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Supplementary Material

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**Kinetic Study of Insertion of Norbornadiene into Palladium-Carbon
Bonds of Complexes Containing the Rigid Bidentate Nitrogen Ligand
Bis(arylimino)acenaphthene**

by

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Table S1. Observed Rate Constants k_{obsd} of the Reaction of Complexes

$\text{Pd}(\text{C}(\text{O})\text{R})\text{X}(\text{Ar-BIAN})$ (**1a-12a**) with Norbornadiene.^a

Compd	Solvent	Temp, ^b °C	[nbd], M	$k_{\text{obsd}} \times 10^2$, ^c s ⁻¹
1a	CH ₂ Cl ₂	5.0	0.061	0.249
1a	CH ₂ Cl ₂	5.0	0.125	0.392
1a	CH ₂ Cl ₂	5.0	0.193	0.532
1a	CH ₂ Cl ₂	5.0	0.256	0.676
1a	CH ₂ Cl ₂	5.0	0.320	0.803
1a	CH ₂ Cl ₂	10.0	0.061	0.346
1a	CH ₂ Cl ₂	10.0	0.125	0.567
1a	CH ₂ Cl ₂	10.0	0.193	0.794
1a	CH ₂ Cl ₂	10.0	0.256	0.937
1a	CH ₂ Cl ₂	10.0	0.320	1.12
1a	CH ₂ Cl ₂	15.0	0.061	0.435
1a	CH ₂ Cl ₂	15.0	0.125	0.747
1a	CH ₂ Cl ₂	15.0	0.193	1.03
1a	CH ₂ Cl ₂	15.0	0.256	1.23
1a	CH ₂ Cl ₂	15.0	0.320	1.43
1a	CH ₂ Cl ₂	19.5	0.061	0.649
1a	CH ₂ Cl ₂	19.5	0.125	0.993
1a	CH ₂ Cl ₂	19.5	0.193	1.29

Table S1. (continued)

Compd	Solvent	Temp, ^b °C	[nbd], M	k _{obsd} x 10 ² , ^c s ⁻¹
1a	CH ₂ Cl ₂	19.5	0.256	1.57
1a	CH ₂ Cl ₂	19.5	0.320	1.86
1a	CH ₂ Cl ₂	24.0	0.061	0.862
1a	CH ₂ Cl ₂	24.0	0.125	1.34
1a	CH ₂ Cl ₂	24.0	0.193	1.78
1a	CH ₂ Cl ₂	24.0	0.256	2.14
1a	CH ₂ Cl ₂	24.0	0.320	2.63
1a	CH ₂ Cl ₂	29.0	0.061	1.21
1a	CH ₂ Cl ₂	29.0	0.125	1.79
1a	CH ₂ Cl ₂	29.0	0.193	2.48
1a	CH ₂ Cl ₂	29.0	0.256	3.03
1a	CH ₂ Cl ₂	29.0	0.320	3.44
1a	THF	19.5	0.061	0.637
1a	THF	19.5	0.125	0.943
1a	THF	19.5	0.193	1.26
1a	THF	19.5	0.256	1.68
1a	THF	19.5	0.320	1.90
1a	2-Me-THF	19.5	0.061	0.557
1a	2-Me-THF	19.5	0.125	0.916
1a	2-Me-THF	19.5	0.193	1.36
1a	2-Me-THF	19.5	0.256	1.79
1a	2-Me-THF	19.5	0.320	2.12
1a	MeCN	19.5	0.0076	1.08
1a	MeCN	19.5	0.015	1.87
1a	MeCN	19.5	0.023	2.85
1a	MeCN	19.5	0.032	3.58
1a	MeC(O)Me	19.5	0.031	0.783
1a	MeC(O)Me	19.5	0.061	1.33
1a	MeC(O)Me	19.5	0.093	1.90
1a	MeC(O)Me	19.5	0.125	2.34
1a	MeC(O)Me	19.5	0.157	2.78
1a	3%(v/v) MeCN in CH ₂ Cl ₂	19.5	0.061	1.08
1a	3%(v/v) MeCN in CH ₂ Cl ₂	19.5	0.125	1.82

Table S1. (continued)

Compd	Solvent	Temp, ^b °C	[nbd], M	k _{obsd} x 10 ² , ^c s ⁻¹
1a	3%(v/v) MeCN in CH ₂ Cl ₂	19.5	0.193	2.41
1a	3%(v/v) MeCN in CH ₂ Cl ₂	19.5	0.256	2.81
1a	3%(v/v) MeCN in CH ₂ Cl ₂	19.5	0.320	3.15
1a	10%(v/v) MeCN in CH ₂ Cl ₂	19.5	0.061	1.84
1a	10%(v/v) MeCN in CH ₂ Cl ₂	19.5	0.125	3.10
1a	10%(v/v) MeCN in CH ₂ Cl ₂	19.5	0.193	3.99
1a	10%(v/v) MeCN in CH ₂ Cl ₂	19.5	0.256	4.98
1a	10%(v/v) MeCN in CH ₂ Cl ₂	19.5	0.320	5.66
1a	17%(v/v) MeCN in CH ₂ Cl ₂	19.5	0.061	2.72
1a	17%(v/v) MeCN in CH ₂ Cl ₂	19.5	0.125	4.54
1a	17%(v/v) MeCN in CH ₂ Cl ₂	19.5	0.193	5.86
1a	17%(v/v) MeCN in CH ₂ Cl ₂	19.5	0.256	7.21
1a	17%(v/v) MeCN in CH ₂ Cl ₂	19.5	0.320	8.87
1a	30%(v/v) MeCN in CH ₂ Cl ₂	19.5	0.032	2.92
1a	30%(v/v) MeCN in CH ₂ Cl ₂	19.5	0.061	4.82
1a	30%(v/v) MeCN in CH ₂ Cl ₂	19.5	0.093	6.58
1a	30%(v/v) MeCN in CH ₂ Cl ₂	19.5	0.125	7.79
1a	30%(v/v) MeCN in CH ₂ Cl ₂	19.5	0.159	9.20

Table S1. (continued)

Compd	Solvent	Temp, ^b °C	[nbd], M	k _{obsd} x 10 ² , ^c s ⁻¹
1a	30%(v/v) MeCN in CH ₂ Cl ₂	19.5	0.225	12.0
1a	30%(v/v) MeCN in CH ₂ Cl ₂	19.5	0.320	15.1
1a	MeCN	19.5	0.032	3.58
1a	MeCN	19.5	0.061	7.71
1a	MeCN	19.5	0.093	10.7
1a	MeCN	19.5	0.125	13.4
1a	MeCN	19.5	0.159	15.8
2a	CH ₂ Cl ₂	5.0	0.061	0.352
2a	CH ₂ Cl ₂	5.0	0.125	0.598
2a	CH ₂ Cl ₂	5.0	0.193	0.793
2a	CH ₂ Cl ₂	5.0	0.256	1.02
2a	CH ₂ Cl ₂	5.0	0.320	1.22
2a	CH ₂ Cl ₂	12.5	0.061	0.569
2a	CH ₂ Cl ₂	12.5	0.125	0.948
2a	CH ₂ Cl ₂	12.5	0.193	1.36
2a	CH ₂ Cl ₂	12.5	0.256	1.64
2a	CH ₂ Cl ₂	12.5	0.320	1.90
2a	CH ₂ Cl ₂	19.5	0.061	0.856
2a	CH ₂ Cl ₂	19.5	0.125	1.40
2a	CH ₂ Cl ₂	19.5	0.193	1.93
2a	CH ₂ Cl ₂	19.5	0.256	2.32
2a	CH ₂ Cl ₂	19.5	0.320	2.75
2a	CH ₂ Cl ₂	29.0	0.061	1.74
2a	CH ₂ Cl ₂	29.0	0.125	2.68
2a	CH ₂ Cl ₂	29.0	0.193	3.64
2a	CH ₂ Cl ₂	29.0	0.256	4.57
2a	CH ₂ Cl ₂	29.0	0.320	5.70
3a	CH ₂ Cl ₂	5.0	0.061	0.388
3a	CH ₂ Cl ₂	5.0	0.125	0.627
3a	CH ₂ Cl ₂	5.0	0.193	0.811
3a	CH ₂ Cl ₂	5.0	0.256	1.03
3a	CH ₂ Cl ₂	5.0	0.320	1.18
3a	CH ₂ Cl ₂	12.5	0.061	0.671
3a	CH ₂ Cl ₂	12.5	0.125	1.08

Table S1. (continued)

Compd	Solvent	Temp, ^b °C	[nbd], M	k _{obsd} × 10 ² , ^c s ⁻¹
3a	CH ₂ Cl ₂	12.5	0.193	1.38
3a	CH ₂ Cl ₂	12.5	0.256	1.69
3a	CH ₂ Cl ₂	12.5	0.320	2.00
3a	CH ₂ Cl ₂	19.5	0.061	0.981
3a	CH ₂ Cl ₂	19.5	0.125	1.62
3a	CH ₂ Cl ₂	19.5	0.193	2.12
3a	CH ₂ Cl ₂	19.5	0.256	2.69
3a	CH ₂ Cl ₂	19.5	0.320	3.08
3a	CH ₂ Cl ₂	29.5	0.061	1.97
3a	CH ₂ Cl ₂	29.5	0.125	3.38
3a	CH ₂ Cl ₂	29.5	0.193	4.41
3a	CH ₂ Cl ₂	29.5	0.256	5.36
3a	CH ₂ Cl ₂	29.5	0.320	6.23
4a	CH ₂ Cl ₂	6.0	0.061	0.156
4a	CH ₂ Cl ₂	6.0	0.125	0.235
4a	CH ₂ Cl ₂	6.0	0.193	0.297
4a	CH ₂ Cl ₂	6.0	0.256	0.394
4a	CH ₂ Cl ₂	6.0	0.320	0.457
4a	CH ₂ Cl ₂	12.5	0.061	0.228
4a	CH ₂ Cl ₂	12.5	0.125	0.354
4a	CH ₂ Cl ₂	12.5	0.193	0.483
4a	CH ₂ Cl ₂	12.5	0.256	0.598
4a	CH ₂ Cl ₂	12.5	0.320	0.699
4a	CH ₂ Cl ₂	19.5	0.061	0.391
4a	CH ₂ Cl ₂	19.5	0.125	0.615
4a	CH ₂ Cl ₂	19.5	0.193	0.756
4a	CH ₂ Cl ₂	19.5	0.256	0.949
4a	CH ₂ Cl ₂	19.5	0.320	1.08
4a	CH ₂ Cl ₂	29.5	0.061	0.774
4a	CH ₂ Cl ₂	29.5	0.125	1.22
4a	CH ₂ Cl ₂	29.5	0.193	1.57
4a	CH ₂ Cl ₂	29.5	0.256	1.92
4a	CH ₂ Cl ₂	29.5	0.320	2.25
5a	CH ₂ Cl ₂	6.0	0.061	0.108
5a	CH ₂ Cl ₂	6.0	0.125	0.182
5a	CH ₂ Cl ₂	6.0	0.193	0.240

Table S1. (continued)

Compd	Solvent	Temp, ^b °C	[nbd], M	k _{obsd} × 10 ² , ^c s ⁻¹
5a	CH ₂ Cl ₂	6.0	0.256	0.282
5a	CH ₂ Cl ₂	6.0	0.320	0.326
5a	CH ₂ Cl ₂	12.5	0.061	0.177
5a	CH ₂ Cl ₂	12.5	0.125	0.275
5a	CH ₂ Cl ₂	12.5	0.193	0.365
5a	CH ₂ Cl ₂	12.5	0.256	0.417
5a	CH ₂ Cl ₂	12.5	0.320	0.508
5a	CH ₂ Cl ₂	19.5	0.061	0.264
5a	CH ₂ Cl ₂	19.5	0.125	0.410
5a	CH ₂ Cl ₂	19.5	0.193	0.513
5a	CH ₂ Cl ₂	19.5	0.256	0.631
5a	CH ₂ Cl ₂	19.5	0.320	0.728
5a	CH ₂ Cl ₂	29.5	0.061	0.588
5a	CH ₂ Cl ₂	29.5	0.125	0.847
5a	CH ₂ Cl ₂	29.5	0.193	1.07
5a	CH ₂ Cl ₂	29.5	0.256	1.30
5a	CH ₂ Cl ₂	29.5	0.320	1.44
6a	CH ₂ Cl ₂	6.0	0.061	0.362
6a	CH ₂ Cl ₂	6.0	0.125	0.666
6a	CH ₂ Cl ₂	6.0	0.193	0.910
6a	CH ₂ Cl ₂	6.0	0.256	1.17
6a	CH ₂ Cl ₂	6.0	0.320	1.39
6a	CH ₂ Cl ₂	12.5	0.061	0.414
6a	CH ₂ Cl ₂	12.5	0.125	0.777
6a	CH ₂ Cl ₂	12.5	0.193	1.06
6a	CH ₂ Cl ₂	12.5	0.256	1.40
6a	CH ₂ Cl ₂	12.5	0.320	1.64
6a	CH ₂ Cl ₂	19.5	0.061	0.596
6a	CH ₂ Cl ₂	19.5	0.125	0.978
6a	CH ₂ Cl ₂	19.5	0.193	1.45
6a	CH ₂ Cl ₂	19.5	0.256	1.75
6a	CH ₂ Cl ₂	19.5	0.320	2.20
6a	CH ₂ Cl ₂	29.5	0.061	0.978
6a	CH ₂ Cl ₂	29.5	0.125	1.77
6a	CH ₂ Cl ₂	29.5	0.193	2.36
6a	CH ₂ Cl ₂	29.5	0.256	3.09

Table S1. (continued)

Compd	Solvent	Temp, ^b °C	[nbd], M	k _{obsd} x 10 ² , ^c s ⁻¹
6a	CH ₂ Cl ₂	29.5	0.320	3.56
7a	CH ₂ Cl ₂	19.5	0.061	1.47
7a	CH ₂ Cl ₂	19.5	0.125	2.20
7a	CH ₂ Cl ₂	19.5	0.193	2.95
7a	CH ₂ Cl ₂	19.5	0.256	3.78
7a	CH ₂ Cl ₂	19.5	0.320	4.46
8a	CH ₂ Cl ₂	19.5	0.061	1.96
8a	CH ₂ Cl ₂	19.5	0.125	3.61
8a	CH ₂ Cl ₂	19.5	0.193	4.98
8a	CH ₂ Cl ₂	19.5	0.256	6.47
8a	CH ₂ Cl ₂	19.5	0.320	7.92
9a	CH ₂ Cl ₂	19.5	0.061	0.829
9a	CH ₂ Cl ₂	19.5	0.125	1.27
9a	CH ₂ Cl ₂	19.5	0.193	1.62
9a	CH ₂ Cl ₂	19.5	0.256	1.92
9a	CH ₂ Cl ₂	19.5	0.320	2.22
10a	CH ₂ Cl ₂	19.5	0.061	1.30
10a	CH ₂ Cl ₂	19.5	0.125	1.97
10a	CH ₂ Cl ₂	19.5	0.193	2.54
10a	CH ₂ Cl ₂	19.5	0.256	3.11
10a	CH ₂ Cl ₂	19.5	0.320	3.56
11a	CH ₂ Cl ₂	19.5	0.160	0.581
11a	CH ₂ Cl ₂	19.5	0.320	0.806
11a	CH ₂ Cl ₂	19.5	0.481	1.12
11a	CH ₂ Cl ₂	19.5	0.642	1.35
11a	CH ₂ Cl ₂	19.5	0.802	1.57
12a	CH ₂ Cl ₂	19.5	0.320	0.176
12a	CH ₂ Cl ₂	19.5	0.642	0.306
12a	CH ₂ Cl ₂	19.5	0.963	0.425
12a	CH ₂ Cl ₂	19.5	1.284	0.545
12a	CH ₂ Cl ₂	19.5	1.604	0.698

^a [Pd] = 3.8 x 10⁻⁴ M. ^b Estimated error in temperature: ±0.5 °C. ^c Estimated error in k_{obsd}: ±2%.

Table S2. Rate Constants k_1 and k_2 of the Reaction of Complexes Pd(C(O)R)X(Ar-BIAN) (**1a-12a**) with Norbornadiene (Standard Deviations in Parentheses).^a

Compd	Temp, ^b °C	$k_1 \times 10^2, \text{s}^{-1}$	$k_2 \times 10^2, \text{s}^{-1} \text{M}^{-1}$
1a	5.0	0.12(1)	2.14(3)
1a	10.0	0.19(3)	2.95(13)
1a	15.0	0.25(5)	3.81(22)
1a	24.0	0.48(4)	6.65(18)
1a	29.0	0.72(8)	8.74(39)
2a	5.0	0.16(2)	3.32(8)
2a	12.5	0.30(6)	5.15(29)
2a	29.0	0.79(8)	15.04(36)
3a	5.5	0.23(3)	2.99(15)
3a	12.5	0.23(3)	5.84(12)
3a	29.5	1.18(19)	16.13(89)
4a	6.0	0.08(1)	1.17(5)
4a	12.5	0.12(1)	1.82(4)
4a	29.5	0.47(4)	5.63(19)
5a	6.0	0.07(1)	0.83(6)
5a	12.5	0.11(1)	1.24(6)
5a	29.5	0.42(4)	3.30(18)
6a	6.0	0.15(3)	3.92(12)
6a	12.5	0.15(4)	4.74(18)
6a	29.5	0.44(9)	9.97(44)

^a Conditions: dichloromethane solvent; [Pd] = 3.8×10^{-4} M, unless noted otherwise.

^b Estimated error in temperature: ± 0.5 °C.