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Dioxomolybdenum(VI)-Catalyzed Reductive Cyclization of Nitroaromatics. Synthesis of Carbazoles and Indoles

Roberto Sanz,[a,*] Jaime Escribano,[a] María R. Pedrosa,[a] Rafael Aguado,[a] and Francisco J. Arnáiz[a,*]

[a] Departamento de Química, Facultad de Ciencias, Universidad de Burgos, Pza. Misael Bañuelos s/n, 09001-Burgos, Spain
Fax: (+34)-947-258-831; e-mail: rsd@ubu.es or farnaiz@ubu.es

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Abstract: Reductive cyclization of nitrobiphenyls and nitrostyrenes to carbazoles and indoles, respectively, is carried out by triphenylphosphine under mild conditions catalyzed by a dichlorodioxomolybdenum(VI) complex. A one-pot procedure for the synthesis of regioselectively functionalized indoles has been developed from commercially available *o*-nitrobenzaldehydes and phosphoranes.

Keywords: carbazoles; cyclization; indoles; molybdenum; nitro compounds; reduction

Indoles and carbazoles are ubiquitous components of both biologically active natural products and important pharmaceuticals.[1] Also, in materials science carbazoles are important building blocks.[2] So, the development of efficient synthetic routes to both core structures with a variety of substitution patterns is a current major objective in organic synthesis.[3] One important route to carbazoles and indoles is the reductive cyclization of nitrobiphenyls and 2-nitrostyrenes, respectively.[4]

Since its discovery in 1962,[5] the Cadogan reduction of 2-nitrobiphenyls by trivalent phosphorus reagents has been recognized as a general route to carbazoles and other nitrogen-containing heterocycles,[6] and remains the most common method to effect deoxygenative cyclizations. The reactions are usually conducted using an excess of $P(OEt)_3$, as both the reductant and solvent, at reflux (156 °C). Also, Cadogan[5b] and Sundberg[7] reported that the deoxygenation of β-substituted *o*-nitrostyrenes with $P(OEt)_3$ afforded 2-substituted (alkyl or aryl) indole derivatives. However, this method furnished very poor yields in the synthesis of 2-ethoxycarbonyl- and 2-acylindoles.[8] The widely accepted mechanism for this transformation involved exhaustive deoxygenation to a singlet nitrene that undergoes C–H insertion in a suitable side chain.[9] Nevertheless, the isolation of *N*-hydroxy derivatives[7a] along with computational studies[10] have shown that an alternative 1,5-electrocyclization of the corresponding nitroso intermediates to nitrones followed by 1,5-H shift and tautomerization, may even be competitive with nitrene formation. *N*-Ethylcarbazoles and *N*-ethoxy- or *N*-ethylindoles are usually formed in these reactions as side products, probably due to alkylation of the nitrogen by the generated triethyl phosphate.[11] This problematic side reaction could, in principle, be avoided by using PPh_3 as a convenient alternative reducing agent due to the non-electrophilic nature of its by-product, triphenylphosphine oxide. However, to the best of our knowledge, only a single methodology has been developed using PPh_3 as a reductant in carbazole synthesis from nitrobiphenyls.[12] Freeman and co-workers have recently described the synthesis of carbazoles by reductive cyclization of 2-nitrobiphenyls using PPh_3 in *o*-dichlorobenzene (*o*-DCB) at reflux (180 °C).[13] Although with this method the formation of undesired alkylated impurities is avoided, it still presents severe drawbacks like the use of highly toxic solvents and the very high temperatures required.

On the other hand, it is known that some dioxomolybdenum(VI) complexes that mimic oxo-transferases are efficient catalysts for oxo-transfer reactions.[14] In this field, we have found that a number of addition compounds of dichlorodioxomolybdenum(VI) are able to catalyze a variety of oxo-transfer processes, in particular the oxidation of thiols to disulfides with DMSO,[15] the deoxygenation of sulfoxides to sulfides with phosphites,[16] and the reduction of *N*-oxides with PPh_3.[17] Herein, we report the synthesis of carbazoles and indoles by the dichlorodioxomolybenum(VI)-catalyzed reductive cyclization of 2-nitrobiphenyls and 2-nitrostyrenes, respectively, with PPh_3.

Our choice of commercially available 2-nitrobiphenyl **1a** as a model substrate for deoxygenation was

prompted by the fact that the expected nitrene (or nitrenoid) intermediate, i.e., 2-biphenylnitrene **2a**,[18] would produce thermally stable and known products from relatively well-defined reaction modes: carbazole **3a** from a formal intramolecular C–H bond insertion and/or 2-aminobiphenyl **4a** from H abstraction (Scheme 1).

As indicated in Scheme 1, deoxygenation is simply achieved by refluxing a solution of **1a** containing PPh_3 (2.4 equivs.) and a catalytic amount of $MoO_2Cl_2(dmf)_2$ (5 mol%). Initially, **1a** and PPh_3 were taken up in toluene, MeCN, THF, DMF and refluxed overnight (Table 1). As shown in Table 1 (entries 1–4) toluene turned out to be the most suitable solvent in order to get a good conversion of nitrobiphenyl **1a**. The use of an inert atmosphere led to a better conversion, probably due to the catalyzed oxidation of PPh_3 to the oxide under air (Table 1, entries 4–6). Interestingly, $P(OEt)_3$, usually used under Cadogan cyclization conditions, was less effective than PPh_3 for deoxygenation of nitrobiphenyl **1a** in the presence of the molybdenum complex (Table 1, entry 7). It is also interesting to note that in the absence of catalyst (Table 1, entry 8) only trace amounts of carbazole **3a** were detected.[19]

Table 1. Conditions for the reductive cyclization of **1a**.

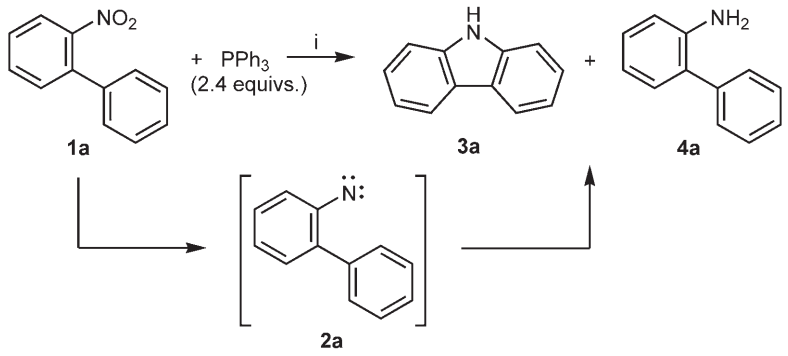
Entry	Solvent	Time [h]	Conversion [%][a]
1	MeCN	24	55
2	DMF[b]	16	0
3	THF	16	67[c]
4	toluene[d]	16	85
5	toluene[e]	16	90
6	toluene[f]	16	>95[g]
7	toluene	16	60[h]
8	toluene	16	<5[i]

[a] Estimated by ^1H NMR analysis of the crude of the reaction. The selectivity of the reaction for the formation of **3a** from **1a** was almost complete and only trace amounts of **4a** could be detected.
[b] Carried out at 110 °C.
[c] 15% of **4a** was generated.
[d] Synthesis grade.
[e] Dried toluene under air atmosphere.
[f] Dried toluene under nitrogen atmosphere.
[g] 83% isolated yield.
[h] $P(OEt)_3$ was used instead PPh_3.
[i] Without catalyst.

In order to simplify the purification process, the excess of PPh_3 was easily transformed into the phosphine oxide by further addition of DMSO and a small amount of the same catalyst (1 mol%) after the complete conversion of the starting nitroaromatic.[20] So, simple removal of the solvent and purification by silica gel column chromatography afforded carbazole **3a**.

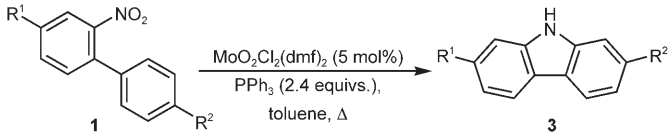
With the conditions for the molybdenum-catalyzed cyclization of 2-nitrobiphenyl **1a** established, our next goal was to test the scope and functional group tolerance of the method. Following known procedures for the Suzuki–Miyaura cross-coupling reactions,[21] we first synthesized a variety of 2-nitrobiphenyls **1b–i** having a range of usual functionalities. Nitroaromatics **1b–i** were treated in the same reaction conditions as described above for **1a**: refluxing toluene ($10\,mL\,mmol^{-1}$) for *ca.* 16 h in the presence of PPh_3 (2.4 equivs.) and $MoO_2Cl_2(dmf)_2$ (5 mol%). The results are summarized in Table 2.

As seen in Table 2, our method tolerates a wide range of functional groups such as alkyls, ethers, carbonyls, halogens, and carboxylic esters. In general, good isolated yields were observed for this process (Table 2, entries 1–7), although minor amounts of the corresponding amines **4** were detected for substrates bearing electron-donating substituents (Table 2, entry 3). As previously noted by Freeman and coworkers the only functional groups that appear to be problematic for this reaction are those with free, acidic protons, such as phenol **1h** and carboxylic acid **1i**.[13] Anyway, whereas Freeman reported no cyclization at all for **1h** and **1i** with PPh_3 in refluxing *o*-DCB,



Scheme 1. Optimization of the reductive cyclization of 2-nitrobiphenyl **1a** to carbazole **3a**. *Reagents and conditions:* i) $MoO_2Cl_2(dmf)_2$ (5 mol%), solvent, reflux, time (see Table 1).

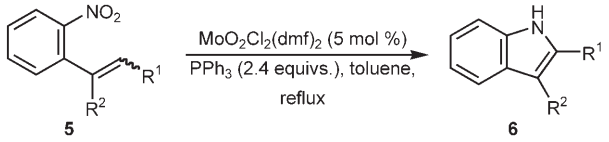
Table 2. Reductive cyclization of nitrobiphenyls **1** to carbazoles **3**.



Entry	Starting material	R^1	R^2	Product	Yield [%][a]
1	**1a**	H	H	**3a**	86[b]
2	**1b**	*t*-Bu	*t*-Bu	**3b**	80
3	**1c**	OMe	H	**3c**	78[c]
4	**1d**	CHO	H	**3d**	70
5	**1e**	COMe	H	**3e**	81
6	**1f**	F	H	**3f**	73
7	**1g**	CO_2Et	H	**3g**	87
8	**1h**	OH	H	**3h**	33[d]
9	**1i**	CO_2H	H	**3i**	30

[a] Isolated yield based on the starting nitrobiphenyl **1**.
[b] Carried out on a 10 mmol scale.
[c] Small amounts (<10%) of the corresponding amine **4c** were detected.
[d] 20% of **1h** and 10% of **4h** were also isolated.

Table 3. Reductive cyclization of 2-nitrostyrenes **5** to indoles **6**.



Entry	Starting material	*E*/*Z*	R^1	R^2	Product	Yield [%][a]
1	**5a**	4/1	Ph	H	**6a**	73[b]
2	**5a**	1/0	Ph	H	**6a**	64
3	**5a**	0/1	Ph	H	**6a**	80
4	**5b**	1/2.3	*n*-C_5H_{11}	H	**6b**	80
5	**5c**	1/2	Me	H	**6c**	77
6	**5d**	10/1	CO_2Et	H	**6d**	75
7	**5e**	1.5/1	CO_2Et	Me	**6e**	84

[a] Isolated yield based on the starting nitrostyrene **5**.
[b] No reaction was observed without catalyst.

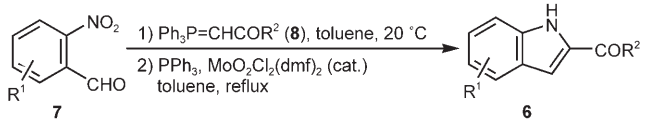
our procedure allows the synthesis of the corresponding carbazoles **3h** and **3i** in modest yields (Table 2, entries 8 and 9). The low yields of these reactions could be due to the ability of nitrobiphenyls **1h** and **i** with acidic protons, to generate alkoxo or carboxylate dioxomolybdenum(VI) complexes,[22] which would not be active catalysts in the process.

Once we had demonstrated the ability of our catalytic method for the synthesis of carbazoles, we decided to explore the deoxygenation and subsequent cyclization of *o*-nitrostyrenes as a method for the synthesis of indole derivatives. *o*-Nitrostilbene **5a** was chosen as a representative β-aryl-*o*-nitrostyrene. Its reductive cyclization with PPh_3 under dioxomolybdenum catalysis afforded 2-phenylindole **6a** in good yield (Table 3, entry 1). It is interesting to note that both the *cis*- and *trans*-isomers of **5a** reacted, although a slightly higher yield was obtained from the former (Table 3, entries 2 and 3).[5b] Then, β-alkyl-*o*-nitrostyrenes **5b** and **c** were prepared by Wittig reaction from 2-nitrobenzaldehyde and obtained in both cases as a mixture of geometrical isomers. When these substrates were subjected to reductive cyclization under the same reaction conditions, the corresponding 2-alkylindoles **6b** and **c** were isolated in good yields (Table 3, entries 4 and 5). Intrigued by the low yields reported for the preparation of indole 2-carboxylates,[5b,7a] our next goal was to test our catalytic procedure in the reductive cyclization of 2-nitrocinnamates. Gratifyingly, treatment of ethyl 2-nitrocinnamate **5d** under the established conditions led to ethyl indole-2-carboxylate **6d** in good yield (Table 3, entry 6). Moreover, 2-nitrocinnamate derivative **5e**, with an additional substituent on the double bond also underwent reductive cyclization to the 2,3-disubstituted indole **6e** in very good yield (Table 3, entry 7).

Among 2-substituted indoles, 2-acylindoles as well as indole 2-carboxylates constitute valuable building blocks for the synthesis of various heterocyclic compounds. Also, regioselectively substituted indoles at the carbocyclic ring are particularly difficult to access following traditional methods due to the different electron-rich nature of each position.[23] In this context, we envisaged that this kind of interesting substitution pattern of indoles could be efficiently obtained in one-pot approach using our molybdenum-catalyzed reductive cyclization. Hence, a Wittig reaction in toluene at room temperature of phosphoranes **8a** (R = OEt) or **8b** (R = Me) with 2-nitrobenzaldehydes **7**, all of them commercially available, gave the corresponding *o*-nitrostyrene derivatives.[24] Without isolation of these derivatives, subsequent addition of PPh_3 and a catalytic amount of $MoO_2Cl_2(dmf)_2$ (10 mol%) was followed by refluxing of the mixture for 24 h.[25] As mentioned above, oxidation of the excess of PPh_3 with DMSO and removal of the solvent, followed by simple column chromatography afforded interesting regioselectively substituted indole derivatives **6f–o** in high to moderate overall yields referred to the starting *o*-nitrobenzaldehydes **7** (Table 4).[26]

Finally, we checked whether 2-nitrobiphenyl **1a** as well as 2-nitrostyrenes **5a** and **b** would also undergo the dioxomolybdenum-catalyzed reductive cyclization to the corresponding heterocyclic derivatives using a commercially available, polymer-bound triphenylphosphine (Scheme 2). The yields of the final compounds were comparable with those obtained using PPh_3, whereas the isolation of the product by simple

Table 4. One-pot synthesis of 2-ethoxycarbonyl- and 2-acetyl-substituted indoles **6** from 2-nitrobenzaldehydes **7**.



Entry	Starting material	R^1[a]	R^2	Product	Yield [%][b]
1	**7a**	H	OEt	**6d**	71
2	**7b**	4-Cl	OEt	**6f**	85
3	**7c**	5-Cl	OEt	**6g**	15
4	**7d**[c]	6-Cl	OEt	**6h**	50
5	**7e**	5,6-(OCH_2O)	OEt	**6i**	81
6	**7f**	7-OMe	OEt	**6j**	45[d]
7	**7a**	H	Me	**6k**	63
8	**7b**	4-Cl	Me	**6l**	93
9	**7c**	5-Cl	Me	**6m**	39
10	**7d**[c]	6-Cl	Me	**6n**	55
11	**7e**	5,6-(OCH_2O)	Me	**6o**	78

[a] Location of R^1 on the final indole derivative **6**.
[b] Isolated yield based on the starting nitrobenzaldehyde **7**.
[c] Although it is commercially available (Sigma), it was synthesized by oxidation of 4-chloro-2-nitrobenzylalcohol.
[d] 25% of the intermediate nitrocinnamate and 10% of ethyl 2-amino-3-methoxycinnamate were also isolated.

filtration of the solid-supported phosphine is much easier. Under these conditions reaction times were a bit longer.

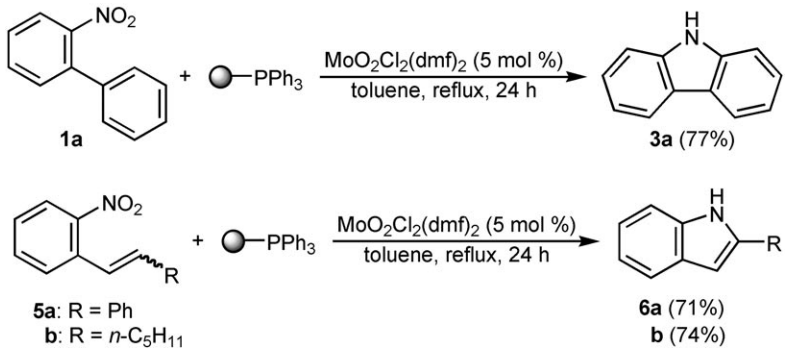
According with our previous reports in this field,[15–17] we proposed that the process probably initiates with the rapid reduction of dioxomolybdenum(VI) with PPh_3. The resulting oxomolybdenum(IV) reacts, as it is formed, with the remaining dioxomolybdenum(VI) leading to a dinuclear, μ-oxo, molybdenum(V) complex,[27] as shown in Scheme 3. Then, the mononuclear oxomolybdenum(IV), or the dinuclear oxomolybdenum(V), or both species, are responsible for the deoxygenation of nitroaromatics **1** and **5** leading to the corresponding nitroso derivatives **9**. Since it is known that the reductive cyclization of 2-nitrosobiphenyl compounds to carbazoles using PPh_3 takes place in benzene at low temperature,[28] we postulated that the second deoxygenation may take place without catalysis. Thus, nitroso intermediates **9** are relatively rapid deoxygenated with a second equivalent of PPh_3 to generate nitrenes (or nitrenoids) **2**, which undergo C–H insertion to afford carbazoles **3** or indoles **6** (Scheme 3). Alternatively, as previously pointed out,[10] nitroso derivatives **9** could undergo direct cyclization before reduction to a nitrene, affording nitrones **10** and finally *N*-hydroxy derivatives **11** which would be further deoxygenated to **3** or **6** (Scheme 3).

In summary, we have developed a dioxomolybdenum(VI)-catalyzed method for the reductive cyclization of nitroaromatics with PPh_3 under milder conditions than all previously reported. A wide range of interesting functionalized carbazole and indole derivatives have been prepared with this methodology showing that it constitutes a synthetically competitive alternative to already established methods for the same kind of reactions.

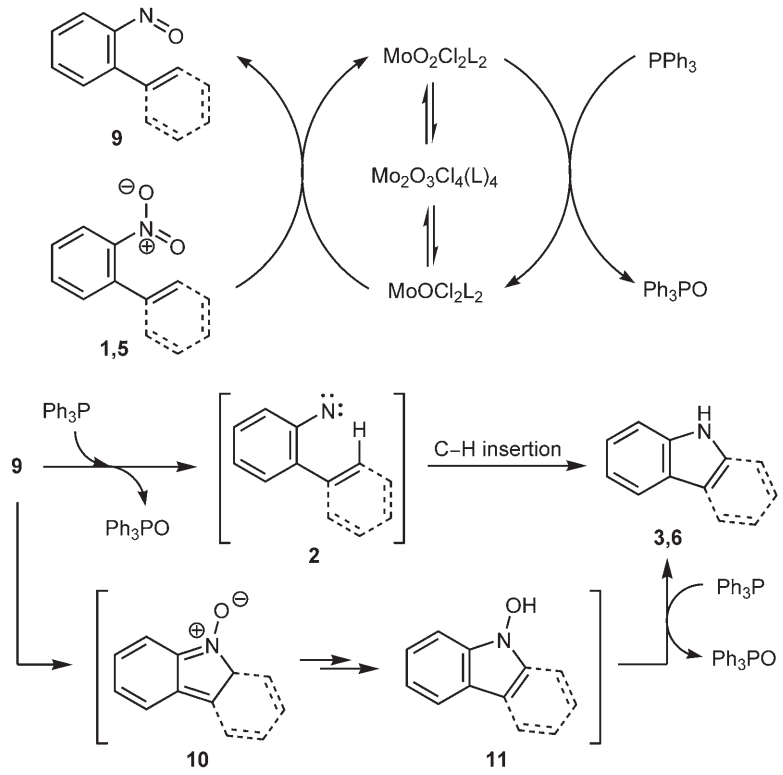
Experimental Section

General Remarks

All reactions were carried out under nitrogen atmosphere unless otherwise specified. CH_3CN, DMF, toluene and THF were analytical grade and purchased from SDS. ^1H and ^{13}C NMR spectra were recorded on a Varian Mercury-Plus 300 or Varian Inova 400 spectrometers. ^1H NMR spectra (300 or 400 MHz) were recorded in $CDCl_3$, DMSO-d_6, or acetone-d_6 and chemical shifts (δ) are reported in ppm from TMS with the residual solvent resonance as internal standard. ^{13}C NMR spectra (75.4 or 100.6 MHz) were measured by using $CDCl_3$, DMSO-d_6, or acetone-d_6 as solvents and internal standards. GC-MS was performed on an Agilent 6890N/5973 mass spectrometer. HR-MS was carried out on a Micromass AutoSpect spectrometer. $Na_2MoO_4 \cdot 2H_2O$ to



Scheme 2. Dioxomolydenum-catalyzed reductive cyclization of 2-nitrobiphenyl **1a** and 2-nitrostyrenes **5a** and **b** with polymer-bound PPh_3.



Scheme 3. Proposed mechanims for the reductive cyclization of nitroaromatics **1** and **5**.

prepare the catalyst was obtained from Acros Organics, and polymer-bound triphenylphosphine (200–400 mesh, loading: 3 mmol g^{-1}) was purchased from Fluka. Other chemicals were purchased from Acros, Fluka and Aldrich and used as received.

$MoO_2Cl_2(dmf)_2$

The catalyst can be prepared as previously described[29] or more readily as we have recently described in almost quantitative yield from $Na_2MoO_4{\cdot}2H_2O$.[16]

General Procedure for Deoxygenation of Nitroaromatics 1 and 5 with PPh_3 Catalyzed by $MoO_2Cl_2(dmf)_2$

To a solution of the nitroaromatic **1** or **5** (1 mmol) and PPh_3 (629 mg, 2.4 mmol) in toluene (10 mL), $MoO_2Cl_2(dmf)_2$ (17.3 mg, 0.05 mmol) was added, and the resulting mixture was stirred at reflux. The completion of the reductive cyclization was monitored by GC-MS or ^1H NMR spectroscopy. In order to completely oxidize the excess of PPh_3, another portion of the catalyst (3.5 mg, 0.01 mmol) and DMSO (0.5 mL) were added and the resulting mixture was refluxed for 30 min. The solvents were removed under reduced pressure and the residue was purified by column chromatography on silica gel (eluent: hexane/EtOAc) to afford the corresponding final product. Characterization data for carbazoles **3** and indoles **6** are listed in the Supporting Information.

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[19] Freeman et al. have described that the conversion of nitrobiphenyls to carbazoles in refluxing toluene is harder negligible. They need to heat up to 180 °C in *o*-DCB to get a good yield of carbazole derivatives, see ref.[13]

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[21] N. Miyaura, A. Suzuki, *Chem. Rev.* **1995**, *95*, 2457–2483; see also ref.[13]

[22] a) F. J. Arnáiz, R. Aguado, M. R. Pedrosa, A. de Cian, J. Fischer, *Polyhedron* **2000**, *19*, 2141–2147; b) F. E. Kühn, A. M. Santos, A. D. Lopes, I. S. Gonçalves, J. E. Rodrígues-Borges, M. Pillinger, C. C. Romao, *J. Organomet. Chem.* **2001**, *621*, 207–217.

[23] R. J. Sundberg, *Indoles*, Academic Press, San Diego, CA, **1996**.

[24] The formation of the intermediates *o*-nitrocinnamates or *o*-nitrochalcones was monitored by GC-MS and usually takes place in 1–2 h.

[25] It was added in two portions: 5 mol % of catalyst at the beginning and further addition of another 5 mol % of catalyst after 12 h.

[26] Although we have not an explanation for the lower yields obtained for 5-chloroindoles **6g** and **6m**, we speculate that it could be due to a decreased efficacy of the reductive deoxygenation [*via* electrophilic attack by the oxomolybdenum(IV)complex] of the nitro group in these cases.

[27] The tendency of oxomolybdenum(IV) and dioxomolybdenum(VI) to comproportionate is well documented: R. H. Holm, *Chem. Rev.* **1987**, *87*, 1401–1449.

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