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Base-Tuned Dehydrogenative and Borrowing Hydrogen Strategies for the Synthesis of Benzimidazoles and *N*-Alkylated Derivatives from *o*-Phenylenediamines and Alcohols Using a Cationic Mn^{I} Catalyst

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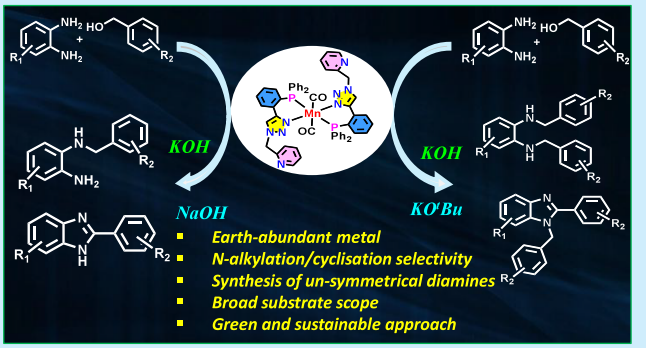
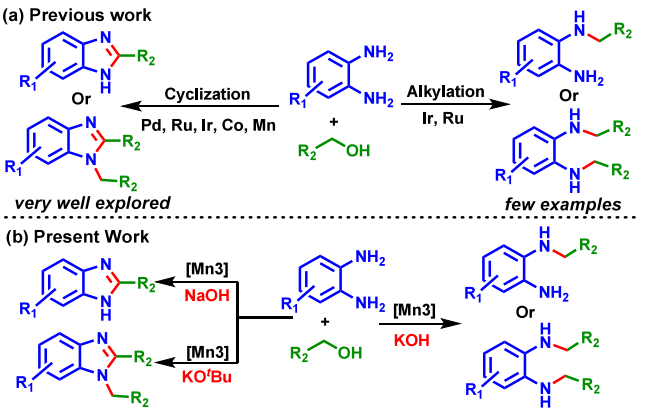
ABSTRACT: The synthesis of a neutral Mn^{I} complex, $[Mn(CO)_3Br(P^{\cap}N_3{}^{\cap}N)$-$\kappa^2$-*P,N*] (**Mn1**), and a cationic Mn^{I} complex, $[Mn(CO)_2(P^{\cap}N_3{}^{\cap}N)_2$-$\kappa^4$-*P,N,P,N*]$BF_4$ (**Mn3**), derived from phosphine- and pyridine-functionalized 1,2,3-triazole ligand *o*-$Ph_2P(C_6H_4)C(CH)$-1,2,3-$N_3(CH_2)$(Py) (**L**), referred to as "$P^{\cap}N_3{}^{\cap}N$", is described. The cationic complex **Mn3** was successfully applied as a catalyst in both base-tuned dehydrogenative and hydrogen borrowing strategies for the synthesis of benzimidazoles and *N*-alkylated derivatives from diamines and alcohols. Notably, this study represents the first example of a base-metal-catalyzed synthesis of mono-*N*-alkylated and unsymmetrical *N,N′*-dialkylated amines. A series of control experiments, complemented by density functional theory (DFT) calculations, provided mechanistic insights, indicating that the formation of a [Mn-H] intermediate constitutes the rate-limiting step in the catalytic cycle.



N-Alkylation[1] of *o*-phenylenediamine derivatives using alcohols represents a versatile transformation offering access to both *N*-alkylated diamines[2] and cyclized products,[3] such as benzimidazoles. This transformation generally proceeds via borrowing hydrogen (BH)[1c,4] or acceptorless dehydrogenative coupling (ADC) pathways[5] catalyzed by transition metals[6] and involving the oxidation of alcohols.[4a,7] The formation of benzimidazoles from *o*-phenylenediamine and alcohols is well-established[3a,c,8] and widely explored due to its synthetic utility and efficiency. In contrast, the selective synthesis of *N,N′*-alkylated diamines remains challenging, as cyclization to benzimidazoles often predominates. As a result, reports on direct *N*-alkylation of *o*-phenylenediamine using alcohols are relatively scarce, requiring careful tuning of reaction parameters to achieve selectivity. Traditionally, alkylated diamines are prepared using benzyl halides in the presence of base.[9] Liu and co-workers developed a diiridium catalyst for diamine alkylation with alcohols, but it favored benzimidazole formation with *o*-phenylenediamine.[10] Kempe reported an iridium-based catalyst for *N*-alkylation, though its substrate scope was narrow.[2a] Wang introduced a ruthenium-based heterogeneous catalyst that achieved selective alkylation with benzyl alcohols while suppressing benzimidazole formation,[2b] albeit requiring excess amine to ensure monoalkylation and avoid side products (Scheme 1). Overall, most catalytic systems rely on precious metals, such as Ir and Ru. More recently, Rit and co-workers employed NHC-based nickel and cobalt catalysts for the dialkylation of *o*-phenylenediamine; however, their systems were less effective for monoalkyla-

Scheme 1. Comparison of Present Work with Prior Reports



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tion.[2c,d] Manganese catalysts, in contrast, have been primarily applied to the synthesis of cyclized products,[3a,8b,11] and their potential in direct alkylation reactions remains underexplored. Notably, Kempe and co-workers demonstrated a manganese-catalyzed, base-switchable strategy enabling access to either *N*-alkylated amines or imines from the same alcohol−amine combination by modulating between BH and ADC pathways highlighting the critical influence of base in steering the reaction outcome.[12,13]

This work reports the application of the cationic Mn^{I} complex for the selective *N*-alkylation and benzimidazole synthesis from *o*-phenylenediamine and alcohols. The catalyst exhibits remarkable selectivity, enabling divergent product formation, either alkylated diamines or benzimidazoles, through simple modulation of the base and reaction conditions. The underlying catalytic mechanism was further elucidated through comprehensive density functional theory (DFT) calculations, providing insights into the electronic structure, metal−ligand bonding, and reactivity of the Mn^{I} complex.

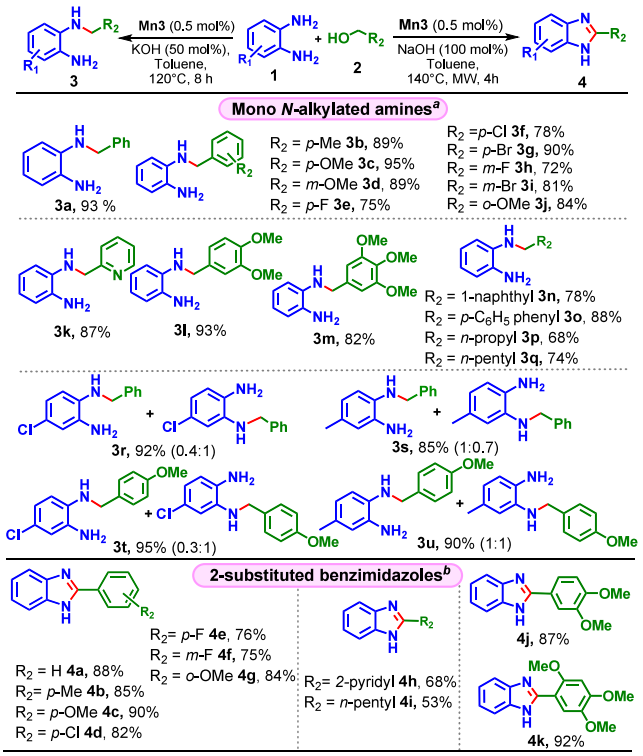
RESULTS AND DISCUSSION

Phosphine *o*-$Ph_2P(C_6H_4)C(CH)$-1,2,3-$N_3(CH_2)(Py)$ (**L**) ($P^{\frown}N_3{}^{\frown}N$) containing 1,2,3-triazoyl and pyridine functionalities was envisioned to form Mn^{I} complexes.[14] The reaction of this ligand with $Mn(CO)_5Br$ in dichloromethane at ambient temperature afforded the neutral complex $[Mn(CO)_3Br$-$(P^{\frown}N_3{}^{\frown}N)$-$\kappa^2$-*P,N*] (**Mn1**), wherein the phosphine and pyridine donors are chelated to the Mn^{I} center. Subsequent halide abstraction from complex **Mn1** with $AgBF_4$ in the presence of acetonitrile gave the cationic complex $[Mn(CO)_3(NCCH_3)(P^{\frown}N_3{}^{\frown}N)$-$\kappa^2$-*P,N*$]BF_4$ (**Mn2**). Heating complex **Mn2** with 1 equiv of ligand **L** in THF resulted in the formation of bis-ligated $[Mn(CO)_2(P^{\frown}N_3{}^{\frown}N)_2$-$\kappa^4$-*P,N,P,N*$]BF_4$ (**Mn3**), involving two *P,N*-chelating arms (Schemes S1−S3).

The catalytic activity of these complexes was evaluated in the *N*-alkylation of *o*-phenylenediamine (**1a**) with benzyl alcohol (**2a**), a transformation that offers access to either mono- or dialkylated diamines or cyclized benzimidazole derivatives (Table S3). Using complex **Mn1** (0.5 mol %) with KOH in toluene at 120 °C for 8 h resulted in 64% conversion with 84% selectivity for the mono-*N*-alkylated product **3a** (entry 1). In contrast, complex **Mn3** demonstrated significantly improved performance under identical conditions, achieving 98 and 95% selectivity for **3a**. Solvent screening revealed that toluene was superior, as other solvents such as acetonitrile, ^{t}amyl alcohol, and dioxane led to lower conversions and a higher prevalence of dialkylated **6a** (entries 6−8) or cyclized products. The influence of the base was also evaluated. No conversion was observed with K_3PO_4, while KO^{t}Bu provided high conversion (97%) but poor selectivity (54%), with major byproducts including the *N,N′*-dialkylated diamine and 1,2-substituted benzimidazole (entries 5 and 9). However, increasing NaOH to 1 equiv and extending the reaction time to 24 h improved the conversion to 72% with 64% selectivity for **4a** (entry 15). Further elevation of the reaction temperature to 140 °C significantly enhanced conversion and selectivity, yielding **4a** in 95% conversion and 93% selectivity (entry 16). Under microwave irradiation at 140 °C with NaOH (100 mol %), **4a** was efficiently obtained within 4 h (entry 17).

The optimized conditions were successfully applied to the mono-*N*-alkylation of diamines by using a broad range of alcohols (Table 1). Benzyl alcohols bearing electron-donating substituents (e.g., *p*-Me, *p*-OMe) afforded excellent yields,

Table 1. Substrate Scope of Mono-*N*-Alkylated Amines and 2-Substituted Benzimidazoles[a,b,c]



[a]Reaction conditions: Diamine **1** (0.5 mmol), alcohols **2** (0.55 mmol), KOH (50 mol %), **Mn3** (0.5 mol %), toluene (2 mL), 120 °C, 8 h, N_2 atm. [b]Diamine **1** (0.5 mmol), alcohols **2** (0.55 mmol), NaOH (100 mol %), **Mn3** (0.5 mol %), toluene (2 mL), 140 °C, microwave irradiation, 4 h. [c]All are isolated yields.

while those containing electron-withdrawing groups (*p*-F, *p*-Cl, or *p*-Br) also delivered good to excellent yields (>75%, **3b**, **3c** and **3e**−**3g**). *meta*-Substituted and heteroatom-containing alcohols also showed good reactivity (**3d**, **3h**−**3i**, and **3k**). Multisubstituted benzyl alcohols including **3l** and **3m** provided excellent yields (93 and 82%, respectively), and 2-naphthylmethanol also performed well, affording **3n** in 78% yield. Aliphatic alcohols such as 1-butanol and 1-hexanol also gave moderate conversions, affording **3p** (68%) and **3q** (74%), respectively. Substituted diamines bearing *p*-Cl and *p*-Me groups also showed high reactivity and selectivity, yielding over 85% alkylated products. The *p*-Cl-substituted diamine afforded regioisomers in differing ratios, whereas the *p*-Me derivative yielded nearly equal amounts of isomers (**3r**−**3u**). With the optimized conditions for cyclization in hand, a wide range of substituted benzyl alcohols was evaluated to probe the substrate scope. Benzyl alcohols bearing electron-donating, electron-withdrawing, and multiple substituents including methoxy groups at the *ortho-*, *meta-*, and *para*-positions readily underwent cyclization to furnish the corresponding 2-substituted benzimidazoles (**4a**−**4g**, **4j**, and **4k**) in good yields. Notably, 2-pyridinemethanol afforded benzimidazole **4h** in 68% yield. In addition, 1-hexanol also afforded compound **4i** in 53% yield.

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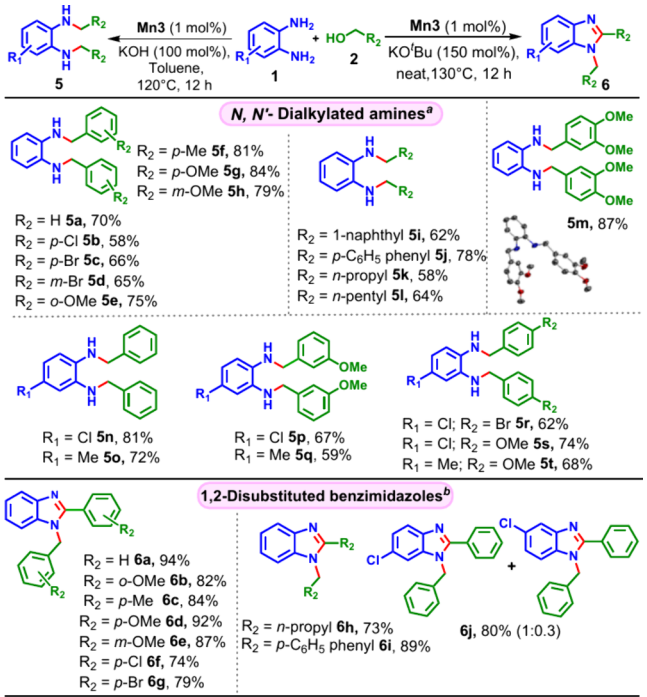
Org. Lett. 2025, 27, 8434−8439

Following the successful selective synthesis of mono-*N*-alkylated diamines and 2-substituted benzimidazoles via base-switchable acceptor-less dehydrogenative and borrowing hydrogen strategies, we next targeted the synthesis of *N*,*N*′-dialkylated diamines and 1,2-disubstituted benzimidazoles. Toward this goal, *o*-phenylenediamine was reacted with 2 equiv of benzyl alcohol under standard conditions (0.5 mol % complex **Mn3**, 50 mol % KOH, toluene, 120 °C, 8 h), affording *N*,*N*′-dialkylated diamines **5a** with 44% selectivity (Table S4, entry 1). Using KO^{t}Bu as the base increased the conversion to 95%, but with reduced selectivity: 24% for **5a** and 40% for 1,2-disubstituted benzimidazole **6a** (entry 2). Increasing the catalyst loading to 1 mol % improved the selectivity for **5a** within 12 h (entry 3), while elevating the base loading to 100 mol % afforded **5a** in 75% yield (entry 5). Attempts using other bases such as NaO^{t}Bu and KO^{t}Bu failed to yield **5a** selectively. Under neat conditions at 130 °C with 100 mol % KO^{t}Bu, a marked increase in the selectivity for **6a** was observed (entry 6). Strikingly, conducting the reaction in air with 150 mol % KO^{t}Bu under neat conditions afforded **6a** in 97% selectivity (entry 7).

Using the optimized conditions, a variety of *N*,*N*′-dialkylated amines were synthesized from substituted benzyl alcohols (Table 2). Benzyl alcohols bearing electron-donating groups (*p*-Me, *p*-OMe, and *m*-OMe) furnished high yields (>80%) of products **5f**−**5h**. Electron-withdrawing substituents (Cl and Br) at the *para*- and *meta*-positions also reacted efficiently, affording moderate yields (>58%, **5b**−**5d**). A naphthalene-substituted alcohol also was well-tolerated, providing **5i** in 62% yield. Notably, 1-butanol and 1-hexanol were well tolerated, yielding **5k** (58%) and **5l** (64%). Additionally, *o*-phenylenediamines bearing *p*-Me and *p*-Cl reacted smoothly with alcohols, delivering moderate to good yields (**5n**−**5t**). Overall, substrates with electron-donating substituents consistently gave higher yields compared to those with electron-withdrawing groups. The substrate scope was further extended to the synthesis of 1,2-disubstituted benzimidazoles. Benzyl alcohols bearing electron-donating groups (e.g., OMe and Me) at various positions gave excellent yields (>80%, **6b**−**6e**). Electron-withdrawing substituents, such as chloro and bromo, provided moderate yields (**6f** and **6g**). In the case of *p*-Cl-substituted diamine, a mixture of regioisomers was observed in a 1:0.3 ratio (**6j**). 1-Butanol also afforded 1,2-disubstituted benzimidazole **6h** in 73% yield.

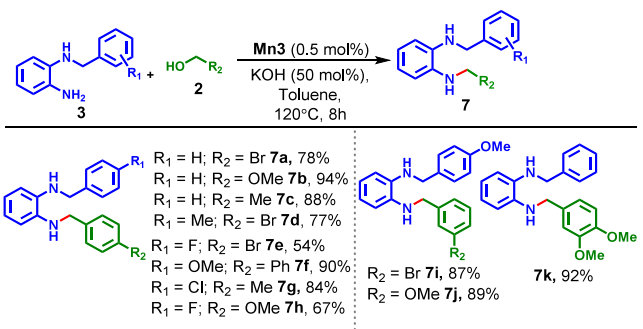
To date, there are no reported methods employing base-metal catalysts for the synthesis of unsymmetrically *N*,*N*′-dialkylated *o*-phenylenediamine derivatives, underscoring a critical gap in sustainable and cost-effective catalysis. The only known method is by Kempe and co-workers using an iridium-based catalyst with a limited substrate scope.[2a] Encouraged by this, monoalkylated amines (**3**) were subjected to further alkylation with various alcohols under the same conditions, affording a series of unsymmetrically dialkylated products (**7a**−**7k**) in high yields (Table 3).

Table 2. Substrate Scope of *N*,*N*′-Dialkylated Amines and 1,2-Substitued Benzimidazoles[a,b,c]



[a]Reaction conditions: Diamine **1** (0.5 mmol), alcohols **2** (1.2 mmol), KOH (100 mol %), **Mn3** (1 mol %), toluene (2 mL), 120 °C, 12 h, N_2 atm. [b]Diamine **1** (0.5 mmol), alcohols **2** (1.2 mmol), KO^{t}Bu (150 mol %), **Mn3** (1 mol %), neat, 130 °C, 12 h, open air. [c]All are isolated yields.

Table 3. Substrate Scope of Unsymmetrical *N*,*N*′-Dialkylated Products[a,b]



[a]Reaction conditions: **3** (0.5 mmol), alcohols **2** (0.55 mmol), KOH (50 mol %), **Mn3** (0.5 mol %), toluene (2 mL), 120°C, 8 h, N_2 atm. [b]All are isolated yields.

To gain deeper insight into the catalytic mechanism, a series of control experiments were performed (Scheme 2). Under the standard conditions for mono-*N*-alkylation, the addition of the radical scavenger TEMPO resulted in 84% conversion while the introduction of elemental mercury to probe the homogeneity of the catalyst led to 80% conversion (Scheme 2a,b). These results effectively rule out both a radical pathway and the involvement of a heterogeneous catalytic system. Under identical conditions, benzyl alcohol underwent partial dehydrogenation, yielding 30% benzaldehyde, as confirmed by GC−MS analysis (Figure S207), along with the release of hydrogen gas (Scheme 2c). *o*-Phenylenediamine failed to yield **3a** with benzaldehyde under identical conditions (Scheme 2d), indicating that the alcohol acts as the source of both hydride and carbonyl moieties. The reaction of **4a** with benzyl alcohol did not produce **6a**, indicating that **4a** does not lead to the formation of **6a** (Scheme 2e). GC−MS analysis after 6 h showed both mono- and dialkylated products, confirming that

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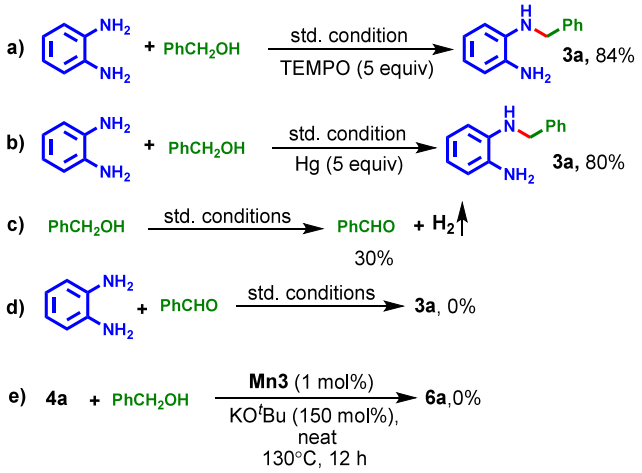
Org. Lett. 2025, 27, 8434−8439

Scheme 2. Control Experiments[a]

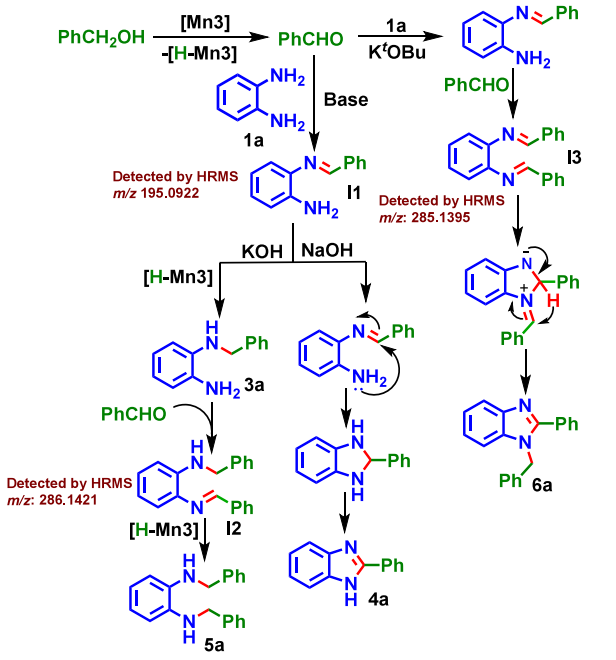


[a]Standard conditions: **Mn3** (0.5 mol %), KOH (50 mol %), toluene (2 mL), 120 °C, 8 h, N_2 atm.

dialkylation follows monoalkylation when 2 equiv of alcohol is used in the presence of KOH (Figure S210).

Based on experimental findings, a plausible mechanism for the formation of different products with different bases is shown in Scheme 3. All of the intermediates formed during the

Scheme 3. Plausible Mechanism



reaction were confirmed by GC−MS and HRMS analysis (Figures S208−S212). KOH, being a stronger base in organic media, enhances the rate of metal hydride formation and thereby promotes hydrogenation, whereas the weaker NaOH leads to a reduced hydride formation rate, favoring cyclization.

To better understand the energies of various steps involved in the reaction, density functional theory (DFT) calculations were carried out using the Gaussian16.C suite of programs employing the B3LYP-D3/def2-TZVP(PCM)//B3LYP-D3/LanL2DZ (Mn, P);6-31G*(rest atoms) level of theory at 298.13 K. The schematic mechanism adapted based on the experimental evidence gathered in this work and from earlier literature precedents[15] is depicted in Figure 1. The DFT

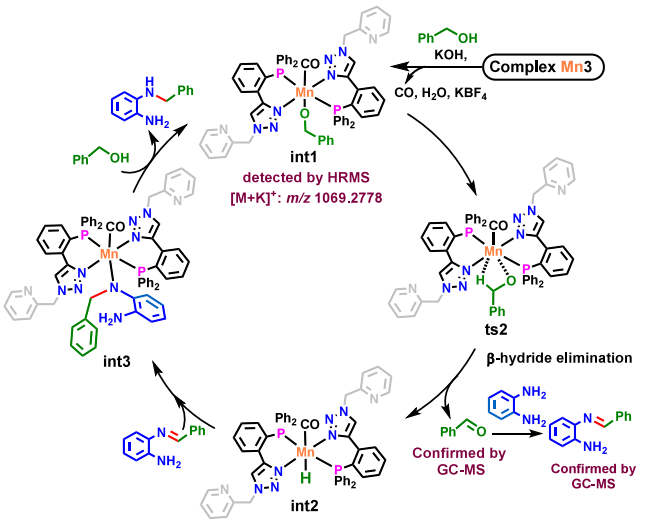


Figure 1. Proposed catalytic cycle for mono-*N*-alkylation of diamine

calculations were performed to understand the structure and bonding nature of the complex **Mn3**; the frontier orbitals corresponding to the d-based orbitals of Mn along with their energies are shown in Figure S215(b), reiterating low-spin Mn(I) with a $(d_{xy})^2(d_{yz})^2(d_{xz})^2$ configuration with a $t_{2g}-e_g$ gap of 3.99 eV. The d_z^2 orbital is significantly destabilized due to the interaction with the p orbital of the phosphorus ligand, reducing this gap as $d_x^2-y^2$ orbital is strongly destabilized (~6.18 eV). The optimized geometry of the catalyst (Figure S215(a)) is consistent with the X-ray geometry. (See Table S5 for comparison.)

We initiated our mechanistic investigation with complex **Mn3** as the precatalyst. The catalytic cycle commences with the dissociation of a CO ligand from complex **Mn3** via transition state **ts1**, with a calculated energy barrier of 85.5 kJ/mol. **ts1** leads to the formation of intermediate **int1**, characterized by the coordination of benzyl alkoxide to the manganese center, a process that is exothermic by −64.2 kJ/mol (Figure 2). This intermediate formation was also observed, upon addition of benzyl alcohol to complex **Mn3**, in the $^{31}P\{^1H\}$ NMR spectrum (Figure S213). The signal corresponding to complex **Mn3** diminishes, while a new peak emerges at 67.1 ppm, which is likely attributed to intermediate **int1**. Further confirmation of the formation of **int1** is supported by HRMS analysis (Figure S214).

Subsequently, *β*-hydride elimination occurs via transition state **ts2**, with an energy barrier of 98.6 kJ/mol, resulting in the formation of Mn−hydride species **int2** and the release of benzaldehyde. This step is expected to be rate-limiting with the competing CO dissociation step **ts1**. The formation of **int2** is mildly exothermic, with a relative energy of −0.9 kJ/mol compared with the starting complex. This is followed by a base-mediated condensation with amines, resulting in the formation of an imine intermediate. The in situ hydrogenation of the imine intermediate by the Mn−H species with the formation of **int3** (30.3 kJ/mol) via **ts3** with an energy barrier of 48.1 kJ/mol, along with another benzyl alcohol, leads to the formation of the dialkylation of diamine with an energy of −8.4 kJ/mol. Depending on the base and reaction conditions, the

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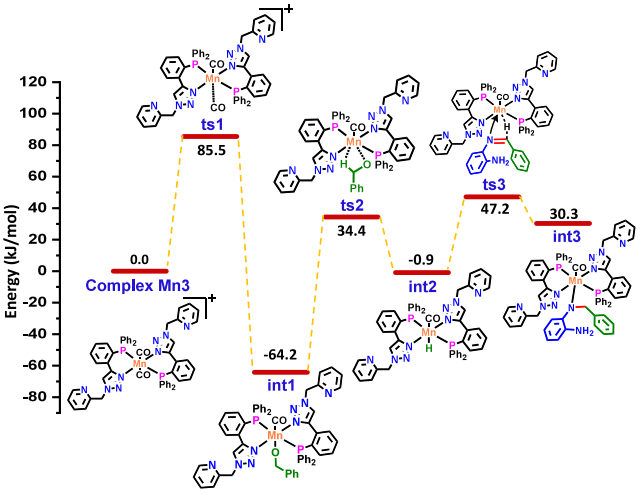

Figure 2. Computed potential energy profile diagram in solvent phase free energies (ΔG, kJ/mol) at the B3LYP-D3/def2-TZVP level of theory for reaction pathways of mono-*N*-alkylation with complex Mn3.

imine can undergo either hydrogenation or cyclization, as shown in Scheme 3. We have conducted a comparative thermodynamics study of all of the products formed during the catalytic cycle in the presence of different bases. The computed potential energy profiles, representing the free-energy changes, are provided in the Supporting Information (Figures S220 and S221).

In conclusion, this work demonstrates the development of a triazole-based *P*,*N*-type ligand-supported cationic Mn^{I} complex capable of promoting base-tunable transformations of *o*-phenylenediamines with alcohols. The system enables the selective formation of mono-*N*-alkylated, *N*,*N*′-dialkylated, and benzimidazole products, depending on the reaction conditions. This represents the first base-metal catalyst achieving all three product classes with high selectivity. The mechanistic insight provided by DFT calculations underscores the importance of Mn−H formation as the rate-determining step and offers a valuable framework for future catalyst design and functional group manipulation in green amine synthesis.

■ ASSOCIATED CONTENT

Data Availability Statement

The data underlying the study are available in the article and in its Supporting Information.

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.5c02197.

Experimental procedures; characterization data, ^{1}H, ^{13}C and ^{31}P NMR spectra, and X-ray crystal structures (PDF)

Accession Codes

Deposition Numbers 2455564−2455566 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via the joint Cambridge Crystallographic Data Centre (CCDC) and Fachinformationszentrum Karlsruhe Access Structures service.

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Notes

The authors declare no competing financial interest.

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