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Diamination of Conjugated Dienes and Trienes Catalyzed by *N*-Heterocyclic Carbene−Pd(0) Complexes

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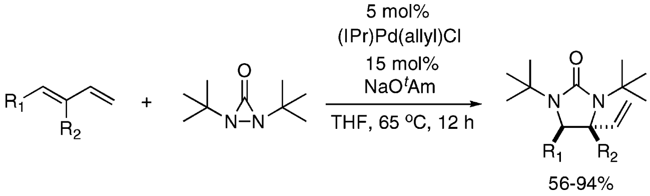
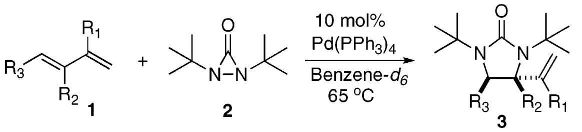


This paper describes a diamination process using di-*t*-butyldiaziridinone as nitrogen source and *N*-heterocyclic carbene−Pd(0) complex as catalyst. A wide variety of conjugated dienes and trienes can be effectively diaminated in good yields with high regio- and stereoselectivities.

N-Heterocyclic carbenes (NHCs) have been shown to be effective ligands for a variety of metal-catalyzed transformations.[1] Compared to phosphines, carbene ligands usually form more stable complexes with metals. Their electron richness and steric bulkiness generally facilitate the oxidative addition and reductive elimination processes which are fundamental steps in many reactions.[1] Recently, we reported a regio- and stereoselective diamination of conjugated dienes and trienes using di-*t*-butyldiaziridinone as nitrogen source and Pd(PPh$_3$)$_4$ as catalyst (Scheme 1).[2,3−8] The unique features displayed by carbene ligands prompted us to examine whether this transformation could also be effective using *N*-heterocyclic carbene−Pd(0) complex as catalyst. Herein we report our preliminary results on this subject.

SCHEME 1



Initial studies were carried out using 1-phenylbutadiene as substrate. Several commercially available NHC−Pd complexes **4**−**9** listed in Figure 1 were examined for the diamination.[9−11] Among these catalysts tested, (NHC)Pd(allyl)Cl complexes **4**−**7** were found to be effective for the diamination (Table 1). More sterically hindered (IPr)Pd(allyl)Cl (**4**) gave a higher conversion than IMesPd(allyl)Cl (**5**) (Table 1, entry 3 vs entry 8), suggesting that the steric hindrance of NHC ligand plays an important role in catalytic activity. One possible reason for this is that the steric hindrance of NHC ligand may facilitate the reductive elimination step in the catalytic cycle.[1] Among the bases examined, sodium *tert*-pentoxide (NaO^{t}Am) was found to be most effective in generating active NHC−Pd(0) catalyst from (NHC)Pd(allyl)Cl precatalyst[9] (Table 1, entries 1−3), possibly due to its good solubility in organic solvent. The amount of base used was found to be crucial, with 3 equiv with respect to Pd being optimal. Using a greater or lesser amount of base led to a decrease in yield. High conversion was obtained in solvents such as benzene, toluene, and THF (Table 1, entries 3−5). High conversion was also obtained without solvent (Table 1, entry 7) but with somewhat diminished isolated yield, possibly due to the polymerization of the diene under the reaction conditions. The diamination was also investigated with in situ generated NHC−Pd complexes from commercially available imidazolium

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10.1021/jo0709394 CCC: $37.00

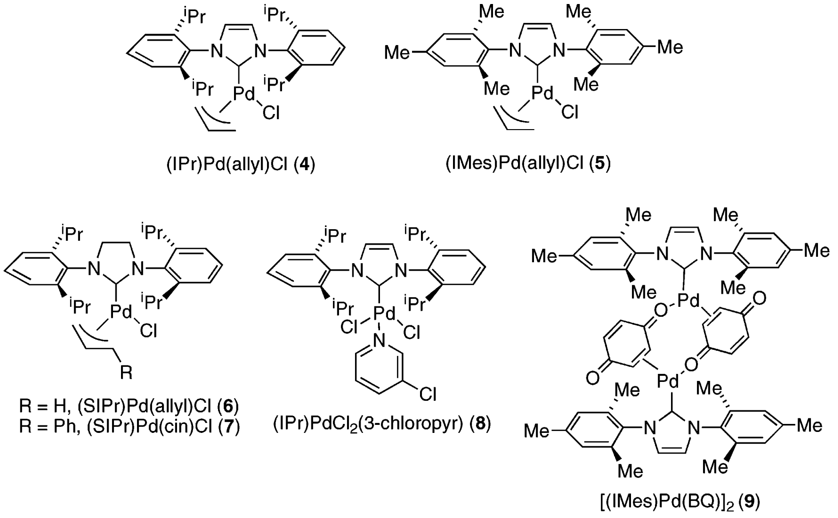
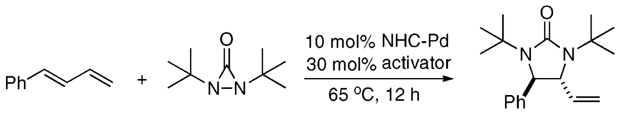


FIGURE 1. NHC−Pd complexes.

TABLE 1. Diamination of 1-Phenylbutadiene with NHC−Pd Complexes[a]



entry	NHC−Pd precatalysts	activator	solvent	conv. (%)[b]
1	(IPr)Pd(allyl)Cl (**4**)	KO^{t}Bu	C_6D_6	70
2		NaO^{t}Bu	C_6D_6	76
3		NaO^{t}Am	C_6D_6	85
4		NaO^{t}Am	toluene	90
5		NaO^{t}Am	THF	95
6		NaO^{t}Am	dioxane	30
7		NaO^{t}Am	none	95
8	(IMes)Pd(allyl)Cl (**5**)	NaO^{t}Am	C_6D_6	45
9	(SIPr)Pd(allyl)Cl (**6**)	NaO^{t}Am	C_6D_6	80
10	(SIPr)Pd(cin)Cl (**7**)	NaO^{t}Am	C_6D_6	80
11	(IPr)PdCl$_2$(3-chloropyr) (**8**)	BuLi[c]	C_6D_6	0
12		EtMgBr[c]	C_6D_6	0
13		ZnEt$_2$[d]	C_6D_6	0
14		NaO^{t}Am	C_6D_6	<5
15	[(IMes)Pd(BQ)]$_2$ (**9**)	none	C_6D_6	<5

[a] All reactions were carried out with diene (0.2 mmol), di-*t*-butyldiaziridinone (**2**) (0.24 mmol), NHC−Pd (0.02 mmol), and activator (0.06 mmol) in solvent indicated (0.6 mL) under Ar at 65 °C for 12 h. [b] Conversion was determined by ^{1}H NMR analysis of the crude reaction mixture. [c] 0.04 mmol used. [d] 0.02 mmol used.

salts **10**−**14** and dihydroimidazolium salts **15**−**16** (Figure 2).[12,13] Thus far, these in situ generated complexes have been found to be much less effective for the reaction. Poor conversion was also obtained using the complex generated from carbene **17** and Pd$_2$(dba)$_3$.[12]

The substrate scope was subsequently examined with 5 mol % (IPr)Pd(allyl)Cl (**4**). As shown in Table 2, various substrates can be effectively diaminated. As in the case of Pd(PPh$_3$)$_4$,[2] the diamination using (IPr)Pd(allyl)Cl (**4**) proceeded highly regioselectively at the internal double bond and also highly stereoselectively. When a conjugated triene was employed, the diamination occurred cleanly at the middle double bond (Table 2, entries 9 and 10). Compared to the previous conditions using Pd(PPh$_3$)$_4$,[2] less NHC−Pd(0) catalyst is used in the current procedure although a longer reaction time is required.

In conclusion, it has been found that (IPr)Pd(allyl)Cl (**4**) is an effective catalyst for the diamination of various conjugated dienes and trienes with di-*t*-butyldiaziridinone as nitrogen source, giving diamination products in good yields and high regio- and stereoselectivities. The feasibility of NHC−Pd(0) complexes as viable catalysts for the diamination opens additional opportunities to develop highly effective catalytic systems by electronic and steric tuning of ligands as well as an asymmetric version of this reaction using chiral carbene ligands.

Experimental Section

All diamination products are known in Table 2, except entries 2 and 9, and gave satisfactory spectroscopic chareaterization.[2]

General Diamination Procedure. A 2.0 mL vial was charged with (IPr)Pd(ally)Cl (0.0171 g, 0.030 mmol) and sodium *tert*-pentoxide (0.0099 g, 0.090 mmol) and a stir bar. The vial was sealed with a septum, evacuated, and then filled with argon three times. THF (0.1 mL) (distilled from sodium) was then added via a syringe. After stirring for 10 min at rt, diene or triene (0.6 mmol) was added (for a solid substrate, it was added earlier along with the Pd catalyst), followed by addition of di-*t*-butyldiaziridinone (0.122 g, 0.72 mmol). Upon being stirred at 65 °C for 12 h, the reaction mixture was purified by flash chromatography (silica gel, hexane:ether = 5:1) to give the diamination compound.

Table 2, Entry 1: Colorless oil; ^{1}H NMR (300 MHz, CDCl$_3$) δ 5.89 (ddd, J = 17.1, 10.2, 8.1 Hz, 1H), 5.16 (d, J = 17.1 Hz, 1H), 5.06 (d, J = 10.2 Hz, 1H), 3.48 (d, J = 8.1 Hz, 1H), 3.24 (q, J = 6.3 Hz, 1H), 1.32 (s, 9H), 1.31 (s, 9H), 1.18 (d, J = 6.3 Hz, 3H);

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[12] For leading references on imidazolium and dihydroimidazolium salts and related carbenes, see: (a) Arduengo, A. J., III; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1991**, *113*, 361. (b) Arduengo, A. J., III; Dias, H. V. R.; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1992**, *114*, 5530. (c) Arduengo, A. J., III; Krafczyk, R.; Schmutzler, R. *Tetrahedron* **1999**, *55*, 14523. (d) Bourissou, D.; Guerret, O.; Gabbaï, F. P.; Bertrand, G. *Chem. Rev.* **2000**, *100*, 39. (e) Herrmann, W. A.; Böhm, V. P. W.; Gstöttmayr, C. W. K.; Grosche, M.; Reisinger, C.-P.; Weskamp, T. *J. Organomet. Chem.* **2001**, *617*−*618*, 616.

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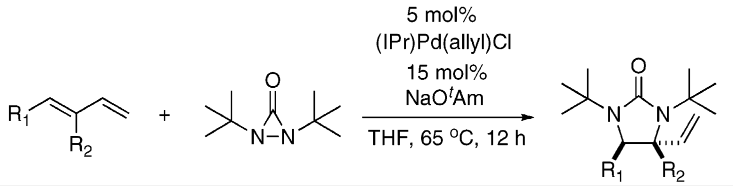
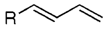
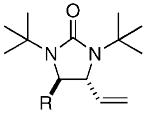
TABLE 2. Catalytic Diamination of Dienes and Trienes[a]



Entry	Substrate	Product	Yield (%)[b]
			
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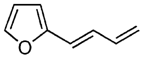
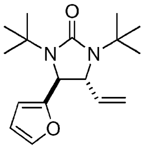
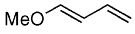
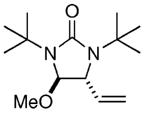
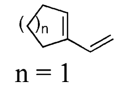
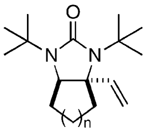
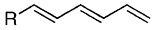
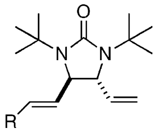
2	R = *n*-Pr		90
3	R = Ph		80
4	R = *p*-MeO-Ph		83
5			84
6			65
			
7	n = 1		74
8	n = 2		56
			
9	R = C_4H_9		84
10	R = C_5H_{11}		83

[a] All reactions were carried out with diene or triene (0.6 mmol), di-*t*-butyldiaziridinone (**2**) (0.72 mmol), NaO^{t}Am (0.09 mmol), and (IPr)Pd(allyl)Cl (0.03 mmol) in THF (0.1 mL) at 65 °C for 12 h. [b] Isolated yield based on diene or triene.

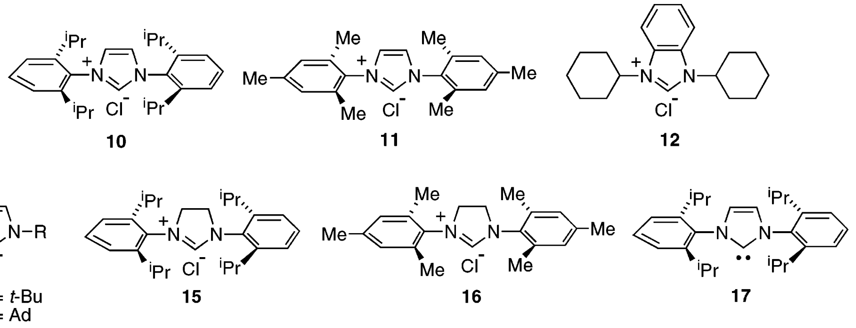


FIGURE 2. Precursors used to generate NHC−Pd complexes.

^{13}C NMR (75 MHz, $CDCl_3$) δ 157.9, 140.1, 115.5, 63.6, 55.4, 53.1, 52.5, 29.1, 28.9, 21.2.

Table 2, Entry 2: Colorless oil; IR (film) 1685 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.89 (ddd, J = 17.1, 10.5, 8.1 Hz, 1H), 5.16 (d, J = 17.1 Hz, 1H), 5.06 (d, J = 10.5 Hz, 1H), 3.64 (d, J = 8.1 Hz, 1H), 3.10 (dd, J = 8.4, 3.0 Hz, 1H), 1.55−1.27 (m, 4H), 1.34 (s, 9H), 1.32 (s, 9H), 0.92 (d, J = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.3, 140.7, 115.1, 60.7, 59.5, 53.1, 52.7, 36.6, 29.1, 29.0, 18.2, 14.3. HRMS calcd. for $C_{16}H_{31}N_2O$ (M + 1), 267.2431; found, 267.2433.

Table 2, Entry 3: Colorless oil; ^1H NMR (300 MHz, $CDCl_3$) δ 7.34−7.25 (m, 5H), 6.01 (ddd, J = 17.1, 9.0, 8.4 Hz, 1H), 5.18 (d, J = 17.1 Hz, 1H), 5.13 (d, J = 9.0 Hz, 1H), 4.14 (d, J = 0.9 Hz, 1H), 3.63 (d, J = 8.4 Hz, 1H), 1.31 (s, 9H), 1.25 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.2, 144.1, 140.9, 128.9, 127.9, 125.9, 115.8, 64.9, 63.3, 53.7, 53.4, 29.0, 28.8.

Table 2, Entry 4: Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.21−7.17 (m, 2H), 6.87−6.82 (m, 2H), 6.00 (ddd, J = 16.8, 9.6, 8.1 Hz, 1H), 5.18 (d, J = 16.8 Hz, 1H), 5.13 (d, J = 9.6 Hz, 1H), 4.09 (d, J = 0.9 Hz, 1H), 3.78 (s, 3H), 3.61 (d, J = 8.1 Hz, 1H), 1.31 (s, 9H), 1.25 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.3, 159.1, 140.9, 136.2, 127.1, 115.7, 114.2, 65.2, 62.8, 55.4, 53.6, 53.4, 29.0, 28.9.

Table 2, Entry 5: Light yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32 (brs, 1H), 6.31 (brs, 1H), 6.24 (d, J = 3.0 Hz, 1H), 6.05−5.90 (m, 1H), 5.24 (d, J = 17.1 Hz, 1H), 5.16 (d, J = 10.2 Hz, 1H), 4.22 (s, 1H), 3.84 (d, J = 8.1 Hz, 1H), 1.33 (s, 9H), 1.24 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.6, 155.9, 141.7, 139.7, 116.5, 110.6, 106.4, 62.0, 57.2, 53.5, 53.3, 28.8, 28.6.

Table 2, Entry 6: Colorless oil; ^{1}H NMR (300 MHz, C_6D_6) δ 5.60−5.48 (m, 1H), 5.00 (d, J = 17.4 Hz, 1H), 4.87 (d, J = 10.2 Hz, 1H), 4.23 (s, 1H), 3.71 (d, J = 8.1 Hz, 1H), 2.89 (s, 3H) 1.42 (s, 9H), 1.35 (s, 9H); ^{13}C NMR (75 MHz, C_6D_6) δ 158.1, 139.7, 116.6, 90.4, 60.4, 53.8, 53.1, 51.1, 29.1, 28.9.

Table 2, Entry 7: Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.97 (dd, J = 17.4, 10.5 Hz, 1H), 5.09 (d, J = 17.4 Hz, 1H), 5.00 (d, J = 10.5 Hz, 1H), 3.33 (t, J = 6.9 Hz, 1H), 2.26−2.20 (m, 1H), 2.07−2.03 (m, 1H), 1.89−1.81 (m, 1H), 1.74−1.70 (m, 1H), 1.54−1.44 (m, 1H), 1.37 (s, 9H), 1.42−1.35 (m, 1H), 1.32 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.9, 145.5, 112.0, 69.5, 67.0, 54.8, 53.2, 39.3, 37.5, 29.8, 28.9, 24.4.

Table 2, Entry 8: Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.13 (ddd, J = 17.4, 10.8, 0.9 Hz, 1H), 5.13 (d, J = 17.4 Hz, 1H), 5.07 (d, J = 10.8 Hz, 1H), 3.01 (dd, J = 9.3, 4.8 Hz, 1H), 2.27−2.22 (m, 1H), 1.81−1.75 (m, 1H), 1.68−1.57 (m, 2H), 1.54−1.46 (m, 3H), 1.36 (s, 9H), 1.33 (s, 9H), 1.30−1.21 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.0, 143.1, 113.0, 64.2, 60.0, 56.3, 52.5, 30.4, 29.8, 29.0, 28.9, 21.3, 19.9.

Table 2, Entry 9: Colorless oil; IR (film) 1685 cm^{-1}; ^{1}H NMR (300 MHz, C_6D_6) δ 5.98 (ddd, J = 17.1, 10.2, 8.4 Hz, 1H), 5.68 (dd, J = 15.3, 8.4 Hz, 1H), 5.46 (dt, J = 15.3, 6.6 Hz, 1H), 5.06 (d, J = 17.1 Hz, 1H), 4.96 (dd, J = 10.2, 1.2 Hz, 1H), 3.59 (d, J = 5.7 Hz, 1H), 3.56 (d, J = 6.3 Hz, 1H), 1.93 (q, J = 6.6 Hz, 2H), 1.48 (s, 9H), 1.46 (s, 9H), 1.30−1.19 (m, 4H), 0.99 (t, J = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, C_6D_6) δ 158.3, 140.6, 132.7, 132.0, 115.8, 63.9, 62.9, 53.6, 53.5, 32.4, 31.9, 29.2, 22.8, 14.3. HRMS calcd. for $C_{19}H_{35}N_2O$ (M + 1), 307.2744; found, 307.2747.

Table 2, Entry 10: Colorless oil; ^{1}H NMR (300 MHz, C_6D_6) δ 5.98 (ddd, J = 17.1, 10.2, 8.4 Hz, 1H), 5.68 (dd, J = 15.3, 8.4 Hz, 1H), 5.47 (dt, J = 15.3, 7.2 Hz, 1H), 5.06 (d, J = 17.1 Hz, 1H), 4.90 (dd, J = 10.2, 0.9 Hz, 1H), 3.59 (d, J = 5.7 Hz, 1H), 3.56 (d, J = 6.3 Hz, 1H), 1.89 (q, J = 6.9 Hz, 2H), 1.48 (s, 9H), 1.46 (s, 9H), 1.31−1.19 (m, 6H), 0.90 (t, J = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, C_6D_6) δ 158.3, 140.7, 132.7, 132.1, 115.8, 63.9, 62.9, 53.6, 53.5, 32.7, 32.0, 29.4, 29.2, 23.1, 14.6.

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Supporting Information Available: ^{1}H and ^{13}C spectra of diamination products. This material is available free of charge via the Internet at http://pubs.acs.org.

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