

Cleavage of the carbon–carbon bond in biphenylene using transition metals

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Abstract

Biphenylene has proven to have a rich chemistry with transition metals. In many cases, the aryl–aryl C–C bond is cleaved to give a metallocycle complex, which can go on to give a variety of reaction products. Insertion reactions with small molecules lead to the formation of new polycyclic aromatic derivatives with the incorporation of functional groups. In several cases, these reactions are selective and catalytic.

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1. Introduction

The cleavage of strong carbon–carbon bonds presents a considerable hurdle in the transformations of organic compounds. Representative examples include homolysis of weak C–C bonds [1] and the retro-Diels Alder reaction [2]. The use of transition metals to mediate C–C bond cleavage has been identified as a successful method in a limited number of cases in which ring strain or proximity is used to promote reaction [3]. A review of C–C activation has recently appeared [4].

In this article, we present a number of examples of cleavage of the strained C–C bond in biphenylene, in which oxidative addition to the metal gives rise to two new metal–aryl bonds. The C–C bond strength in biphenylene can be estimated as shown in [Scheme 1](#).

The bond strength is given by difference in the heats of formation of biphenylene and the 2,2'-biphenyl diradical. The latter can be obtained by comparing the cleavage of two C–H bonds in biphenyl (ΔH_{f1}) with the difference in the heat of formation of biphenyl versus the 2,2'-biphenyl diradical plus two hydrogen atoms [5].¹

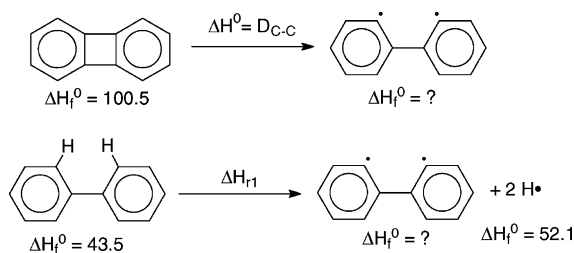
The C–C bond strength for biphenylene obtained in this way (65.4 kcal/mol) is some 53 kcal/mol less than the C–C bond in biphenyl itself, making it an excellent target for C–C cleavage. One can combine the advantage of cleavage of a weak C–C bond with the formation of two strong metal–aryl bonds, improving the overall thermodynamics of the oxidative addition. For third row transition metals, metal–aryl bond strengths have been measured to be

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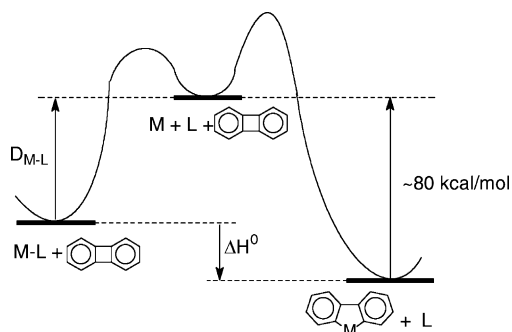
¹ Calculated using ΔH_f data from [5]. ΔH_f (biphenyl) = 43.5 kcal/mol, ΔH_f (biphenylene) = 100.5 kcal/mol, ΔH_f (H^\bullet) = 52.1 kcal/mol, ΔH_f ($C_6H_5^\bullet$) = 81.0 kcal/mol, ΔH_f (C_6H_6) = 19.8 kcal/mol.



$$\begin{aligned} \Delta H_{r1} &= 2(D_{Ar-H}) = 2(113.3) = 226.6 \\ \Delta H_{r1} &= \Delta H_f^\circ + 2(52.1) - 43.5 \\ \Delta H_f^\circ &= \Delta H_{r1} - 2(52.1) + 43.5 = 165.9 \\ D_{C-C} &= 165.9 - 100.5 = \mathbf{65.4 \text{ kcal/mol}} \end{aligned}$$

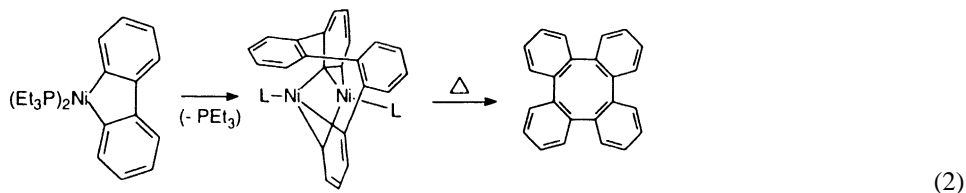
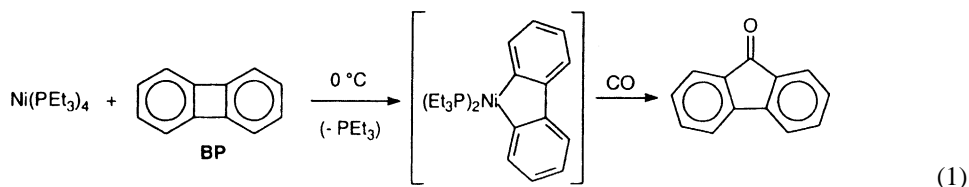
Scheme 1.

~71–75 kcal/mol, which means that oxidative addition of a metal fragment to biphenylene should be exothermic by ~80–85 kcal/mol! Of course, some energy must also be expended to generate the reactive metal fragment, but there is ample energy available for this (Scheme 2).



Scheme 2.

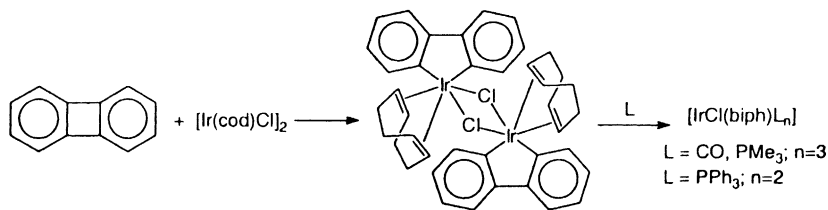
found that Ni⁰ complexes react with biphenylene to give C–C insertion products, and isolation of metastable derivatives was possible with triethylphosphine as a ligand (Eq. (1)). Eisch also demonstrated a number of insertion reactions as evidence for the C–C cleavage, including CO insertion to give fluorenone, alkyne insertion to give phenanthrene, and oxidation to give dibenzofuran and 2-hydroxybiphenyl. In the absence of added substrate, a dinuclear complex was formed in which phosphine was lost and a new aryl–aryl C–C bond was formed. Upon heating to 150 °C, this species decomposes to give tetraphenylene (Eq. (2)) [8].



As biphenylene is an appropriate target for C–C bond cleavage, it is no surprise that several early examples have appeared in the literature. In 1964, a report appeared indicating that biphenylene and Cr(CO)₆ react at 225 °C to give traces of fluorenone (5%) and bis-biphenylene ethylene (1–2%) [6]. Chatt had reported earlier that no reaction of biphenylene occurred with Fe(CO)₅, Ni(CO)₄, Ni(PPh₃)₂(CO)₂, or PtCl₂(PPh₃)₂ [7]. In 1985, Eisch and co-workers

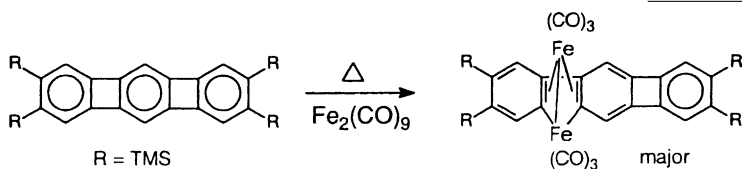
Vollhardt and co-workers also investigated a nickel system that activated biphenylene. They found that Ni(cod)(PMe₃)₂ reacts with biphenylene at 25 °C to give tetraphenylene. Only small quantities of the insertion complex could be seen over the course of the reaction. At 100 °C, conversion of biphenylene into tetraphenylene was catalytic using 10% catalyst. Several other substituted biphenylenes were also found to form tetraphenylenes [9].

In another example, Crabtree and co-workers demonstrated that Ir^I can add to biphenylene to give stable insertion adducts [10]. The insertion adduct, a 16-electron Ir^{III} compound, reacted with CO, PhC≡CPh, PR₃ or NaBH₄ but in no case showed disruption of the metallacycle ring (Eq. (3)).



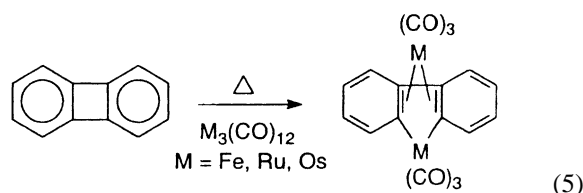
(3)

C–C biphenylene insertion with iron has been seen by Vollhardt and co-workers upon heating tetra(trimethylsilyl)-[3]-phenylene with Fe₂(CO)₉ [11]. Three products were obtained, two of which contained metallacycles resulting from insertion of Fe(CO)₃ into the C–C bond (Eq. (4)). A second Fe(CO)₃ moiety bridges to the diene portion of the metallacycle as has been seen in other dibenzoferrrole structures [12].



(4)

In related studies, Yeh and co-workers recently reported the thermal reaction of biphenylene with Fe₃(CO)₁₂ to give the dibenzoferrrole (Eq. (5)). Similar reactions occur with Ru₃(CO)₁₂ and Os₃(CO)₁₂, although harsher reaction conditions are required and some C–H activation is seen with osmium [13].



(5)

An interesting case of biphenylene hydrogenolysis has been reported by Caubère using an in situ organometallic reducing agent. A combination of *t*-amyl alcohol, NaH, 2,2'-bipyridine, and Ni(OAc)₂ gives a 'complex reducing agent' that was capable of converting biphenylene to biphenyl at 65 °C in high

yield [14]. In a somewhat similar report, Pd(O₂CMe)₂ was found to react with biphenylene at 100 °C in acetic acid solution to give biphenyl and Pd(0) metal [15].

Reactions of biphenylene with samarium or ytterbium powders in DME have also been reported to give

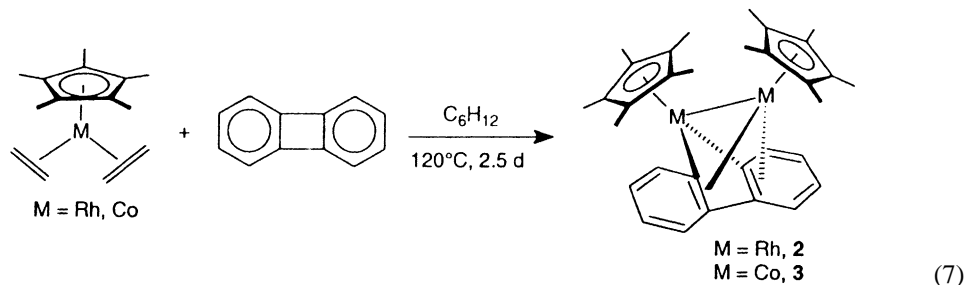
C–C insertion adducts, but the species are very sensitive and could not be isolated in pure form [16]. Other than this handful of examples, the chemistry of biphenylene with transition metal complexes has remained largely unexplored. Below we report further stoichiometric and catalytic chemistry of late transition metal complexes with biphenylene to give functionalized products that have been discovered in our group over the last 7 years.

2. Results and discussion

2.1. Reactions with Cp*Rh and Cp*Co

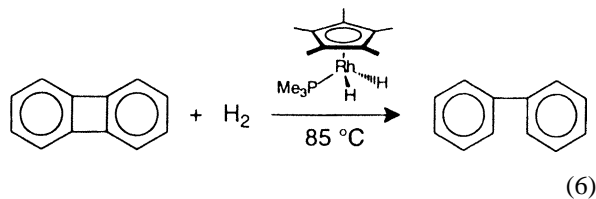
The phenyl hydride complex Cp*Rh(PMe₃)(Ph)H serves as a convenient thermal source of the reactive 16-electron fragment [Cp*Rh(PMe₃)]. At 65 °C, biphenylene reacts to give a C–H activation product at the α-carbon within a few hours [17]. Lithiation is also known to occur selectively at this position [18]. When the temperature is raised to 85 °C, the C–H activation product is observed to isomerize into the C–C insertion adduct. If this isomerization is carried out in the presence of a large excess of deuterated biphenylene, only 50% of the C–C insertion product contains deuterated ligand. Therefore, the reductive elimination of biphenylene and the direct isomerization processes

occur at the same rate. Scheme 3 shows the mechanism proposed for these interconversions, in which η^2 -arene complexes are proposed as (unseen) intermediates. There is ample precedent for such η^2 -arene complexes in C–H activation reactions of this metal fragment [19], and a similar species is invoked to explain the intramolecular C–C bond activation. This work clearly shows that while C–H activation can be



kinetically preferred, C–C activation is thermodynamically preferred, a result not too surprising in light of the arguments pertaining to Scheme 2 above.

The related dihydride $\text{Cp}^*\text{Rh}(\text{PMe}_3)_2\text{H}_2$ was found to be a catalyst for the hydrogenolysis of biphenylene to biphenyl (Eq. (6)) [17]. The obvious intermediate in this reaction is $\text{Cp}^*\text{Rh}(\text{PMe}_3)(\eta^2\text{-}2,2'\text{-biphenyl})$, **1**, but this possibility can be ruled out as **1** does not react with 1 atm hydrogen at 130 °C (**1** is coordinatively saturated). Rather, a mechanism invoking hydride migration to the Cp^* ring was suggested as seen in the exchange reaction with D_2 [20].

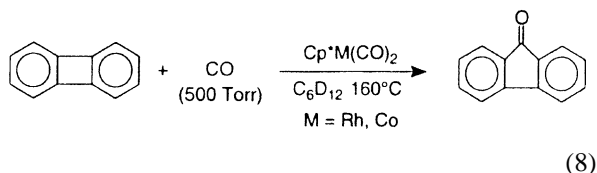


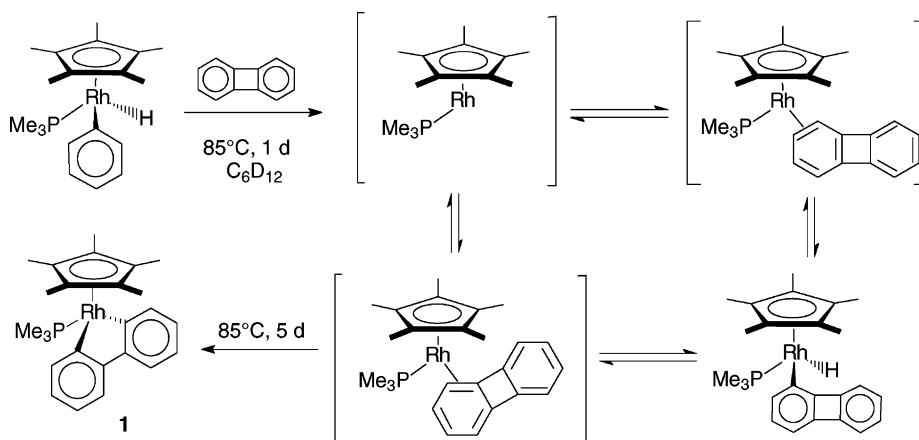
In an effort to probe the reactivity of related derivatives containing additional vacant coordination sites, the reactions of $\text{Cp}^*\text{M}(\text{C}_2\text{H}_4)_2$ ($\text{M} = \text{Co}, \text{Rh}$) with biphenylene were examined. Both ethylenes are known to be labile in these complexes [21], leaving one site for C–C activation and a second for additional reaction chemistry. In both cases, thermolysis in solution with biphenylene (1 equivalent) leads to the formation of a dinuclear product in which C–C

insertion occurs, but a second Cp^*M unit coordinates to the metallacycle in an η^5 fashion (Eq. (7)). The two metal centers in these complexes differ in that the β -carbons are bound to only one of the metals, unlike the α -carbons, as revealed in their X-ray structures. In solution, however, the β -carbons flip-flop between the two metals, equilibrating the Cp^* rings. For cobalt, the barrier is 11.4 kcal/mol, whereas for rhodium, the barrier is 16.8 kcal/mol.

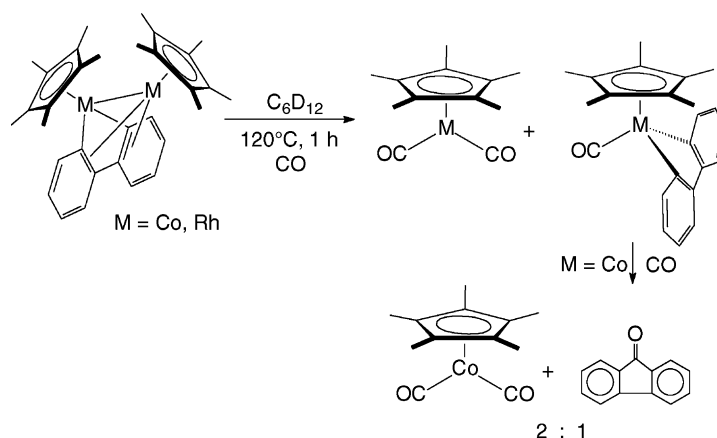
The dinuclear rhodium complex **2** reacts with CO at 120 °C to give a 1:1 mixture of $\text{Cp}^*\text{Rh}(\text{CO})_2$ and $\text{Cp}^*\text{Rh}(\text{CO})(\eta^2\text{-}2,2'\text{-biphenyl})$. The dinuclear cobalt complex **3** appears to react similarly. The intermediate insertion adduct is apparently unstable, however, as a second equivalent of $\text{Cp}^*\text{Co}(\text{CO})_2$ is seen instead along with one equivalent of fluorenone (Scheme 4). Curiously, cobalt complex **3** reacts with PMe_3 at 120 °C to give the cobalt analog of **1**, $\text{Cp}^*\text{Co}(\text{PMe}_3)(\eta^2\text{-}2,2'\text{-biphenyl})$, whereas the dinuclear rhodium complex **2** is unreactive with PMe_3 under these conditions. Neither **2** nor **3** reacts with hydrogen (500 Torr) at 170 °C.

The observation of fluorenone with **3** suggested the possibility for catalytic carbonylation of the C–C bond in biphenylene. Indeed, both $\text{Cp}^*\text{Co}(\text{CO})_2$ and $\text{Cp}^*\text{Rh}(\text{CO})_2$ were found to be catalysts for CO insertion at 160 °C (Eq. (8)). The rhodium complex was unchanged during the reaction, and rates of approximately one turnover per day were seen under 500 Torr CO. Cobalt was a faster catalyst (~ 3 turnovers per day), but decomposition set in after only a few turnovers.





Scheme 3.

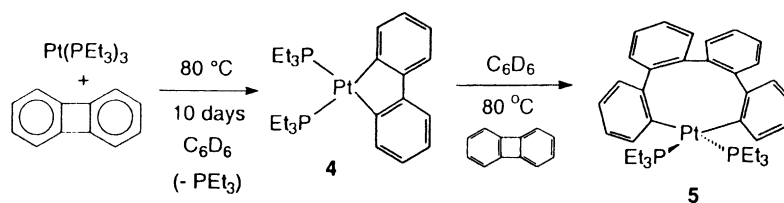


Scheme 4.

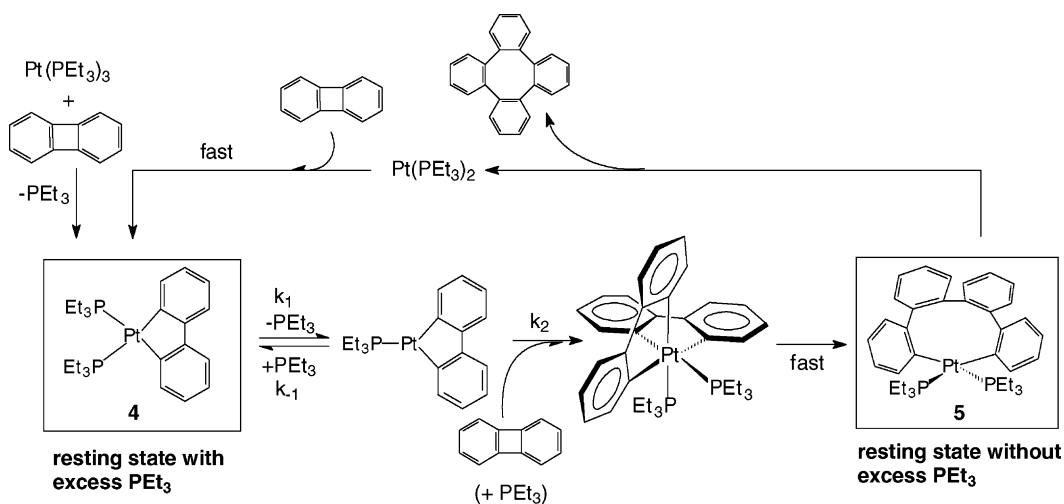
2.2. Reactions with $Pt(PEt_3)_2$ and $Pd(PEt_3)_2$

PtL_2 fragments are well known to be reactive towards oxidative addition reactions [22]. We examined the reactivity of $Pt(PEt_3)_3$ with biphenylene analogous to the earlier studies by Eisch and co-workers with

nickel [8]. $Pt(PEt_3)_3$ reacts with biphenylene at $80^\circ C$ to give a C–C cleavage adduct **4**. Upon heating isolated **4** with more biphenylene at $80^\circ C$, a second C–C cleavage occurs to give a 2,2'''-tetraphenyl complex **5** as shown in Eq. (9). Heating **5** at $115^\circ C$ in the presence of PEt_3 leads to the formation of $Pt(PEt_3)_3$ and tetraphenylene [23].

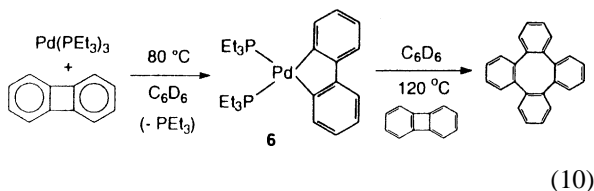


(9)



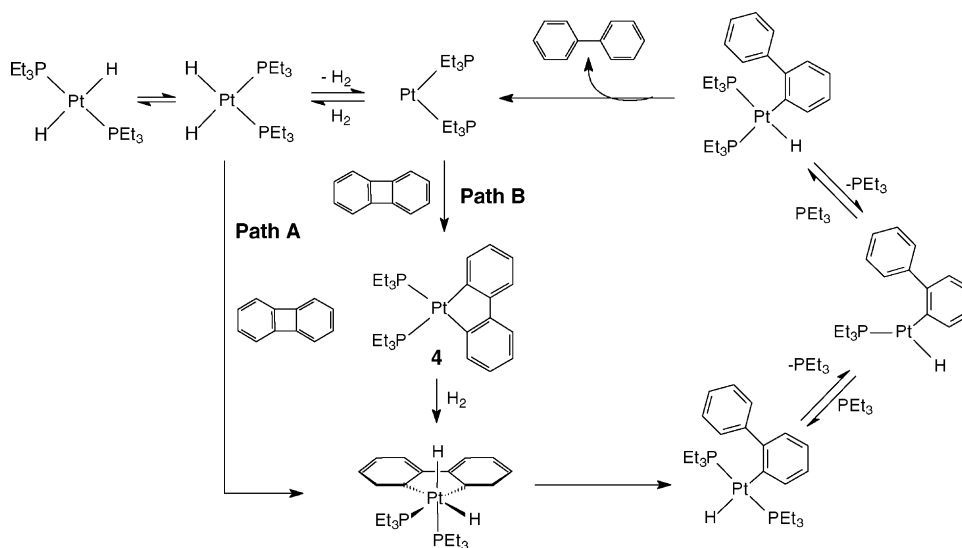
Either $\text{Pt}(\text{PEt}_3)_3$, **4**, or **5** serve as catalysts for the dimerization of biphenylene to make tetraphenylene. A detailed mechanistic study of the catalysis showed that the relative amounts of biphenylene and PEt_3 determine the ratios of the resting state species during the catalysis as well as the overall rate of catalysis. Scheme 5 shows the mechanism that was identified. The competition of biphenylene versus PEt_3 for the tri-coordinate intermediate can be seen to be the critical branch point in the catalysis, consistent with the kinetics. Also, the second C–C activation gives a Pt^{IV} complex that was shown to be a transient intermediate by independent synthesis. Ultimately, catalyst death occurs by way of aromatic C–H bond activation by the tri-coordinate intermediate leading to an inactive $\text{PtL}_2(\text{aryl})_2$ complex [23].

Examination of $\text{Pd}(\text{PEt}_3)_3$ produced similar results, with the C–C insertion complex **6** (analogous to **4**) being observed as the resting state (Eq. (10)). No species analogous to **5** was seen, however. The rate using $\text{Pd}(\text{PEt}_3)_3$ was ~ 16 turnovers per day at 120°C , about 100 times faster than with the platinum analog [23].



We have also examined the use of hydrogen with the above catalyst systems for the hydrogenolysis of the C–C bond of biphenylene. $\text{Pt}(\text{PEt}_3)_3$ slowly catalyzes the hydrogenolysis (one turnover per 12 days at 120°C , 0.9 atm H_2) [24]. As the catalysis proceeds, $\text{Pt}(\text{PEt}_3)_3$ is replaced first with *trans*- $\text{Pt}(\text{PEt}_3)_2\text{H}_2$ and then with *trans*- $\text{Pt}(\text{PEt}_3)_2(\alpha\text{-biphenyl})\text{H}$, which remains as the catalysis continues. The latter complex can be isolated and shown independently to react with hydrogen to give biphenyl and $\text{Pt}(\text{PEt}_3)_2\text{H}_2$, but the reaction is strongly inhibited by added PEt_3 , indicating that phosphine loss is required prior to elimination of biphenyl [25]. The mechanism proposed for this reaction is shown in Scheme 6. While addition of H_2 to $\text{Pt}(\text{PEt}_3)_2$ is likely to give *cis*- $\text{Pt}(\text{PEt}_3)_2\text{H}_2$, Trogler has established that the *trans* isomer is in equilibrium with a small amount of the *cis* isomer [26]. Oxidative addition of the C–C bond of biphenylene to the dihydride is believed to give the Pt^{IV} intermediate *cis,cis,cis*- $\text{Pt}(\text{PEt}_3)_2(2,2'\text{-biphenyl})\text{H}_2$. Of the two other isomers possible, the one with *trans* hydrides is inconsistent with a *cis* addition of H_2 , and the other possibility, the *trans,cis,cis* isomer with *trans* PEt_3 groups was independently prepared and shown to react too slowly to be involved in the catalytic cycle.

The palladium complex $\text{Pd}(\text{PEt}_3)_3$ was found to be a faster catalyst for biphenylene hydrogenolysis (2.2 turnovers per day at 70°C , 0.9 atm H_2). The only species observed in solution was



Scheme 6.

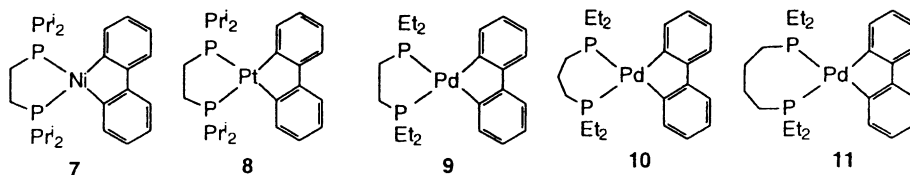
$\text{Pd}(\text{PEt}_3)_2(2,2'\text{-biphenyl})$ (**6**), consistent with path B in [Scheme 6](#) and with H_2 oxidative addition as being the rate determining step. *trans*- $\text{Pd}(\text{PEt}_3)_2(\alpha\text{-biphenyl})\text{H}$ could be generated from **6** plus hydrogen in the presence of an excess of PEt_3 , but it immediately eliminated biphenyl upon attempted removal of the PEt_3 . $[\text{Ni}(\text{dippe})\text{H}]_2$ proved to be the most efficient hydrogenolysis catalyst, giving 16 turnovers per day at 50°C , 0.9 atm H_2 . $\text{Ni}(\text{dippe})(2,2'\text{-biphenyl})$ (**7**) was the resting state, again consistent with H_2 addition to the C–C insertion adduct as the pathway for reaction [\[24\]](#). An η^2 -biphenylene adduct was observed at room temperature, similar to that seen in $\text{Ni}(\text{dippe})(\eta^2\text{-naphthalene})$ [\[27\]](#).

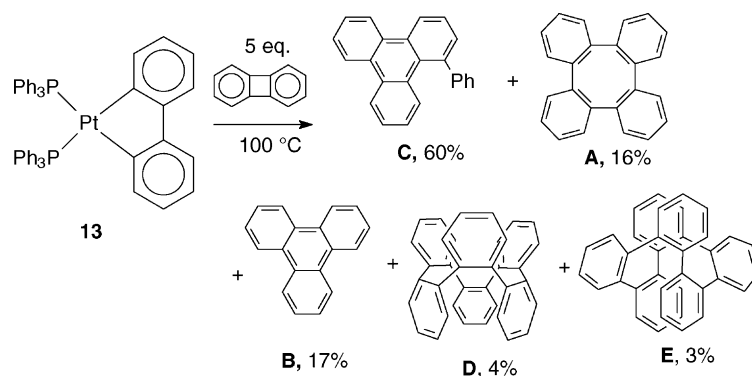
2.3. Reactions of PtL_2 and PdL_2 chelates and related derivatives

Chelating phosphines were also examined with platinum. As the rate determining step involves phosphine loss (and isomerization to a *cis* isomer) from *trans*- $\text{Pt}(\text{PEt}_3)_2(\alpha\text{-biphenyl})\text{H}$, the chelate would

enforce a *cis* geometry, thereby obviating the rate determining step. Use of $\text{Pt}(\text{dippe})\text{H}_2$ (which is known to be in equilibrium with its dimer [\[28\]](#)) did indeed eliminate $\text{Pt}(\text{L})_2(\alpha\text{-biphenyl})\text{H}$ as the resting state, with the dihydride now being the major species seen, but the rate was still no faster than in the PEt_3 case. Only traces of the C–C insertion adduct **8** were seen. The mechanism of reaction was believed to be consistent with a sequence similar to path A in [Scheme 6](#). Use of the larger chelate *dipp*p with a 3-carbon linker in $\text{Pt}(\text{dipp})\text{H}_2$ gave catalysis at virtually the same rate as the *dippe* complex [\[24\]](#).

Three chelating phosphines were examined with palladium. The derivatives $\text{L}_2\text{Pd}(2,2'\text{-biphenyl})$ where $\text{L}_2 = \text{depe}$, *depp*, or *depb* (**9–11**) were prepared and reacted with excess biphenylene at 95°C under 0.9 atm H_2 . The rates of catalytic hydrogenolysis by all three complexes was 0.7 ± 0.2 turnovers per day, showing little effect of chelate size. As mentioned above, the nickel *dippe* chelate was by far the best catalyst for hydrogenolysis [\[24\]](#).



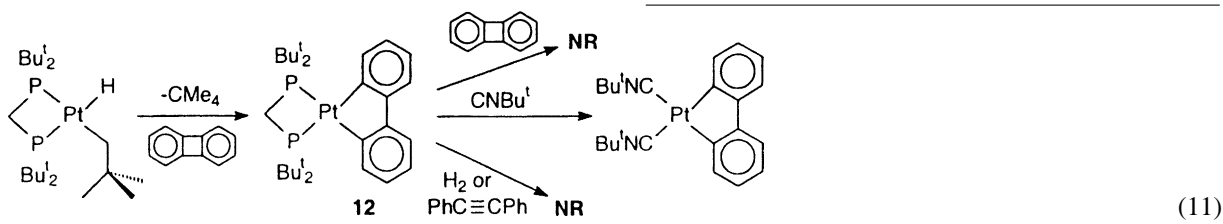


Scheme 7.

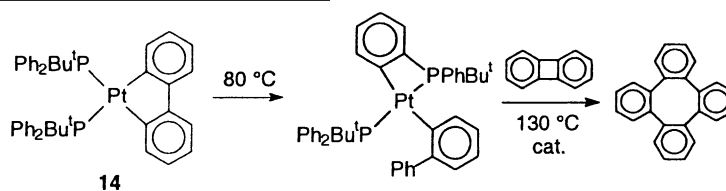
Smaller chelate rings were found to have a greater effect upon reactivity. $\text{Pt}(\text{dtbpm})(\text{neopentyl})\text{H}$ has been reported to be a convenient precursor to the reactive $[\text{Pt}(\text{dtbpm})]$ fragment [29]. Reaction of this compound with biphenylene leads to the Pt^{II} C–C insertion adduct **12**, as with the other PtL_2 systems. This adduct proved to be quite stable however, and was unreactive with H_2 , diphenylacetylene, or more biphenylene. Bu^tNC was found to displace the phosphine chelate, but in no case were the Pt–aryl bonds disturbed (Eq. (11)). The isopropyl analog, $\text{Pt}(\text{dippm})(\text{neopentyl})\text{H}$ does not even react with biphenylene, but forms a $[\text{Pt}(\text{dippm})]_2$ dimer [30].

indicated in Scheme 7. The formation of triphenylene was found to involve reaction with the benzene solvent rather than cleavage of a biphenyl C–C bond [30].

The bis- PPh_2Bu^t C–C insertion complex **14** was prepared by treating PtCl_4^{2-} with dilithiobiphenyl followed by PPh_2Bu^t . Upon heating to $80\text{ }^\circ\text{C}$, **14** undergoes C–H activation of one of the phosphine phenyl groups and then eliminates a biphenyl–H bond, producing an orthometallated derivative (Eq. (12)). This orthometallation is apparently reversible, however, as the derivative is a slow catalyst for the conversion of biphenylene into tetraphenylene at $130\text{ }^\circ\text{C}$ (approximately one turnover per week) [30].



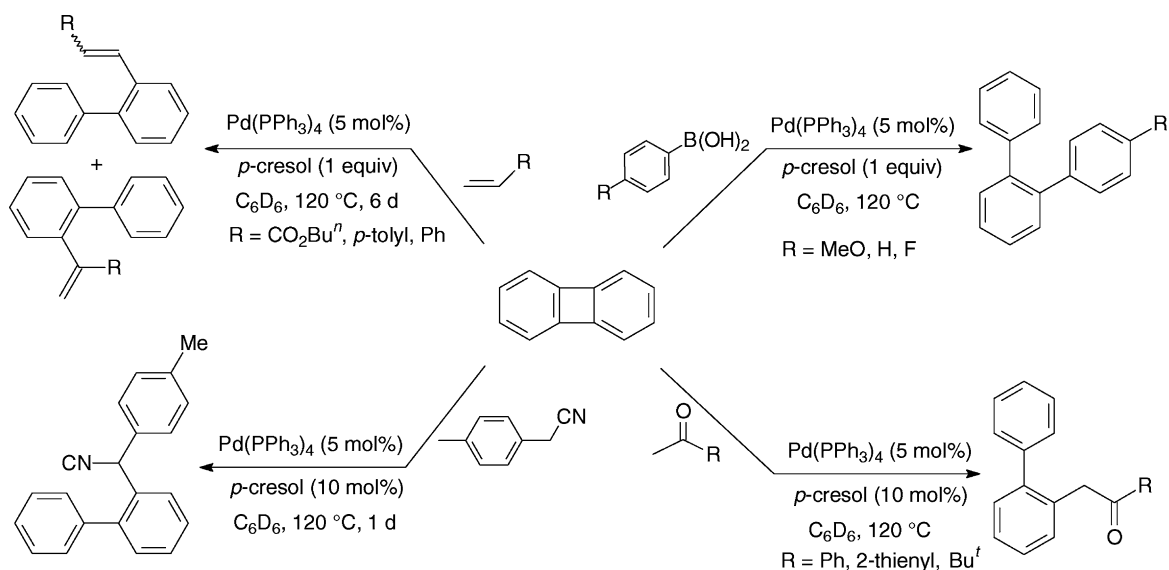
(11)



(12)

$\text{Pt}(\text{PPh}_3)_3$ does not react with biphenylene, but the insertion adduct **13** can be prepared independently from dilithiobiphenyl and $\text{PtCl}_2(\text{PPh}_3)_2$. While the $[\text{Pt}(\text{PPh}_3)_2]$ fragment does not appear to cleave the C–C bond of biphenylene, **13** reacts with biphenylene in a stoichiometric reaction to give oligomers as

Palladium triphenylphosphines derivatives proved to be elusive, but biphenylene C–C cleavage could be carried out catalytically to give a variety of functionalized products. In these reactions, $\text{Pd}(\text{PPh}_3)_4$ was reacted with biphenylene at $120\text{ }^\circ\text{C}$ in the presence of a catalytic amount of *p*-cresol. The mildly



Scheme 8.

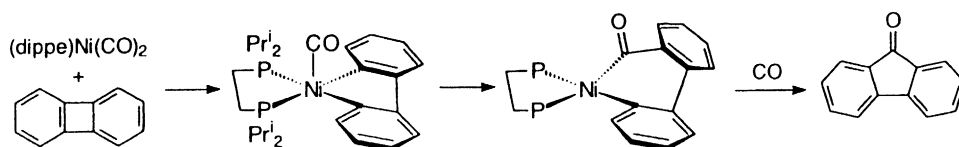
acidic alcohol cleaved one Pd–aryl bond, allowing insertion of an olefin into the remaining Pd–aryl bond. The β -elimination leads to the isolation of vinyl-biphenyl derivatives (Scheme 8). In another application, the acid-cleaved intermediate was reacted with aryl-boronic acids to give new triaryl derivatives. In a third case, substrates with weakly acidic hydrogens such as methyl ketones or benzylnitriles can undergo coupling with the *o*-biphenyl ligand to give *o*-biphenyl substituted derivatives. Careful attention to pH appeared to be a requirement to obtaining good product yields (>80%). While the C–C insertion adduct Pd(PPh₃)₂(2,2'-biphenyl) is not observed in these reactions, its presence is strongly implicated by the nature of the products obtained [31].

2.4. Reactions with Ni(dippe)

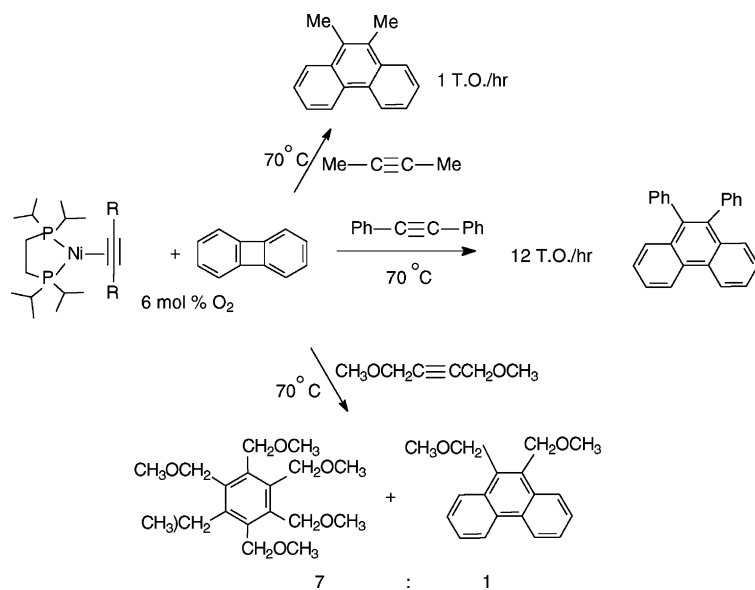
As mentioned earlier, the hydride dimer [Ni(dippe)-H]₂ serves as a convenient source of the nickel fragment [Ni(dippe)], and this fragment reacts with biphenylene to give the C–C insertion adduct **7**.

Reaction of **7** with diphenylacetylene leads cleanly to 9,10-diphenylphenanthrene and Ni(dippe)(h²-PhC-CPh). The formation of the phenanthrene was found to be catalytic, with dimethylacetylene and bis-(methoxymethyl)acetylene also giving phenanthrenes (Scheme 9). An investigation of the reaction mechanism showed, however, that the catalysis was accelerated by the addition of small quantities of O₂, and it appears that oxidation of the phosphine ligand leads to a more active ‘naked’ catalyst center. In this regard, Ni(PPh₃)₂(PhCCPh) + O₂ also produced a very active catalytic system [32].

In related reactions, Ni(dippe)(CO)₂ was found to catalyze the insertion of CO into biphenylene to give fluorenone at 95 °C. The dicarbonyl is the resting point during the catalysis, but if the reaction is starved for CO, then a CO-inserted adduct can be seen to build up (Eq. (13)). Addition of xylol isocyanide rather than CO leads to the catalytic formation of fluorenimine in a reaction similar to the CO insertion. Once again, an intermediate is observed in which the isocyanide has inserted into one of the Ni–aryl bonds.



(13)

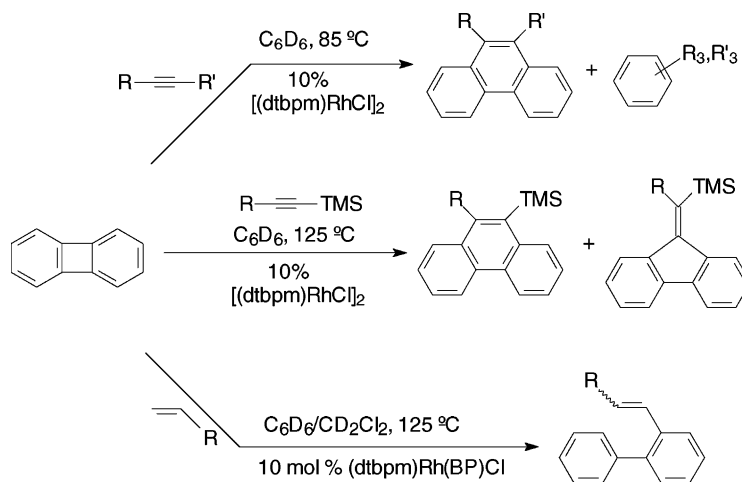


Scheme 9.

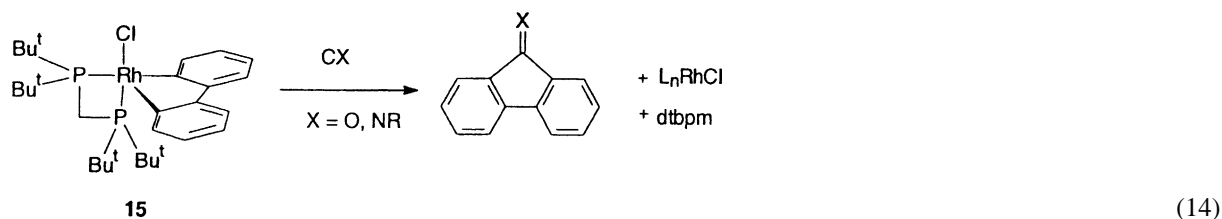
2.5. Related metal reactions

Recently, the cleavage of the C–C bond of biphenylene by a rhodium bis-phosphine complex has been observed. The dimer $[(\text{dippm})\text{Rh}(\text{Cl})]_2$ reacts with biphenylene at 85°C to give a Rh(III) insertion adduct **15** with a square pyramidal structure. Adduct **15** reacts with CO and isonitriles to

give fluorenone and fluorenimine products stoichiometrically (Eq. (14)). Alkenes and alkynes react to give a variety of insertion adducts as shown in Scheme 10. The alkene and alkyne insertion reactions are catalytic, whereas the reactions with the strong p-acceptors CO and CNR lead to stable adducts of the type $(\text{dippm})\text{RhCl}(\text{CX})$ ($\text{X} = \text{O}, \text{NR}$) [33].



Scheme 10.



One last example of biphenylene C–C cleavage has been seen using a nickel P–N chelating complex. In this example, biphenylene and diphenylacetylene react with $\text{Ni}[\text{Pr}'_2\text{PC}_2\text{H}_4\text{NMe}_2]\text{-(PhCCPh)}$ (**16**) to give 9,10-diphenylphenanthrene catalytically at 80 °C (Eq. (15)). Unlike the reaction with dippe as a ligand, air is not required and high yields of the organic product are obtained. The greater reactivity of this

complex is attributed to the lability of the NMe_2 group. The initial catalyst is formed by reaction of $\text{Ni}(\text{COD})_2$ with the PN chelate, followed by addition of diphenylacetylene. A single crystal X-ray structure of the complex is shown in Fig. 1. The acetylene can be seen to lie in the NiPN plane, with a slightly asymmetric binding of the acetylene, as seen in the Ni–C distances of 1.845(3) and 1.904(3) [34].

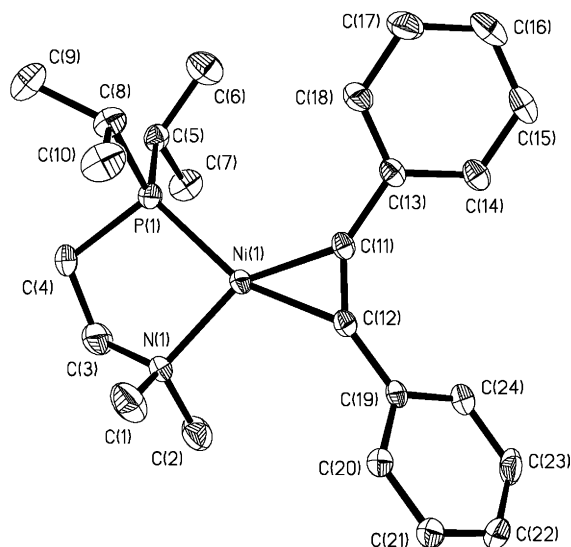
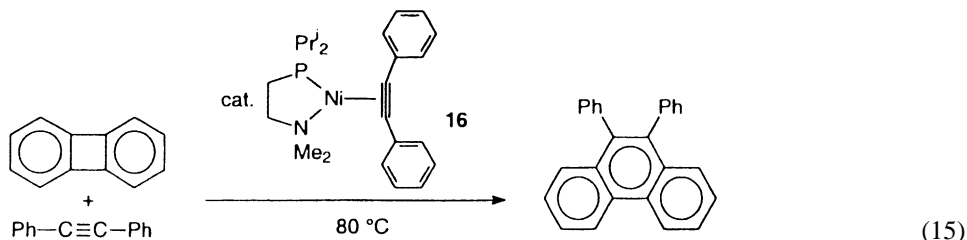


Fig. 1. ORTEP drawing of $\text{Ni}[\text{Pr}'_2\text{PC}_2\text{H}_4\text{NMe}_2]\text{-(PhCCPh)}$. Selected distances (Å) and angles (°): Ni(1)–C(11), 1.845 (3); Ni(1)–C(12) 1.904 (3); C(11)–C(12), 1.291 (5); N(1)–Ni(1)–P(1), 89.44 (8).

3. Conclusions

A variety of late transition metal complexes containing electron-rich ligands have been found to be capable of cleaving the C–C bond of biphenylene. In many cases, the insertion adduct can be isolated and characterized. These adducts participate in a wide variety of insertion reactions with small unsaturated molecules including CO, isonitriles, olefins, and alkynes to give functionalized products. In many cases, the reactions are catalytic. Transition metal catalyzed biphenylene C–C bond functionalization has proven to be a rich area for development of new routes to functionalized aromatic compounds.

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References

- [1] E.M. Arnett, R.A. Flowers, *Chem. Soc. Rev.* 22 (1993) 9.
- [2] A.J.H. Klunder, J. Zhu, B. Zwanenburg, *Chem. Rev.* 99 (1999) 1163;
R. Bloch, G. Mandville, *Recent Res. Dev. Org. Chem.* 2 (1998) 441.
- [3] W.D. Jones, *Nature, News and Views* 364 (1993) 676.
- [4] M. Murakami, Y. Ito, in: S. Murai (Ed.), *Topics in Organometallic Chemistry*, Vol. 3, Springer, New York, 1999, pp. 96–129.
- [5] H.Y. Afeefy, J.F. Liebman, S.E. Stein, Neutral thermochemical data, in: W.G. Mallard, P.J. Linstrom (Eds.), *NIST Chemistry WebBook*, NIST Standard Reference Database Number 69, February 2000, National Institute of Standards and Technology, Gaithersburg MD, 20899 (<http://webbook.nist.gov>).
- [6] E.R. Atkinson, P.L. Levins, T.E. Dickelman, *Chem. Ind.* (1964) 934.
- [7] J. Chatt, R.G. Guy, H.R. Watson, *J. Chem. Soc.* (1961) 2332.
- [8] J.J. Eisch, A.M. Piotrowski, K.I. Han, C. Krüger, Y.H. Tsay, *Organometallics* 14 (1985) 224.
- [9] H. Schwager, S. Spyroudis, K.P.C. Vollhardt, *J. Organomet. Chem.* 382 (1990) 191.
- [10] Z. Lu, C.-H. Jun, S.R. de Gala, M. Sigalas, O. Eisenstein, R.H. Crabtree, *J. Chem. Soc., Chem. Commun.* (1993) 1877;
Z. Lu, C.-H. Jun, S.R. de Gala, M.P. Sigalas, O. Eisenstein, R.H. Crabtree, *Organometallics* 14 (1995) 1168.
- [11] B.C. Berris, G.H. Hovakeemian, Y.-H. Lai, H. Mestdaph, K.P.C. Vollhardt, *J. Am. Chem. Soc.* 107 (1985) 5670.
- [12] R. Victor, R. Ben-Shoshan, *J. Chem. Soc., Chem. Commun.* (1974) 93;
R.E. Davis, B.L. Barnett, R.G. Amiet, W. Merk, J.S. McKennis, R. Pettit, *J. Am. Chem. Soc.* 96 (1974) 7108.
- [13] W.-Y. Yeh, S.C.N. Hsu, S.-M. Peng, G.-H. Lee, *Organometallics* 17 (1998) 2477.
- [14] S. Becker, Y. Fort, R. Vanderesse, P. Caubère, *J. Org. Chem.* 54 (1989) 4848.
- [15] N.F. Gol'dshleger, E.T. Epel'baum, I.B. Nazarova, O.S. Roshchupkina, Yu.M. Shul'ga, *Russ. J. Gen. Chem.* 63 (1993) 926.
- [16] Y. Chauvin, N. Marchal, H. Olivier, L. Saussine, *J. Organomet. Chem.* 445 (1993) 93.
- [17] C. Perthuisot, W.D. Jones, *J. Am. Chem. Soc.* 116 (1994) 3647.
- [18] J.M. Blatchy, R. J. Taylor, *J. Chem. Soc.* (1964) 4641.
- [19] W.D. Jones, L. Dong, *J. Am. Chem. Soc.* 111 (1989) 8722;
S.T. Belt, L. Dong, S.B. Duckett, W.D. Jones, M.G. Partridge, R.N. Perutz, *J. Chem. Soc., Chem. Commun.* (1991) 266;
R.M. Chin, L. Dong, S.B. Duckett, W.D. Jones, *Organometallics* 11 (1992) 871.
- [20] W.D. Jones, V.L. Kuykendall, A.D. Selmezy, *Organometallics* 10 (1991) 1577;
R.M. Chin, L. Dong, S.B. Duckett, M.G. Partridge, W.D. Jones, R.N. Perutz, *J. Am. Chem. Soc.* 115 (1993) 7685.
- [21] L.P. Seiwel, *J. Am. Chem. Soc.* 96 (1974) 7134;
W.D. Jones, R.M. Chin, *J. Organomet. Chem.* 472 (1994) 311.
- [22] M. Hackett, G.M. Whitesides, *J. Am. Chem. Soc.* 110 (110) (1988) 1436;
M. Hackett, G.M. Whitesides, *J. Am. Chem. Soc.* 110 (1988) 1449.
- [23] B.L. Edelbach, R.J. Lachicotte, W.D. Jones, *J. Am. Chem. Soc.* 120 (1998) 2843.
- [24] B.L. Edelbach, D.A. Vicic, R.J. Lachicotte, W.D. Jones, *Organometallics* 17 (1998) 4784.
- [25] P.J. Stang, M.H. Kowalski, *J. Am. Chem. Soc.* 111 (1989) 3356.
- [26] R.S. Paonessa, W.C. Trogler, *J. Am. Chem. Soc.* 104 (1982) 1138.
- [27] R. Benn, R. Mynott, I. Topalovic, F. Scott, *Organometallics* 8 (1989) 2299;
F. Scott, C. Kruger, P. Betz, *J. Organomet. Chem.* 387 (1990) 113.
- [28] D.J. Schwartz, R.A. Anderson, *J. Am. Chem. Soc.* 117 (1995) 4014.
- [29] P. Hofmann, G. Unfried, *Chem. Ber.* 125 (1992) 659.
- [30] N. Simhai, C.N. Iverson, B.L. Edelbach, W.D. Jones, *Organometallics* 20 (2001) 2759.
- [31] T. Satoh, W.D. Jones, *Organometallics* 20 (2001) 2916.
- [32] B.L. Edelbach, R.J. Lachicotte, W.D. Jones, *Organometallics* 18 (1999) 4040.
- [33] C.N. Iverson, W.D. Jones, *Organometallics* 20 (2001) 5745.
- [34] C. Müller, R.J. Lachicotte, W.D. Jones, *Organometallics* 21 (2002) 1975.