Nickel(0)-induced geminal bond cleavages leading to carbon–carbon double bonds: intermediacy of nickel(0)–carbene complexes as a unifying hypothesis [1]

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Abstract

The possibility of effecting geminal bond cleavages of organic monomers with nickel(0) complexes to achieve olefinic dimers has been investigated both in stoichiometric reactions between monomers of the type R_2CE_2 and $R_2C=E$ and the complexes $(Cod)_2Ni$, $(Et_3P)_4Ni$ and $(Bpy)(Cod)Ni$ and in nickel(0)-catalytic α-elimination reactions of α-lithioorganic sulfones, $RR'C(Li)(SO_2R'')$. Substrates for the stoichiometric geminal bond cleavages comprised geminal dihalides, aminomethyl sulfides, cyclopropenes, thioketones and ketones. Reductive dimerization to the olefin or its hydroxy derivatives was found to occur to a varying degree in most cases, including the catalytic decomposition of the α-lithioorganic sulfones. Accordingly, this method offers considerable promise in organic synthesis. A gamut of known nickel(0) chemistry, results of chemical-trapping and spectroscopic evidence are marshaled in support of the proposal that such geminal bond cleavages and reductive coupling processes most likely proceed via nickel(0)–carbene intermediates of the type $R_2C=Ni \cdot L_n$.

Keywords: Nickel; Carbene complexes; Lithiosulfones; Phosphonium ylides; Oxidative addition; Cleavage; Synthesis
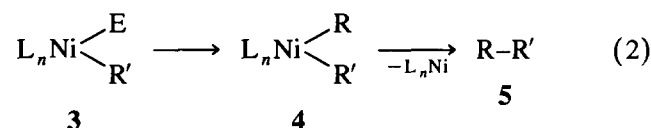
1. Introduction

Nickel(0) complexes, when provided with appropriate ligands (1), have been found to undergo oxidative addition with a wide range of *sigma*-bonds between carbon and both metals and nonmetals [1]:

$$L_nNi + R'-E \longrightarrow L_nNi\begin{array}{c} E \\ R' \end{array} \qquad (1)$$

1   2

3
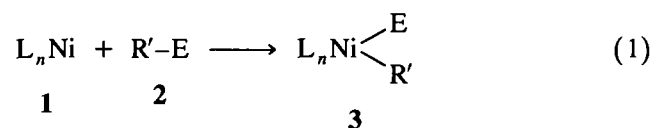
Such intermediates as 3 are crucial precursors in a number of useful carbon–heteroatom bond cleavages as exemplified by the deoxygenation of epoxides [2], the desulfurization of dibenzothiophenes [3] and the Kumada carbon–carbon cross-coupling reaction [4], in which 3 is suggested to form from a vinylic or aryl halide (2: R'–E, E = $-\overset{|}{C}=\overset{|}{C}-X$) and then to undergo alkylation with an alkyl Grignard reagent to produce 4. Reductive elimination finally yields the coupling product 5 and regenerates 1 for the next catalytic cycle:

$$L_nNi\begin{array}{c} E \\ R' \end{array} \longrightarrow L_nNi\begin{array}{c} R \\ R' \end{array} \xrightarrow[-L_nNi]{} R-R' \qquad (2)$$

3   4   5

Similar oxidative additions of nickel(0) complexes into *sigma*-carbon–carbon bonds have been observed to occur with remarkable facility in situations where the C–C bond is present in a strained ring, such as in benzocyclopropene [5] and in biphenylene [6] (6, Eq. (3)). In the latter case, it is noteworthy that $(Et_3P)_4Ni$ produces the nickelacyclopentadiene 7 at 0°C but

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$(\text{Cod})_2\text{Ni}$ is unreactive towards **6** under analogous conditions.

$$\tag{3}$$
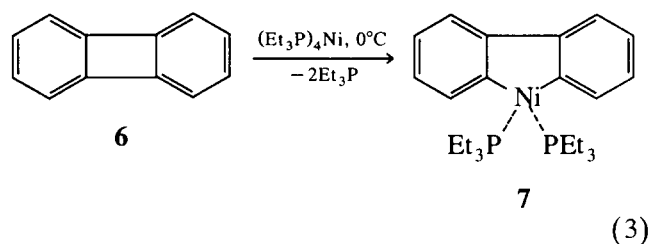
Because the foregoing studies of nickel(0) insertions into single C–E bonds have led to both useful synthetic applications and valuable mechanistic insights, we were curious to learn to what extent such nickel(0) insertions would be attainable with geminal C–E bonds (**8**, Eq. (4)). A priori, the product of oxidative addition could be the geminal dinickelo intermediate **9** or the nickel(0)–carbene complex **10**. In the latter case, the transformation of the C–NiE linkage into NiE_2 could provide the thermodynamic driving force. The Ni–Cl bond energy in NiCl_2, for example, is estimated at 87 kcal mol^{-1}.


$$\tag{4}$$
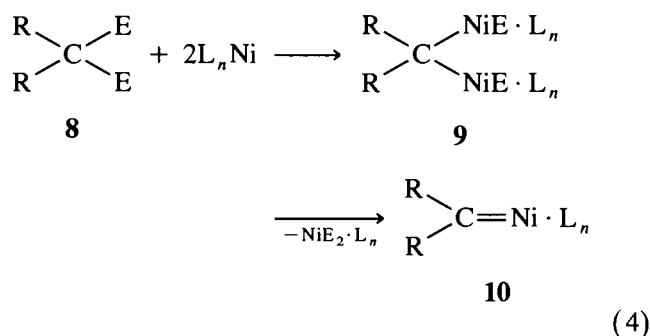
As a further variant of **8**, the reactivity of geminal C–E bonds belonging to the same heteroatom, as in $\text{R}_2\text{C=S}$ and $\text{R}_2\text{C=O}$, towards nickel(0) complexes was also pertinent to this study. The present report, therefore, gives our findings from a broad survey of the stoichiometric interactions of nickel(0) complexes such as (Bpy)(Cod)Ni (**11**) and $(\text{Et}_3\text{P})_4\text{Ni}$ (**12**), with a variety of substrates such as R_2CX_2, $\text{R}_2\text{C(NR}'_2\text{)(SR''})$, cyclopropenes, $\text{R}_2\text{C=S}$ and $\text{R}_2\text{C=O}$. Furthermore, evidence is provided that with α-lithiosulfones, $\text{R}_2\text{C(Li)(SO}_2\text{Ph)}$, a nickel(0)-catalyzed α-elimination of lithium benzenesulfinate takes place. Finally, the course of such novel reactions and the chemical or physical detection of nickel intermediates are adduced in support of the vital intermediacy of nickel(0)–carbene complexes (**10**), rather than alkylene(dinickel) derivatives (**9**), in such coupling processes. The unifying hypothesis of nickel (0)–carbene intermediates in these carbon–carbon couplings should prove of great heuristic value in subsequent mechanistic studies and synthetic applications.

2. Results

2.1 Geminal dihalides

The interaction of the simplest dihalides CH_2X_2 (**13**) with (Bpy)(Cod)Ni has already been shown to give ethylene in moderate yields [7] (Eq. (5)). We found that the homocoupling of either α,α-dichlorotoluene (**14**) or dichloro(diphenyl)methane (**15**) by $(\text{Et}_3\text{P})_4\text{Ni}$ proceeded at 25°C in high yield; noteworthy is the exclusive formation of *trans*-stilbene (**16**) from **14** (Eq. (6)).


$$\tag{5}$$
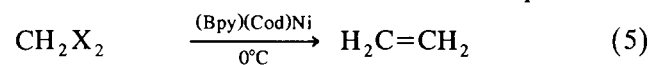
| **13a**: X = Br | 40–60% |
| **13b**: X = Cl | 25% |

$$\tag{6}$$
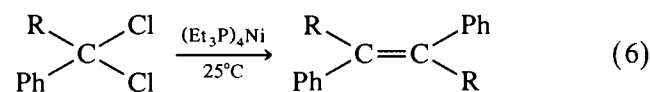
| **14**: R = H | **16**: R = H, 98% |
| **15**: R = Ph | **17**: R = Ph, 93% |

In an attempt to trap any organonickel intermediate, such as **9** or **10** formed in the course of these coupling reactions, the individual reactions of CH_2Br_2 (**13a**) and PhCHCl_2 (**14**) with $(\text{Et}_3\text{P})_4\text{Ni}$ in THF were conducted in the presence of 1 equiv. benzophenone (**18**). In each case hydrolytic workup yielded significant amounts of the cross-coupled product with **18** (Eq. (7)):

$$\tag{7}$$
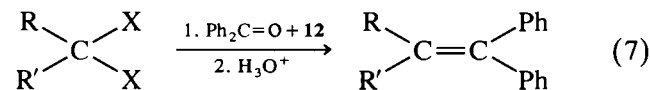
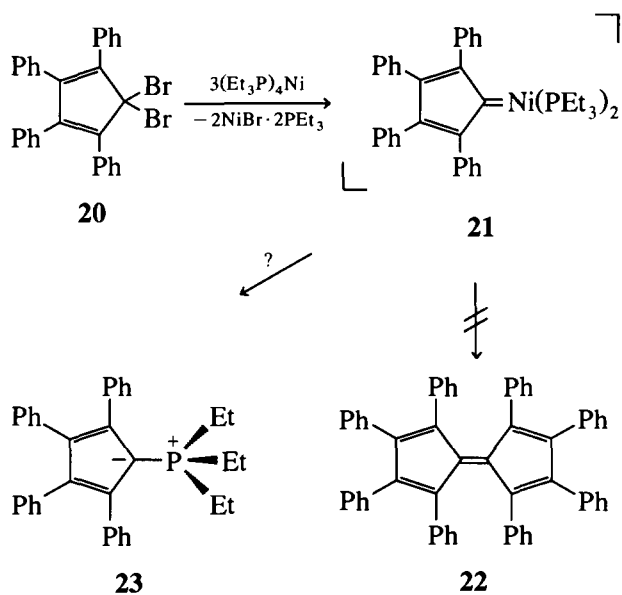| **13a**: R, R' = H; X = Br | **18**: 8% |
| **14**: R = H; R' = Ph; X = Cl | **19**: 47% |

However, similar attempts to detect the formation of **19** from the reaction of **15** with **12** in the presence of benzaldehyde failed.

An attempt was then made to isolate the possible nickel–carbene intermediate **21** from the interaction of 5,5-dibromo-1,2,3,4-tetraphenylcyclopentadiene (**20**) with 3 equiv. **12**. This hope was predicated on the great F-strain that might hinder formation of the expected coupling product **22** (Scheme 1). Although the expected $\text{NiBr}_2 \cdot 2\text{PEt}_3$ did precipitate from the reaction mixture and little, if any, **22** did form, the only other isolable product proved to be triethylphosphonium tetraphenylcyclopentadienide (**23**) [8] in a surprising yield of 70%. Since free carbenes are unlikely intermediates in these coupling reactions (cf. infra), carbene complex **21** may be a possible precursor.

2.2. (N,N-Diphenylamino)methyl phenyl sulfide (24)

The reaction of sulfide **24** with 1 equiv. of either (Bpy)(Cod)Ni (**11**) or $(\text{Et}_3\text{P})_4\text{Ni}$ (**12**), followed by hy-

Scheme 1.

Scheme 3.

of **31** obtained, a turnover number of 10 can be estimated.

A similar attempt to catalyze an α-elimination of lithium benzenesulfinate from lithioorganic sulfone **32** with $Ni(acac)_2$ gave no detectable analogous carbene-coupling product **33** but, unexpectedly, yielded at least 31% **34**, apparently arising from **32** by a β-lithium-hydride elimination (Eq. (8)):

$$(8)$$
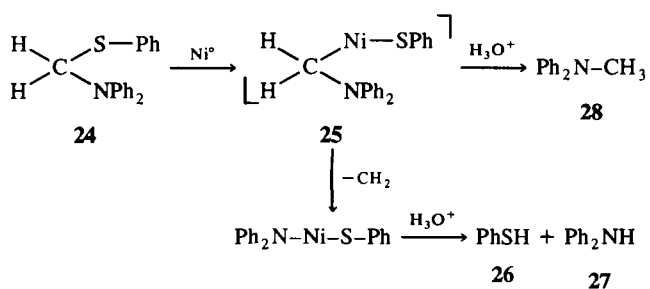
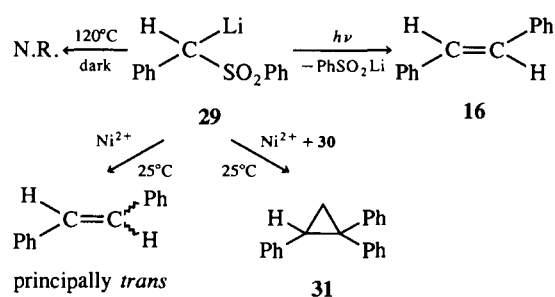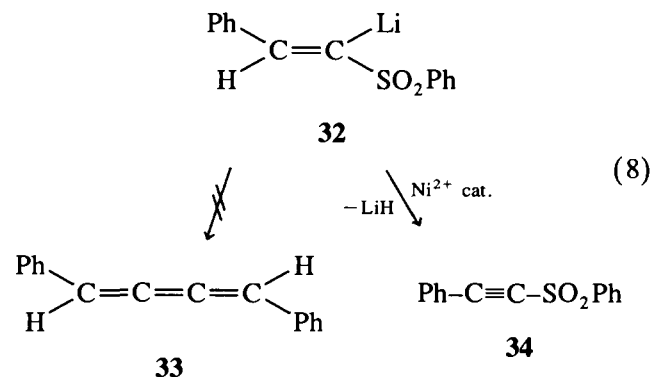drolytic workup, yielded thiophenol (**26**) and diphenylamine (**27**) as the major products, with small, varying amounts of methyl(diphenyl)amine (**28**). The last product undoubtedly stems from the expected intermediate **25**, but the small amount of **28** suggests that **25** is unstable to α-elimination (Scheme 2).

2.3. α-Lithioorganic sulfones

α-Lithiobenzyl phenyl sulfone (**29**) is stable to the α-elimination of lithium benzenesulfinate when heated up to 120°C for 4 h in the dark; irradiation of a solution of **29** in THF at 254 nm at 25°C over a week yields only trans-stilbene (**16**) [9]. When a solution of **29** in THF was treated with 3 mol.% nickel(II) acetylacetonate $(Ni(acac)_2)$ and allowed to stand in the dark, a mixture of the stilbenes (principally **16**) was isolated. Finally, when a solution of **29** in THF was mixed with 4 equiv. 1,1-diphenylethylene (**30**) and 3 mol.% $Ni(acac)_2$ and allowed to stand in the dark, a 29% yield of 1,1,2-triphenylcyclopropane (**31**) was isolated (a control run without $Ni(acac)_2$ produced only 6% of **31**) (Scheme 3). From the amount of $Ni(acac)_2$ employed and the yield

In the absence of such a β-hydrogen, as with **35**, then 40% of the product (**36**) in such a nickel-catalyzed reaction (turnover no. ≈ 10) arose from the desired α-elimination (Eq. (9)).
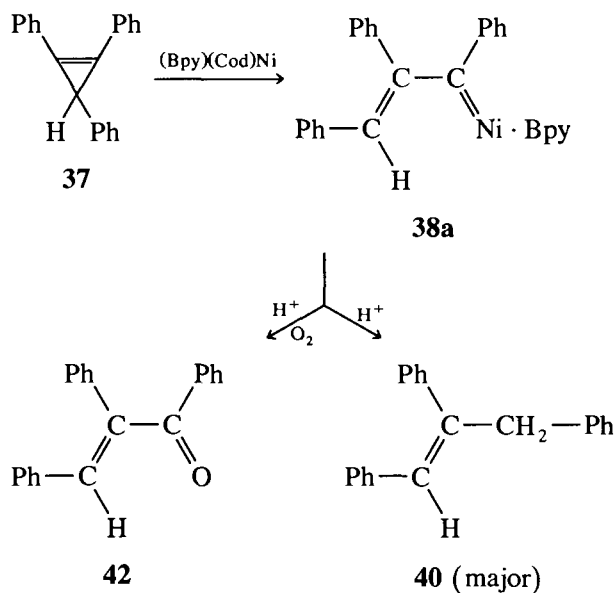
$$(9)$$
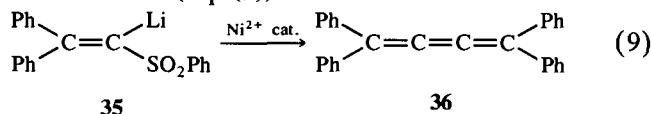
2.4. 1,2,3-Triphenylcyclopropene (37)

The cleavage of strained cyclopropene **37** would be an example of cleaving geminal bonds to carbon if nickel–carbene **38** were to result (asterisked σ- and π-bonded to C_1).

$$(10)$$

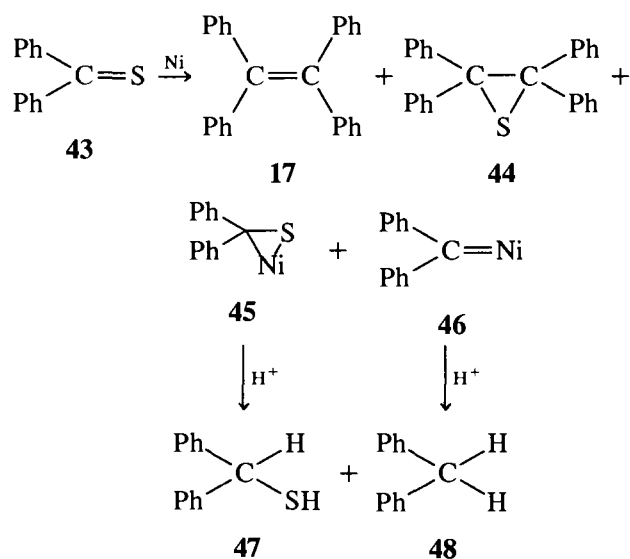Scheme 2.

Scheme 4.

Scheme 5.
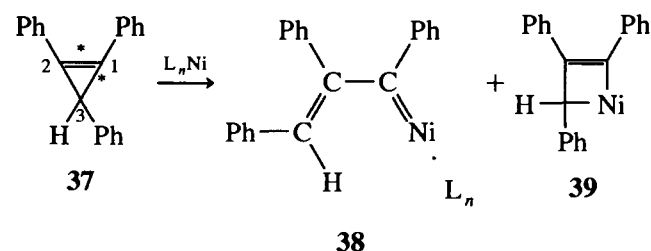
However, the alternative structure of a nickelacy-clobutene (**39**) might also result from such a cleavage (Eq. (10)).

When **37** was treated with $(Et_3P)_4Ni$ in THF, orange crystals of the composition **37** · Ni · 2 PEt_3 were isolated, whose XRD showed it to be a coordination complex of intact **37** with the Ni · 2 PEt_3 unit [8]. In contrast, the interaction of **37** with (Bpy)(Cod)Ni in THF rapidly produced a deep green solution. A brief heating at reflux and solvent removal gave a dark green residue whose ^{13}C NMR spectrum in C_6H_6 displayed a prominent peak at 251 ppm. Such a signal lies in the region characteristic of the carbon in nickel(0)–carbene complexes [10]. This spectral evidence is consistent with at least some of the ring cleavage product having structure **38**.

Protolysis of such green residues with carefully de-oxygenated aqueous 6N-HCl produced a 4:1 mixture of (Z)- and (E)-1,2,3-triphenylpropenes (**40**, **41**). When the 6N-HCl for protolysis was not carefully deoxygenated, 1,2,3-triphenylpropenone (**42**) was also isolated. These additional chemical observations also accord with the structure of the principal component from the cleavage of **37** by (Bpy)(Cod)Ni as being **38a** (Scheme 4). Efforts are underway to obtain crystals of **38a** suitable for an XRD confirmation of its structure [8].

2.5. Thiobenzophenone (43)

The interaction of **43** (containing 40% Ph_2CO) with 1.8 equiv. $(Cod)_2Ni$ in toluene led to 92% te-traphenylethylene (**17**) and 6% tetraphenylthiirane (**44**). A similar interaction of **43** with (Bpy)(Cod)Ni gave,

upon hydrolytic workup, small amounts of diphenyl-methane (**48**, 4%) and benzhydryl mercaptan (**47**, 7%), in addition to **17**. The latter products are consistent with the persistence of intermediates **45** and **46** up to the hydrolysis step (Scheme 5).

2.6. Aromatic ketones

Nickel(0) complexes interacted with aromatic ke-tones in varying degrees, depending on the ligands on nickel. Admixing benzophenone (**18**) with 0.5 equiv. $(Cod)_2Ni$ produced an orange–red solution which displayed an intense triplet signal in its ESR spectrum [11]. However, hydrolysis with deoxygenated, aqueous 6N-HCl led only to the recovery of **18** and not to benzpina-col (**49**). However, treatment of **18** with $(Et_3P)_4Ni$ in THF allowed the isolation of 8% **49** and an analogous treatment of 9-fluorenone (**50**) with (Bpy)(Cod)Ni yielded 25% of the corresponding pinacol (**52**) and 40% of 9-fluorenol (**53**). The SET equilibria involved are thus greatly influenced both by the donor ligands on
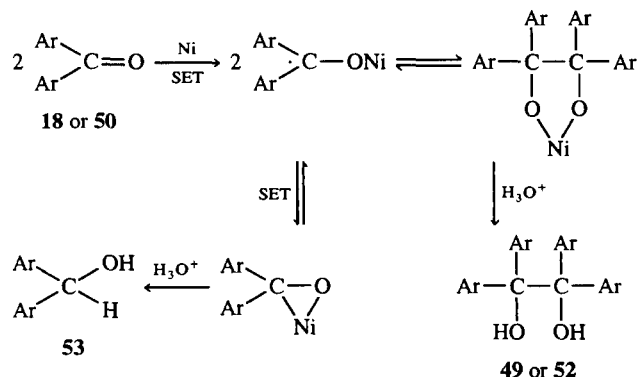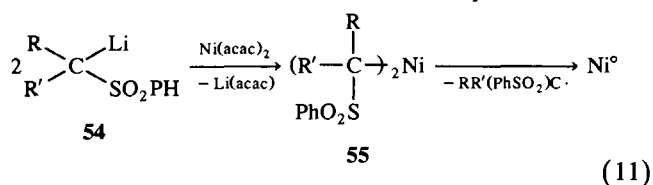
Scheme 6.

nickel and the conjugation of the aromatic ketone acceptor (Scheme 6). That neither diphenylmethane nor fluorene was isolated from the reactions of these ketones shows that nickel(0) cannot cleave both bonds of the C = O group.
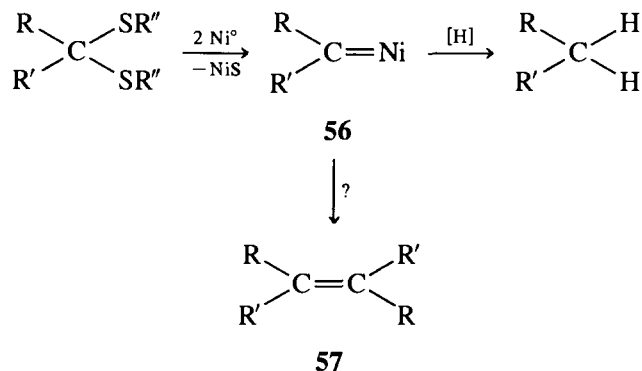
3. Discussion

3.1. Applications in synthesis

The present investigation has demonstrated that geminal bonds between carbon on the one hand, and halogen, sulfur, sulfur and nitrogen, sulfur and lithium and even carbon in strained rings, on the other hand, can be efficiently cleaved by nickel(0) complexes in a stoichiometric or catalytic manner. With α-lithioorganic sulfones, the nickel(II) acetylacetonate introduced as a promoter is undoubtedly alkylated by **54** and the resulting organonickel intermediate **55** then decomposes (cf. Eq. (2)) to produce nickel(0), the actual catalyst for the lithium benzenesulfinate-elimination (Eq. (11)).

$$2 \overset{R}{\underset{R'}{>}}C\overset{Li}{\underset{SO_2PH}{<}} \xrightarrow[-Li(acac)]{Ni(acac)_2} (R'—\overset{R}{\underset{PhO_2S}{\overset{|}{\underset{|}{C}}}}{\rightarrow}_2 Ni \xrightarrow[-RR'(PhSO_2)C \cdot]{} Ni^\circ$$

54   **55**

(11)

For the stoichiometric cleavages, complexes such as $(Cod)_2Ni$, $(Et_3P)_4Ni$ or $(Bpy)(Cod)Ni$ can be effective but there is evidence that $(Bpy)(Cod)Ni$ is the most reactive, readily cleaving, for example, the cyclopropene ring in 1,2,3-triphenylcyclopropene (**37**, Scheme 4), where $(Cod)_2Ni$ and $(Et_3P)_4Ni$ do not. In turn, $(Et_3P)_4Ni$ generally proved to be more reactive, both in SET and cleavage reactions, than $(Cod)_2Ni$, as demonstrated both by the bimolecular reduction of benzophenone (**18**) into its pinacol (**49** (Scheme 6)) and by the coupling of geminal dichlorides **14** and **15** (Eq. (6)).

For the formation of olefins by nickel(0)-induced bimolecular reduction, the monomolecular geminal dihalides R_2CX_2 have proved to be very satisfactory starting reactants (Eq. (6)); thioketones can also be used but there are more difficulties in preparing the required $R_2C=S$ in high purity and in protecting such reagents against adventitious hydrolysis. As has been shown in this study, aldehydes and ketones are completely unsuitable reactants for the nickel(0) bimolecular reduction into olefins. For this reason, we are currently exploring the practicality of employing thioketals $RR'C(SR'')_2$ in place of either thioketones or ketones [12]. The well-known transformation of such thioketals into the corresponding methylene derivative by Raney nickel encourages us to believe that plausible intermediate **56** (cf. infra) might be diverted into olefin **57** (Scheme 7).

$$\overset{R}{\underset{R'}{>}}C\overset{SR''}{\underset{SR''}{<}} \xrightarrow[-NiS]{2\ Ni^\circ} \overset{R}{\underset{R'}{>}}C=Ni \xrightarrow{[H]} \overset{R}{\underset{R'}{>}}C\overset{H}{\underset{H}{<}}$$

56

$$\downarrow ?$$

$$\overset{R}{\underset{R'}{>}}C=C\overset{R'}{\underset{R}{<}}$$

57

Scheme 7.

The nickel(0)-catalyzed coupling of α-lithioorganic sulfones (**54**), which offers an additional preparatively useful route to bimolecular olefins, actually has a clear precedent in the nickel-catalyzed coupling of Grignard reagents of allylic sulfones into conjugated alkatrienes [13]. Our work demonstrates that the nickel(0)-catalyzed α-elimination of lithium benzenesulfinate from **54** is generally applicable to lithium salts of alkyl, vinylic and allenic sulfones [12]. Especially noteworthy is that this coupling provides a new approach to the synthesis of cumulenes (cf. Eq. (9)) and a side reaction, the β-elimination of LiH, a novel conversion of a vinyl sulfone into an acetylenic sulfone (cf. Eq. (8)). Since this report presents a wide-ranging survey of nickel(0)-induced cleavages, the yields for such sulfone and related reactions have not yet been optimized.

Any extensive discussion of the organic synthetic value of the single nickel(0)-induced cyclopropene ring cleavage observed in this work (Scheme 4) would be premature. However, it should be remarked that this is the first such cleavage reported of a simple cyclopropene, to our best knowledge, where there is not the additional strain of a benzocyclopropene system [5], and that such cyclopropenes (**37a**) are available by the methylenation of acetylenes with a variety of carbene and carbenoid sources, such as diazoalkanes with metal catalysts or the Simmons–Smith reaction [14]. Such cleavages of cyclopropenes with Ni^0 appear to generate nickel(0)–carbenes (**38a**) (cf. infra), whose protolysis could give largely the syn-alkyl olefin (**58**) and whose capture with alkynes could provide the corresponding cyclopentadiene (**59**) (Scheme 8). Indeed, we have now observed that 1,2,3-triphenylcyclopropene (**37**) reacts with diphenylacetylene (**61**) in the presence of catalytic amounts of Ni^0 (from $Ni(acac)_2$ and EtMgCl in THF) to form 1,2,3,4,5-pentaphenylcyclopentadiene (**68** or **59** where R, R' and R'' = Ph) in 44% yield.

3.2. Mechanistic considerations

The bimolecular reductive couplings of such derivatives as R_2CX_2, $R_2C(Li)(SO_2R')$ and $R_2C=S$ observed
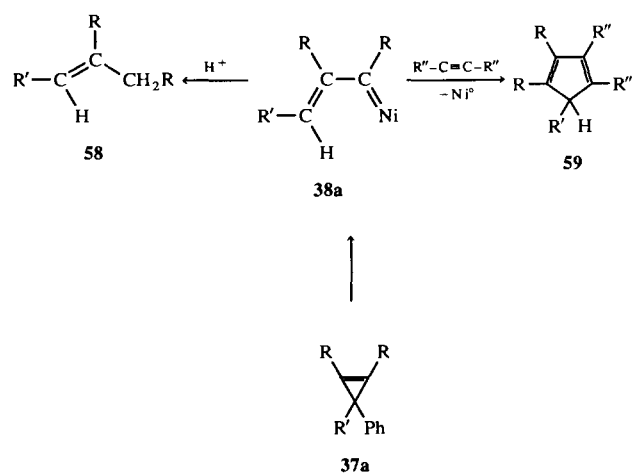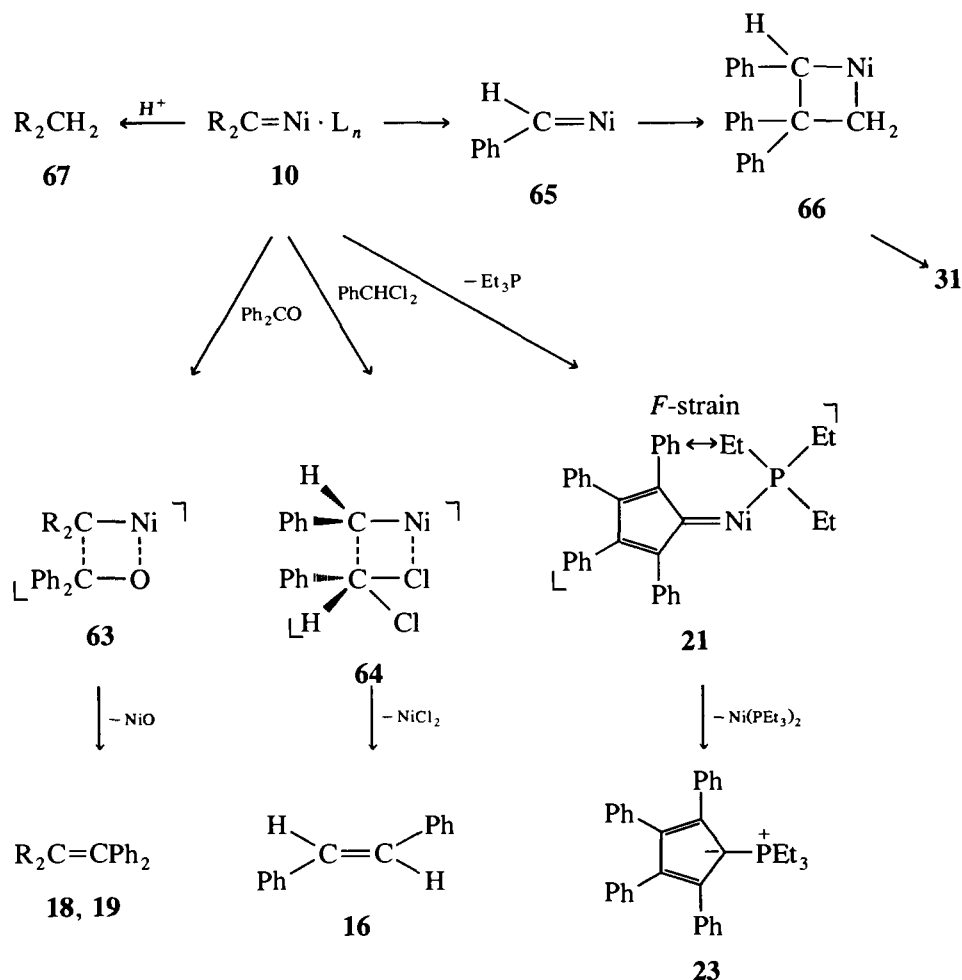
Scheme 8.

in this study clearly do not involve any free carbene R_2C. Were such free carbenes generated, a number of rearrangements would be expected to occur which are not in fact observed. If in the coupling of **35** to **36** (Eq. (9)) the intermediate **60** were ever formed, it would

undergo the well-known, rapid isomerization to diphenylacetylene (**61**) [15] (Eq. (12)). No **61** could be detected among the reaction products.

$$\longrightarrow \quad Ph-C{\equiv}C-Ph \qquad (12)$$
$$\mathbf{61}$$
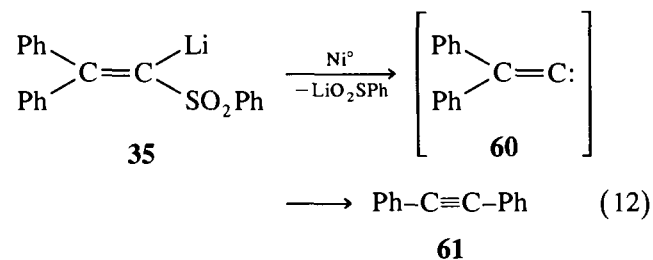
Thus the most likely intermediates in such coupling are organonickel reagents, such as **9**, **10** or possibly $R_2C(NiE \cdot L_n)E$ (**62**), the insertion product of one equiv. Ni^0 with the substrate R_2CE_2 (**8**). Within the last five years a number of genuine nickel(0)–carbene complexes have been fully characterized by spectroscopic and XRD methods, thereby establishing both the existence and considerable stability of such intermediates [10]. Their behavior upon oxidation exactly parallels that suggested to occur in transforming **38a** into **42** in Scheme 4. However, if **9** or **62** were the key intermedi-

Scheme 9.

ates in these coupling processes, the chemical trapping of such intermediates from $PhCHCl_2$ by benzophenone should have led to the isolation of either the alcohol (Eq. (13)) or the halohydrin (Eq. (14)), rather than the olefin (19, Eq. (7)):

$$Ph\text{---}CH_2\text{---}\underset{\underset{OH}{|}}{CPh_2} \quad (13)$$

(not observed)

$$Ph\text{---}\underset{\underset{Cl}{|}}{CH}\text{---}\underset{\underset{OH}{|}}{CPh_2} \quad (14)$$

(not observed)
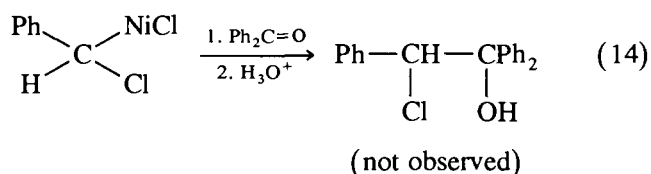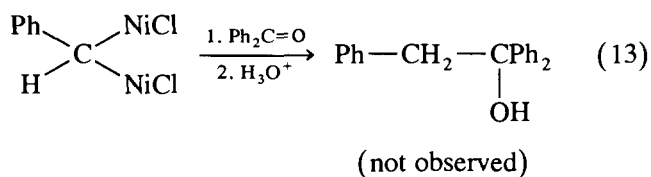
Based on the evidence of reaction products and chemical trapping experiments, therefore, the intermediate most consistent with all these data is the nickel(0)–carbene complex 10. The evidence can be globally viewed in Scheme 9: (1) the trapping of 10 with benzophenone (18) via 63; (2) the exclusive formation of trans-stilbene (16) via the transition state 64 having minimalized steric hindrance; (3) the formation of phosphonium cyclopentadienide 23, whose formation from nickel(0)–carbene complex 21 may be fostered by the destabilizing F-strain in 21; (4) the generation of 1,1,2-tricyclopropane (31) from 29 and Ni^0 with 1,1-diphen-

ylethylene (30) which would form via 65 and adduct 66; and (5) the formation of methylene derivative 67 in the protolytic workup of certain nickel(0) cleavage reactions, such as the 1,2,3-triphenylpropene (40) isolated from the 1,2,3-triphenylcyclopropene reaction and the diphenylmethane (48) found in the thiobenzophenone cleavage. In these suggested pathways for the observed transformations, it cannot as yet be determined whether bracketed structures 21, 63 and 64 are persistent intermediates or whether they are transition state configurations on the way to σ-bond metatheses (63 and 64) or reductive elimination (21).

Further evidence supporting the presence of nickel(0)–carbene intermediates in these cleavages is the ^{13}C NMR signal at 251 ppm observed in the reaction product of 1,2,3-triphenylcyclopropene (37) and (Bpy)(Cod)Ni. Although such a signal is strongly indicative of at least a significant portion of complex 38 being present (Eq. (10)), neither the available spectral nor chemical evidence can rule out the possibility of equilibria between 38 and nickelacyclobutene 39 or between 38 and the starting cyclopropene 37. Current efforts to obtain XRD data on the reaction product may elucidate this uncertainty. An indication that such equilibria may be possible stems from our observation that the nickel-catalyzed decomposition of α-lithiobenzyl phenyl sulfone (29) in the presence of diphenylacetylene produces in moderate yield 1,2,3-triphenylcyclopropene (37) and 1,2,3,4,5-pentaphenylcyclopen-
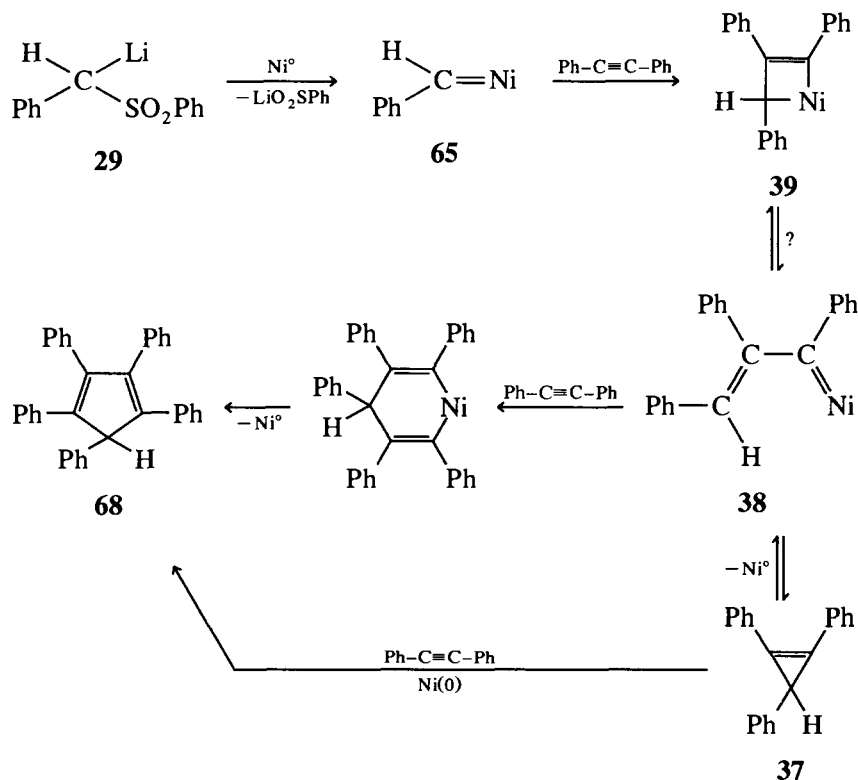
Scheme 10.

tadiene (68), possibly via 39 [9] (Scheme 10). Further corroboration of these suggested equilibria comes from our aforementioned finding that 37 reacts with diphenylacetylene by nickel(0)-catalysis to produce 68.

Clarification of these tantalizing mechanistic hypotheses and of their advantageous consequences for novel organic syntheses continues to receive our devoted attention.

4. Experimental section

4.1. General procedures

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 sodium metal-benzophenone ketyl mixture prior to use. The IR spectra were recorded on a Perkin-Elmer instrument, model 457 and samples were measured either as mineral oil mulls or as KBr films. The NMR spectra (^{1}H and ^{13}C) were recorded on a Bruker spectrometer, model EM-360 and tetramethylsilane (TMS) was used as the internal standard. The chemical shifts reported are expressed in the δ-scale and in parts per million (ppm) from the reference TMS signal. The gas chromatographic analyses were carried out on 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 on a Thomas-Hoover Unimelt capillary melting point apparatus and uncorrected. The (Cod)$_2$Ni was prepared according to a procedure adapted from those of Semmelhack [16] and of Schunn [17]. The yield of product has been improved to 95% by purifying the starting materials with extreme care.

The (Et$_3$P)$_4$Ni was prepared according to the method of Cundy [18] and the (Cod) (Bpy)Ni by procedure of Dinjus et al. [19]. The 2,2-diphenylethyl phenyl sulfone and the 9,9'-bifluorenylidene were synthesized by published procedures [20,21].

4.2. Reactions of nickel(0) complexes with geminal dihalogen compounds

4.2.1. Reaction of (Et$_3$P)$_4$Ni with α,α-dichlorotoluene (14)

To a solution of 1.40 g (2.64 mmol) (Et$_3$P)$_4$Ni in 20 ml THF was added dropwise at 25°C 0.17 ml (0.21 g, 1.30 mmol) α,α-dichlorotoluene. The reaction mixture was allowed to stir for 2 h and then was quenched with degassed 6N-HCl under Ar. After Et$_2$O extraction the organic layer was neutralized with sodium bicarbonate, dried over anhydrous magnesium sulfate and evaporated under reduced pressure. A flash column chromato-

graphic separation gave 240 mg *trans*-stilbene (16) (98%), which was identified by its IR and NMR spectra.

4.2.2. Reaction of (Et$_3$P)$_4$Ni with α,α-dichlorotoluene (14) in the presence of benzophenone

To the mixture of (Et$_3$P)$_4$Ni (1.30 g, 2.45 mmol) and 0.22 g benzophenone (1.22 mmol) was added 0.16 ml α,α-dichlorotoluene (0.20 g, 1.24 mmol) at 0°C. The reaction mixture was allowed to stir for 1 h before quenching with degassed aqueous 6N hydrochloric acid. The workup procedure was the same as described above. *Trans*-stilbene (90 mg, 40%) and one other product, triphenylethylene (19) (150 mg, 47%) were separated by flash column chromatography (Et$_2$O: hexanes, 1 : 8). Benzophenone was also recovered (100 mg, 46%). The triphenylethylene exhibited the following properties. M.p. 71–72°C; ^{1}H NMR (CDCl$_3$): δ7.29 (m, 8H), 7.08 (m, 4H), 6.96 (s, 1H); ^{13}C NMR (CDCl$_3$): δ 143.4, 142.7, 140.4, 137.4, 130.4, 129.5, 128.5, 128.2, 127.9, 127.7, 127.4, 126.7.

4.2.3. Reaction of (Cod)$_2$Ni with dichlorodiphenylmethane (15)

To a yellow solution of (Cod)$_2$Ni (0.95 g, 3.45 mmol) in 15 ml toluene was added 0.34 ml dichlorodiphenylmethane (0.42 g, 1.77 mmol) at 25°C. A small amount of nickel mirror was observed to form on the wall of the flask. The black reaction mixture was allowed to stir for 1 h and then was quenched with degassed 6N-HCl. The two products were separated by flash column chromatography (elutant 5% ethyl acetate in hexanes) and spectroscopically identified as benzophenone (4%) and tetraphenylethylene (17) (93%). M.p. 223–224°C; ^{1}H NMR (CDCl$_3$): δ 7.11–7.01 (m, 20H); ^{13}C NMR (CDCl$_3$): δ 143.72, 140.98, 131.30, 127.62, 126.38, MS m/e 332 (M$^+$), 198,167,77.

4.2.4. Reaction of (Et$_3$P)$_4$Ni with dichlorophenylmethane (15) in the presence of benzaldehyde

To the deep red solution of (Et$_3$P)$_4$Ni (420 mg, 7.9 × 10^{-4} mol) in 20 ml THF was added first 0.08 ml dichlorodiphenylmethane (100 mg, 4.0 × 10^{-4} mol) and then 0.04 ml benzaldehyde (40 mg, 4 × 10^{-4} mol). The reaction mixture was allowed to reflux for 2 h before quenching with degassed aqueous 6N hydrochloric acid. The two products separated by flash column chromatography (elutant 5% ethylacetate in hexanes) were spectroscopically identified as tetraphenylethylene (17) (95%) and benzophenone (1%). Benzaldehyde was also recovered.

4.2.5. Reaction of (Et$_3$P)$_4$Ni with 5,5-dibromotetraphenylcyclopentadiene (20)

To a solution of (Et$_3$P)$_4$Ni (970 mg, 1.83 mmol) in 30 ml THF was added 5,5-dibromotetraphenylcyclopentadiene (320 mg, 6.06 × 10^{-4} mol) at 25°C and the

resulting solution was stirred for 15 h. The solution was then evaporated to dryness in vacuo and the residue was extracted with warm cyclohexane (3 × 10 ml). The hot extracts were filtered and the filtrate allowed to stand at 25°C for several days to complete the crystallization. After the supernatant liquid was removed via a cannula, pale yellow crystals of triethylphosphonium tetraphenyl-cyclopentadienide (**23**) were obtained (70%). M.p. 200–202°C; ^{1}H NMR (C_6D_6): δ 7.59–6.82 (m, 20H), 1.21–1.02 (m, 6H), 0.50–0.41 (m, 9H).

4.2.6. Reaction of $(Et_3P)_4Ni$ with methylene bromide (13a) in the presence of benzophenone

To the mixture of 0.05 ml methylene bromide (120 mg, 6.87 × 10^{-4} mol) and benzophenone (130 mg, 6.87 × 10^{-4} mol) in 20 ml THF was added 730 mg $(Et_3P)_4Ni$ (1.37 mmol) at 25°C. The reaction mixture was then refluxed for 3 h before quenching with degassed 6N-HCl. Both 1,1-diphenylethylene (10 mg, 8%) and benzpinacol (10 mg, 8%) were isolated by means of flash column chromatography. Some benzophenone was also recovered (77%). The 1,1-diphenylethylene (**18**) exhibited the following spectral signals. ^{1}H NMR (CDCl$_3$): δ 7.21 (m, 10H), 5.39 (s, 2H); ^{13}C NMR (CDCl$_3$): δ 149.97, 141.37, 128.18, 128.08, 127.62, 114.19. Benzpinacol, m.p. 183–185°C: ^{1}H NMR (CDCl$_3$): δ 7.31–7.15 (m, 20H), 3.01 (br, 2H). ^{13}C NMR (CDCl$_3$): δ 141.20, 128.61, 127.29, 126.94, 83.0.

4.3. Reactions of nickel(0) complexes with thiobenzophenone (43)

4.3.1. Reaction of (Bpy)(Cod)Ni with thiobenzophenone (43)

To the purple solution resulting from admixing $(Cod)_2Ni$ (800 mg, 2.91 mmol) with 2,2'-bipyridine (450 mg, 2.91 mmol) in 15 ml toluene was added 450 mg thiobenzophenone (1.46 mmol, aged sample was a mixture of about 60% thiobenzophenone and benzophenone). The black reaction mixture was allowed to stir for 1 h at 25°C and then quenched with degassed aqueous 6N-HCl under Ar. Hydrogen sulfide was evolved upon quenching. The workup procedure was the same as described as above. Diphenylmethane (10 mg, 4%) and benzhydryl mercaptan (20 mg, 7%) were isolated by flash column chromatography (THF: hexanes, 1:50) and spectroscopically identified. Some benzophenone was also recovered. ^{1}H NMR spectrum of Ph_2CH–SH (CDCl$_3$): δ 8.0–7.0 (m, 20H), 5.53 (d, 1H), 2.26 (d, 1H).

4.3.2. Reaction of $(Cod)_2Ni$ with thiobenzophenone (43)

To a yellow solution of $(Cod)_2Ni$ (480 mg, 1.75 mmol) in 15 ml toluene was added 220 mg thioben-

zophenone (**43**, newly purchased sample, containing < 10% benzophenone, 1.0 mmol). After the black solution was stirred at 25°C for 1 h, it was worked up in the usual hydrolytic fashion. Upon flash column chromatographic separation (5% ethyl acetate in hexanes) tetraphenylethylene (**17**, 92%) and tetraphenylthiirane (**44**, 6%) were isolated. **17**: ^{1}H NMR δ 7.0–7.6 (m); MS *m/e* 332 (M$^+$), 198, 167, 77, **44**: ^{1}H NMR (CDCl$_3$): δ 7.6–7.0; ^{13}C NMR (CDCl$_3$): δ 143, 133, 127.5, 126, 86; MS *m/e* 364 (M$^+$), 332, 198, 167, 77.

4.4. Reaction of (Bpy)(Cod)Ni with 9-fluorenone (50)

To the purple solution resulting from admixing $(Cod)_2Ni$ (430 mg, 1.55 mmol) with 2,2'-bipyridine (240 mg, 1.55 mmol) in 30 ml THF was added 280 mg 9-fluorenone (1.55 mmol). The solution, which became deep green immediately, was allowed to stir at 25°C for 30 min and then was brought to reflux for 15 h before quenching with degassed 6N-HCl under argon. The products, 9,9'-dihydroxy-9,9'-bifluorenyl (70 mg, 25%), and 9-fluorenol (70 mg, 30%) were isolated by means of flash column chromatography (ethylacetate; hexanes, 1:3). Spectral data. **53**: ^{1}H NMR (CDCl$_3$): δ 7.64–7.28 (m, 8H), 5.55–5.52 (d, 2H), 1.93–1.90 (d, 1H); ^{13}C NMR (CDCl$_3$): δ 145.67, 140.00, 129.05, 127.79, 125.11, 119.95, 75.23. **52**: ^{1}H NMR (CDCl$_3$): δ 7.32–7.00 (m, 16H), 3.27–3.25 (s, 2H). ^{13}C NMR (CDCl$_3$): δ 145.17, 140.55, 129.01, 126.96, 125.15, 119.15, 86.40.

4.5. Reactions of α-lithioorganic sulfones

4.5.1. Reaction of α-lithiobenzyl phenyl sulfone (29) with 1,1-diphenylethylene promoted by $Ni(acac)_2$

To a solution of 620 mg (2.67 mmol) benzyl phenyl sulfone in 20 ml THF was added dropwise 1.70 ml (2.67 mmol, 1.6 M in hexane) *n*-butyllithium at 25°C. The solution changed immediately from colorless to orange. Thereupon a solution of 2 ml 1,1-diphenylethyl-ene (2.04 g, 11.3 mmol) and 20 mg nickel(II)acetyla-cetonate (7.79 × 10^{-5} mol) in 5 ml THF was added. The reaction flask was carefully covered with aluminum foil and the reaction was allowed to proceed at 25°C for 7 days. After the usual hydrolytic workup and flash column chromatography, 200 mg 1,1,2-triphenyl-cyclopropane (**31**) (30%) was isolated. ^{1}H NMR (CDCl$_3$): δ 7.3–6.8 (m, 15H), 2.8 (q, 1H), 1.9 (q, 1H), 1.7 (q, 1H); ^{13}C NMR (CDCl$_3$): δ 147.0, 140.2, 138.7, 131.2, 131.0, 129.2, 128.5, 128.3, 127.9, 127.4, 126.2, 125.9, 125.6, 39.3, 32.4, 20.9.

When a similar reaction was carried out without $Ni(acac)_2$, only 6% 1,1,2-triphenylcyclopropane was formed.

4.5.2. Reaction of phenyl(E)-2-phenylvinyl sulfone with methyllithium, promoted by Ni(acac)₂

To the solution of 490 mg phenyl (E)-2-phenylvinyl sulfone (2.0 mmol) in 20 ml THF was added dropwise 1.71 ml CH₃Li(2.4 mmol, 1.4 M in Et₂O) at $-90°C$. After the yellow solution of 32 was allowed to stir at $-90°C$ for 15 min, 15 mg $(5.84 \times 10^{-5}$ mol) Ni(acac)₂ in 5 ml THF was added. The reaction mixture was then allowed to come to 25°C gradually. The reaction flask was carefully covered with aluminum foil and was allowed to stand at 25°C for 7 days. The 1-phenyl propyne (1%) and Ph–C≡C–SO₂Ph (0.15 g, 31%) were separated by flash column chromatography. Ph–C≡C–SO₂Ph (34): m.p. 74–76°C. ¹H NMR (CDCl₃): δ 8.09–7.26 (m, 10H), ¹³C NMR (CDCl₃): δ 141.92, 134.12, 132.76, 131.55, 129.36, 128.69, 127.40, 117.94, 93.49, 85.41. 1-phenyl propyne: ¹H NMR (CDCl₃): δ 7.39–7.21 (m, 5H), 1.99 (s, 3H); ¹³C NMR (CDCl₃): δ 131.40, 128.09, 127.38, 124.06, 85.66, 79.73, 4.06.

4.5.3. Reaction of 2,2-diphenylethenyl phenyl sulfone with methyllithium promoted by Ni(acac)₂

To the mixture of 640 mg 2,2-diphenylethenyl phenyl sulfone (2.0 mmol) and 15 mg Ni(acac)₂ $(5.84 \times 10^{-5}$ mol) in 30 ml THF was added 1.71 ml methyllithium (2.4 mmol, 1.4 M in Et₂O) at 0°C. The reaction mixture of 35 was allowed to stir at 0°C for 4 h before quenching with degassed 6N-HCl. The tetraphenylbutatriene (36) (190 mg, 27%) and starting sulfone (28%) were isolated by means of flash column chromatography. Tetraphenylbutatriene (36): m.p. 236–237°C. ¹H NMR (CDCl₃): δ 7.58–7.33 (m, 20H); ¹³C NMR (CDCl₃): δ 151.99, 138.77, 129.43, 128.39, 127.95, 122.71.

4.6. Reaction of (Bpy)(Cod)Ni with 1,2,3-triphenyl-cyclopropene (37)

To the purple solution resulting from admixing (Cod)₂Ni (480 mg, 1.75 mmol) with 2,2'-bipyridine (270 mg 1.75 mmol) in 20 ml THF was added 470 mg 1,2,3-triphenylcyclopropene (1.75 mmol) in 5 ml THF at 25°C. The solution, which changed to deep green immediately, was allowed to stir at 25°C for 15 h and then heated at reflux for 1 h. The reaction mixture was concentrated in vacuo and the residue analyzed by ¹³C NMR in dry C₆D₆ (no (CH₃)₄Si added). A prominent peak appeared at δ 251 ppm. The reaction mixture was quenched with degassed 6N-HCl under Ar in the usual manner. The 1,2,3-triphenylpropene (14%, Z:E = 4:1, estimated from NMR) was isolated by means of flash column chromatography.

When the foregoing reaction was conducted at 25°C for 4 h and then hydrolyzed with carefully degassed aqueous 6N-HCl, only the (E)- and (Z)-1,2,3-triphenyl-propenes (40 and 41) were formed. When ordinary

oxygen-containing aqueous 6N-HCl was employed, some 1,2,3-triphenylpropenone (42) was formed: MS m/e 284 (M⁺); IR cm⁻¹ 1665.

4.7. Reaction of (Et₃P)₄Ni and related Ni⁰ complexes with (N,N-diphenylamino) methyl phenyl sulfide (24)

Interaction of 1.0 mmol 24 with 1.1 mmol (Cod)₂Ni, (Bpy)(Cod)Ni or (Et₃P)₄Ni in 10 ml THF was allowed to proceed for 4 h at 25°C. With (Cod)₂Ni a black precipitate and a nickel mirror were observed; with (Bpy)(Cod)Ni the purple color of the complex was completely discharged; and with (Et₃P)₄Ni a clear brown solution persisted. Usual hydrolytic workup showed that 24 had been completely consumed in the reactions with (Bpy)(Cod)Ni and with (Et₃P)₄Ni, but about 50% 24 remained from the reaction with (Cod)₂Ni. The principal products (> 90%) were thiophenol (26) and diphenylamine (27); 5–15% methyl(diphenyl)amine (28) and other unidentified side-products were also detected.

4.8. Reaction of 1,2,3-triphenylcyclopropene (37) with diphenylacetylene (61) catalyzed by nickel(0)

To a mixture of 1,2,3-triphenylcyclopropene (0.36 g, 1.34 mmol), 0.48 g diphenylacetylene (2.68 mmol) and nickel(II) acetylacetonate (0.01 g, 0.04 mmol) in 30 ml THF was added dropwise 0.13 ml ethylmagnesium chloride (0.27 mmol, 2.0 M in Et₂O). The solution, which changes to dark brown immediately, was allowed to stir at 25°C for 3 h and then heated at reflux for 2 h. The workup procedure was the same as described above. The 1,2,3,4,5-pentaphenylcyclopentadiene (100 mg, 17%; 44% based on the unrecovered 37) and hexaphenylbenzene (20 mg, 4%) were separated by flash column chromatography. Some diphenylacetylene (69%) and 1,2,3-triphenylcyclopropene (61%) were also recovered. The pentaphenylcyclopentadiene exhibited the following spectral signals. ¹H NR (CDCl₃): δ 7.50–7.13 (m), 5.06 (s); MS m/e 446, 119, 58; hexaphenylbenzene: ¹H NMR (CDCl₃): δ 6.84 (m); ¹³C NMR (CDCl₃): δ 125.13, 126.54, 131.36, 140.60 and 140.28.

experiments on certain of the foregoing nickel(0) cleavages.

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