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Palladium complex-catalyzed intermolecular reductive *N*-heterocyclization: novel synthesis of quinazoline derivatives from 2-nitrobenzaldehyde or 2-nitrophenyl ketones with formamide

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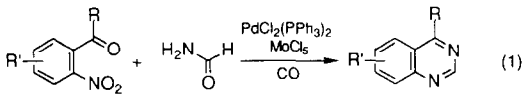
Abstract

A combination of the palladium complex $PdCl_2(PPh_3)_2$ with $MoCl_5$ shows a high catalytic activity for the intermolecular reductive *N*-heterocyclization of 2-nitrobenzaldehyde or 2-nitrophenyl ketones with formamide to give the corresponding quinazoline derivatives in moderate yields. For example, in the reaction of 2-nitrobenzaldehyde with formamide, quinazoline was obtained in 46% yield. We assume that the present reaction proceeds via an active nitrene intermediate which would be generated by selective deoxygenation of nitro group by carbon monoxide.

Keywords: Palladium; Molybdenum; Carbon monoxide; Nitrene; Reductive *N*-heterocyclization

1. Introduction

The synthesis of *N*-heterocyclic compounds using transition metal catalysts is one of the most stimulating fields and many approaches have already been reported [1]. Especially from an industrial point of view, the catalytic synthesis of *N*-heterocyclic compounds from nitroarenes is attractive [2]. In the course of our studies on transition metal complex-catalyzed *N*-heterocyclization reactions [3], we have recently developed the palladium- and ruthenium-catalyzed intramolecular reductive *N*-heterocyclization of ortho-substituted nitroarenes into 2*H*-indazoles [3a, c], indoles [3b, c] and 4(3*H*)-quinazolinone derivatives [3d]. On the basis of these studies, we have directed our attention to intermolecular reductive *N*-heterocyclization reactions. Here, we report a novel synthesis of quinazoline derivatives by the *intermolecular* reductive *N*-heterocyclization of 2-nitrobenzaldehyde or 2-nitrophenyl ketones with formamide catalyzed by the palladium complex $(PdCl_2(PPh_3)_2)$–$MoCl_5$ system (Eq. (1)).



(1)

Since Griess succeeded in the synthesis of the first 2-cyano-3,4-dihydro-4-oxoquinazoline by the reaction of cyanogen with anthranilic acid in 1869, a large number of quinazoline derivatives have been synthesized, because quinazoline derivatives constitute a fundamental skeleton in drugs and agriculture chemicals [4]. For example, prazosin is now widely used as an antihypertensive drug clinically with considerable success [4b]. In spite of their biological and industrial interest, however, catalytic methods for synthesis of quinazolines have rarely been reported. To our knowledge, the present reaction is the first example of a transition metal complex-catalyzed synthesis of quinazoline derivatives.

2. Results and discussion

2.1. Catalytic activity and effects of co-catalysts

First, the catalytic activities of several transition metal complexes were examined in the reaction of 2-nitro-

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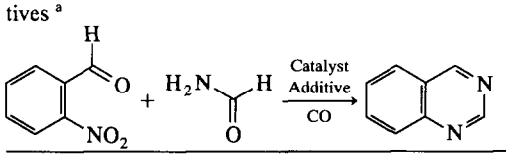
benzaldehyde with formamide and the results are summarized in Table 1. As can be seen, a palladium complex combined with $MoCl_5$ showed the best catalytic activity (run 1). Addition of $SnCl_2$ and $FeCl_3$ also showed moderate effects (runs 3 and 4), but $AlCl_3$ and $ZnCl_2$ were ineffective (runs 5 and 6). In the absence of a Lewis acid, the catalytic activity of the palladium complex was low (run 7). Phosphorus ligands did not affect the present reaction (runs 8–10). The catalytic activities of other Group 8–10 metal complexes were low (runs 11–14).

The effect of the reaction temperature, under a 20 kg cm^{-2} initial carbon monoxide pressure, was examined. The yield of quinazoline was 13% at 80 °C and a maximum yield of 46% was observed at 120 °C. Above 140 °C, the yield deceased and palladium metal was deposited during the reaction.

2.2. Synthesis of quinazoline derivatives

In the presence of a catalytic amount of $PdCl_2(PPh_3)_2$ and $MoCl_5$ under a 20 kg cm^{-2} initial carbon monoxide pressure, the reductive *N*-heterocyclization of 2-nitrobenzaldehydes or 2-nitrophenyl ketones with formamide proceeded effectively to give the corresponding quinazoline derivatives in moderate yields with a considerable amount of tarry compounds (Table 2). The reaction of 2-nitrobenzaldehyde, 2′-nitroacetophenone, 5′-methyl-2′-nitroacetophenone and 2′-nitropropiophenone with formamide afforded the corresponding quinazoline derivatives in 19–46% yields (runs 1 and 15–17). In the presence of $MoCl_5$, 7-chloroquinazoline was obtained from 4′-chloro-2′-nitrobenzaldehyde in only 8% yield, but with the the use of tin(II) chloride the yield of 7-chloroquinazoline increased to 18% (run 18). 2-Nitrobenzaldehyde dimethyl acetal could also be employed in the present reaction, and quinazoline was obtained in 47% yield (run 19). Furthermore, from the

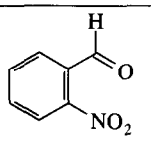
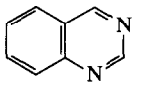
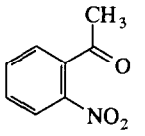
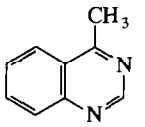
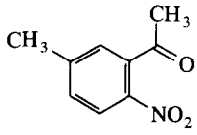
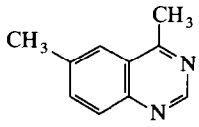
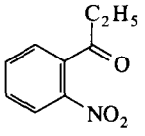
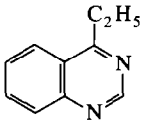
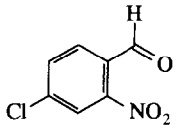
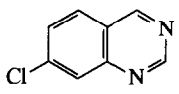
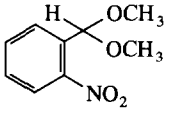
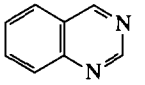
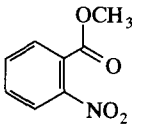
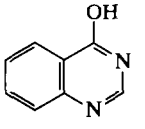
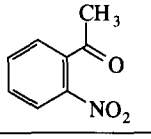
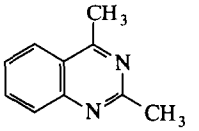
Table 1
Catalytic activities of transition metal complexes and effect of additives [a]



Run No.	Catalyst	Additive	Conversion/% [b]	Yield/% [c]
1 [d]	$PdCl_2(PPh_3)_2$	$MoCl_5$	100	46
2 [d,e]	$PdCl_2(PPh_3)_2$	$MoCl_5$	100	25
3	$PdCl_2(PPh_3)_2$	$SnCl_2$	100	36
4	$PdCl_2(PPh_3)_2$	$FeCl_3$	100	36
5	$PdCl_2(PPh_3)_2$	$AlCl_3$	100	19
6	$PdCl_2(PPh_3)_2$	$ZnCl_2$	100	15
7	$PdCl_2(PPh_3)_2$	–	100	12
8	$PdCl_2(PBu_3)_2$	$SnCl_2$	100	30
9 [f]	$PdCl_2$(bipy)	$SnCl_2$	100	28
10	$PdCl_2(PhCN)_2$	$SnCl_2$	100	33
11	$RhCl(PPh_3)_3$	$SnCl_2$	100	17
12	$PtCl_2(PPh_3)_2$	$SnCl_2$	100	12
13	$NiCl_2(PPh_3)_2$	$SnCl_2$	100	5
14	$RuCl_2(PPh_3)_3$	$SnCl_2$	100	4

[a] 2-Nitrobenzaldehyde (3.0 mmol), formamide (5.0 ml), catalyst (0.10 mmol), additive (1.0 mmol), CO (20 kg cm^{-2}), 100°C, 16 h.
[b] Conversion of 2-nitrobenzaldehyde determined by GLC.
[c] Yield of quinazoline determined by GLC.
[d] At 120°C.
[e] $MoCl_5$ (0.20 mmol) was employed for 48 h.
[f] Bipy = 2,2′-bipyridine.

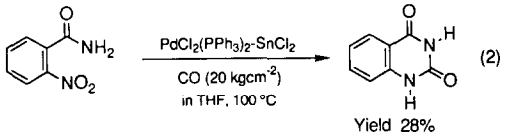
Table 2
Synthesis of quinazoline derivatives [a]

Run No.	Substrate	Product	Yield/% [b]
1			46 [c]
15			44
16			44
17			19
18 [d]			18
19			47 [b]
20			40
21 [e]			5

[a] Substrate (2.0 mmol), formamide (5.0 ml), $PdCl_2(PPh_3)_2$ (0.10 mmol), $MoCl_5$ (1.0 mmol), under CO (20 kg cm^{-2}) for 16 h.
[b] Isolated yields.
[c] GLC yields.
[d] $SnCl_2$ (1.0 mmol) was employed instead of $MoCl_5$.
[e] Acetamide (20 mmol) and 1,4-dioxane (5.0 ml) were employed instead of formamide.

reaction of methyl 2-nitrobenzoate, 4-hydroxyquinazoline was obtained in 40% yield (run 20). When acetamide was employed instead of formamide, only a trace amount of the corresponding 2-substituted quinazoline was obtained (run 21).

In the case of 2-nitrobenzamide, a reductive *N*-carbonylation reaction proceeded alternatively to give 1,3-dihydro-2,4-quinazolidinone in 28% yield (Eq. (2)).



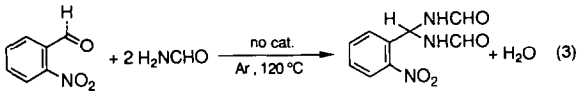
(2)

2.3. Reducing agent for nitro group

Several reducing agents were examined in this reductive *N*-heterocyclization of 2-nitrobenzaldehyde with formamide. Under a 20 kg cm^{-2} initial carbon monoxide pressure, carbon dioxide was generated and detected in the gas phase in 360% yield, based on the amount of 2-nitrobenzaldehyde charged. This result can be explained by the generation of a transition metal nitrene intermediate [2a,c,5]. Under water gas shift reaction conditions (20 kg cm^{-2} of carbon monoxide and 10 mmol of water), quinazoline was obtained in 29% yield. Furthermore, under a 20 kg cm^{-2} pressure of hydrogen or synthesis gas (20 kg cm^{-2} of carbon monoxide and 20 kg cm^{-2} of hydrogen), the yields of qunazoline decreased to 9% and 12%, respectively. Consequently, carbon monoxide is the best reducing agent for the present intermolecular reductive *N*-heterocyclization reaction.

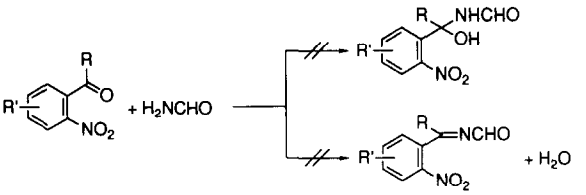
2.4. Mechanism

In the absence of a palladium complex and/or cocatalyst, 2-nitrobenzaldehyde reacted with formamide to give the corresponding 2-nitrobenzaldiformamide (Eq. (3)):



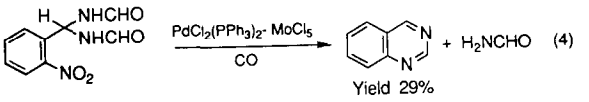
(3)

Indeed, Ittyerah and Pandya [6] have already reported that 2-nitrobenzaldehyde reacted with formamide at 60–70 °C for 8 h to afford the corresponding 2-nitrobenzaldiformamide in 40% yield. Moreover, Adachi [7] has reported that quinazolines were prepared by an intramolecular cyclization of 2-nitrobenzaldiformamide using zinc–acetic acid or iron–hydrochloric acid as reducing agent.



Scheme 1.

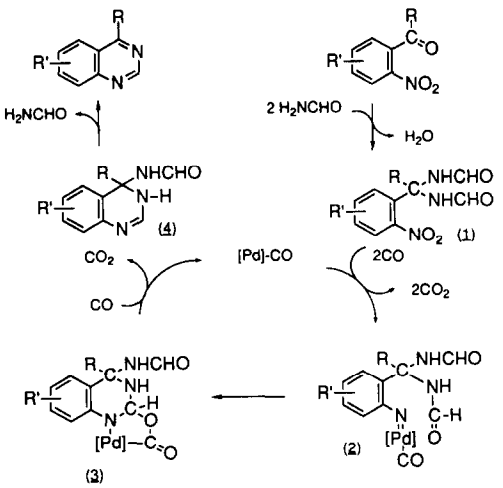
In our reaction, when the generated 2-nitrobenzaldiformamide was treated in the presence of a catalytic amount of $PdCl_2(PPh_3)_2$ and $MoCl_5$ under CO pressure (20 kg cm^{-2}) at 100 °C for 16 h, quinazoline was obtained in 29% yield (Eq. (4)):



(4)

This result suggests that the 2-nitrobenzaldiformamide seems to be a possible intermediate in the present reductive *N*-heterocyclization reaction. Other intermediates such as one-to-one adduct of 2-nitrobenzaldehyde with formamide and its dehydrated product could not be observed in the present reaction (Scheme 1).

On the basis of the above results, the most plausible mechanism is illustrated in Scheme 2. First, the carbonyl group of 2-nitrobenzaldehydes or 2-nitrophenyl ketones is condensed with two molecules of formamide to give the corresponding bisamide (**1**). Second, deoxygenation of the nitro group of (**1**) with carbon monoxide gives a nitrene intermediate (**2**), and subsequent intramolecular nucleophilic addition of nitrene to the carbonyl group of the bisamide affords the metallacyclic intermediate **3** [2a,c,5,8]. Then decarboxylation and concomitant reductive elimination of 3,4-dihydro-4-(*N*-formylamino)quinazoline (**4**) regenerate the active cata-



Scheme 2.

lyst species. Finally, dehydroamidation of (4) gives the quinazoline derivative [10]. For this process, Leconte et al. [11] have already reported that the formation of a carbon–nitrogen double bond resulted from the reductive elimination of palladium metal from a similar five-membered metallacycle intermediate followed by decarboxylation.

The effects of Lewis acids such as $MoCl_5$, $SnCl_2$ and $FeCl_3$ may be explained as follows. The coordination of the oxygen atoms of the nitro group to the Lewis acids weakens the N–O bond and makes the deoxygenation easy to generate the nitrene intermediate [3a–c].

3. Conclusion

We have succeeded in developing the first transition metal complex-catalyzed intermolecular reductive *N*-heterocyclization reaction and it offers a novel synthetic method to obtain quinazoline derivatives from 2-nitrobenzaldehyde or 2-nitrophenyl ketones with formamide. We anticipate that this intermolecular reductive *N*-heterocyclization will be applicable to the construction of other *N*-heterocyclc ring systems.

4. Experimental section

4.1. Materials

The reagents employed were dried and purified before use by the usual procedures. Carbon monoxide (> 99.9%) was used without further purification. Transition metal complexes, such as $PdCl_2(PPh_3)_2$ [11], $PdCl_2(PBu_3)_2$ [12], $PdCl_2$(bipy) [13], $PdCl_2(PhCN)_2$ [14], $RhCl(PPh_3)_3$ [15], $PtCl_2(PPh_3)_2$ [16], $NiCl_2(PPh_3)_2$ [17] and $RuCl_2(PPh_3)_3$ [18], were prepared by the literature methods. $MoCl_5$, $SnCl_2$, $FeCl_3$, $AlCl_3$, and $ZnCl_2$ were commercially available and used without further purification. 2′-Nitropropiophenone and 5′-methyl-2′-nitroacetophenone were prepared by the literature method [19].

4.2. General reaction procedure

A mixture of 2-nitrobenzaldehyde (2.0 mmol), $PdCl_2(PPh_3)_2$ (0.10 mmol), $MoCl_5$ (1.0 mmol) and dry formamide (5.0 ml) was placed in a 50 ml stainless-steel autoclave (Yuasa Giken; SUS 316) equipped with a glass liner and a magnetic stirring bar. The unit was sealed and then purged three times with 20 kg cm^{-2} pressurization–depressurization cycles of carbon monoxide. The reactor was then pressurized with carbon monoxide to 20 kg cm^{-2} (at room temperature) and heated to 120 °C within 10 min with stirring and held at this temperature for 16 h. The reaction was terminated by rapid cooling, and gaseous products were discharged. The resulting brown solution was analyzed by GLC. Isolation of the products was effected as follows.

Water (150 ml) was added to the reaction mixture and organic products were extracted with diethyl ether (50 ml × 3). The ether layer was dried with anhydrous Na_2SO_4 and after evaporation of the ether, the products were isolated by Kugelrohr distillation. The identification of the products was confirmed by ^1H and ^{13}C NMR and GC–MS. The GLC analyses were carried out on a Shimadzu GC-8A chromatograph equipped with a glass column (3 m × 3 mm i.d.), packed with silicone OV-17 (2% on Chromosorb W (AW-DMCS), 80–100 mesh) and PEG-HT (5% on Uniport HP, 60–80 mesh). The ^1H NMR spectra were recorded at 270 MHz with a JEOL GSX-270 spectrometer. The ^{13}C NMR spectra were recorded at 25.05 MHz with a JEOL JNM FX-100 spectrometer and/or at 67.8 MHz with JEOL GSX-270 spectrometer. Samples were dissolved in $CDCl_3$, and the chemical shift values were expressed relative to tetramethylsilane as an internal standard. Mass spectra were obtained on a Shimadzu QP-2000 spectrometer. The spectral and analytical data for the products are shown below.

4.2.1. Quinazoline

Colorless solid; b.p. 150 °C/10 mmHg (Kugelrohr distillation); ^1H NMR ($CDCl_3$, 270 MHz), δ 7.64 (ddd, 1H, H-6, J = 8.1, 6.8, 1.2 Hz), 7.87–7.93 (m, 2H, H-7, 8), 8.03 (d, 1H, H-8, J = 8.8 Hz), 9.33 (s, 1H, H-2), 9.39 (s, 1H, H-4); ^{13}C NMR ($CDCl_3$, 25.05 MHz) δ 126.4 (s, C_{4a}), 126.9 (d, C_5), 127.7 (d, C_6), 128.0 (d, C_8), 133.9 (d, C_7), 149.6 (s, C_{8a}), 154.8 (d, C_2); mass spectrum (electron impact), m/z 130 (M^+, base peak), 103 ($M^+ - CHN$, 71.5), 76 ($M^+ - 2CHN$, 56.3).

4.2.2. 4-Methylquinazoline

Colorless solid; b.p. 170 °C/10 mmHg (Kugelrohr distillation); ^1H NMR ($CDCl_3$, 270 MHz), δ 2.94 (s, 3H, CH_3), 7.62 (ddd, 1H, H-6, J = 8.3, 6.8, 1.2 Hz), 7.87 (ddd, 1H, H-7, J = 8.3, 6.8, 1.5 Hz), 8.01 (d, 1H, H-5, J = 8.3 Hz), 8.07 (ddd, 1H, H-8, J = 8.3, 1.2, 0.7 Hz), 9.16 (s, 1H, H-2); ^{13}C NMR ($CDCl_3$, 67.8 MHz), δ 21.69 (CH_3), 124.43 (C_{4a}), 125.03 (C_5), 127.64 (C_6), 128.86 (C_8), 133.72 (C_7), 149.47 (C_{8a}), 154.39 (C_2), 168.27 (C_4); mass spectrum (electron impact), m/z 144 (M^+, base peak), 129 ($M^+ - CH_3$, 25.3), 103 ($M^+ - CH_3CN$, 32.8), 76 ($M^+ - CH_3CNCHN$, 30.4).

4.2.3. 4,6-Dimethylquinazoline

Colorless solid; b.p. 250 °C/10 mmHg (Kugelrohr distillation); ^1H NMR ($CDCl_3$, 270 MHz), δ 2.55 (s, 3H, CH_3), 2.89 (s, 3H, CH_3), 7.67 (dd, 1H, H-7, J = 8.5, 2.0 Hz), 7.78 (m, 1H, H-5), 7.89 (d, 1H, H-8, J = 8.5 Hz), 9.10 (s, 1H, H-2); ^{13}C NMR ($CDCl_3$,

25.05 MHz), δ 21.6 (q, CH_3), 21.8 (q, CH_3), 123.5 (d, C_5), 124.0 (s, C_{4a}), 128.3 (d, C_8), 135.4 (d, C_7), 137.3 (s, C_6), 147.7 (s, C_{8a}), 153.4 (d, C_2), 166.9 (s, C_4); mass spectrum (electron impact), *m/z* 158 (M^+, base-peak), 143 ($M^+ - CH_3$, 18.4), 117 ($M^+ - CH_3CN$, 18.1), 90 ($M^+ - CH_3CNCHN$, 31.0).

4.2.4. 4-Ethylquinazoline

Colorless liquid; b.p. 200 °C/5 mmHg (Kugelrohr distillation); ^1H NMR ($CDCl_3$, 270 MHz), δ 1.47 (t, 3H, CH_3, $J = 7.6$ Hz), 3.32 (q, 2H, CH_2, $J = 7.6$ Hz), 7.64 (t, 1H, H-6), 7.88 (t, 1H, H-7), 8.04 (d, 1H, H-5, $J = 8.2$ Hz), 8.13 (d, 1H, H-8, $J = 8.3$ Hz), 9.23 (s, 1H, H-2); ^{13}C NMR ($CDCl_3$, 67.8 MHz), δ 12.71 (CH_3), 27.71 (CH_2), 123.75 (C_{4a}), 124.56 (C_5), 127.54 (C_6), 129.14 (C_8), 133.52 (C_7), 149.75 (C_{8a}), 154.64 (C_2), 172.49 (C_4); mass spectrum (electron impact), *m/z* 158 (M^+, 67.9), 157 ($M^+ - H$, base-peak), 130 (35.8), 103 ($M^+ - EtCN$, 29.7), 76 ($M^+ - EtCNCHN$, 36.4).

4.2.5. 7-Chloroquinazoline

Colorless solid; b.p. 200 °C/10 mmHg (Kugelrohr distillation); ^1H NMR ($CDCl_3$, 270 MHz), δ 7.64 (dd, 1H, H-6, $J = 8.8$, 2.0 Hz), 7.90 (d, 1H, H-5, $J = 8.8$ Hz), 8.07 (d, 1H, H-8, $J = 2.0$ Hz), 9.35 (s, 1H, H-2), 9.40 (s, 1H, H-4); mass spectrum (electron impact), *m/z* 166 ($M[^{37}Cl]^+$, 33.8), 164 ($M[^{35}Cl]^+$, base peak), 137 ($M[^{35}Cl]^+ - CHN$, 48.6), 110 ($M[^{35}Cl]^+ - 2CHN$, 34.1).

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