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1,10-Phenanthroline Derivatives: A New Ligand Class in the Heck Reaction. Mechanistic Aspects

Walter Cabri,* Ilaria Candiani, and Angelo Bedeschi

Farmitalia Carlo Erba, Process Research, via Giovanni XXIII, 23, 20014-Nerviano (MI), Italy

Roberto Santi

Istituto Guido Donegani, via Fauser, 4, 28100-Novara, Italy

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Mechanistic studies concerning the use of 1,10-phenanthroline derivatives as palladium ligands in the Heck reaction are described. The work is focused on the steering factors for the coordination of unsaturated systems onto palladium(0) and palladium(II) complexes.

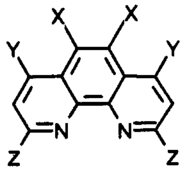
Introduction

The application of metal-catalyzed carbon–carbon bond formation methodologies to the synthesis of polyfunctional compounds is related to the capability of the catalyst to control the chemo-, regio-, and stereoselectivity of the reaction at a reasonable rate under mild conditions. The ligands on the metal play a key role in tuning the catalyst reactivity by a balance of steric and electronic factors and the identification of the best class of ligands for a given reaction is based on the elucidation of the factors that affect each step of the catalytic cycle.

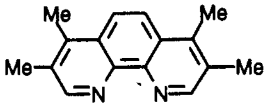
During the course of studies on the Heck reaction (palladium-catalyzed arylation of olefins),[1] we found that the use of bidentate phosphines as palladium ligands leads to control of the regioselectivity of the intermolecular arylation of several classes of terminal olefins.[2] However, the arylation of hindered enamides or disubstituted enol ethers must be carried out at high temperature and the formation of reduced products (arenes) was sometimes observed.[2a]

Focusing our attention on the coordination–insertion process of the π-system onto a palladium(II) oxidative-addition complex (Scheme I, b),[2,3] we identified 1,10-phenanthroline and its derivatives as a potentially useful class of ligands. The flat nature of 1–7 should favor the approach of the π-systems to the metal by a decrease of the steric hindrance above and below the coordination plane (Figure 1). Furthermore, the electron-donor properties of 1–7 should favor the oxidative-addition process of the aryl derivative onto the corresponding palladium(0) complex (Scheme I, a) and hamper the key step of the reduction pathway, the coordination of trialkylamine on the palladium(II) oxidative-addition complex.[4]

In spite of the number of applications of 1,10-phenanthroline derivatives in palladium-catalyzed olefin–CO copolymerizations,[5] where the coordination–insertion of the olefin to a palladium()II) complex is a crucial step, there is no reported survey on the use of these ligands for "simple" carbon–carbon bond formation in the Heck reaction.[6,7]



	X	Y	Z
1	H	H	H
2	Me	H	H
3	H	Me	H
4	H	H	Me
5	H	Ph	H
6	H	Ph	Me



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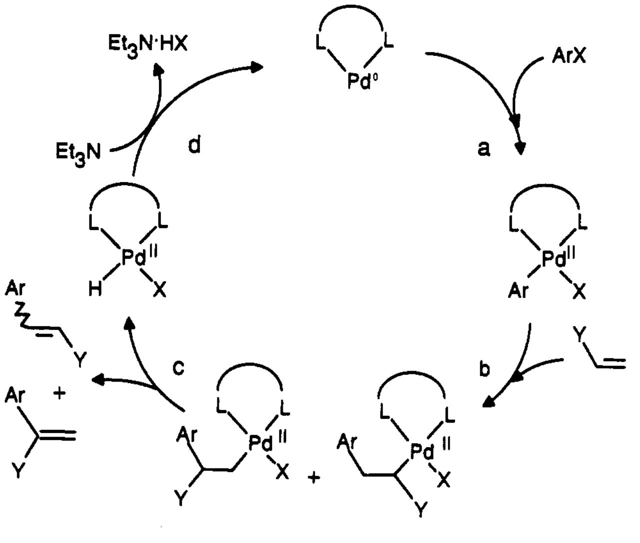
Scheme I



In this paper, we report the results of a study on the use of 1,10-phenanthroline and its derivatives in palladium-catalyzed arylation of terminal olefins.

Results and Discussion

We started with the comparison of the performances of catalysts generated *in situ* from Pd(OAc)$_2$ and several

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[•] Abstract published in *Advance ACS Abstracts*, November 1, 1993.

[1] Heck, R. F. *Palladium Reagents in Organic Syntheses*; Academic Press: London, 1985.

[2] (a) Cabri, W.; Candiani, I.; Bedeschi, A.; Santi, R. *J. Org. Chem.* **1992**, *57*, 3558. (b) Cabri, W.; Candiani, I.; Bedeschi, A.; Penco, S.; Santi, R. *J. Org. Chem.* **1992**, *57*, 1481. (c) Cabri, W.; Candiani, I.; Bedeschi, A.; Santi, R. *J. Org. Chem.* **1990**, *55*, 3654.

[3] Cabri, W.; Candiani, I.; DeBernardinis, S.; Francalanci, F.; Penco, S. *J. Org. Chem.* **1991**, *56*, 5796.

[4] For palladium-catalyzed reduction of aryl triflates using trialkylamines as hydride source, see: (a) ref 3. (b) Saa, J. M.; Dopico, M.; Martorell, G.; Garcia-Raso, A. *J. Org. Chem.* **1990**, *55*, 991.

[5] (a) Pisano, C.; Mezzetti, A.; Consiglio, G. *Organometallics* **1992**, *11*, 20. (b) Drent, E. Eur. Pat. Appl. 229408, 1986, *Chem. Abstr.* **1988**, *108*, 6617.

[6] For a preliminary screening among bidentate nitrogen ligands, see: (a) Cabri, W.; Candiani, I.; Bedeschi, A.; Santi, R. *Synlett* **1992**, 871.

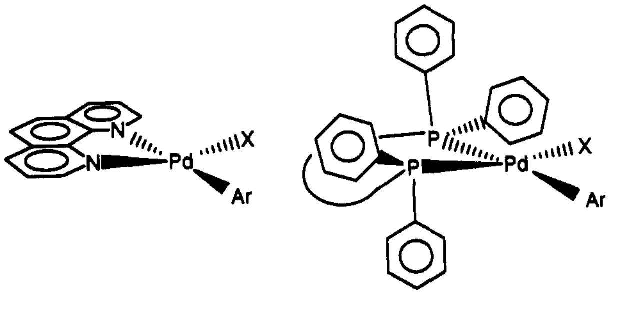
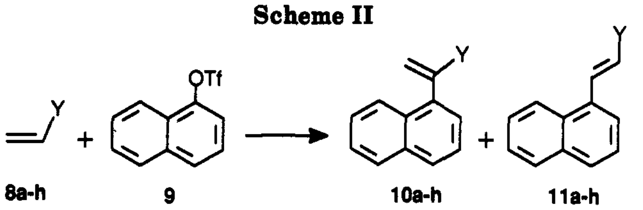


Figure 1.

Scheme II



Y: a,$COOCH_3$; b,On-Bu; c,Ph; d,$N(COCH_2CH_2CH_2)$; e,$N(COCH_3)CH_3$; f,CH_2OH; g,$CONH_2$; h,CN.

commercially available 1,10-phenanthroline derivatives 1–7[8] in the reaction between methyl acrylate (**8a**) or butyl vinyl ether (**8b**) and 1-naphthyl triflate (**9**) (Scheme II) (Table I, entries 1–14). These two terminal olefins differ from electronic properties: **8a** is an electron-poor olefin (poor σ-donor and good π-acceptor) and **8b** is an electron-rich one (good σ-donor and poor π-acceptor).

Except for the $Pd(OAc)_2/4$ system (entry 4), all the 1,10-phenanthroline-containing catalysts gave good results in the arylation of methyl acrylate (**8a**) (entries 1–3, 5–7).

The arylation of butyl vinyl ether (**8b**) afforded selectively the branched product **10b** irrespective of the ligand (entries 8–14). However, only with **4** and **6** were complete conversion achieved (entries 11 and 13), while with phenanthrolines **1–3**, **5**, and **7** extensive catalyst decomposition was observed.

The catalyst generated from 2,9-dimethy-1,10-phenanthroline (**4**) gave the best performances and the reaction outcome was not dependent on the temperature (from 100 °C to rt) and the solvent (i.e. dioxane, THF, DMSO, NMP, CH_3CN, CH_3OH, toluene). Furthermore, the regioselectivities of the arylations of styrene (**8c**) and enamides **8d,e** (entries 15–17) were comparable to the ones obtained with bidentate phosphine ligands[2] and, as expected from our working hypothesis, higher reaction rates were observed. The arylation of enamides **8d,e** were carried out at 40 °C (entries 16 and 17) instead of 100 °C and the presence of the reduced product, naphthalene, was never detected.[2a] In contrast, no reaction took place with allyl alcohol (**8f**) (entry 18) and among the electron-poor olefins **8a,g,h** only the arylation of acrylamide (**8g**) gave satisfactory results (entries 4, 19, 20).

The good performances, in terms of reaction rates and yields, observed in the arylation of heterosubstituted olefins catalyzed by $Pd(OAc)_2/4$ can be related to a higher stability of the corresponding palladium(0) complex and to a more effective catalytic cycle due to an easier oxidative addition step (Scheme I, a) because of the increased charge density on the metal in the palladium(0) complex and/or to a faster olefin insertion (Scheme I, b) because of the steric influence of the two methyl groups present in the coordination plane.

The comparison of the performances of ligands PPh_3, DPPP, and 1,10-phenanthrolines **1–7** in the competitive arylation of **8a** and **8b** by **9** is reported in Table II. With PPh_3, preferential formation of **11a** was observed (entry 1). On the contrary, the arylation of butyl vinyl ether (**8b**) prevailed when DPPP was the ligand (entry 2), but even better selectivities, up to >99/1, were observed with 1,10-phenanthroline derivatives **1–7** (entries 3–9).

With bidentate ligands the coordination–insertion step of the olefin onto the palladium(II) oxidative-addition complex takes place by dissociation of the trifluoromethanesulfonate anion[2,9] and consequently preferential arylation of the good σ-donor **8b** with respect to the poor σ-donor **8a** was observed.

Although the results of the reaction catalyzed by $Pd(OAc)_2/1$ (entry 3) appear to be in contrast with the ones previously observed (Table I, entries 1 and 8), the selectivity toward **10b** can be explained with the ability of electron-poor olefins to coordinate palladium(0) complexes containing a bidentate nitrogen ligand[10] and the high reactivity of electron-rich olefins toward cationic palladium(II) complexes.[2] Therefore, methyl acrylate (**8a**) behaves as a coligand, stabilizing the palladium(0) complex (Scheme III,[11] **27** ⇄ **28**), and butyl vinyl ether (**8b**) reacts with the palladium(II) oxidative-addition complex (**29** ⇄ **31**).

The above explanation disclosed a way to increase the conversion of the arylation of **8b** catalyzed by $Pd(OAc)_2/1$ (Table III). In fact, better performances were observed by adding electron-poor olefins **8a**, **8g**, **8h**, and **16** as coligands (cf, entry 1 and entries 2–8). The addition of **8a** to the arylation of **8c**, **8d**, and **8f** showed the same effect with an acceleration of the reaction rate avoiding catalyst decomposition (entries 9–15). In contrast, when two or more electron-withdrawing groups were present on the π-system of the coligand, the conversion in the arylation of **8b** decreased because of the formation of a stable palladium(0) complex (**27**) (entries 16–18). Prior dissociation of the coligand is necessary in order to generate the catalytically active species $L_2Pd(0)$ **28**.[12]

The addition of PPh_3[13] or acetate anions[14] (Table III, entries 19–22) increased the conversion of the arylation of

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[7] There are some applications of bidentate nitrogen ligands in palladium-catalyzed cross coupling between aryl, aroyl, vinyl, and benzyl halides and organometallic derivatives. Tin: (a) Sustman, R.; Lau, J. *Tetrahedron Lett.* **1985**, *26*, 4907. (b) Wright, M. E.; Lowe-Ma, C. K. *Organometallics* **1990**, *9*, 347. Magnesium, zinc, and tin: (c) van Asselt, R.; Elsevier, C. J. *Organometallics* **1992**, *11*, 1999. The reaction between a vinylboronate ester and aryl halides was recently carried out in the presence of **1** as palladium ligand. The Heck products were isolated in 8–40% yield. See: (d) Hunt, A. R.; Stewart, S. K.; Whiting, A. *Tetrahedron Lett.* **1993**, *34*, 3599.

[8] It is worth noting from a preparative point of view that 1,10-phenanthrolines **1** and **4** are cheaper than the bidentate phosphine ligands giving the best performances in the Heck reaction, DPPP and DPPF.

[9] Isolated $PdI(COCH_3)L_2$ complexes, where L_2 was bpy or tmeda, do not react with alkenes. However, the insertion process proceeds in the presence of AgOTf as sequestrating agent of iodide. See: Markies, B. A.; Rietveld, M. H. P.; Boersma, J.; Spek, A. L.; van Koten, G. *J. Organomet. Chem.* **1992**, *424*, C12.

[10] (a) Ito, T.; Takahashi, Y.; Ishii, Y. *J. Chem. Soc., Chem. Commun.* **1972**, 629. (b) Cucciolito, M. E.; Panunzi, A.; Ruffo, F.; De Felice, V. *Gazz. Chim. Ital.* **1989**, *119*, 461.

[11] Scheme III represent a general mechanistic scheme of the reaction carried out in the presence of coligands. However, in order to simplify the comprehension we described the complexes formed using the combination of ArOTf (substrate), vinyl butyl ether (**8b**) (reactant), methyl acrylate (**8a**) (coligand), and 1,10-phenanthroline (**1**) (ligand).

[12] Negishi, E.-i.; Takahashi, T.; Akiyoshi, K. *J. Chem. Soc., Chem. Commun.* **1986**, 1336.

[13] Vicente, J.; Abad, J.-A.; Jones, P. G. *Organometallics* **1992**, *11*, 3512.

[14] Cabri, W.; Candiani, I.; DeBernardinis, S.; Francalanci, F.; Penco, S.; Santi, R. *J. Org. Chem.* **1991**, *56*, 5796.

Table I. Palladium-Catalyzed Arylation of Terminal Olefins 8a–h by 1-Naphthyl Triflate (9). Bidentate Nitrogen Ligands 1–7 Effect[a]

entry	ligand (cat., mol %)[c]	olefin	T, °C	t, h	conv,[b] %	10/11[b]	product (yield, %)[d]
1	**1** (5)	**8a**	80	2.5	100	<1/99	**11a** (94)[e]
2	**2** (2.5)	**8a**	80	4	100	<1/99	**11a** (96)[e]
3	**3** (2.5)	**8a**	80	8	100	<1/99	**11a** (97)[e]
4	**4** (2.5)	**8a**	80	24	24	<1/99	**11a** (20)[e]
5	**5** (2.5)	**8a**	80	1.2	100	<1/99	**11a** (98)[e]
6	**6** (2.5)	**8a**	80	6	100	<1/99	**11a** (98)[e]
7	**7** (2.5)	**8a**	80	3	100	<1/99	**11a** (98)[e]
8	**1** (5)	**8b**	80	24	30	>99/1	**12** (25)
9	**2** (2.5)	**8b**	80	24	22	>99/1	**12** (16)
10	**3** (2.5)	**8b**	80	24	5	>99/1	
11	**4** (2.5)	**8b**	40	2.5	100	>99/1	**12** (95)
12	**5** (2.5)	**8b**	80	24	15	>99/1	**12** (11)
13	**6** (2.5)	**8b**	80	2	100	>99/1	**12** (88)
14	**7** (2.5)	**8b**	80	24	25	>99/1	**12** (16)
15	**4** (2.5)	**8c**	60	0.8	100	35/65[f]	**10c** + **11c** (98)
16	**4** (2.5)	**8d**	40	12	100	>99/1	**10d** (95)
17	**4** (2.5)	**8e**	40	24	100	>99/1	**10e** (94)
18	**4** (2.5)	**8f**	80	24	4	>99/1	
19	**4** (2.5)	**8g**	80	4	100	<1/99	**11g** (98)
20	**4** (2.5)	**8h**	80	24	70	<1/99	**11h** (69)[g]

[a] All reactions were carried out under argon in the presence of 1 mmol of **9**, 5 mmol of the olefin, and 1.2 mmol of Et_3N in 2.7 mL of DMF. [b] Determined by GLC. [c] The molar ratio between $Pd(OAc)_2$ and the ligand was 1.1. [d] Isolated yields. 1-Acetyl naphthalene (**12**) was isolated after acidic workup. [e] The *E*/*Z* ratio of **11a** determined by GLC was >99/1. [f] The *E*/*Z* ratio of **11c** determined by GLC was 74/26. [g] The *E*/*Z* ratio determined by ^1H NMR was 89/11.

Chart I

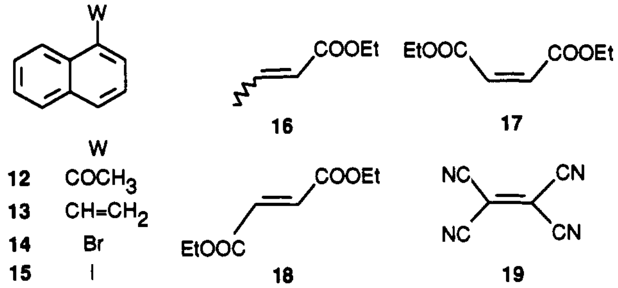

Table II. Competitive Arylation of 8a and 8b by 9. Ligand Effect[a]

$$\mathbf{8a} + \mathbf{8b} + \mathbf{9} \xrightarrow[\text{DMF/80 °C}]{\text{Pd(OAc)}_2\text{/ligand}} \mathbf{11a} + \mathbf{10b} + \mathbf{11b}$$

entry	ligand	conv, %[b]	t, h	11a[c]	10b[c]	11b[c]
1	PPh_3	98	24	75	21	4
2	DPPP	100	1	28	72	
3	**1**	100	6	8	92	
4	**2**	85	24	1	99	
5	**3**	79	24	<1	>99	
6	**4**	100	1	<1	>99	
7	**5**	85	16	<1	>99	
8	**6**	100	2	<1	>99	
9	**7**	75	6	<1	>99	

[a] All reactions were carried out at 80 °C under argon in the presence of 1 mmol of **9**, 5 mmol of **8a**, 5 mmol of **8b**, 1.2 mmol of Et_3N, 5 mol % of $Pd(OAc)_2$, and 5.5 mol % of the ligand in 2.7 mL of DMF. [b] Determined by GLC. [c] Determined by GLC. In the reaction carried out with **1**–**7** as ligands, the presence of **13** (2–4%) was sometimes observed.

8b by an alternative mechanism involving the stabilization of the cationic palladium(II) complex (**29** ⇄ **30**). The reaction was completely inhibited by adding halide anions (entries 23–25) because of the formation of a stable neutral square-planar palladium(II) complex (**30**).[2b,15] The reaction mixture remained reddish and no catalyst decomopsition was observed.

As far as the leaving group is concerned, triflate is best in this kind of reaction. In fact, arylation of **8b** by 1-naphthyl bromide (**14**) and 1-naphthyl iodide (**15**) carried out in the presence of **1** (Table IV, entries 2, 3) or **4** (entries 5, 6) afforded selectively but in low yields **10b**. Generally, the olefin arylation by aryl halides follows the ligand dissociation pathway.[2a,b] On the contrary, in this case, the regioselectivities observed suggest that the coordination–insertion process takes place by dissociation of the halide anions and the reaction proceeds till the concentration of the halide anions inhibits the dissociation process (**30** ⇄ **31**). When **8a** was used instead of **8b** no reaction was observed. The poor σ-donor **8a** is not able to compete with halide anions in the coordination of square-planar palladium(II) complexes **30**.

The aryl triflate substitution has practically no effect on the reaction between aryl triflates **20**–**26** and **8b** catalyzed by bidentate phosphine ligands containing catalyst.[2a,b] On the contrary, the aromatic ring substituents strongly affected the reaction carried out in the presence of **4** as ligand (Table V). In fact, with electron-releasing substituents (CH_3, CH_3O) the arylation afforded selectively the branched products but very low conversions were obtained because of catalysts decomposition (entires 1–3). On the other hand, with electron-withdrawing groups complete conversion and a decrease of the regioselectivity control were observed (entries 4–7). The amount of linear products (up to 16%) is related with the σ_P of the substituents and increases in the series $CH_3CO < COOCH_3 < CN < NO_2$.[16] The presence of an electron-withdrawing group on the aryl triflate favors the formation of the linear products *via* **39**. In fact, there is a competition between the carbon of the aryl moiety and the metal to migrate onto the carbon of the π-system having the higher charge density (Figure 2, **39** *vs* **40**).

The regioselectivity control exerted by **4** is lower with respect to bidentate phosphine ligands because the two nitrogens increase the charge density on the metal.

It is worth noting that the arylation of **8b** by **26** carried

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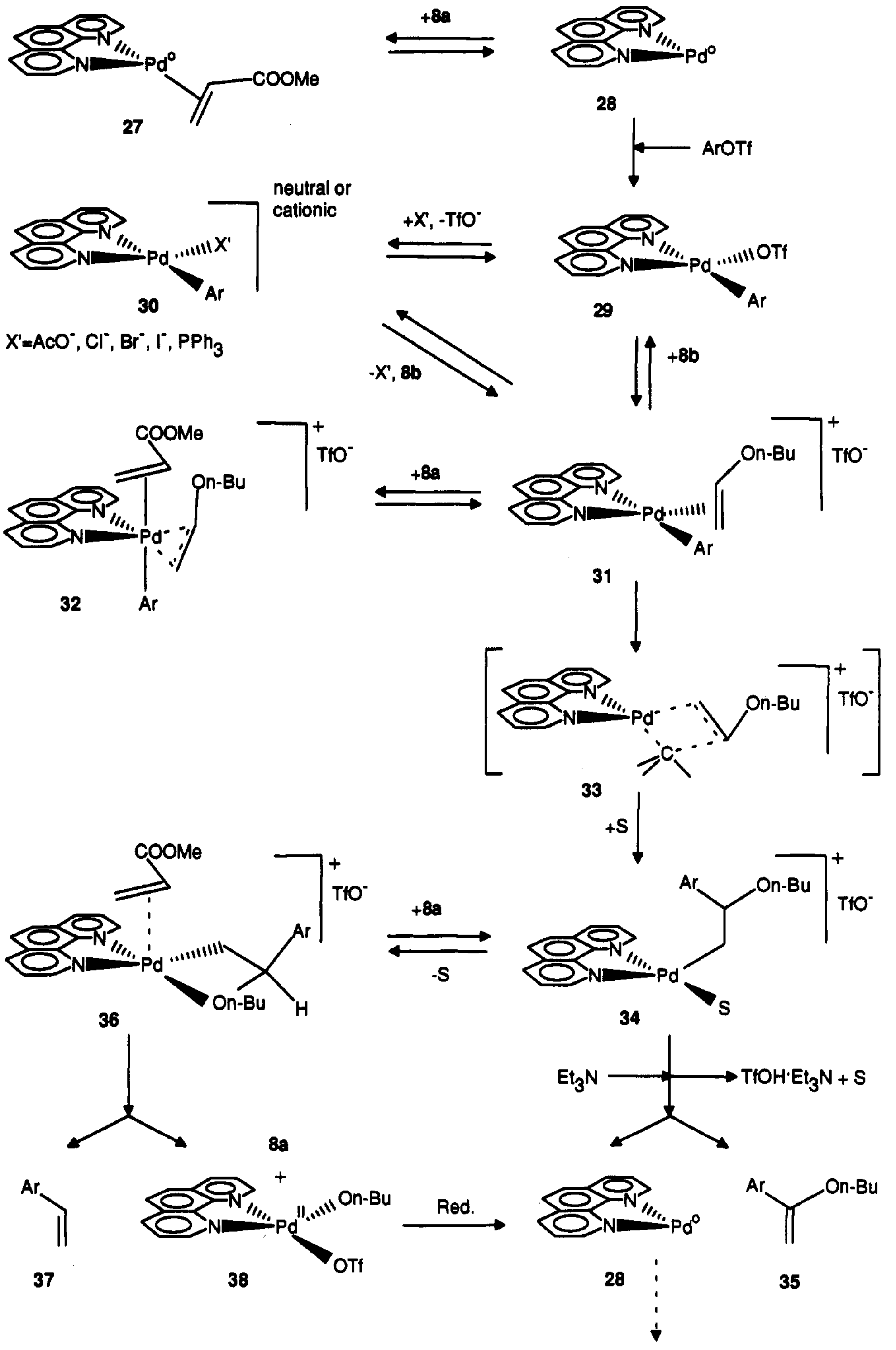
[15] The addition of halide salts favor the cross-coupling reaction between aryl triflates and tin derivatives. See: Echavarren, A. M.; Stille, J. K. *J. Am. Chem. Soc.* **1987**, *109*, 5478. On the contrary, negative results were obtained in the Heck reaction carried out in the presence of bidentate phosphine ligands. See: refs 2a and 2b.

[16] March, J. *Advanced Organic Chemistry*, 3rd ed.; Wiley Interscience: New York, 1985; pp 242–244.

Scheme III



out at 60 °C for 2.5 h afforded after acidic workup methyl ketone **26i** in 74% yield. In order to achieve complete conversion, the corresponding reaction catalyzed by the DPPP-containing catalyst was carried out at 100 °C for 3.5 h. The arylated product was obtained with higher regioselectivity (99/1 *vs* 84/16) but in lower yield **26i** (54%).[2a]

Pentacoordinated Species? The results reported in Tables I–IV clearly indicate that the scenario is more complicated with respect to the corresponding reactions with bidentate phosphine ligands. The stabilization of the palladium(0) complexes by electron-poor olefins has already been discussed. However, the olefin can be involved as coligand at any step of the catalytic cycle with bidentate nitrogen ligands.

In fact, the synthesis of several neutral and cationic pentacoordinated palladium(II) and platinum(II) complexes has been reported[17] and the formation of pentacoordinated species such as **32** can not be ruled out.[17b] However, on the basis of the Thorn–Hoffman calculations,

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[17] Pentacoordinated platinum(II) neutral complexes: (a) De Felice, V.; Funicello, M.; Panunzi, A.; Ruffo, F. *J. Organomet. Chem.* **1981**, *403*, 243. Pentacoordinated platinum(II) cationic complexes: (b) Sanchez, A.; Castellari, C.; Panunzi, A.; Vitagliano, A. *J. Organomet. Chem.* **1990**, *388*, 243. Pentacoordinated palladium(II) neutral complexes: (c) Albano, V. G.; Castellari, C.; Cucciolito, M. E.; Panunzi, A.; Vitagliano, A. *Organometallics* **1990**, *9*, 1269.

Table III. Reaction between 8b, 8c, 8d, 8f, and 1-Naphthyl Triflate (9) Catalyzed by Pd(OAc)$_2$/1. Additive Effect[a]

entry	olefin	additive[b] (equiv)	t, h	conv,[c] %	10/11	product[d] (yield, %)
1	**8b**		24	30	>99/1	**12** (25)
2	**8b**	**8a** (1)	7.5	95	>99/1	**12** (84) + **13** (4)[e]
3	**8b**	**8a** (1)	24	100	>99/1	**12** (90) + **13** (4)[e]
4	**8b**	**8a** (0.5)	24	93	>99/1	**12** (81) + **13** (5)[e]
5	**8b**	**8g** (1)	24	65	>99/1	**12** (60) + **13** (4)[e]
6	**8b**	**8h** (1)	24	75	>99/1	**12** (67) + **13** (5)[e]
7	**8b**	**8h** (0.5)	24	93	>99/1	**12** (76) + **13** (5)[e]
8	**8b**	**16** (1)	24	50	>99/1	**12** (46)
9	**8c**		8	96	28/72	**10c** + **11c** (86)
10	**8c**	**8a** (0.5)	8	99	27/73	**10c** + **11c** (90)
11	**8c**	**8a** (1)	3.5	100	23/77	**10c** + **11c** (88)
12	**8d**		6	76	67/33	**10d** (45) + **11d** (18)
13	**8d**	**8a** (1)	18	100	67/33	**10d** (58) + **11d** (27)
14	**8f**		24	50	73/27	**10f** (28) + **11f** (9)
15	**8f**	**8a** (1)	24	82	70/30	**10f** (48) + **11f** (18)
16	**8b**	**17** (1)	24	27	>99/1	**12** (25)
17	**8b**	**18** (1)	24	7	>99/1	
18	**8b**	**19** (1)	24	0		
19	**8b**	PPh_3 (0.08)	24	90	>99/1	**12** (84)
20	**8b**	LiOAc (1)	24	55	>99/1	**12** (51)
21	**8b**	NaOAc (1)	24	56	>99/1	**12** (50)
22	**8b**	KOAc (1)	24	60	>99/1	**12** (57)
23	**8b**	LiCl (1)	24	0		
24	**8b**	LiBr (1)	24	0		
25	**8b**	LiI (1)	24	0		

[a] All reactions were carried out at 80 °C under argon in the presence of 1 mmol of **9**, 5 mmol of **8b**, 1.2 mmol of Et_3N, 5 mol % of $Pd(OAc)_2$, and 5.5 mol % of **4** in 2.7 mL of DMF. [b] The equivalents of coligand are calculated with respect to **9**. [c] Determined by GLC. [d] Isolated yields. [e] The amount of **13** was determined by GLC.

Table IV. Reaction between 8b and 1-Naphthyl Derivatives 9, 14, and 15 Catalyzed by Pd(OAc)$_2$/1 or Pd(OAc)$_2$/4. Leaving Group Effect[a]

entry	substrate	ligand	t, h	conv,[b] %	10b/11b	12[c] yield, %
1	**9**	**1**	24	30	>99/1	25
2	**14**	**1**	24	6	>99/1	
3	**15**	**1**	24	35	>99/1	30
4	**9**	**4**	0.2	100	>99/1	95
5	**14**	**4**	24	14	>99/1	9
6	**15**	**4**	2.5	20	>99/1	15
7	**15**	**4**	4	45	68/32[d]	28

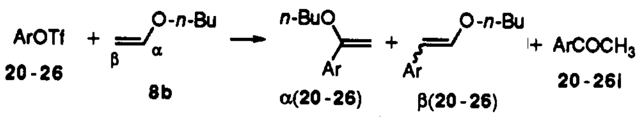
[a] All reactions were carried out at 80 °C under argon in the presence of 1 mmol of the naphthyl derivative, 5 mmol of the olefin, 1.2 mmol of Et_3N, 5 mol % of $Pd(OAc)_2$, and 5.5 mol % of the ligand in DMF. [b] Determined by GLC. [c] Isolated yields. [d] The E/Z ratio of **11b** determined by GLC was 50/50.

pentacoordinated complexes are not involved in the insertion process.[18] The energy barrier for the rotation of an olefin in a tetracoordinated complex like **31**, in order to generate the transition state **33** where the metal, the carbon of the aryl moiety, and the olefin are coplanar, is lower than the corresponding process in a pentacoordinated complex like **32**.

The detection of 1-vinylnaphthalene (**13**) in the reactions carried out in the presence of the coligands (Table II and Table III, entries 2–7) suggests that the electron-poor olefin is somehow coordinated to the metal in the insertion complex **36**.[19] In fact, we have never observed the elimination of O-n-Bu with formation of the corresponding vinyl derivative in the arylation of butyl vinyl ether (**8b**).

Taking into consideration 2,9-dimethyl-1,10-phenanthroline (**4**) as ligand, the low conversion of the arylation of electron-poor olefins **8a** and **8h** (Table I, entries 4, 20)

Table V. Reaction between Aryl Triflates 20–26 and 8b Catalyzed by Pd(OAc)$_2$/4. Aryl Triflate Substituent Effect[a]



	Ar		Ar
20	4-CH_3OPh	**24**	4-$CH_3OC(O)Ph$
21	4-CH_3Ph	**25**	4-CNPh
22	Ph	**26**	4-NO_2Ph
23	4-CH_3COPh		

entry	substrate	catalyst, mol %	t, h	conv,[b] %	α/β[b]	E/Z[b]	$ArCOCH_3$[c] (yield, %)
1	**20**	5	24	20	>99/1		**20i** (16)
2	**21**	5	24	26	>99/1		**21i** (20)
3	**22**	5	15	78	>99/1		**22i** (70)
4	**23**	2.5	1.3	100	98/2	50/50	**23i** (93)
5	**24**	2.5	2.5	100	96/4	30/70	**24i** (90)
6	**25**	5	1.5	100	88/12	39/61	**25i** (84)
7	**26**	2.5	2.5	100	84/16	32/68	**26i** (74)

[a] All reactions were carried out at 60 °C under argon in the presence of 1 mmol of aryl triflate, 5 mmol of **8b**, 1.2 mmol of Et_3N, $Pd(OAc)_2$, and **4** in DMF. [b] Determined by GLC. [c] Isolated yields after acidic treatment.

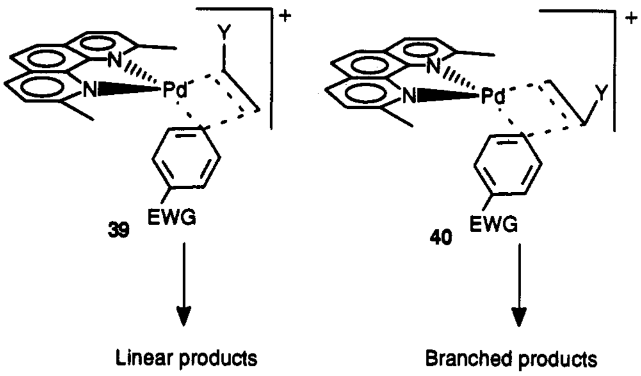


Figure 2.

can be related to the charge increase onto the metal and therefore to a high stabilization of the palladium(0) complex. However, steric factors can play an important role in this case too. In fact, the presence of the two methyl in plane can favor the formation of a pentacoordinated palladium(II) species like **32** by a destabilization of the corresponding square-planar complex **31**.[20]

Conclusions

1,10-Phenanthroline and its derivatives gave promising results in the Heck reaction. Good reaction rates, regioselectivities, and yields were obtained in the arylation of heterosubstituted olefins by aryl triflates bearing electron-withdrawing substituents using the catalytic system generated *in situ* from $Pd(OAc)_2$ and 2,9-dimethyl-1,10-phenanthroline (**4**).

Furthermore, a mechanistic scheme that explains the effects of several variables (ligand, coligand, olefin, leaving group, and aryl substituent) on the reaction course was proposed. In particular, the flat nature of 1,10-phenanthroline derivatives (Figure 1), in accord with our starting hypothesis, allows the reaction to be carried out under mild conditions because of the facile approach of the olefin to the metal in the tetracoordinated cationic palladium(II) complex (**29** $\rightleftarrows$ **31**).

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Further studies are under way in order to overcome the problems related to the stability of the palladium(0) complexes generated in the presence of bidentate nitrogen ligands under the Heck reaction conditions.

Experimental Section

All compounds were identified and characterized through their 200-MHz ^{1}H NMR spectra, mass spectra, mp (Kofler apparatus and uncorrected), or bp from bulb-to-bulb distillation conducted with a Büchi Kugelrohr apparatus. GC analyses were carried out with a Nordibond OV-1 column (25 m length, i.d. 0.32 mm) and a flame ionization detector.

Solvents were degassed prior use. Et_3N was distilled over CaH_2. Compounds **1–7**, **8a–h**, **16–19**, PPh_3, DPPP, **14**, and **15** were commercially available from Aldrich and used as received. Aryl triflates **9** and **20–26** are known compounds[2b] and were prepared from the corresponding phenols by a standard procedure in 85–95% yields.[15] Compounds **11a**,[2a] **11b**,[2c] **10c**,[2a] **11c**,[2a] **10d**,[2a] **10e**,[2a] **11h**,[2a] **12**,[21] **13**,[21] **20–26i**,[21] and **β26**[22] are known, and their structures were determined by comparison of their physical and spectroscopic data with the reported values.

Representative procedure for Tables I–V. Table I, entry 1. To a stirred solution of triflate **9** (0.276 g, 1.0 mmol) in DMF (2.7 mL) at rt under argon were sequentially added triethylamine (0.167 mL, 1.2 mmol), **8a** (0.450 mL, 5.0 mmol), **1** (0.010 g, 0.055 mmol), and $Pd(OAc)_2$ (0.011 g, 0.05 mmol). The reaction temperature was raised to 80 °C. After 2.5 h the conversion was complete (GLC), the reaction was cooled to rt, diluted with CH_2Cl_2 (30mL), washed with brine (3 × 10 mL), dried (Na_2SO_4), and filtered, and the solvent was removed *in vacuo*. The crude was purified by flash chromatography (hexane/ethyl acetate 8/2 by volume), affording **11a** (0.199 g, 94% yield).

At the end of the reactions carried out with olefin **8b**, the mixture was treated with HCl (2%) for 0.5 h in order to obtain the corresponding methyl ketone.

(*E*)-3-(1-Naphthyl)propenamide (11g): white solid; mp 175–177 °C (CH_2Cl_2/hexane) (lit.[21a] mp 175 °C); IR ($CHCl_3$) 3530, 3410, 1730, 1635, 1590, 1375 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 8.19 (J = 15.8 Hz, 1H), 8.22–7.2 (m, 7H), 7.75 (bs, 1H), 7.20 (1H), 6.65 (d, J = 15.8 Hz, 1H); GLC-MS *m/e* (rel intensity) 197 (M$^+$), 180, 154, 153 (100), 151, 126. Anal. Calcd for $C_{13}H_{11}NO$: C, 79.16; H, 5.62; N, 7.10. Found: C, 79.14; H, 5.64; N, 7.06.

(*E*/*Z*)-1-Butoxy-2-(4-acethylphenyl)ethylene (β23): pale yellow oil; ^{1}H NMR ($CDCl_3$) δ 7.9–7.75 (m, 2H), 7.64 (d, J = 8.5 Hz, 1H, *Z* isomer), 7.27 (d, J = 8.4 Hz, 1H, *E* isomer), 7.17 (d, J = 13.0 Hz, 0.5H, *E* isomer), 6.33 (d, J = 7.0 Hz, 0.5H, *Z* isomer), 5.84 (d, J = 13.0 Hz, 0.5H, *E* isomer), 5.24 (d, J = 7.0 Hz, 0.5H, *Z* isomer), 3.98 (t, J = 6.4 Hz, 1H, *Z* isomer), 3.87 (t, J = 6.4 Hz, 0.5H, *E* isomer). 2.56 (s, 3H), 1.85–1.1 (m, 4H), 1.0–0.8 (m, 3H). The GLC-MS were identical for the two isomers: *m/e* (rel intensity) 218 (M$^+$), 162, 147 (100).

(*E*/*Z*)-1-Butoxy-2-(4-(methoxycarbonyl)phenyl)ethylene (β24): waxy solid; ^{1}H NMR ($CDCl_3$) δ 7.95–7.86 (m, 2H), 7.28–7.20 (m, 2H), 7.12 (d, J = 12.9 Hz, 0.3H, *E* isomer), 6.30 (d, J = 6.9 Hz, 0.7H, *Z* isomer), 5.83 (d, J = 12.9 Hz, 0.3H, *E* isomer), 5.23 (d, J = 6.9 Hz, 0.7H, *Z* isomer), 3.97 (t, J = 6.4 Hz, 1.4H, *Z* isomer), 3.86 (t, J = 6.4Hz, 0.6H, *E* isomer), 1.8–1.2 (m, 4H), 1.0–0.8 (m, 3H). The GLC-MS were identical for the two isomers: *m/e* (rel intensity) 234 (M$^+$), 203, 179, 178 (100), 147, 119, 91.

(*E*/*Z*)-1-Butoxy-2-(4-cyanophenyl)ethylene (β25): waxy solid; ^{1}H NMR ($CDCl_3$) δ 7.65–7.25 (m, 4H), 7.12 (d, J = 13.0 Hz, 0.4H, *E* isomer), 6.34 (d, J = 7.0 Hz, 0.6H, *Z* isomer), 5.79 (d, J = 13.0 Hz, 0.4H, *E* isomer), 5.20 (d, J = 7 Hz, 0.6H, *Z* isomer), 3.98 (t, J = 6.5 Hz, 1.2H, *Z* isomer), 3.87 (t, J = 6.5 Hz, 0.8H, *E* isomer), 1.8–1.1 (m, 4H), 1.0–0.75 (m, 3H). The GLC-MS were identical for the two isomers: *m/e* (rel intensity) 201 (M$^+$), 145 (100), 116.

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