by coordination of the PPh_2 group to a second metal atom.

Alkynylphosphines also undergo regiospecific double-insertion reactions with Ni–benzyne complexes. Addition of $Ph_2PC{\equiv}CR$ (R = Me, Ph) to **41** leads to the formation of a 2,3-bis(diphenylphosphino)naphthalene coordinated to a Ni^0 fragment (**58**) that can readily be oxidized to a stable Ni^{II} complex by addition of Br_2 (**59**) (*Scheme 11*) [64][65]. In this sequence, the alkynylphosphine is thought to insert into the Ni–aryl bond with the same regioselectivity as for **6b**,**c**. The Ni–vinyl bond in the five-membered nickelacycle is likely to be stabilized by partial coordination of the PPh_2 group to Ni to form a transient phosphanickelacyclopropane fragment.

5. Conclusions. – The insertions of alkynes into the M–C bonds of nickelacycles show very good regioselectivities, and these reactions, therefore, may have applications for the preparation of polycyclic products. In the past, the observed regioselectivities have generally been attributed to steric factors, and electronic factors such as frontier orbitals have been neglected. Our calculations indicate that such orbital interactions between the alkyne triple-bond and the M–C bond can often provide reasonable models for the experimental data, and can accurately reproduce most of the observed regioselectivities in the case of nickel. Unfortunately, in some cases, such as the insertion of $CF_3C{\equiv}CCO_2H$ into the model complex **16**, the computed transition states leading to both regioisomers are too close in energy to reproduce the experimental regiospecificity. For these cases, a more elaborate combined molecular-mechanics quantum-mechanics method will probably be needed.

The calculations have shown that the electron distribution in the Ni–C bond is a very important factor that depends greatly on the ligand *trans* to that bond. This model is currently being extended to analogous Pd systems, and subsequently will be applied to the M–C bonds of metallacycles containing Ru and Mn. This work should provide a

Scheme 11



41a X = H
41b X = F

R = Me, Ph
59

R' = Et, RC≡CPPh2
58

better understanding of this synthetically useful insertion reaction and, thus, allow better control of the regiochemistry by specific modification both of the alkyne substituents and of the auxiliary ligands in the complexes or catalysts used.

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Experimental Part

General. All experiments, unless otherwise specified, were carried out under Ar by standard *Schlenk* techniques. All solvents were dried and degassed prior to use. IR Spectra: *Perkin-Elmer 1800 FT-IR*; ν in cm^{-1}. NMR Spectra: *Varian XL-200E* (^1H: 200 MHz; ^{13}C: 50.3 MHz; ^{31}P: 81.0 MHz), *Varian Gemini-300BB* or *Varian Mercury-300* (^1H: 300 MHz; ^{13}C: 75.4 MHz; ^{31}P: 121.4 MHz), or *Varian Inova-500* (^1H: 500 MHz; ^{13}C: 125.7 MHz). The chemical shifts (δ) for ^1H and ^{13}C are given in ppm relative to residual signals of the solvent. The spectra of all nuclei (except ^1H) were ^1H-decoupled. The coupling constants (J) are given in Hz. The substitution pattern of the naphthalene compound **32** was investigated by use of the GOESY pulse sequence on the *Inova-500* spectrometer. EI-MS *Fisons VG Autospec* spectrometer; m/z (rel. %).

Diethyl 2,4-Diphenylnaphthalene-1,3-dicarboxylate (**47**). A solution of $[Ni(\eta^2\text{-}C_6H_4)(PEt_3)_2]$ (**41a**) in hexane (40 ml) at $-50°$, freshly prepared by reduction of $[NiBr(o\text{-}C_6H_4Br)(PEt_3)_2]$ (520 mg, 0.98 mmol) with Li [30], was treated with a soln. of $PhC{\equiv}CCO_2Et$ (0.36 ml, 2.16 mmol) in THF (5 ml). The mixture was allowed to warm to r.t. and was stirred for an additional 2 h. Monitoring by ^{31}P-NMR spectroscopy showed that **41a** had completely reacted. Remaining Ni^0 complexes were destroyed by addition of acetone (2 ml), and the mixture was filtered through *Celite*. The solvent was removed by rotary evaporation and the residue was purified by TLC to yield 200 mg (48%) of **47**. The unsymmetrical substitution pattern of **47** was clearly established by NMR spectroscopy. IR (KBr): 1732 (C=O). ^1H-NMR (300 MHz, (D_6)acetone): 0.70 ($t, J = 7.1$, Me); 0.95 ($t, J = 7.1$, Me); 3.65 ($q, J = 7.1$, CH_2O); 4.11 ($q, J = 7.1$, CH_2O); 7.38–7.42 (m, 8 arom. H); 7.48–7.52 (m, 2 arom. H); 7.58 ($dd, J = 6.2, 1.2$, H−C(6)); 7.60 ($dd, J = 2.0, 0.9$, H−C(5)); 7.69 ($ddd, J = 8.4, 6.2, 2.0$, H−C(7)); 7.98 ('dt', $J = 8.4, 1.0$, H−C(8)). ^{13}C-NMR (75.4 MHz, (D_6)acetone): 13.10, 13.36 (2 Me); 60.52, 61.24 (2 CH_2); 125.46, 127.11, 127.49 (3 CH of naph); 128.01 (m-CH of Ph); 128.16 (CH of naph); 128.31 (m- and p-CH of Ph); 128.41 (p-CH of Ph); 129.36 (C(3)); 129.66, 130.41 (2 o-CH of Ph); 131.27, 132.30, 133.14 (3 C); 134.42 (C(8a)); 137.35, 138.29 (2 C of Ph); 138.91 (C(4a)); 167.44 (C(3)−*C*O); 168.00 (C(1))−*C*O). EI-MS ($C_{28}H_{24}O_4$): 424 (100, M^+), 379 (27), 351 (25), 307 (30), 305 (28), 276 (40).

3-Ethyl 1,2-Dimethyl 4-Phenylnaphthalene-1,2,3-tricarboxylate (**33**). A soln. of $PhC{\equiv}CCO_2Et$ (0.41 ml, 2.5 mmol) in THF (5 ml) was added at $-20°$ to a THF soln. (25 ml) of $[Ni\{o\text{-}C_6H_4C(CO_2Me){=}C(CO_2Me)\text{-}\kappa C,C\}(dcpe)]$ (**30**), freshly prepared by slow addition of DMAD (55 µl, 0.45 mmol) to $[Ni(\eta^2\text{-}C_6H_4)(dcpe)]$ (254 mg, 0.45 mmol) [58]. The mixture was stirred for 16 h at r.t. and heated for 1 h to 60°. The mixture was worked up as described above to yield 53 mg (30%) of **33**, the structure of which was determined by the HMBC-NMR pulse sequence and confirmed by X-ray analysis of crystals obtained from an Et_2O soln. layered with hexane. IR (KBr): 1736, 1724 (C=O). ^1H-NMR (200 MHz, $CDCl_3$): 0.93 ($t, J = 7.2$, Me); 3.81 (s, MeO); 3.97 ($q, J = 7.2$, OCH_2); 4.03 (s, MeO); 7.30–7.67 (m, 8 arom. H); 8.04 ('dt', $J = 8.2, 1.0$, H−C(8)). ^{13}C-NMR (50.3 MHz, $CDCl_3$): 13.66 (CH_2*Me*); 53.01 (CH_2); 61.38 (MeO); 125.46 (C(2)); 125.96 (C(6)); 127.37 (CH of naph); 127.97 (m-CH of Ph); 128.07 (CH of naph); 128.53, 128.65 (2 CH); 129.29 (C(3)); 129.86 (o-CH of Ph); 129.95 (C(4)); 132.63 (C(1)); 133.27 (C(8a)); 136.49 (C of Ph); 140.65 (C(4a)); 166.57 (C(2)−*C*O); 167.64 (C(3)−*C*O); 168.06 (C(1)−*C*O). EI-MS ($C_{23}H_{20}O_6$): 392 (100, M^+), 347 (87), 301 (65), 202 (44).

Trimethyl 4-Methylnaphthalene-1,2,3-tricarboxylate (**32**). As described above, a soln. of $MeC{\equiv}CCO_2Me$ (0.25 ml, 2.5 mmol) in THF was added to a soln. of $[Ni\{o\text{-}C_6H_4C(CO_2Me){=}C(CO_2Me)\text{-}\kappa C,C\}(dcpe)]$ (**30**) (0.45 mmol). The isolated solid (78 mg) was a 2 : 1 mixture of **32** (38%) and alkyne cyclotrimerization products that could not be separated. The substitution pattern of **32** was confirmed with the help of the GOESY-NMR pulse sequence. IR (KBr): 1726 (C=O). ^1H-NMR (300 MHz, $CDCl_3$): 2.72 (s, Me); 3.91, 3.94, 4.01 (3s, 3 MeO); 7.60–7.72 (m, H−C(2), H−C(3)); 8.00 ($dd, J = 7.5, 2.0$, H−C(8)); 8.13 ($dd, J = 7.9, 2.0$, H−C(5)). GOESY-NMR (500 MHz, $CDCl_3$): irradiation of δ 2.72 showed magnetization transfer to δ 8.13 (strong) and δ 3.94 (weak). ^{13}C-NMR (50.3 MHz, $CDCl_3$): 16.38 (Me); 52.65, 52.86, 52.99 (3 MeO); 124.90 (C(6)); 125.41, 126.56, 128.48, 128.82 (3 CH); 129.08 (C(3)); 129.36, 131.78 (2 C); 133.36 (C(8a)); 135.34 (C(4a)); 166.75 (C(2)−*C*O); 168.28 (C(3)−*C*O); 169.06 (C(1)−*C*O). EI-MS ($C_{17}H_{16}O_6$): 316 (50, M^+), 285 (100), 269 (73), 198 (78).

X-Ray Crystallography. The crystal was mounted on a glass fibre and the data recorded on a *Nonius KappaCCD* at 200 K. The structure was solved by direct methods (SIR92) [66], and expanded with use of *Fourier* techniques (DIRDIF94) [67]. The diffractions were measured by a 95 mm *CCD* camera, and the intensities of the reflections were processed by use of the computer programs *Denzo* and *Scalepak* [68]. The non-H-atoms were refined anisotropically by full-matrix least squares, while the H-atoms were located in a difference electron-density map and then refined. The maximum and minimum peaks in the final difference-*Fourier* map were 0.14 and $-0.16\ e/\text{Å}^3$, respectively. The calculations were performed with use of the crystallographic software packages maXus and teXsan [69]: $a = 9.8769(3)$ Å, $b = 11.4383(3)$ Å, $c = 17.2654(4)$ Å, $\beta = 94.774(1)°$, monoclinic ($P2_1/c$), $V = 1943.79(7)\ \text{Å}^3$, $Z = 4$, $D_x = 1.341\ \text{g/cm}^3$, $F(000) = 824$, $\mu = 0.097\ \text{mm}^{-1}$, $\theta_{\max} = 26.022°$, radiation $=$ MoK_α (graphite monochromated), multi-scan absorption correction (0.940 to 0.989), 30478 reflections (3846 independent, 2633 observed $[I > 2\sigma(I)]$), 322 parameters, $R = 0.036$, $wR = 0.0409$, $s = 1.128$.

The crystallographic data (excluding structure factors) have been deposited with the *Cambridge Crystallographic Data Centre* as deposition No CCDC-164220. Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (FAX: +44(1223)336033; email: deposit@ccdc.cam.ac.uk).

Computational Details. Density-functional calculations were performed with the Amsterdam Density-Functional program ADF1999 [70]; Ni was described by a triple-ζ STO basis set, and double-ζ-plus polarization STO basis sets were employed for all other atoms. The frozen-core approximation was used for the 1s electrons of C, N, O, and F atoms, up to and including the 2p electrons of Ni and P and the 3d electrons of Br. Geometry optimizations included the gradient corrections due to *Becke* [71] and *Perdew* [72] as well as the quasi-relativistic corrections of *Snijders* and co-workers [73]. The optimization procedure developed by *Versluis* and *Ziegler* was employed [74]. Calculations on free alkynes were performed in C_{3v} or C_s symmetry as appropriate. Calculations on the Ni species were performed without symmetry constraints. For the insertion reactions of HCCH, all stationary points were characterized as either minima (no imaginary frequencies) or transition states (one imaginary frequency). Because of the size of the molecules involved, stationary points located with substituted alkynes were not characterized in this way. However, computed geometries were in all cases closely related to those of the HCCH analogues.

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