Synthesis of Aromatic Compounds by Catalytic C–C Bond Activation of Biphenylene or Angular [3]Phenylene

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Abstract: Substituted phenanthrenes and picenes were easily prepared by reaction of biphenylene or angular [3]phenylene with various alkynes in the presence of a catalytic amount of $[IrCl(cod)]_2/dppe (cod=1,5-cyclooctadiene, dppe=1,2-bis(diphenylphosphino)ethane).$ The reaction is based on C–C bond activation of the cyclobutane ring. The reaction tolerates the presence of bulky groups on the alkyne, such as the ferrocene moiety. In addition, a catalytic system based on [RhCl-(cod)]_2/dppe enabled the, hitherto unreported, reaction of biphenylene with nitriles to provide phenanthridines.

Introduction

Synthesis of aromatic compounds that possess extended π conjugated systems is of considerable interest because of their potential use in organic electronic materials.^[1] Substances that contain the phenanthrene motif belong in this class of compounds. As a typical example, picene has recently been shown to exhibit superconducting properties.^[2] Although there are a number of synthetic procedures that could be used for the preparation of phenanthrenes,^[3] picenes,^[4] and their extended aromatic and heteroaromatic congeners,^[5] the development of new, selective, and efficient procedures is highly desirable. Especially, the use of synthetic methodologies based on catalytic C-C bond activation followed by annulation reactions with unsaturated substrates is synthetically attractive. Potentially suitable starting materials are biphenylene (1), which contains a strained cyclobutane ring, and its higher congeners, the polyphenylenes.^[6] Although a number of transition-metal complexes have been reported to undergo oxidative addition to the biphenylene C-C bond to give rise to dibenzometallacycles,^[7] only a handful of reports has dealt with the subsequent reaction with alkynes to result in the formation of a new aromatic ring.^[7e,8,9] In this report, we present new conditions for the reaction of the strained cyclobutadiene rings of bi- and polyphenylenes with alkynes or nitriles to give aromatic compounds.

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Results and Discussion

We were interested whether C-C bond activation of 1 could be carried out simply by using commercially available ligands and if the subsequent reaction with various carboncarbon (alkynes) and carbon-nitrogen (nitriles) triple bonds was achievable. Further attention was focused on the insertion of sterically hindered alkynes that bore a ferrocene moiety. To this end, we screened the reaction of 1 with 1phenylpropyne (2a) in the presence of a catalytic amount of $[IrCl(cod)]_2$ (10 mol%, cod=1,5-cyclooctadiene) and various mono- (PPh₃) and bidentate ligands (1,1-bis(diphenylphosphino)methane (dppm), 1,2-bis(diphenylphosphino)ethane (dppe), 1,3-bis(diphenylphosphino)propane (dppp), and 1,4-bis(diphenylphosphino)butane (dppb)). From numerous experiments, dppe emerged as the most suitable ligand. In the presence of dppe, 9-phenyl-10-methylphenanthrene (3a) was obtained in 83% isolated yield (Table 1,

Table 1. Reaction of **1** with **2**.



[a] Determined by ¹H NMR spectroscopy, isolated yields are in parentheses. [b] Signals of the internal standard were covered by signals of the products, which disabled determination of the yield by ¹H NMR spectroscopy. [c] The reaction was carried out in *m*-xylene at 160 °C.

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entry 1). The reaction did not proceed with the bidentate ligands dppm, dppp, or dppb. In the presence of monodentate ligand PPh₃ (20 mol%), **3a** was formed in 39% yield. Interestingly, when 2a was used in four-fold excess with respect to 1, the yield of 3a dropped to 28%. The reaction with diphenylacetylene (2b) yielded 3b in 47% isolated yield (Table 1, entry 2). The reaction with di(p-tolyl)acetylene (2c) gave the best yield of 3c (NMR spectroscopy: 75%; isolated: 57%) when two equivalents of alkyne were used (Table 1, entry 3). When one equivalent of 2c was used a 47% isolated yield was obtained. In the case of di(p-carbomethoxyphenyl)acetylene (2d) the reaction proceeded well to form 3d in reasonable yield (NMR spectroscopy: 40%; isolated: 11%). Problems associated with the isolation of 3d in an analytically pure form were responsible for the poor isolated yield (Table 1, entry 4). Unlike aryl-substituted alkynes, four equivalents of 4-octyne (2e) were required to obtain a high isolated yield of dipropylphenanthrene (3e, 80%, Table 1, entry 5). When 1.5, 2, or 3 equivalents of alkyne were used 3e was formed in 27, 31, and 96% yield (by NMR spectroscopy), respectively.

We turned out our attention to sterically hindered alkynes substituted with a ferrocenyl moiety. Ferrocenyl alkynes are, due to the steric bulk exerted by the ferrocene group, interesting reaction partners for cycloaddition with other unsaturated compounds. In addition, cycloaddition reactions could be a suitable methodology for incorporation of the electrochemically active ferrocene moiety into more complex molecular systems. Although ferrocenyl alkynes are readily available, there is only a handful of papers that deal with their application in transition-metal-catalyzed cyclotrimerizations.^[10] The reaction with propynylferrocene (2 f, 1 equiv) proceeded to give 9-methyl-10-ferrocenylphenanthrene (3 f)in 53% isolated yield (Table 1, entry 6). Adjustment of the alkyne/1 ratio did not lead to any improvement in yield. Moreover, once again, problems with efficient separation of the product from the starting material were encountered. Gratifyingly, the reaction with 1-ferrocenyl-2-(4-carbomethoxyphenyl)acetylene (2g, 1 equiv) gave rise to 3g in good isolated yield (51%, Table 1, entry 7). The structure of **3g** was unequivocally confirmed by a single-crystal X-ray analysis (Figure 1). The reaction also proceeded surprisingly well with diferrocenylacetylene $(2h, 1 \text{ equiv})^{[11]}$ to give 9,10diferrocenylphenanthrene (3h) in a good isolated yield (42%, Table 1, entry 8), although the reaction had to be performed in m-xylene at 160 °C. It should be emphasized that this is the first example of a cycloaddition reaction with sterically hindered ferrocenyl alkyne **2h**.^[12]

The structure of **3h** was unequivocally confirmed by a single-crystal X-ray analysis (Figure 2). Currently, it is not clear why successful reaction requires a substrate-dependent alkyne/**1** ratio, which varies from 1:1 to 4:1. Possibly, it could be related to subtle changes in the intrinsic reactivity of the triple bond induced by electronic and steric effects.

With regards to the scope of the reaction with respect to the alkyne, the reaction proceeded only with internal alkynes, but alkyl or aryl group substitution was acceptable.



Figure 1. X-ray structure of 3g.



Figure 2. X-ray structure of 3h.

Interestingly, the reactions with alkynes that bore electronwithdrawing (such as dimethylacetylene dicarboxylate (DMAC) and methyl propynoate) or electron-donating groups (such 1-[(triisopropyl)silyloxy]octyne) did not proceed. Also, the reaction with di-*O*-toluoyl-1-(propyn-1-yl)deoxyribose^[13] did not provide the expected products.

The successful synthesis of phenanthrenes 3 prompted us to study the, hitherto unreported, reaction of 1 with nitriles 4 to give phenanthridines 5. The Ir-based catalytic system reported above did not bring about the desired reaction with 4, but substitution of the iridium complex for [RhCl-(cod)₂ in combination with dppe yielded the expected products 5 (Table 2, conditions A). The successful course of the reaction required an increased catalyst loading (20 mol%) and reaction temperature (190-200 °C) and use of the appropriate nitrile as a solvent. The reaction with acetonitrile (4a) gave phenanthridine 5a in 26% isolated yield (Table 2, entry 1). The use of benzonitrile (4b) led to phenanthridine **5b** in reasonable yield (46%, Table 2, entry 2). Reaction of 1 with benzonitriles 4c or 4d, which bear Cl or CF₃ electron-withdrawing groups, yielded phenanthridines 5c and 5d in reasonable isolated yields of 57 and 39%, respectively

Table 2. Reaction of 1 with 4.

1



2	4b	<⊂ →−CN	5b	46 (50) ^[b]	92 ^[b]
3	4 c	CI-CN	5 c	57	40
4	4 d	F ₃ C-CN	5 d	39	78
5	4e	CN N	5e	80	25 ^[b]

[[]a] Isolated yield; the yield obtained by ¹H NMR spectroscopy is given in parentheses. [b] The reaction was carried out at 180°C, 18 h.

(Table 2, entries 3 and 4). Gratifyingly, the reaction with 2cyanopyridine (4e) proceeded quantitatively and gave phenanthridine 5e in 80% isolated yield (Table 2, entry 5). Next, we tried to reduce the amount of the catalyst required. After some experimentation, we discovered that the cationic complex $[Rh(cod)_2BF_4]$ (10 mol%) and dppe (10 mol%) under microwave (MW) irradiation could bring about the transformation of 1 to phenanthridines 5 with better efficiency in most cases (Table 2, conditions B). Phenanthridines 5a, 5b, and 5d were obtained in 40, 92, 78% isolated yields, respectively. Phenanthridine 5c was obtained in a similar isolated yield (40%); only 5e was obtained in a substantially lower isolated yield of 25%.

After screening the reactions of 1 with various alkynes and establishing suitable reaction conditions, we set out to attempt a similar process with angular tetrakis(trimethylsilyl)-[3]phenylene 6.^[14] We presumed that two consecutive C-C bonds activations followed by reaction with an alkyne 2 could open a new pathway for the synthesis of 5,6,7,8-substituted picenes 7.

Although it was reported that $[Co{(CH_2=CH_2)_2}Cp]$ (Cp = cyclopentadienyl) reacted with angular [3]phenylene to yield a bis-cobalt complex,^[15] its subsequent reactions with other substrates have been not been reported as yet. However, very recently, Vollhardt et al. have reported a Ni-catalyzed reaction of polyphenylenes with alkynes.^[6] We assumed that a similar intermediate could also form upon reaction with the iridium catalytic system and could further react with alkynes. To this end, angular [3]phenylene 6 was heated in the Ir-catalyzed reaction with symmetrically substituted alkynes (Scheme 1). The reaction of 6 with 2e yielded only a small amount (8%) of the picene derivative 7a. A much better result was obtained in the reaction with 2b, which gave picene 7b as the sole product in 27% isolated yield. A single-crystal X-ray analysis unequivocally confirmed the structure of the picene framework (Figure 3). A similar result was also observed in the reaction with 2c; picene de-



Scheme 1. Reaction of 6 with alkynes 2.



Figure 3. X-ray structure of 7b.

rivative 7c was isolated in 13% yield. Although the yields of the substituted picenes 7 may seem low, these are yields of the analytically pure compounds. Conversions of 6 were about 50% (25-30% starting material was recovered) and we encountered difficulties in separation of the desired products from byproducts. Interestingly, we did not detect products of monoinsertion in the reaction mixtures. The reaction with 2h was also attempted, however, the successful course of the reaction required the use of *m*-xylene as a solvent and a higher reaction temperature (160°C). Moreover, only compound 8-the product of monoinsertion-was obtained, in 25% isolated yield (Scheme 2). Because the oxi-



Scheme 2. Reaction of 6 with diferrocenylacetylene (2h).

dative addition proceeded from the more hindered edge of 6, it is presumed that further oxidative addition of the catalyst to the remaining cyclobutane ring in 8 is prevented by the steric hindrance caused by the bulky ferrocene moieties.

Unlike in the Ni-catalyzed reaction, we did not observe the addition products formed by cleavage of the outer-rim

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Scheme 3. Possible products of the reaction of 6 with 2b under iridium catalysis.

level are 0, 28, and 52 kJ mol⁻¹, respectively (Table 3). By comparison, the empirical correction of the dispersion interaction at the B97D level leads to the values 0, 23, and 38 kJ mol⁻¹, respectively. Single-point calculations at the MP2 level (for the B3LYP optimized structures) lead to very similar values (0, 22, and 33 kJ mol⁻¹, respectively). The energy differences for the derivatives with trimethylsilyl (TMS) and phenyl substituents are even larger (Table 3). Hence, it can be concluded that if dispersion interactions are neglected, the relative stabilities of these aromatic systems substantially change. As the empirical corrections of dispersion interactions are not available for iridium, in the following study we decided to optimize the structure at the B3LYP level and correct of the energy by a single-point calculation at the MP2 level.

Although 7 is thermodynamically favored over isomers 9 and 10, the introduction of phenyl substituents leads to an inversion of the thermodynamic stability. The most stable isomer corresponds to the backbone 10, followed by the derivative 9, and the isomer highest in energy is derived from 7. Hence, we observed exclusive formation of the thermodynamically disfavored product. The course of the reaction is influenced by the interplay between steric, dispersion, and coordination effects, therefore we cannot reduce the size of

Table 3. Comparison of the energies^[a] $[kJmol^{-1}]$ of **9** and **10** relative to the energy of **7** (0 kJmol⁻¹) calculated at different levels of theory.

	Benzo[c]chrysenes 9			Helicenes 10		
	B3LYP	B97D	MP2//B3LYP	B3LYP	B97D	MP2//B3LYP
$R^1 = R^2 = H^{[b]}$	28	23	22	52	38	33
$R^1 = TMS, R^2 = H^{[b]}$	27	19	22	53	12	11
$R^1 = TMS, R^2 = Ph^{[c]}$	-16	-11	-9	-29	-24	-21

[a] Energies at 0 K. [b] Basis set p-VTZ. [c] Basis set p-VDZ.

the investigated system and calculate the whole potentialenergy surface. We opted to calculate the relative stabilities of iridium-containing intermediates, which are formed by the opening of a four-membered ring from the inner or outer rim of 6 (or 11/12 in the second step), to determine the formation of the given product isomers (Table 4 and Scheme 4).

Table 4. Relative energies $[kJ\,mol^{-1}]$ of iridacycle intermediates calculated at the MP2//B3LYP level.^{[a]}

Intermediate	R	=H	R=TMS		
6 _in	0.0	(0.0)	0.0	(0.0)	
6_out	12.7	(12.7)	12.7	(12.7)	
11_in	0.0	(0.0)	0.0	(0.0)	
11_out	65.3	(54.7)	65.3	(54.7)	
12_in	-13.1	(-18.5)	-13.1	(-18.5)	
12_out	69.4	(54.4)	69.4	(54.4)	

[a] Energies are given at 0 K and the values in parentheses refer to the relative Gibbs energies at 298 K.

The reaction proceeded in nonpolar solvent, therefore, only neutral forms of the intermediates with the active form of the catalyst [IrCl(dppe)] were considered. Opening of the four-membered ring of **6** from the inner-rim side leads to the iridiacycle intermediate **6**_in, whereas ring opening from the outer rim leads to the **6**_out intermediate (Scheme 4). The formation of the **6**_out intermediate is disfavored by more than 10 kJ mol⁻¹; this effect is even more pronounced in the presence of TMS substituents (R=TMS; Table 4). The reactions of **6**_in and **6**_out with **2b** lead to the formation of **11** and **12**, respectively. Based on the stabilities of the iridiacycle intermediates, a preference for the formation of **11** is expected and, additionally, the TMS groups contribute to a larger selectivity of the reaction.

The opening of the four-membered ring of **11** can also proceed from the inner- or outer-rim side. Opening from the inner-rim side leads to the intermediate **11**_in (Scheme 4) and is thermodynamically favored relative to opening from the outer-rim side by about 60 kJ mol⁻¹ (Table 4). The reaction of intermediate **11**_in with **2b** leads to the formation of isomer **7** and, thus, explains the exclusive observation of this product in the iridium-catalyzed reaction. For completeness, we have also followed the opening of the four-membered ring of **12**. Similarly to the reaction of **11**, opening from the inner-rim side is more favored by about 60 kJ mol⁻¹ and, therefore, the overall reaction pathway via **12** would yield the isomer **9**

the isomer 9.

The results suggest that the first reaction step, which gives intermediates **11** or **12**, is the selectivity-determining step. For the reactants that do not bear TMS groups a minor formation of the intermediate product **12** formed by outer-rim opening could be observed. The TMS-substituted reactants were investigated and the reaction proceeds exclusively to form **11**. The second step proceeds selectively due to the large energy preference for attack



Scheme 4. B3LYP/cc-pVDZ:LANL2DZ calculated structures of possible intermediates in the reaction of 6 with the iridium catalyst. R=H or TMS. Notation 6_in stands for the intermediate formed by the opening of a four-membered ring of a compound 6 from the inner rim, all other intermediates are denoted analogously. The aromatic part of the synthesized skeleton is depicted in yellow and the phenyl rings of the dppe ligand are grey.

of the inner-rim of intermediates **11** or **12**, which explains why only derivatives of **7** were observed.

The fact that the reaction proceeds towards the thermodynamically disfavored products (the derivative 7 is more than 20 kJ mol^{-1} higher in energy than 10 and about 10 kJ mol^{-1} higher in energy than 9) is most probably determined by the relative stabilities of the iridacycle intermediates. Therefore, the reaction course could also depend crucially on ligands and other features of the transition-metal catalyst. This and other aspects of the reaction will be subject of future studies.

Conclusion

We have demonstrated that a simple [IrCl(cod)]₂/dppebased catalytic system is suitable for reaction of 1 with various alkynes 2 to give 9,10-substituted phenanthrenes 3. Moreover, this methodology was extended to angular [3]phenylene, which outlines a new pathway for the preparation of 5,6,7,8-substituted picene derivatives 7. In a similar manner, a [RhCl(cod)]₂/dppe catalytic system is convenient for the, hitherto unreported, reactions of 1 with nitriles 4 to produce substituted phenanthridines 5. Exploratory calculations, based on the investigation of the relative stabilities of the iridiacycle intermediates, suggest that opening of the four-membered ring of 6 from the inner-rim region is favored relative to opening from the outer-rim region. The selectivity of the reaction is enhanced by the TMS substitution of the reactants. These results explain the exclusive observation of the picene derivatives 7.

Experimental Section

General procedure for alkyne insertion into biphenylene: Under Ar, $[IrCl(cod)_2]_2$ (13.4 mg, 0.02 mmol) and dppe (15.9 mg, 0.04 mmol) were added to a vial equipped with a septum. Toluene (1.5 mL) or *m*-xylene (1.5 mL) was added by syringe and the mixture was stirred until dissolution was achieved (\approx 5 min). Compound 1 (30.4 mg, 0.2 mmol) and alkyne 2 (0.2–0.8 mmol) were added and the reaction mixture was heated in an oil bath for 3.5–6.5 h. The volatile compounds were removed under reduced pressure and purification of the residue by column chromatography on silica gel yielded 3.

Compound 3 f: Compound **1** (30.4 mg, 0.2 mmol), **2 f** (45 mg, 0.2 mmol), 130 °C, 4 h. Column chromatography (5:1 hexane/CH₂Cl₂) yielded **3 f** as an orange solid (40 mg, 53%). $R_{\rm f}$ (5:1 hexane/CH₂Cl₂)=0.48; m.p. 161 °C; ¹H NMR (300 MHz, C₆D₆): δ =2.69 (s, 3 H), 4.01 (s, 5H), 4.18 (apparent t, 2H), 4.35 (apparent t, 2H), 7.43–7.51 (m, 4H), 7.94–8.00 (m, 1H), 8.54–8.62 (m, 2H), 9.50 ppm (d, *J*=7.5 Hz, 1H); ¹³C NMR (75 MHz, CDCl₃): δ =19.23, 67.31 (2 C), 69.71 (5 C), 72.96 (2 C), 86.02, 122.37, 122.65, 124.95, 125.05, 125.39, 125.95, 126.74, 127.92, 129.46, 129.69, 131.04, 131.80, 131.93, 132.45 ppm; IR (KBr): $\bar{\nu}$ =503, 720, 746, 826, 999, 1105, 1442, 1491 cm⁻¹; MS (ES +): *m/z* (%): 376 (100) [*M*]⁺, 171 (3); HRMS: *m/z* calcd for C₂₅H₂₀Fe: 376.0909; found: 376.0908.

General procedure for nitrile insertion: Under Ar, $[RhCl(cod)_2]_2$ (19.8 mg, 0.04 mmol), dppe (31.8 mg, 0.08 mmol), and **1** (30.4 mg, 0.2 mmol) were added to a vial equipped with a septum. Nitrile **4** (1.5 mL) was added (solid nitriles (2.0 mmol) were dissolved in THF (1 mL) before addition). The reaction mixture was heated in an oil bath or in a MW reactor. Excess of **4** was removed under reduced pressure (oil pump, 100 °C). Column chromatography of the residue on silica gel yielded **5**.

Compound 5c: Compound **4c** (1.5 mL), oil bath, 190 °C, 4 h. Column chromatography (5:1 hexane/EtOAc) yielded **5c** (41 mg, 80%) as a colorless solid. $R_{\rm f}$ (5:1 hexane/EtOAc) =0.2; ¹H NMR (300 MHz, CDCl₃): δ = 7.43 (ddd, J=7.5, 5.1, 1.5 Hz, 1H), 7.62–7.96 (m, 5H), 8.03 (d, J=8.1 Hz, 1H), 8.26 (d, J=7.8 Hz, 1 Hz), 8.50 (d, J=8.4 Hz, 1H), 8.62 (dd, J=8.1, 1.5 Hz, 1H), 8.69 (d, J=8.4 Hz, 1H), 8.81 ppm (d, J=4.8 Hz, 1H); ¹³C NMR (75 MHz, CDCl₃): δ =121.97, 122.01, 123.34, 124.18, 124.72, 125.15, 127.30 (2 C), 128.70, 128.86, 130.41, 130.55, 133.59, 137.02, 143.52, 148.68, 158.32 ppm (2 C). Spectral characteristics were in agreement with the published data.^[16]

General procedure for picene synthesis: Under Ar, $[IrCl(cod)_2]_2$ (13.4 mg, 0.02 mmol) and dppe (15.9 mg, 0.04 mmol) were added to a vial equipped with a septum. Toluene (1 mL) was added by syringe and the

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mixture was stirred until dissolved (5 min). Compound 6 (51.4 mg, 0.1 mmol) and alkyne 2 (2–8 equiv) were added and the reaction mixture was heated in an oil bath at 130 °C for 5 h. The volatile compounds were removed under reduced pressure and column chromatography of the residue, followed by preparative TLC or crystallization, yielded 7.

Compound 7b: Compound **6** (44 mg, 0.086 mmol), **2b** (30.1 mg, 0.17 mmol), 4 h. Filtration through a short pad of silica gel (CH₂Cl₂), column chromatography (20:1, then 10:1 hexane/CH₂Cl₂) yielded **7b** (20 mg, 27%) as a yellowish solid. $R_{\rm f}$ (10:1 hexane/CH₂Cl₂) = 0.32; m.p. 313°C; ¹H NMR (300 MHz, CDCl₃): δ =0.21 (s, 18H), 0.57 (s, 18H), 6.00–6.19 (m, 6H), 6.55–6.70 (m. 4H), 6.86–6.92 (m, 2H), 6.92–7.00 (apparent t, J=7.8, 7.8, 0.9 Hz, 2H), 7.16–7.23 (m, 2H), 7.32–7.45 (m, 4H), 7.78 (s, 2H), 8.97 (s, 2H), 9.19 ppm (s, 2H); ¹³C NMR (150 MHz, CDCl₃): δ =1.63 (3C), 2.06 (3C), 121.13, 125.45, 125.64 (2C), 126.19, 126.80, 127.75, 128.22, 129.52, 129.83, 130.42, 130.56, 131.25, 132.27, 133.40 (2C), 135.32, 136.86, 138.18, 139.88, 140.35, 142.71, 142.93 ppm; IR (KBr): \bar{v} = 2953, 1440, 1250, 1122, 853, 839, 757, 699 cm⁻¹; MS (ES+): *m*/*z* (%): 894 (80) [*M*+Na]⁺, 893 (100), 822 (14), 821 (19), 783 (10), 390 (4); HRMS: *m*/*z* calcd for C₈₈H₆₂Si₄: 871.3977; found: 871.3986.

The computational DFT study was performed by using the B3LYP^[17-20] functional as implemented in the Gaussian 09 package.^[21] Basis sets cc-VTZ or cc-VDZ for molecules without iridium (explicitly denoted in Table 3) and a combination of LAN2DZ for iridium and cc-VDZ for the remaining atoms of the iridium-containing intermediates (denoted as LAN2DZ:cc-pVDZ) were used.^[22,23] Frequency analysis was performed for all optimized structures to assure that they corresponded to the minima on the potential-energy surface and to calculate the zero-point energy. The MP2 single-point calculations were performed for the optimized geometries. The zero-point energy and Gibbs energy corrections were calculated at the B3LYP level and added to the MP2 energies. All energies given in the paper refer to 0 and 298 K. The test calculations on the effect of the dispersion interactions were made at the levels of theory B3LYP/cc-pVTZ, B97D/cc-pVTZ,^[24] and MP2/cc-pVTZ//B3LYP/ccpVTZ. Note that the use of B3LYP energies alone lead to different mechanistic predictions. The B3LYP level does not cover the dispersion interactions, which however play an important role in the studied reaction. Therefore, the B3LYP energies cannot be considered as correct.

CCDC-835379 (**3h**), CCDC-835380 (**7b**), and CCDC-835381 (**3g**) contain 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.

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