

Nickel(II)-Carbene Intermediates in Reactions of Geminal Dihaloalkanes with Nickel(0) Reagents and the Corresponding Carbene Capture as the Phosphonium Ylide^[‡]

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Keywords: Nickel(0) reagents / Nickel(II)-carbenes / Phosphonium ylides / α -Elimination / Carbon-carbon bond formation

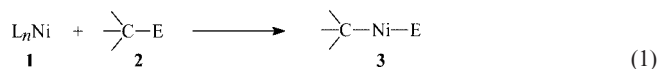
In a previous study of geminal bond cleavages of substrates of the type R_2CE_2 [$E_2 = X_2, O, S, Li(SO_2Ph)$] by nickel(0) reagents [L_nNi , $L_n = (Cod)_2, (Et_4P)_4$], leading to $R_2C=CR_2$ as products, the tentative hypothesis had been proposed that such reactions likely proceed via nickel(0)-carbene intermediates (J. J. Eisch, Y. Qian, M. Singh, *J. Organomet. Chem.* **1996**, 512, 207). Because such proposed nickel(0)-carbenes do not satisfactorily account for reactions encountered with such α -eliminations, a detailed reexamination of the reaction of these nickel(0) reagents with geminal dihalides has been undertaken. For example, two reactions of such presumed nickel(0)-carbenes remained anomalous: (1) the failure of 5,5-dibromotetraphenylcyclopentadiene to form its expected dimer, octaphenylphenylfulvalene and instead the formation of triethylphosphonium tetraphenylcyclopentadienide in its reaction with $(Et_3P)_4Ni$; and (2) the presumed capture of intermediate $R_2C=Ni^0$ in presence of the trapping agent (benz-

aldehyde or benzophenone). As to the first anomaly, a detailed study has shown that no trace of octaphenylfulvalene was formed. As to the second anomaly, the R_2C fragment could be trapped by the carbonyl reagents only in reactions involving $(Et_3P)_4Ni$, but not in reactions with $(Cod)_2Ni$. This finding compels one to conclude that the carbonyl reagent is capturing the Wittig reagent, $R_2C=PEt_3$, and not $R_2C=Ni^0$. Based upon all present data, the mechanism of such C=C bond dimerizations is best explicable in terms of nickel(II)-carbenes. The triethylphosphonium tetraphenylcyclopentadienide formed here has by single-crystal X-ray structure determination, complemented by ^{13}C NMR spectroscopic data, been found to have the zwitterionic structure $Ph_4Cp^- - ^+PEt_3$ as its paramount resonance contributor.

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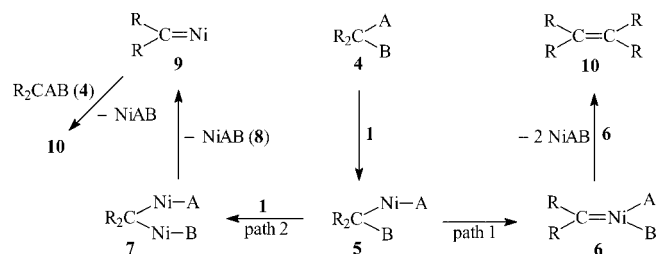
Introduction

The oxidative addition of nickel(0) complexes (L_nNi , **1**) into σ -covalent bonds between carbon and a wide variety of heteroatoms or even another carbon [**2**; $E = X, O$ (of epoxide ring or allylic ether), N, C, S, P, Al]^[2,3] produces organonickel intermediates (**3**) pivotal in olefin isomerization,^[3] olefin and diolefin oligomerization,^[3] desulfurization of aromatic sulfur heterocycles,^[4] epoxide deoxygenation^[5] and the Kumada carbon-carbon cross coupling^[6] [Equation (1)].



A recent study of nickel(0)-induced α -eliminations from geminal disubstituted alkanes **4** leading directly to carbon-

carbon π -bond coupling also appears to involve such oxidative addition by nickel(0) to produce **5**^[7] (Scheme 1). However, in this situation adduct **5** could lead to C=C bond coupling via two distinctly different routes: (1) **5** could itself undergo an α -elimination yielding a nickel(II)-carbene complex (**6**); or (2) alternatively, **5** could undergo a second oxidative addition with **1** to produce dinickelaalkane **7**, which upon elimination of NiAB (**8**) would yield nickel(0)-carbene complex **9**. Then via a dimerization-elimination of nickel(II)-carbene **6** (path 1) or by a coupling process through nickel(0)-carbene **9** and **4** (path 2) the olefin dimer **10** would result. This previous global investigation of α -eliminations of geminally disubstituted hydrocarbons by nickel(0) re-



Scheme 1.

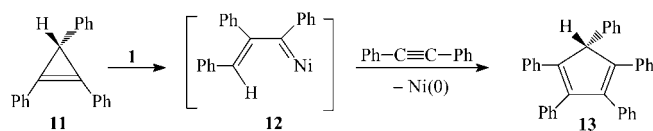
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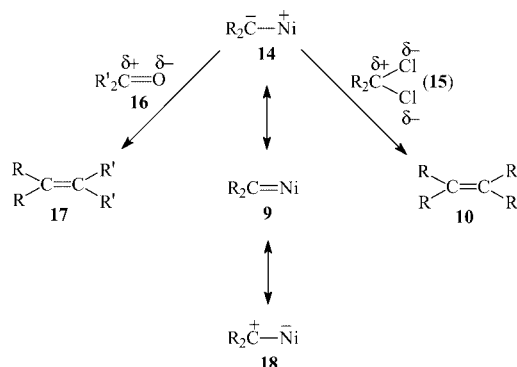
gents has embraced in its survey dihalo, sulfonyl lithio, ketonic, thioketonic and even cyclopropene reagents.^[7]

Since the ring-opening and alkyne-insertion reactions of 1,2,3-triphenylcyclopropene (**11**) with nickel(0) complexes to produce intermediate **12** seemed to be explicable only in terms of path 2 (Scheme 2; Diels–Alder capture of **12** by diphenylacetylene and subsequent Ni⁰-elimination to yield **13**), we made the preliminary hypothesis that all such geminal disubstituted derivatives would similarly involve nickel(0)-carbene intermediates.



Scheme 2.

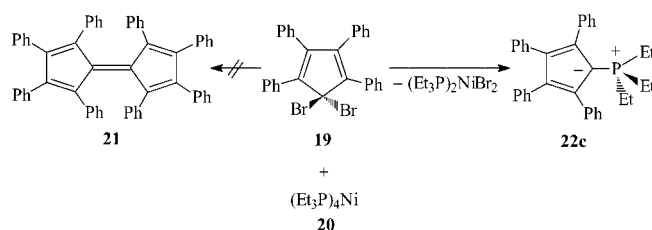
But in extending path 2 to the reactions of L_nNi (**1**) with geminal dichlorides, for example, one would have to invoke the unlikely polarization **14** to explain the coupling with R_2CCl_2 (**15**) to form olefin dimer **10** or the purported capture of **9** as **17** with an aldehyde or ketone $R_2C=O$ (**16**), benzaldehyde or benzophenone for **9** in ref.^[7] (Scheme 3). On the contrary, with late transition metal or Fischer carbenes, the carbene center is known to exhibit *electrophilic* (**18**), rather than nucleophilic (**14**) character. Accordingly, resonance structure **14** would be only a minor contributor to the actual π -electron distribution in **9**.



Scheme 3.

Because of these incongruities between the experimental observations made in the reactions of geminal dihalides (e.g. **15**) with nickel(0) reagents **1** and the postulated role of nickel(0)-carbenes (Scheme 1; path 2: **4** $\rightarrow$ **5** $\rightarrow$ **7** $\rightarrow$ **9** $\rightarrow$ **10**), we have reinvestigated these reactions in a more searching manner. We have tried to detect and identify all possible by-products and side products. Most of all, we have striven to explain the anomalous course of the attempted carbon–carbon π -bond coupling of 5,5-dibromotetraphenylcyclopentadiene (**19**) by tetrakis(triethylphosphane)nickel(0), $(Et_3P)_4Ni$ (**20**).

Instead of dimerizing to octaphenylfulvalene (**21**), the corresponding phosphonium ylide or Wittig reagent **22c** was formed in high yield^[7] (Scheme 4). Any acceptable reaction mechanism, in our opinion, would have to explain how such Wittig reagents could readily arise in the course of such couplings. We will show that only the intermediacy of nickel(II)-carbene complexes (Scheme 1; path 1: **4** $\rightarrow$ **5** $\rightarrow$ **6** $\rightarrow$ **10**) can readily lead to Wittig reagents *in situ*.

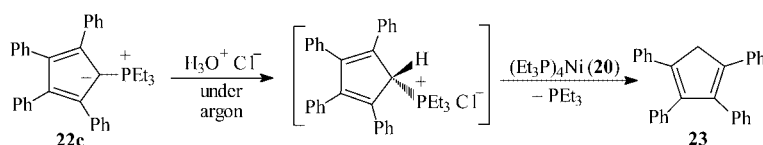


Scheme 4.

Results and Discussion

Anomalous Reaction of 5,5-Dibromotetraphenylcyclopentadiene (**19**) with $(Et_3P)_4Ni$ (**20**)

The reaction mixture of a 1:3 molar ratio of **19** and **20** in THF at room temp. was freed of volatiles and the resulting residue was extracted with warm cyclohexane. The extract deposited 70% of triethylphosphonium tetraphenylcyclopentadienide (**22c**).^[8a] From the concentrated and cooled cyclohexane filtrate were obtained 80% of the expected $(Et_3P)_2NiBr_2$. Finally, treating the last filtrate with deoxygenated 6 N aqueous HCl led upon hydrolytic workup to the isolation of 1,2,3,4-tetraphenylcyclopentadiene (**23**, 24%) as the only detectable organic product with no sign of fulvalene **21**. The hydrocarbon **23** can be considered as the expected reductive cleavage product of phosphonium ylide **22c** by **20** and acid, shown in Scheme 5, a reaction having ample precedent.^[8b] From this detailed analysis of the reaction products, we therefore conclude that the formation of phosphonium ylide in Scheme 3 has proceeded essentially to completion without the generation of any **21**. The failure of any fulvalene like **21** to form in such a reaction cannot be ascribed to any inherent instability of these substituted fulvalenes. Both 1,2,3,4-tetraphenylfulvalene (m.p. 202 °C)^[9a] and octaphenylfulvalene [**21**, m.p. 170 °C (dec.)]^[9b] have been prepared as brilliant orange-red solids and have been found to be indefinitely stable below 100 °C.



Scheme 5.

The Stability and Structure of Triethylphosphonium Tetraphenylcyclopentadienide (**22c**)

Although the phosphonium ylide **22c** has all the structural features of a typical Wittig reagent, it is stable to air and moisture when stored at room temperature and does not react with either benzaldehyde or benzophenone in warm cyclohexane to give a fulvene, the expected Wittig methylenation reaction product. But the corresponding triphenylphosphonium cyclopentadienide has also been shown by Ramirez and Levy not to react with cyclohexanone even at elevated temperatures.^[10] In both instances, the delocalization of the anionic charge and Hückel aromaticity of such a cyclopentadienyl ring could be viewed as the cause for the inertness of such Wittig reagents.

The single-crystal X-ray structure determination of phosphonium ylide **22c** (Figure 1 and Tables 1 and 2) sheds light on the extent of delocalization of the negative charge in the cyclopentadienyl moiety of **22c**, namely the relative importance of resonance structures **22a**, **22b** and **22c**, as well as the relative importance of the neutral phosphorane resonance structure **22d**, often invoked with Wittig reagents. It should be noted that this XRD structure of **22c** is not the first trisubstituted phosphonium cyclopentadienide whose structure has been determined in the crystalline state. The crystal structure of triphenylphosphonium cyclopentadienide (**24**) has been determined by X-ray crystallography and the question of the degree of ylide-ylenic character in the cyclopentadienyl carbon–phosphorus bond carefully addressed.^[11a] This prior work has been most valuable in our present attempt to evaluate the relative contributions of resonance structures **22a–22d**.

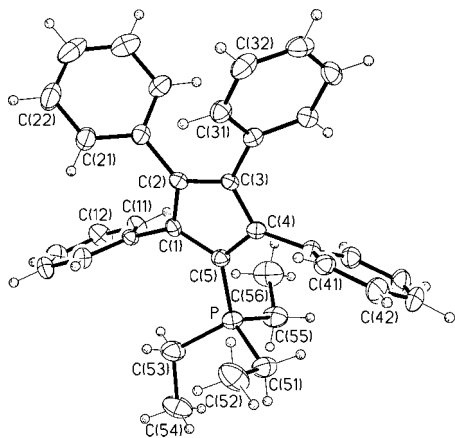


Figure 1. ORTEP projection of triethylphosphonium tetraphenylcyclopentadienide (**22c**) with ellipsoids at the 30% probability level.

In Table 1 are listed the experimentally determined C(5)–P and C–C bond lengths of greatest relevance in evaluating the relative contributions of resonance structures **22a–22d**. The observed C–C bond lengths within the cyclopentadienyl ring, as shown in **22d**, can be profitably compared with those of the cyclopentadienyl anion.^[12] Of analogous use is a comparison of C(5)–P bond length in **22a–d** with

Table 1. Selected bond lengths and angles of triethylphosphonium tetraphenylcyclopentadienide (**22c**).

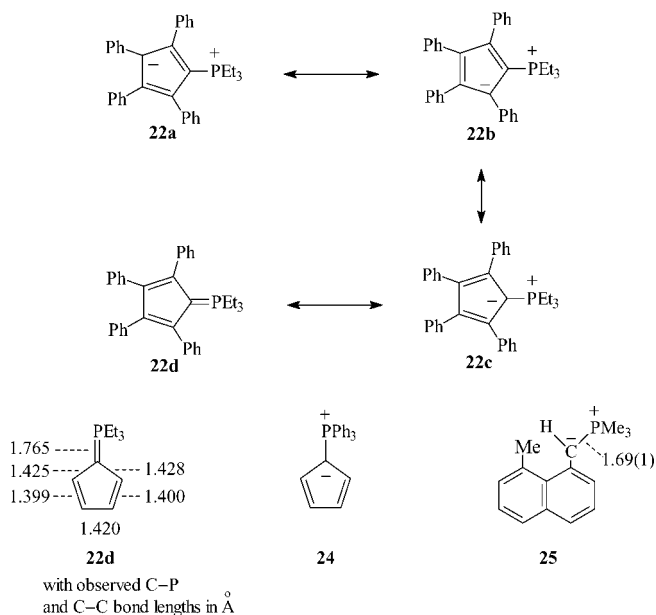
Bond lengths [Å]			
P–C(5)	1.756(5)	C(1)–C(16)	1.492(6)
P–C(51)	1.807(5)	C(2)–C(3)	1.420(7)
P–C(53)	1.812(6)	C(2)–C(26)	1.483(7)
P–C(55)	1.825(5)	C(3)–C(4)	1.400(6)
C(1)–C(2)	1.399(6)	C(3)–C(36)	1.476(6)
C(1)–C(5)	1.425(6)	C(4)–C(5)	1.428(6)
Bond angles [°]			
C(5)–P–C(51)	112.3(3)	C(4)–C(3)–C(2)	108.5(4)
C(5)–P–C(53)	112.0(3)	C(3)–C(4)–C(5)	107.4(5)
C(5)–P–C(55)	113.6(2)	C(1)–C(5)–C(4)	108.1(4)
C(2)–C(1)–C(5)	107.4(4)	C(1)–C(5)–P	126.6(4)
C(1)–C(2)–C(3)	108.6(4)	C(4)–C(5)–P	125.0(4)

Table 2. Crystal data and structure refinement for triethylphosphonium tetraphenylcyclopentadienide (**22c**).

Empirical formula	C ₃₅ H ₃₅ P
Formula weight	486.60
Diffractometer	Siemens P4 (scintillation counter)
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system	monoclinic
Space group	P2(1)
Unit cell dimensions	$a = 10.757(2)$ Å; $a = 90^\circ$ $b = 11.076(2)$ Å; $\beta = 94.57(2)^\circ$ $c = 11.988(3)$ Å; $\gamma = 90^\circ$
Volume	1423.8(5) Å ³
Z	2
Density (calculated)	1.135 mg/m ³
Absorption coefficient	0.117 mm ^{−1}
$F(000)$	520
Crystal size	0.32 × 0.28 × 0.24 mm
θ range for data collection	2.45–22.50°
Index ranges	−11 ≤ h ≤ 11, 0 ≤ k ≤ 11, 0 ≤ l ≤ 12
Reflections collected	2076
Independent reflections	1970 [$R(\text{int}) = 0.0205$]
Completeness to $\theta = 22.50^\circ$	99.6%
Absorption correction	none
Max. and min. transmission	0.9724 and 0.9635
Refinement method	full-matrix least squares on F^2
Data/restraints/parameters	1970/1/325
Goodness-of-fit on F^2	0.795
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0371$, $wR2 = 0.0645$
R indices (all data)	$R1 = 0.0715$, $wR2 = 0.0722$
Absolute structure parameter	0.04(17)
Largest diff. peak and hole	0.118 and −0.168 e Å ^{−3}

that of the similar phosphonium ylide **24** and that of naphthalene derivative **25**.^[13a]

In the first place, the clearly alternating C–C bond lengths of the cyclopentadienyl ring (1.40 ± 0.02 Å) of **22a–d** indicate that resonance structures **22a** and **22b** make relatively lesser contributions to the π -electron distribution. In the cyclopentadienyl anion of KCp(18-crown-6), however, the ring C–C bond lengths range from 1.37 to 1.41 Å with a mean of 1.40 Å. The distances in **22a–d** might be considered the same within experimental error, if their bond length alternation did not so nicely parallel the C–C bonding in resonance structures **22c** or **22d**.



The question of ionic or double character of the carbene–carbon bonding with phosphorus can reasonably be judged on the basis of the carbene C–P bond in **25**, one of the few open-chain phosphoranes with alkyl substituents, whose XRD structures have been measured. At 1.69 Å the C–P bond in **25** should have more C=P bond character than that in **22a–d**, 0.08 Å longer. Another indication of lessened C=P bonding in **22a–d** results from comparing the bond lengths of the C–P bonds of the three ethyl groups attached to phosphorus, 1.81 Å, with the carbene C(5)–P bond, 1.77 Å. A change in the C(sp³) hybridization of the ethyl in **22** to the C(sp²) hybridization of the phenyl in Ph₄P⁺ (1.81 → 1.79 Å) suggests that the sp²-hybridized carbene–carbon–phosphorus bond length would be 1.79 Å for an ordinary single C–P bond. This length is so close to the observed 1.77 Å as to indicate that there is markedly less phosphorane character in **22**, as suggested by **22c** than there is in **25** (C–P bond of 1.69 Å) or even in **24** (C–P bond of 1.72 Å). Therefore, the carbon–phosphorus linkage is best represented by the single resonance structure **22c**. The greater zwitterionic character in the carbene–carbon–phosphorus bond of **22c**, compared with that of **24**, can be attributed to the following electronic stabilization: (1) the

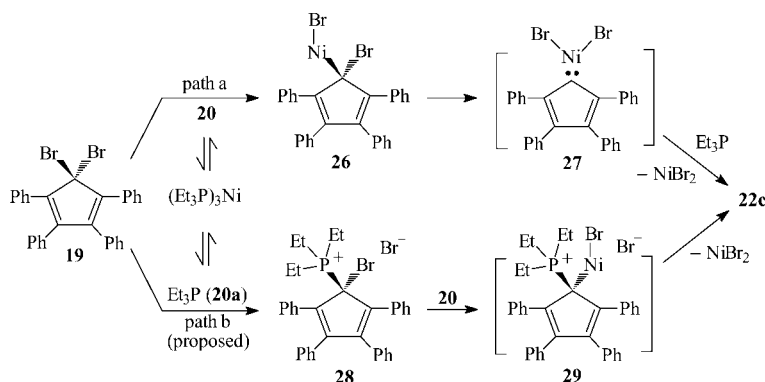
presence of electron-donating ethyl groups on P, instead of phenyl groups, stabilizing the cationic P-center; and (2) the presence of π -electron-withdrawing phenyl groups on the cyclopentadienyl ring, instead of hydrogens, stabilizing the anionic C-center. Assigning a reliable percentage of ylene character to the C–P bond, however, seems to be beset with great uncertainty.^[11b]

The ¹³C NMR spectrum of **22c** provides confirmation of the higher charge density of carbon C(5) over that of centers C(1) or C(4).^[13b] The doublet centered at δ = 124.85 ppm displays the largest ¹³C–³¹P coupling (60 Hz) whereas the doublets at δ = 127.10 ppm and 127.80 ppm are split by 25 Hz and 18 Hz, respectively. As expected, the doublet with the largest splitting must be assigned to C(5), which is closest to the phosphorus. Since C(5) is the closest to phosphorus and its signal is the most shielded, it would thus have a higher electron density than those of C(1) and C(4).

Possible Mechanistic Routes to Triethylphosphonium Tetraphenylcyclopentadienide (**22c**)

Two quite divergent pathways leading from 5,5-dibromotetraphenylcyclopentadiene (**19**) and (Et₃P)₄Ni (**20**) to **22c** can be envisioned, the one an integral part of the nickel(II)-carbene pathway proposed here for the coupling of geminal dihalides to yield dimeric olefins via intermediates analogous to **26** and **27** (cf. *infra*) (path a; Scheme 6) and the other involving an initially formed quaternary phosphonium salt (**28**), followed by oxidative addition of Ni⁰ from **20** to produce **29** and concluded by elimination of NiBr₂ (path b).^[14] Clearly, the latter route would involve no nickel–carbene complex as such.

As will be discussed below, there is ample precedent for the coupling of geminal dihalides by Ni⁰ reagents, either (Et₃P)₄Ni (**20**) or (Cod)₂Ni (**34**), via intermediates like **26** and **27**, when steric factors do not prevent their coupling. Thus, the feasibility of path a is evident. On the other hand, path b requires as its first step the slow quaternization of Et₃P (**20a**) by **19** to form **28**, a process known to require a combination of higher temperatures, peroxides and/or ultraviolet radiation to be initiated and widely considered to involve free-radical chain reactions.^[15a,15b] By contrast, it

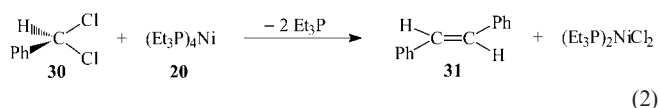


Scheme 6.

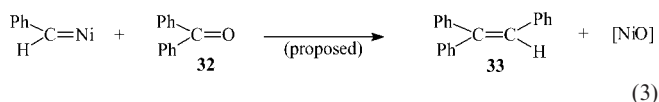
should be noted that the reaction of **19** with **20** proceeds readily at room temperature in oxygen- and peroxide-free THF with no special illumination. Furthermore, the reaction of putative intermediate **28** with **20** to yield the necessary **29** is obviously fraught with steric hindrance. Finally and decisively, the attempted interaction of **19** with **20a** in THF, with the conditions under which **19** and **20** react completely (18 h at 25 °C), failed altogether. Since this proposed first step of path b has been attempted in this study without success, path b can be dismissed as a viable alternative to path a.

Reactions of α,α -Dichlorotoluene (**30**) with Nickel(0) Reagents

In our previous report we observed that a 1:2 mixture of α,α -dichlorotoluene (**30**) and $(\text{Et}_3\text{P})_4\text{Ni}$ (**20**) reacted in THF at 25 °C to give 98% of *trans*-stilbene (**31**) [Equation (2)].^[16]

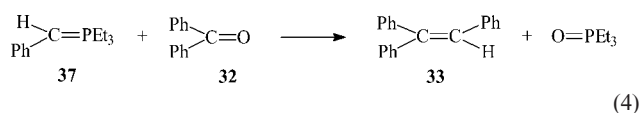


In a parallel reaction conducted at 0 °C, the 1:2 mixture of **30** and **20** was allowed to react in the presence of 1 equiv. of benzophenone (**32**). Hydrolytic workup led to the isolation of 40% of **31** and 47% of triphenylethylene (**33**). The formation of **33** was at first thought to have originated from a Wittig-like reaction of the nickel(0)-carbene, $\text{PhCH}=\text{Ni}$, with **32** through the elimination of NiO [Equation (3)].



But the present findings, employing $(\text{Cod})_2\text{Ni}$ (**34**) with **30**, tend to rule out this interpretation. Certainly, a 1:2 mixture of **30** and **34** reacted equally smoothly in THF at 25 °C to produce a high yield of *trans*-stilbene (96%). But the corresponding attempted trapping experiment involving a 1:2:1 mixture of **30**, **34** and **32** again led only to a high conversion to *trans*-stilbene (94%) with no detectable amount of the trapping product **33**. If the nickel(0)-carbene, $\text{PhCH}=\text{Ni}$, were the source of **33**, it should also have been present in this mixture and therefore have been trapped. Since no such

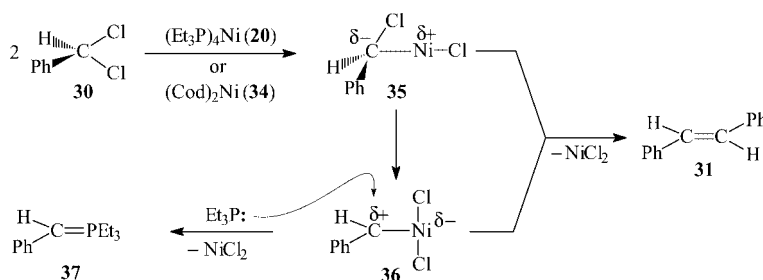
trapping product was detected, we suggest an alternative and mechanically more reasonable source of **33**. We now propose, instead, that a nickel(II)-carbene (**36**) is generated in these coupling reactions and that coupling occurs through the reaction between **36** and oxidative-addition product **35**. The matched polarities of carbon–nickel bond of **35** and the Fischer-carbene-carbon–nickel(II) bond of **36** should foster rapid C–C bond formation to yield **31**. Only in the C–C couplings employing reagent **20** would the triethylphosphane be present to undergo a competitive reaction with the electrophilic carbon of nickel(II)-carbene **36**, leading to the displacement of nickel(II) chloride as its Et_3P complex and the generation of phosphane ylide **37** (Scheme 7). The reaction of benzophenone (**32**) with this Wittig reagent, rather than the dubious reaction with the previously suggested nickel(0)-carbene, is therefore concluded to be the actual source of the triphenylethylene (**33**) [Equation (4)].



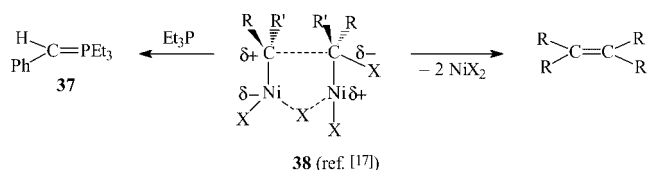
The observation of phosphonium ylide **22c** as the ultimate Wittig-like reagent from dibromo compound **19** and nickel reagent **20**, as well as the aforementioned detection of **37** in the reaction of geminal dichloro compound **30** with **20**, show that phosphonium ylides can occur as intermediates in such C–C bond-coupling reactions. That they are necessary intermediates, however, seems most unlikely.^[17]

Generalized Mechanism for the Nickel(0)-Promoted Coupling of Geminal Disubstituted Hydrocarbons

The foregoing coupling mechanism, having nickel(II)-carbenes as key intermediates, can be rationally applied to the other geminal dihalohydrocarbons already studied, namely dibromomethane, dichlorodiphenylmethane and 5,5-dibromo-1,2,3,4-tetraphenylcyclopentadiene (**19**) (Scheme 8).



Scheme 7.

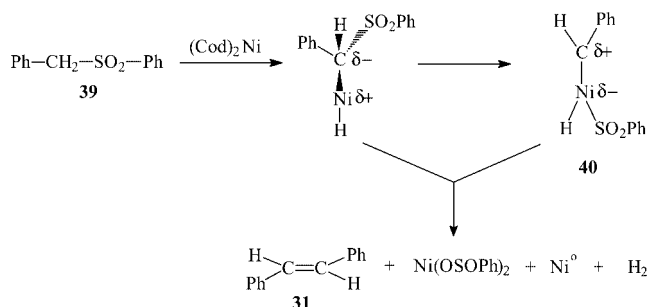


Scheme 8.

Considering **38** as an appropriate activated complex,^[18] it is clear that when R and R' are space-filling groups as in the reaction of 5,5-dibromotetraphenylcyclopentadiene (**19**) (R and R' combined as a 1,4-tetraphenylbutadienylenegroup), then C–C bond formation will be relatively slow and the Et₃P attack will form the Wittig reagent selectively. With R and R' as phenyl groups, C–C bonding is still possible but backside attack at the pseudo-tertiary carbene-carbon by Et₃P should be slow. This view is in agreement with our previous finding that the reaction of (Et₃P)₄Ni with dichlorodiphenylmethane in the presence of benzaldehyde leads to 95% of tetraphenylethylene with no sign of triphenylethylene, the expected Wittig reaction product expected to arise from benzaldehyde and Ph₂C=PEt₃.^[19]

Finally, with R = Ph and R' = H, as was presented in Scheme 5, C–C bond formation would occur along the internuclear line in **38** with the phenyl groups *trans* to each other for steric reasons. In this case, the carbene-carbon is pseudo-secondary and hence more accessible to backside attack by Et₃P and thus the formation of the corresponding Wittig reagent. With R and R' as H in dihalomethanes, the frontside C–C coupling in **38** and the backside attack by Et₃P should be of comparable facility and therefore C–C coupling and Wittig-reagent formation both are possible and in fact observed.

The coupling mechanism operative with other geminal disubstituted hydrocarbon derivatives, such as thioketones and α -lithioorganic sulfones, is also most likely one involving analogous nickel(II)-carbene intermediates.^[20] Even the behavior of benzylic sulfones toward nickel(0) reagents indicates the possible intermediacy of nickel(II)-carbene complexes. Benzyl phenyl sulfone (**39**), for example, reacted with (Cod)₂Ni in toluene at 25 °C over an extended period to give the deposition of nickel metal. Hydrolytic workup gave a 40% yield of *trans*-stilbene (**31**) with no trace of bibenzyl (Scheme 9). The absence of bibenzyl is consistent with the absence of reductive cleavage of the C–S bond. The formation of *trans*-stilbene can be readily explained through the



Scheme 9.

oxidative addition process depicted in Scheme 9, which would lead to a nickel(II)-carbene (**40**) and thus to C–C bond coupling analogous to that in Scheme 7.

Conclusions

The bond cleavages of geminal dihalides of the type R₂CX₂ by nickel(0) reagents is best depicted as leading to dimers R₂C=CR₂ via nickel(II)-carbenes by the following sequence of reactions: (1) oxidative addition of Ni⁰ to produce XR₂C–Ni–X; to provide the nickel(II)-carbene, R₂C⁺–NiX₂[–]; (3) C=C bond formation between XR₂C^{6–}–NiX₂[–] and R₂C⁺–NiX₂[–] because of opposite polarities. If step 3 is too slow in the reactions involving (Et₃P)₄Ni, then any free Et₃P can displace the NiX₂ from R₂C⁺–NiX₂[–] and capture the R₂C ligand as the Wittig reagent, R₂C=PEt₃. Such a Wittig reagent, rather than the previously assumed nickel(0)-carbene, R₂C=Ni⁰, is responsible for the formation of R₂C=CR'R'' when R'R''C=O is added to such reaction mixtures.

Triethylphosphonium tetraphenylcyclopentadienide (**22c**), the Wittig reagent obtained in high yield from the unsuccessful attempt to couple 5,5-dibromotetraphenylcyclopentadiene to produce octaphenylfulvalene (cf. supra: slow step 3), was subjected to X-ray crystallographic structure determination. Such structural data, together with its ¹³C NMR chemical shifts and ¹³C–³¹P coupling constants, are clearly consistent with the electronic structure **22c**, where the ring C(5)–P bond is essentially a zwitterionic single C–P bond and the negative charge of the *pseudo*-cyclopentadiene anion greatest on C(5).

Experimental Section

General Procedures and Techniques: All reactions were carried out under a positive pressure of anhydrous, oxygen-free argon. All solvents employed with organometallic compounds were dried and distilled from a sodium metal/benzophenone ketyl mixture prior to use. The preparation and purification of oxygen- and moisture-sensitive reagents were carried out under argon with the use of Schlenk techniques.^[21] The IR spectra were recorded with a Perkin–Elmer instrument, model 457 and samples were measured either as mineral oil mulls or as KBr films. The NMR spectra (¹H and ¹³C) were recorded with a Bruker spectrometer, model AM-360 and tetramethylsilane (TMS) was used as the internal standard. The chemical shifts reported are expressed on the δ -scale and in parts per million (ppm) from the reference TMS signal. The gas-chromatographic analyses were carried out with a Hewlett–Packard instrument, model 5880, provided with a 6 ft OV-101 packed column or with a Hewlett–Packard instrument, model 5890, having a 30 m SE-30 capillary column, respectively. Melting points were determined with a Thomas-Hoover Unimelt capillary melting point apparatus and are uncorrected. The (Cod)₂Ni was prepared according to a procedure adapted from those of Semmelhack^[22] and of Schunn.^[23] The yield of product has been improved to 95% by purifying the starting materials with extreme care.

The (Et₃P)₄Ni was prepared according to the method of Cundy^[24] and the (Cod)(Bpy)Ni by the procedure of Dinjus et al.^[25] The α , α -dichlorotoluene, dichlorodiphenylmethane and dibromomethane

were purchased at 98+% of purity and their purity further checked by gas chromatography.

The 5,5-dibromotetraphenylcyclopentadiene (**19**) was prepared for the first time by the following procedure developed in this laboratory. A solution of 3.76 g (10.0 mmol) of 1,2,3,4-tetraphenylcyclopentadiene (**23**) in 80 mL of CCl_4 was treated with 3.65 g (20.5 mmol) of *N*-bromosuccinimide (99%) and the suspension heated at reflux until all suspended solid had risen to the surface (90 min). During the heating, a small illuminated UV lamp was focused on the reaction flask. The hot solution was then filtered from the succinimide and the filtrate freed of solvent in a rotary evaporator. The pale yellow solid residue of 5.1 g was essentially pure **19** because the peak at $\delta = 4.0$ ppm in the ^1H NMR spectrum of the starting diene was absent. Recrystallization from 95% ethanol yielded 4.4 g (83%) of pure **19**, m.p. 154–155 °C. $\text{C}_{29}\text{H}_{20}\text{Br}_2$ (528.30): C 65.31, H 3.78; found C 65.69, H 3.82.

The sample of octaphenylfulvalene (**21**) was prepared by the following route. A suspension of 1.50 g (2.80 mmol) of **19**, prepared in the foregoing method, and 5.0 g (76 mmol) of zinc dust in 50 mL of benzene was treated with a crystal of iodine as an activator and was then stirred under reflux for 6 h. The resulting deep red suspension was filtered hot. The filtrate was freed of solvent in a rotary evaporator to leave a deep red gummy residue. Stirring this residue with hot portions of a 1:1 (v/v) mixture of benzene/95% ethanol gave a deep red extract. Concentration and cooling of the extract gave 710 mg (69%) of brilliant orange-red solid (**21**), which had multiplets of proton signals between $\delta = 7.0$ ppm and 7.4 ppm in the ^1H NMR spectrum and whose mass spectrum at 70 eV had a parent peak at $m/z = 736$, characteristic of fulvalene **21**. No peaks were present indicative of any **19** or any other bromine-containing component (with isotopic ^{79}Br and ^{81}Br components). This sample melted at 170 °C with decomposition, despite several recrystallizations from 95% ethanol/toluene. $\text{C}_{58}\text{H}_{40}$ (736.77): calcd. C 94.54, H 5.46; found C 94.10, H 5.16.

X-ray Crystallographic Study of Triethylphosphonium Tetraphenylcyclopentadienide (22**). Crystal Mounting and Data Collection:** Data were collected at room temperature with a Siemens P4 diffractometer equipped with a scintillation counter. An orange crystal was mounted on a glass fiber with epoxy cement and a unit cell determined from the angular settings of 25 centered reflections. Systematic absences in the diffraction data indicated either the monoclinic space groups $P2_1$ or $P2_1/m$. *E* statistics initially indicated the noncentrosymmetric alternative, and the structure that was developed in this setting proved to be incompatible with mirror-plane symmetry. All non-hydrogen atoms were refined with anisotropic thermal parameters and hydrogen atoms were treated as idealized contributions. The correctness of the reported hand was affirmed by the value of the refined Flack parameter: 0.04(17). All software used was contained in the SHELXTL and data collection libraries of programs provided by the Siemens Corporation (Madison, WI). The pertinent crystal data and structure refinement are presented in Table 2. CCDC-628202 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Preparation of Triethylphosphonium Tetraphenylcyclopentadienide (22c**) from 5,5-Dibromotetraphenylcyclopentadiene (**19**) and $(\text{Et}_3\text{P})_4\text{Ni}$ (**20**):** A solution of 1.94 g (3.66 mmol) of **19** in 60 mL of THF was treated with 640 mg (1.20 mmol) of **20** at 25 °C. The dark red solution was stirred for 18 h and then the THF was removed under reduced pressure. The dark residue was extracted with warm cyclohexane (6 10-mL portions of deoxygenated solvent). The hot ex-

tracts were filtered, concentrated to 2/3 of volume and chilled to deposit 1.24 g of amber-colored **22c** (70%). Recrystallization from cyclohexane yielded pale orange **22c**, m.p. 200–202 °C, which was submitted to X-ray single-crystal determination (Table 2). ^1H NMR (C_6D_6): $\delta = 0.41$ – 0.50 (m, 9 H), 1.02 – 1.21 (m, 6 H), 6.82 – 7.59 (m, 304) ppm. ^{13}C NMR (C_6D_6): $\delta = 15.98$ (d), 20.17 (3), 124.85 (d), 127.10 (d), 127.80 (m, high intensity), 132.45 (d) ppm. The $J_{\text{C,P}}$ values of the doublets at $\delta = 124.85$, 127.10 and 127.80 ppm are 60, 25 and 18 Hz, respectively.

The original cyclohexane filtrate from which **22c** had crystallized was concentrated to dryness under reduced pressure and the residue dissolved in dry, deoxygenated C_6H_6 . The ^1H NMR spectrum of this solution displayed only very broad absorptions, characteristic of the presence of paramagnetic components. Hence, the entire C_6D_6 solution was treated with deoxygenated 6 N aqueous HCl. Hydrolytic workup yielded 107 mg of a reddish solid, whose ^1H NMR spectrum showed it to be largely **23** (m.p. 180–181 °C, 24%, ^1H NMR peak at $\delta = 4.0$ ppm).

The deep red reaction residue remaining after the cyclohexane extraction of the reaction mixture was redissolved in THF and cooled to -78 °C. Long dark red needles of $(\text{Et}_3\text{P})_2\text{NiBr}_2$ were formed (440 mg, 80%).^[26] The ^1H NMR spectrum showed no aromatic proton absorptions.

Attempted Reaction of 5,5-Dibromotetraphenylcyclopentadiene (19**) with Triethylphosphane (**20a**). Test of the First Proposed Step, **19** + **20** → **28**, of Path b in Scheme 6:** A solution of 3.88 g (7.32 mmol) of **19** and 0.87 g (7.4 mmol) of **20a** dissolved in 120 mL of anhydrous, deoxygenated THF was allowed to stand under an argon atmosphere for 18 h at 25 ± 5 °C in a Schlenk flask sheathed in aluminum foil, so as to exclude light. During this time, the initially pale yellow solution did not change color nor did any solid precipitate. All volatiles were then removed under reduced pressure at 25 °C and the resulting residue was shown to be essentially pure **19** by ^1H and ^{13}C NMR spectroscopic analysis.

Reaction of $(\text{Cod})_2\text{Ni}$ (34**) with α,α -Dichlorotoluene (**30**):** In our previous report on the reactions of geminal dihaloalkanes with nickel(0) reagents^[7] the experimental details for the individual reactions of α,α -dichlorotoluene, dichlorodiphenylmethane and dibromomethane with $(\text{Et}_3\text{P})_4\text{Ni}$ or for the reaction of dichlorodiphenylmethane with $(\text{Cod})_2\text{Ni}$ have already been published. The following experiment is described here for the first time.

A solution of $(\text{Cod})_2\text{Ni}$ (**34**, 1.35 g, 4.90 mmol) and α,α -dichlorotoluene (**30**, 0.40 g, 2.40 mmol) in 20 mL of THF was stirred for 2 h at 25 °C. Quenching with deoxygenated 6 N HCl under argon. Usual workup (diethyl ether extraction, neutralization with solid NaHCO_3 , solvent removal and flash chromatography) permitted the isolation of only *trans*-stilbene (**31**) (225 mg, 96%).

Reactions of $(\text{Cod})_2\text{Ni}$ (34**) with α,α -Dichlorotoluene (**30**) in the Presence of Benzophenone (**28**):** A reaction run almost identical to the foregoing was conducted, except that 1 equiv. of benzophenone (**32**) was present. The analogous workup of the reaction mixture and flash chromatography led only to *trans*-stilbene (94%), with 90% of the benzophenone recovered.

Reaction of $(\text{Cod})_2\text{Ni}$ (34**) with Benzyl Phenyl Sulfone (**39**):** A solution of **34** (1.24 g, 4.50 mmol) and **39** (1.05 g, 4.50 mmol) in 60 mL of dry, deoxygenated toluene became black upon mixing the components. The black mixture was stirred at 25 °C for 4 h and then at reflux for 3 h, during which latter period a nickel mirror appeared on the flask wall. Hydrolysis of the mixture with deoxygenated, aqueous 6 N HCl led to gas evolution. Separation and drying of the toluene layer, removal of solvent and flash

chromatography led to the isolation of *trans*-stilbene (0.81 g, 39%) and recovered **39**. No sign of bibenzyl was seen in the ^1H NMR spectrum of the crude reaction product.

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- [11] a) H. L. Ammon, G. L. Wheeler, P. H. Waats Jr, *J. Am. Chem. Soc.* **1973**, *95*, 6158–6163; b) in ref.^[11a], such percentages for **24** ranged from 20% to 80%, depending upon the method of calculation.
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- [14] A referee has been helpful in suggesting the possibility of path b as an alternative possibility for producing **22c** from **19** and **20** without the intermediacy of a nickel(II)-carbene. In addition, the same referee suggested the key experiment for deciding on the viability of path b as a competing mechanism, namely whether or not **19** and **20a** would react with each other at 25 °C.
- [15] a) F. Ramirez, N. McKelvie, *J. Am. Chem. Soc.* **1957**, *79*, 5829–5830. b) Although this report appeared 50 years ago, it has not been repudiated since and in fact is treated as reliable in a classic monograph on organophosphorus reactions: R. F. Hudson, *Structure and Mechanism in Organo-Phosphorus Chemistry*, Academic Press, New York, **1965**, pp. 297–299.
- [16] When the THF solution of the final reaction mixture was concentrated to half its volume and then cooled to 0 °C, dark red crystals of bis(triethylphosphane)nickel(II) chloride were deposited, mp. 113–115 °C (68%); D. T. Doughty, G. Gordon, R. P. Stewart Jr, *J. Am. Chem. Soc.* **1979**, *101*, 2645–2648.
- [17] A referee has proposed that in such coupling reactions of geminal dihalides with $(\text{Et}_3\text{P})_4\text{Ni}$ (**20**) perhaps metal carbenes are not involved at all, that maybe they are just phosphonium ylide adducts, $\text{R}_3\text{P}^+-\text{CR}_2-\text{NiCl}_2$ and, as Milstein and co-workers have shown, that ylides could be converted to metal-carbenes by late transition metal compounds (M. Gandelman, K. M. Naing, B. Rybtchinski, E. Poverenov, Y. Ben-David, N. Ashkenazi, R. M. Gauvin, D. Milstein, *J. Am. Chem. Soc.* **2005**, *127*, 15265–15272). Admittedly, our work has shown that phosphonium ylide **22c** is readily formed from dibromo compound **19** and $(\text{Et}_3\text{P})_4\text{Ni}$ (**20**) and that **30** and **20** produce Wittig reagent **37** in solution, which is capable of being captured in a Wittig reaction with benzophenone. Despite the presence of **37** in such reactions, such phosphonium ylides or their complexes with NiCl_2 cannot be essential intermediates in these coupling reactions, because **30** can be converted into olefin dimer **31** in over 90% yield either by $(\text{Et}_3\text{P})_4\text{Ni}$ or by $(\text{Cod})_2\text{Ni}$. Obviously, the latter nickel(0) complex could not involve any phosphonium ylide. In fact, any phosphonium ylide generated with **30** may be in ready equilibrium with the crucial carbene intermediate **36a** (**36** with coordinated Et_3P):

$$\text{Et}_3\text{P}^+-\text{CHPh}-\text{NiCl}_2^- \rightleftharpoons \text{H} \begin{array}{c} \delta- \\ \text{C} \\ \delta+ \end{array} \begin{array}{c} \text{Cl} \\ | \\ \text{Ph} \end{array} \begin{array}{c} \delta+ \\ \text{Ni} \\ \delta- \end{array} \begin{array}{c} \text{PEt}_3 \\ | \\ \text{Cl} \end{array} \quad (\text{36a})$$
- [18] The likelihood of a bridging halide between the nickel centers in the proposed activated complex **38** is supported by the known dimeric structure of η^4 -tetraphenylcyclobutadiene–nickel(II) bromide where the two units of the monomer are held together by two $\text{Ni} \cdots \text{Br} \cdots \text{Ni}$ bridges.
- [19] The failure to detect triphenylethylene in this trapping experiment with benzaldehyde can stem from either of two causes: (1) the supposed ylide, $\text{Ph}_2\text{C}=\text{PEt}_3$, is too slow to react with PhCHO , before it reacts thus: $\text{Ph}_2\text{C}=\text{PEt}_3 + \text{Ph}_2\text{C}(\text{Cl})\text{NiCl} \rightarrow \text{Ph}_2\text{C}=\text{CPh}_2 + (\text{Et}_3\text{P})_2\text{NiCl}_2$; or (2) in analogy with Scheme 7, Et_3P is unable, for steric reasons, to react with $\text{Ph}_2\text{C}-\text{NiCl}_2$ (**36**) before coupling occurs via **38**.
- [20] The α -elimination of lithium benzenesulfinate from $\text{Ph}-\text{CHLi}-\text{SO}_2\text{Ph}$ cannot be effected by heating this dry salt under argon at 90–120 °C for 5 h. No trace of either *cis*- or *trans*-stilbene could be detected upon hydrolytic workup and 90% of the starting sulfone was recovered. By contrast, irradiation of $\text{Ph}-\text{CHLi}-\text{SO}_2\text{Ph}$ in THF under argon in a quartz tube in a Rayonet rotating reactor (model 100), equipped with lamp-tubes of 254 nm wavelength for 24 h and subsequent hydrolysis yielded upon liquid chromatography on silica gel with a hexane eluent: (a) a 1:1.3 mixture of *cis*- and *trans*-stilbenes (33%); and (b) *cis*- and *trans*-1,2,3-triphenylcyclopropanes (25%), besides recovered $\text{Ph}-\text{CH}_2-\text{SO}_2-\text{Ph}$. The cyclopropanes were identified by their C–H proton singlets at $\delta = 2.82$ (*cis*) and 2.73 (*trans*) ppm (CDCl_3) and the mass spectrum of the mixture: MS (70eV): $m/z = 270$ [M], 179, 178, 152, 89, 77 (Y. Qian, Masters Thesis, SUNY-Binghamton, **1992**, p. 57; Y. Qian, Research Notebook No. 1, May 22, **1991**, p. 36). More to the point of this study, however, is the finding that 1–10 mol-% of $\text{Ni}(\text{acac})_2$ can cause the catalytic elimination of LiOSOPh from $\text{Ph}-\text{CHLi}-\text{SO}_2\text{Ph}$ in THF from 0 °C to reflux, leading to variable proportions of solely *trans*-stilbene and *trans*-1,2,3-triphenylcyclopropane, as attested to by their IR, ^1H NMR and

mass spectra on pure samples separated by column chromatography (silica gel/hexane). In two separate further experiments, one with 1,1-diphenylethylene and the other with diphenylacetylene, the benzyldiene fragment from Ph-CHLi-SO₂Ph was trapped as 1,1,2-triphenylcyclopropane and 1,2,3-triphenylcyclopropene, respectively (ref.^[7]; Y. Qian, Doctoral Dissertation, SUNY-Binghamton, **1996**, pp. 117–118; Y. Qian, Research Notebook No. 1, October 19, **1991**, p. 66). The detailed mechanisms of these carbenoid oligomerizations are under further investigation.

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