

Bis-Triazolylidenes of Manganese and Rhenium and Their Catalytic Application in N-Alkylation of Amines with Alcohols

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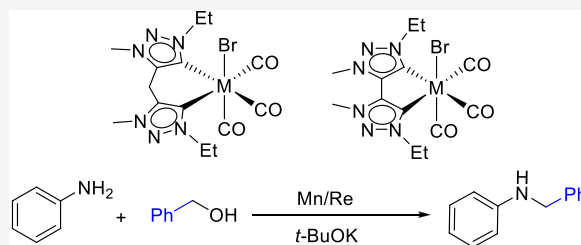


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ABSTRACT: A new family of air-stable Mn and Re complexes bearing bidentate bis(1,2,3-triazol-5-ylidene) ligands with the general formula $[M(\text{bis-triazolylidene})(\text{CO})_3\text{X}]$ ($M = \text{Mn}$ or Re ; $\text{X} = \text{Cl}$ or Br), containing a methylene linker or a direct link between the two triazolylidene ligands, is presented. All complexes have been applied as catalysts for the N-alkylation of anilines with benzylic alcohols. The Mn complex bearing a bis-triazolylidene with a methylene bridge between the two triazolylidene fragments was shown to be a highly efficient catalyst, affording the corresponding amine in 92% yield in the presence of a low base loading ($t\text{-BuOK}$, 0.1 equiv). Comparison between Mn complexes bearing imidazolium- and triazolium-derived N-heterocyclic carbene ligands showed that Mn triazolylidenes displayed higher catalytic activity when a low base loading was used.



INTRODUCTION

N-Alkylation of amines with alcohols via the borrowing hydrogen (BH) approach has emerged as an atom economical and waste-free strategy for producing N-alkylated amines.¹ A diverse range of catalytic systems have been developed for these transformations.² The traditional ones are based on precious metals, such as Ir,^{3–7} Ru,^{3,8–11} and Rh.¹² Due to their high cost, toxicity, and limited availability, numerous efforts have been dedicated to developing non-noble metal catalysts with Fe, Mn, Co, and Ni.^{13–16} Among these metals, Mn is tremendously attractive because it represents the third most abundant transition metal in the earth's crust and is an economical, nontoxic, and environmentally benign metal.^{17–19} Since the seminal works of Beller²⁰ and Milstein in 2016,²¹ using Mn pincer complexes in BH processes, the field of Mn catalysis has attracted a great deal of attention from the scientific community. However, a majority of the Mn catalytic systems developed so far are based on phosphine ligands.^{20–25}

With the aim of developing phosphine-free catalytic systems with cheap metals, our research team has recently focused on the preparation of active Mn catalysts using N-heterocyclic carbene ligands (NHCs).^{26–29} Recently, we disclosed the excellent catalytic efficiency of *fac*- $[\text{Mn}(\text{bis-NHC}^{\text{Me}})(\text{CO})_3\text{Br}]$, bearing a simple bidentate NHC in reduction reactions, namely, in hydrosilylation^{27–29} and in the electrocatalytic reduction of CO_2 .²⁶ Later, other authors showed the capability of this complex to efficiently catalyze the N-alkylation of anilines with alcohols,^{30a} the α -alkylation of ketones with alcohols,^{30b} and, more recently, the transformation of α,β -unsaturated ketones to α -methylated ketones using methanol.³¹ Apart from classical imidazolium-derived NHCs, we are also interested in the chemistry of manganese with mesoionic carbenes (MICs).^{32–35} MICs, especially those derived from

1,2,3-triazolylidenes, make up an interesting subclass of NHCs that have advanced to become a prominent class of ligands in catalysis.^{36–38} In many cases, their strong σ -donor and weak π -acceptor properties yield metal complexes with enhanced catalytic activities and stability.³⁸ Despite these interesting features, the chemistry and catalysis of Mn with MICs have remained elusive.^{35,36}

In this work, we report the synthesis and characterization of a new family of tricarbonyl Mn(I) complexes bearing bis(1,2,3-triazol-5-ylidene) ligands and their catalytic performance in the N-alkylation of anilines with alcohols. In addition, related Re(I) triazolylidene complexes have been prepared and applied in this catalytic process to compare the activity of Mn and Re complexes. We have investigated the effect on catalysis of Mn and Re complexes (i) having a methylene bridge and a direct bond between the two triazolylidene fragments and (ii) bearing imidazolium- and triazolium-derived NHCs.

RESULTS AND DISCUSSION

Synthesis and Characterization of Mn and Re Complexes. C4-linked bis-triazole **I** was prepared according to the well-established copper-catalyzed click $[3 + 2]$ cycloaddition reaction previously described in the literature.³⁹ Compound **I** was then methylated with methyl triflate and subjected to anion exchange with tetra-*n*-butylammonium

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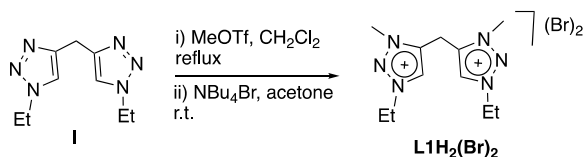
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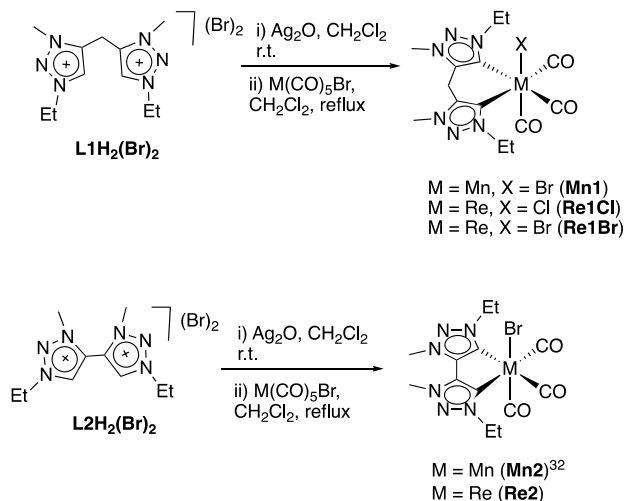
bromide, following the same procedure previously described by us for $L2H_2(Br)_2$,³⁴ to afford the corresponding bromide salt $L1H_2(Br)_2$ in good yield (Scheme 1). Compound $L1H_2(Br)_2$ was characterized by 1H and ^{13}C nuclear magnetic resonance (NMR) spectroscopy, mass spectrometry (ESI-HRMS), and elemental analysis.

Scheme 1. Synthesis of Bis-Triazolium Salt $L1H_2(Br)_2$



Coordination of pro-ligands $L1H_2(Br)_2$ and $L2H_2(Br)_2$ to manganese and rhenium was investigated using the Ag transmetalation route. Transmetalation involving the formation of triazolylidene silver(I) intermediates is a well-established procedure for the synthesis of triazolylidenes of late transition metals.^{38–40} This methodology has been previously utilized by Albrecht and co-workers for the coordination of triazolium triflate salt $L1H_2(OTf)_2$ to Ir³⁹ and by us for the synthesis of complex **Mn2**.³² The Ag transmetalation procedure allowed the isolation of new bis-triazolylidene complexes **Mn1**, **Re1**, and **Re2** as crystalline solids in moderate yields (Scheme 2).

Scheme 2. Synthesis of Mn and Re Complexes Bearing Triazolylidene Ligands



All complexes have been fully characterized by NMR and IR spectroscopy, elemental analysis, and, in the case of complex **Mn1**, single-crystal X-ray diffraction studies (Figure 1). The coordination of $L1H_2(Br)_2$ and $L2H_2(Br)_2$ was corroborated by the disappearance of the signals corresponding to the triazolium protons at 9.00 ppm (for **L1**) and 9.43 ppm (for **L2**) in 1H NMR spectra and the appearance of the characteristic resonance of the carbene carbon between 164 and 174 ppm in the ^{13}C NMR spectra. Consistent with the proposed structures, the IR spectra of all complexes displayed the typical patterns for *fac*-tricarbonyl ligands.^{25,26,29,33} As expected, the values of the symmetrical CO stretching vibrations of **Mn1** and **Re1** appear at wavenumbers (1995 and 1999 cm^{-1} , respectively) lower than those reported for the corresponding imidazole-2-ylidene analogous *fac*-[Mn(bis-

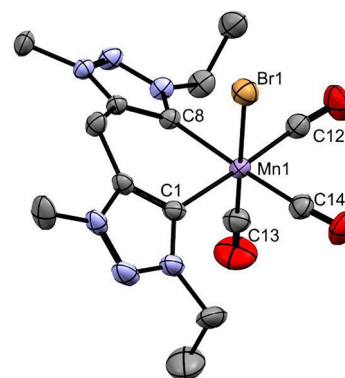


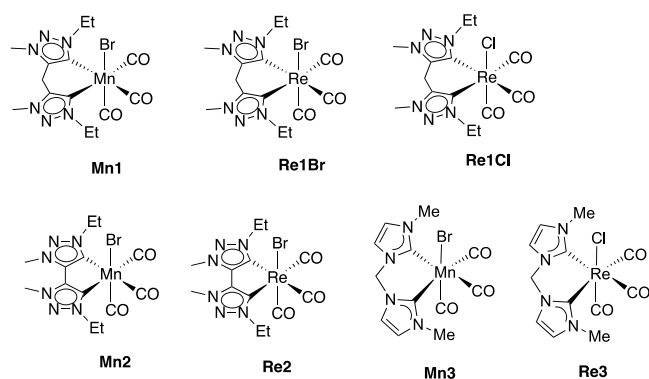
Figure 1. ORTEP diagram of complex **Mn1** using 50% probability-level ellipsoids. Selected bond lengths: Mn1–Br1, 2.5749(7) Å; Mn1–C1, 2.065(4) Å; Mn1–C8, 2.057(3) Å; Mn1–CCO, between 1.770(4) and 1.830(4) Å.

$NHC^{Me})(CO)_3Br]$ (2004 cm^{-1})²⁵ and *fac*-[Re(bis- $NHC^{Me})(CO)_3Cl]$ (2006 cm^{-1}),⁴¹ corroborating the stronger donor capacity of the triazolylidene ligands. Related rhenium(I) tricarbonyl complexes containing combinations of pyridine, triazole, and triazolylidene ligands have been recently reported by Sarkar and co-workers.⁴²

It is worth mentioning that methylene-bridged bis-triazolium salts have been shown to undergo significant structural changes and chemical transformations under metalation conditions with silver oxide.⁴³ An elegant work reported by Sarkar and co-workers described the unexpected formation of a new bis-mesoionic carbene ligand, obtained through activation of the methylene protons of the CH_2 linker when a bis-triazolium salt was treated with Ag_2O .⁴³ Intrigued by this work, we decided to isolate the Ag-bis-triazolylidene complex generated by reaction of $L1H_2(Br)_2$ with Ag_2O under the conditions used in the synthesis of **Mn1**. Interestingly, we confirmed that the major product obtained in this reaction corresponds to the expected Ag-bis-triazolylidene adduct (Figures S16 and S17). However, the formation of a [triazolium][$AgBr_2$] compound, as a minor product, formed by methylene bridge breaking was detected, indicating that activation of the methylene bridge protons occurs under these conditions (Figure S18).

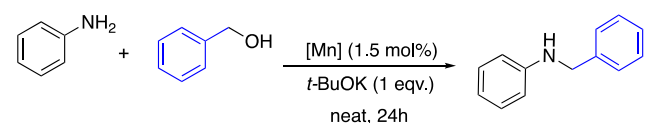
The molecular structure of bis-triazolylidene **Mn1** was unequivocally evidenced by X-ray diffraction studies (Figure 1). Selected bond distances are listed in the corresponding figure caption. The geometry around the Mn(I) center is that of a slightly distorted octahedron, containing a chelating ditriazolylidene, one Br, and *fac*-carbonyl ligands in the coordination sphere. The chelating ditriazolylidene has a bite angle of 84.25(14)°, similar to that found in an iridium complex of this ligand.⁴⁰ The Mn–Br bond length is 2.5749(7) Å, and the Mn–C_{CO} distances vary between 1.770(4) and 1.830(4) Å. The dihedral angle between the two triazolylidene rings is 33.50(18)°, reflecting a twisted backbone of the ligand as expected due to the presence of the methylene spacer in the ligand structure.

With these complexes in hand, we investigated their catalytic application in the N-alkylation of amines with alcohols, using aniline and benzyl alcohol as model substrates. Initially, for the sake of comparison, we evaluated the performance of complexes depicted in Chart 1 under catalytic conditions similar to those reported by Ke and co-workers using [Mn(bis- $NHC^{Me})(CO)_3Br]$ (**Mn3**),³⁰ which we used as a benchmark. In addition, we also explored the activity of Re bis-NHC

Chart 1. Mn and Re Complexes Applied as Catalysts for the N-Alkylation of Aniline with Benzyl Alcohol

complex **Re3** to compare the efficiency of imidazolium- and triazolium-derived NHC complexes (Chart 1). It must be noted that Re-NHC complexes have not been previously investigated in this reaction, although BH processes catalyzed by other Re compounds have been recently described in the literature.^{44–46}

As shown in Table 1, when the reactions were performed at 50 °C in the presence of 1 equiv of *t*-BuOK and 1.5 mol %

Table 1. Screening of the Catalytic Activity of Bis-Imidazolylidenes and Bis-Triazolylidenes of Mn and Re in the N-Alkylation of Aniline with Benzyl Alcohol at 50 and 100 °C^a

| entry | complex | T (°C) | η (%) ^b |
|-------|------------------------|--------|-------------------------|
| 1 | Mn1 | 50 | 42 |
| 2 | Mn2 | 50 | <15 |
| 3 | Mn3 | 50 | >99 |
| 4 | Re1Br | 50 | <14 |
| 5 | Re1Cl | 50 | <3 |
| 6 | Re2 | 50 | 0 |
| 7 | Re3 | 50 | 0 |
| 8 | Mn1 | 100 | >99 |
| 9 | Mn2 | 100 | 45 |
| 10 | Mn3 | 100 | >99 |
| 11 | Re1Br | 100 | >99 |
| 12 | Re1Cl | 100 | 81 |
| 13 | Re2 | 100 | 63 |
| 14 | Re3 | 100 | 79 |
| 15 | Mn(CO) ₅ Br | 100 | <12 |
| 16 | Re(CO) ₅ Br | 100 | 39 |
| 17 | – | 100 | <5 |

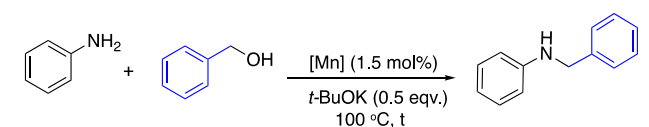
^aReaction conditions: aniline (0.5 mmol), benzyl alcohol (0.75 mmol), *t*-BuOK (1 equiv), catalyst (1.5 mol %), neat conditions, 24 h.

^bYields determined by GC using 1,3,5-trimethoxybenzene as the internal standard.

catalyst for 24 h, **Mn3** bearing the imidazolium-based NHC reached full conversion to the corresponding amine, while MIC complex **Mn1** gave an only 42% yield; no formation of imine was detected (Table 1, entries 3 and 1). Interestingly, under these conditions, the manganese complex bearing two triazolylidene ligands directly bonded (**Mn2**) was inactive

(Table 1, entry 2), indicating that the presence of a methylene bridge between the two rings is crucial for the activity of the Mn complexes. Moreover, at 50 °C, all of the Re complexes tested, **Re1–Re3**, were inactive (Table 1, entries 4–7). When the temperature of the reaction was increased to 100 °C, the activity of the Mn and Re complexes increased (Table 1, entries 8–14). Interesting trends can be observed. (i) Mn and Re complexes bearing the bis-triazolylidene ligand with a methylene bridge between the two rings, **Mn1** and **Re1Br**, yielded quantitative conversion to the corresponding amine (Table 1, entries 8 and 11, respectively), while the corresponding complexes containing the two triazolylidene rings directly bonded were less active [**Mn2** and **Re2** afforded 45% and 63% yields, respectively]. (ii) As expected, the Re complex bearing Br instead of Cl, **Re1Br** versus **Re1Cl**, afforded a slightly higher yield (Table 1, entries 11 and 12, respectively). (iii) At 100 °C, both **Mn1** and **Mn3** complexes bearing triazolylidene and imidazolylidene ligands gave full conversion to the corresponding amine (Table 1, entries 8 and 10, respectively), while for rhenium, the complex containing the triazolylidene ligand displayed activity higher than that of the analogous imidazolylidene complex [**Re1Br** and **Re3** (Table 1, entries 11 and 14, respectively)]. It was also confirmed that the presence of the NHC ligands is crucial for the catalytic efficiency of these complexes, because Mn(CO)₅Br and Re(CO)₅Br displayed very low reactivities (Table 1, entries 15 and 16, respectively). In addition, no catalytic reaction occurred in the absence of a catalyst (Table 1, entry 17).

Taking into consideration these preliminary results and having in mind the importance of reducing the base loading in BH reactions, we decided to explore the reactivity of Mn and Re NHC complexes using a smaller amount of base (0.5 equiv). The results are summarized in Table 2. Interestingly, we observed that under these conditions, **Mn1** afforded a quantitative amount of amine in 2 h (Table 2, entry 1). The

Table 2. Screening of the Catalytic Activity of Bis-Imidazolylidenes and Bis-Triazolylidenes of Mn and Re in the N-Alkylation of Aniline with Benzyl Alcohol Using 0.5 equiv of *t*-BuOK at 100 °C^a

| entry | complex | time (h) | η (%) ^b |
|-------|--------------|----------|-------------------------|
| 1 | Mn1 | 2 | >99 |
| 2 | Mn2 | 2 | 22 |
| 3 | | 24 | 25 |
| 4 | Mn3 | 2 | 26 |
| 5 | | 24 | 38 |
| 6 | Re1Br | 2 | <5 |
| 7 | | 24 | <15 |
| 8 | Re2 | 2 | <5 |
| 9 | | 24 | <15 |
| 10 | Re3 | 2 | <5 |
| 11 | | 24 | <11 |

^aReaction conditions: aniline (0.5 mmol), benzyl alcohol (0.75 mmol), *t*-BuOK (0.5 equiv), catalyst (1.5 mol %), neat conditions.

^bYields determined by GC using 1,3,5-trimethoxybenzene as the internal standard.

kinetic profile of the reaction catalyzed by **Mn1** (Figure S30) showed no induction period; the reaction reached a 62% yield of the amine in the first 15 min of reaction. In comparison, **Mn3** afforded an only 26% yield of the corresponding amine under similar reaction conditions, reaching a 38% yield after reaction for 24 h; formation of byproducts was not detected by GC (Table 2, entries 4 and 5, and Figure S31). Under these catalytic conditions, **Mn2** afforded an only 25% yield of the amine, and formation of trace amounts of the corresponding imine was detected by GC (Figures S22 and S23). All rhenium complexes, **Re1Br**, **Re2**, and **Re3**, were rather inactive in the BH reaction when the amount of base was decreased from 1 to 0.5 equiv [in all cases, traces of imine were formed (Figures S26–S29)].

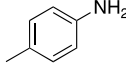
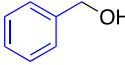
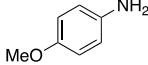
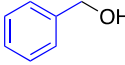
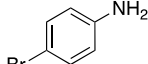
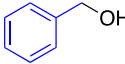
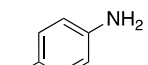
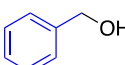
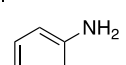
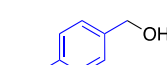
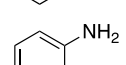
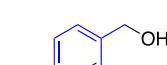
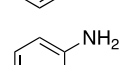
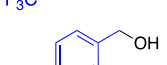
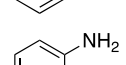
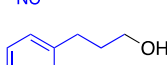
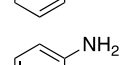
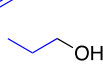
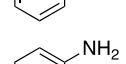
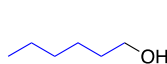
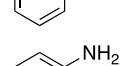
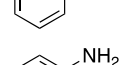
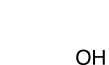
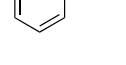
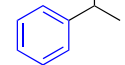
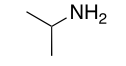
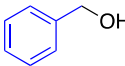
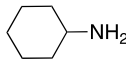
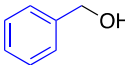
Encouraged by the results obtained using **Mn1** as a catalyst for the N-alkylation of aniline with benzyl alcohol, we decided to optimize the reaction conditions by exploring the effect of solvents in the catalytic reaction. The reaction did not work when acetonitrile was used as a solvent, but a high yield (87%) was obtained using toluene (Table S1). Nevertheless, neat conditions were the best choice. We also investigated the catalytic activity of **Mn1** using different types of bases, such as NaOH, KOH, K₂CO₃, and Cs₂CO₃, but in all cases, lower yields of the corresponding amine were obtained compared to that with *t*-BuOK (Table S1). Finally, we investigated the effect of further decreasing the amount of base. Gratifyingly, we found that **Mn1** can catalyze the N-alkylation of aniline with benzyl alcohol using 0.1 equiv of base, if the amount of catalyst and benzyl alcohol is increased [2 mol % **Mn1** and 2.5 equiv of alcohol (Table S2)], affording a 92% yield of the amine in 16 h.

Finally, as shown in Table 3, the scope of the reaction mediated by **Mn1**, using the optimized conditions of Table 2 (1.5 mol % **Mn1** and 0.5 equiv of *t*-BuOK, at 100 °C, during 2 h), was explored using several amines and alcohols. Functional groups such as Me, OMe, Br, I, and CF₃ were well tolerated (Table 3, entries 1–6), while the reaction of aniline with 4-cyanobenzyl alcohol afforded an only 12% yield of the corresponding amine (Table 3, entry 7). The reaction can also be performed using aliphatic alcohols; excellent yields were obtained using 3-phenyl-1-propanol, 1-propanol, and 1-hexanol (Table 3, entries 8–10, respectively). In contrast, a very low yield of the corresponding amine was obtained using MeOH [16% yield (Table 3, entry 11)]. In addition, the secondary alcohol 1-phenylethanol afforded an only 23% yield of the amine (Table 3, entry 12). No reaction was observed using aliphatic amines such as isopropylamine and cyclohexylamine, which represents a limitation of our catalytic system; the starting materials were recovered intact (Table 3, entries 13 and 14). Reaction of the primary aliphatic amine dodecylamine with benzyl alcohol afforded a 21% yield of the alkylated amine (Table 3, entry 15).

CONCLUSIONS

A new family of Mn(I) and Re(I) tricarbonyl complexes bearing bis-triazolyldiene ligands have been prepared and fully characterized. These complexes have shown interesting reactivity in the catalytic N-alkylation of anilines with benzyl alcohols. From the preliminary screening experiments, several conclusions can be reached. (i) Complex **Mn1** bearing a bis-triazolyldiene displayed an activity higher than that of the related imidazolium-derived NHC complex **Mn3** when the reaction was carried out with 0.5 equiv of base at 100 °C. (ii) A

Table 3. N-Alkylation of Functionalized Amines and Alcohols Catalyzed by **Mn1**^a

| Entry | Amine | Alcohol | η (%) ^b |
|-------|---|---|--------------------|
| 1 |  |  | 94 |
| 2 |  |  | 83 |
| 3 |  |  | 93 |
| 4 |  |  | 98 |
| 5 |  |  | 90 |
| 6 |  |  | 95 |
| 7 |  |  | 12 |
| 8 |  |  | 91 |
| 9 |  |  | >99 |
| 10 |  |  | 95 |
| 11 |  | MeOH | 16 |
| 12 |  |  | 23 |
| 13 |  |  | 0 |
| 14 |  |  | 0 |
| 15 |  |  | 21 |

^aReaction conditions: aniline (0.5 mmol), benzyl alcohol (0.75 mmol), *t*-BuOK (50 mol %), **Mn1** (1.5 mol %), neat conditions, 100 °C, 2 h. ^bYields determined by ¹H NMR using 1,3,5-trimethoxybenzene as the internal standard.

significantly higher activity of the methylene-bridged bis-triazolyldienes of Mn and Re was obtained compared to those of related complexes with the two triazolyldiene ligands directly bonded (**Mn1** vs **Mn2**). (iii) The activity of **Mn1** was

higher than that of its **Re1** counterpart. Further studies to consolidate the observed trends are ongoing in our laboratories. In addition, mechanistic studies are being carried out, aiming to rationalize the structure–activity correlation.

EXPERIMENTAL SECTION

General Considerations. Syntheses of ligands and metal complexes were performed under a nitrogen atmosphere in dried and degassed solvents using standard Schlenk techniques. Solvents were purified using appropriate drying agents. Deuterated solvents were degassed and stored over molecular sieves. All other reagents were purchased from commercial suppliers and used without further purification. Catalytic experiments were carried out under a nitrogen atmosphere. Elemental analysis was performed in our laboratories at ITQB-NOVA by C. Almeida. ESI-HRMS data were provided by the Mass Spectrometry Unit (UniMS), ITQB/IBET. Infrared spectra were recorded on samples as KBr pellets using a Bruker IFS 66/S ATR-FTIR spectrometer. The preparation of compounds **1**, **L2H₂(Br)₂**, **Mn2**, **Mn3**, and **Re3** was performed following the procedures described in the literature.^{32,26,40} ¹H and ¹³C NMR spectra were recorded on a Bruker Avance III 400 MHz spectrometer. The chemical shifts are expressed as δ (parts per million) relative to residual solvent signals, and J values are given in hertz.

Synthesis and Characterization of L1H₂(Br)₂. In an ampule, ditiatriazole **1** (0.250 g, 1.21 mmol) was dissolved in dry dichloromethane (10 mL), and methyl trifluoromethanesulfonate (0.53 mL, 4.83 mmol) was added at 0 °C. The mixture was then heated to 50 °C and stirred for 16 h. After the mixture had cooled to room temperature, diethyl ether was added to the mixture to yield a beige precipitate that was collected by filtration and dried under vacuum. The residue was redissolved in a minimum amount of acetone (5 mL) and treated with tetra-*n*-butylammonium bromide (1.34 g, 4.15 mmol). After the mixture had been stirred for 10 min, **L1H₂(Br)₂** precipitated from the solution. The solid was isolated by filtration and dried under vacuum to give a beige hygroscopic pure sample of **L1H₂(Br)₂** (0.350 g, 73% yield). ¹H NMR (400 MHz, DMSO-*d*₆): δ_{H} 9.00 (s, 2H, CH_{trz}), 4.85 (s, 2H, CH_{2linker}), 4.65 (q, ³J_{HH} = 7.3 Hz, 4H, NCH₂CH₃), 4.30 (s, 6H, NCH₃), 1.54 (t, ³J_{HH} = 7.3 Hz, 6H, NCH₂CH₃). ¹³C{¹H} NMR (100 MHz, DMSO-*d*₆): δ_{C} 137.27 (C_{trz}-NCH₃), 129.26 (CH_{trz}), 48.85 (C_{trz}-NCH₂CH₃), 38.09 (C_{trz}-NCH₃), 17.99 (C_{trz}-CH_{2linker}), 14.06 (C_{trz}-NCH₂CH₃). ESI-HRMS (m/z): 235.1662, calcd for C₁₁H₁₉N₆ [M - 2Br - H]⁺ 235.1671, and 118.0867, calcd for C₁₁H₁₉N₆ [M - 2Br]²⁺ 118.0874. Anal. Calcd for C₁₁H₂₀Br₂N₆: C, 33.35; H, 5.09; N, 21.22. Found: C, 33.71; H, 5.41; N, 20.88.

General Procedure for the Synthesis of Complexes Mn1, Re1, and Re2. The appropriate pro-ligand **L1H₂(Br)₂** or **L2H₂(Br)₂** (0.50 mmol) was dissolved in dry dichloromethane; Ag₂O (0.75 mmol) was added, and the mixture was stirred for 4 h at room temperature. Then, the corresponding metal precursor [M(CO)₃X, where M = Mn or Re and X = Cl or Br] was added, and the mixture was heated under reflux for 72 h. After cooling to room temperature, the solution was filtered through a pad of Celite, and the solution was concentrated to dryness. The remaining residue was washed with Et₂O (3 × 15 mL) to yield the corresponding Mn and Re complexes as pure solids.

Characterization of Mn1. The yellow crystalline solid was isolated from CH₂Cl₂/hexane recrystallization. Isolated yield of **Mn1**: 0.122 g (54% yield). ¹H NMR (400 MHz, DMSO-*d*₆): δ_{H} 4.78–4.72 (q, ³J_{HH} = 7.3 Hz, 4H, NCH₂CH₃), 4.32 (d, ²J_{HH} = 18.0 Hz, 1H, CH_{2linker}), 4.22 (s, 3H, NCH₃), 4.17 (s, 3H, NCH₃), 4.10 (d, ²J_{HH} = 18.4 Hz, 1H, CH_{2linker}), 1.59 (t, ³J_{HH} = 7.2 Hz, 3H, NCH₂CH₃), 1.54 (t, ³J_{HH} = 7.2 Hz, 3H, NCH₂CH₃). ¹³C{¹H} NMR (100 MHz, DMSO-*d*₆): δ_{C} 221.36 (CO), 217.51 (CO), 165.31 (C_{carbene}-Mn), 142.10 (C_{trz}-NCH₃), 48.89 and 47.77 (C_{trz}-NCH₂CH₃), 36.11 (C_{trz}-NCH₃), 21.10 (C_{trz}-CH_{2linker}), 15.79 (C_{trz}-NCH₂CH₃). Selected IR data (KBr): ν (CO) 1995 s, 1908 s, 1884 s cm⁻¹. Anal. Calcd for C₁₄H₁₈BrMnN₆O₃: C, 37.11; H, 4.00; N, 18.54. Found: C, 37.00; H, 4.25; N, 18.50.

Characterization of Re1Cl. The white crystalline solid was isolated from CH₂Cl₂/hexane recrystallization. Isolated yield of **Re1Cl**: 0.067 g (25% yield). ¹H NMR (400 MHz, DMSO-*d*₆): δ_{H} 4.70–4.58 (m, 4H, NCH₂CH₃), 4.26 (d, ²J_{HH} = 18.0 Hz, 1H, CH_{2linker}), 4.18 (s, 6H, NCH₃), 4.06 (d, ²J_{HH} = 18.3 Hz, 1H, CH_{2linker}), 1.52 (t, ³J_{HH} = 7.3 Hz, 6H, NCH₂CH₃). ¹³C{¹H} NMR (100 MHz, DMSO-*d*₆): δ_{C} 198.50 (CO), 194.80 (CO), 164.39 (C_{carbene}-Re), 142.47 (C_{trz}-NCH₃), 48.55 (C_{trz}-NCH₂CH₃), 36.18 (C_{trz}-NCH₃), 21.42 (C_{trz}-CH_{2linker}), 15.83 (C_{trz}-NCH₂CH₃). Selected IR data (KBr): ν (CO) 1999 s, 1877 s, 1864 s cm⁻¹. Anal. Calcd for C₁₄H₁₈ClN₆O₃Re: C, 31.14; H, 3.36; N, 15.56. Found: C, 30.80; H, 3.51; N, 15.29.

Characterization of Re1Br. The beige crystalline solid was isolated from CH₂Cl₂/hexane recrystallization. Isolated yield of **Re1Br**: 0.222 g (76% yield). ¹H NMR (400 MHz, DMSO-*d*₆): δ_{H} 4.70–4.61 (m, 4H, NCH₂CH₃), 4.27 (d, ²J_{HH} = 18.0 Hz, 1H, CH_{2linker}), 4.18 (s, 6H, NCH₃), 4.08 (d, ²J_{HH} = 18.0 Hz, 1H, CH_{2linker}), 1.52 (t, ³J_{HH} = 7.3 Hz, 6H, NCH₂CH₃). ¹³C{¹H} NMR (100 MHz, DMSO-*d*₆): δ_{C} 197.59 (CO), 194.20 (CO), 162.02 (C_{carbene}-Re), 142.53 (C_{trz}-NCH₃), 48.68 (C_{trz}-NCH₂CH₃), 36.22 (C_{trz}-NCH₃), 21.53 (C_{trz}-CH_{2linker}), 15.83 (C_{trz}-NCH₂CH₃). Selected IR data (KBr): ν (CO) 1990 s, 1876 s, 1862 s cm⁻¹. Anal. Calcd for C₁₄H₁₈BrN₆O₃Re: C, 28.77; H, 3.10; N, 14.38. Found: C, 28.42; H, 3.22; N, 14.63.

Characterization of Re2. The beige crystalline solid was isolated from CH₂Cl₂/hexane recrystallization. Isolated yield of **Re2**: 0.120 g (42% yield). ¹H NMR (400 MHz, DMSO-*d*₆): δ_{H} 4.64–4.57 (m, 4H, NCH₂CH₃), 4.53 (s, 6H, NCH₃), 1.54 (t, ³J_{HH} = 7.1 Hz, 6H, NCH₂CH₃). ¹³C{¹H} NMR (100 MHz, DMSO-*d*₆): δ_{C} 198.87 (CO), 189.84 (CO), 174.29 (C_{carbene}-Re), 143.62 (C_{trz}-NCH₃), 48.82 (C_{trz}-NCH₂CH₃), 39.43 (C_{trz}-NCH₃), 15.83 (C_{trz}-NCH₂CH₃). Selected IR data (KBr): ν (CO) 1999 s, 1892 s, 1858 s cm⁻¹. Anal. Calcd for C₁₃H₁₆BrN₆O₃Re: C, 27.37; H, 2.83; N, 14.73. Found: C, 27.01; H, 2.78; N, 14.78.

General Procedure for the Catalytic N-Alkylation of Amines with Alcohols. The samples were typically prepared as follows. Manganese or rhenium complexes, *t*-BuOK, amine, and alcohol were introduced into a small Schlenk tube (10 mL) under a nitrogen atmosphere, which was closed with a screw-tap, and the reaction mixture was stirred and heated to the appropriate temperature. After the desired time, the reaction mixture was analyzed by GC-FID using 1,3,5-trimethoxybenzene as the internal standard. The identity of the N-alkylated amine was assessed by comparison with a commercially available pure sample. In the case of the scope of the reaction with functionalized anilines and alcohols, the reaction mixture was analyzed by ¹H NMR using 1,3,5-trimethoxybenzene as the internal standard.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.organomet.3c00046>.

¹H and ¹³C NMR spectra of all compounds, IR and HRMS spectra, X-ray experimental details and molecular structure of [triazolium][AgBr₂], catalytic time conversion profiles, and optimization of catalytic reactions (PDF)

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The authors declare no competing financial interest.

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