Methylene-Linked Bis-NHC Half-Sandwich Ruthenium Complexes: Binding of Small Molecules and Catalysis toward Ketone Transfer Hydrogenation

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ABSTRACT: The complex [Cp*RuCl(COD)] reacts with LH2Cl (L = bis(3-methylimidazol-2-ylidene)) and LiBu4 in tetrahydrofuran at 65 °C furnishing the bis-carbene derivative [Cp*RuCl(L)] (2). This compound reacts with NaBPh4 in MeOH under dinitrogen to yield the labile dinitrogen-bridged complex [{[Cp*Ru(L)]2(μ-N2)}[BPh4]] (4). The dinitrogen ligand in 4 is readily replaced by a series of donor molecules leading to the corresponding cationic complexes [Cp*Ru(X)(L)][BPh4] (X = MeCN 3, H, C6H6 6, CH2CH2COOMe 8b, CHPh 9). Attempts to recrystallize 4 from MeNO2/EtOH solutions led to the isolation of the nitrosyl derivative [Cp*Ru(NO)(L)][BPh4] (5), which was structurally characterized. The allenylidene complex [Cp*Ru(C≡C≡C=CPh3)(L)][BPh4] (10) was also obtained, and it was prepared by reaction of 2 with HC≡CC(OH)Ph2 and NaBPh4 in MeOH at 60 °C. Complexes 3, 4, and 6 are efficient catalyst precursors for the transfer hydrogenation of a broad range of ketones. The dihydrogen complex 6 has proven particularly effective, reaching TOF values up to 455 h⁻¹ at catalyst loadings of 0.1% mol, with a high functional group tolerance on the reduction of a broad scope of aryl and aliphatic ketones to yield the corresponding alcohols.

INTRODUCTION

The catalytic transfer hydrogenation (TH) of carbonyl groups to afford their corresponding alcohols is considered a useful synthetic tool to produce valuable building blocks for the pharmaceutical industry.1−3 This methodology has an advantage in the use of alcohols,4 water,5 or formic acid6 instead of molecular hydrogen or metal hydrides as sources of the hydrogen atoms transferred in the reaction. Catalytic TH using transition metal complexes has received a great deal of attention due to its selectivity, efficiency, safety, broad scope, and compatibility with Green Chemistry principles. Homogeneous complexes based on transition metals such as Ir,7−9 Ru,8a or Rh10 are often used as catalysts for TH.1 However, the development of more efficient and selective transfer hydrogenation catalysts is still in demand. Among them, ruthenium complexes possess higher activity, selectivity, and cheaper cost in comparison to those of rhodium or iridium.10

NHC ligands have been successfully used as ancillary ligands in the design and synthesis of homogeneous catalysts.11 These ligands are considered an alternative to phosphine ligands due to their stronger sigma-donor properties that confer a greater stability to the corresponding metallic complexes, and facilitate the modulation of their stereoelectronic properties.12 Chelation is a strategy used to stabilize the M-NHC bond and provide more robust complexes with different topological properties, namely steric hindrance, bite angle, or fluxional behavior.13 In contrast to their monodentate counterparts, the chemistry of transition-metal complexes based on bis(NHC) ligands have been far less explored.14 Ruthenium(II)−NHC complexes have been recently used in a wide range of organic reactions including TH reactions.1,11a,16 However, the synthesis and catalytic application of their related hydrocarbon chain-linked bis(NHC) complexes is scarce in the literature and their potential synthetic applicability still needs to be studied. To the best of our knowledge, only a few reports have been described about the use of hydrocarbon chain-linked bis(NHC) complexes of ruthenium in TH of ketones19 and hydrogenation of olefins.20

Following the recent works carried out in our research group in the preparation of TpRu complexes bearing the methylene...
linked bis(NHC) ligand bis(3-methylimidazol-2-ylidene) methane (L).21 We focused our attention in the preparation of homologous pentamethylcyclopentadienyl (Cp*) ruthenium complexes with the same ligand in order to compare the effect of the replacement of the supporting ligand Tp by Cp* on the reactivity of the metal center. We have now found that this modification enhances reactivity, and that several of the new complexes prepared in this way are efficient catalyst precursors for TH reactions of carbonyl groups.

**RESULTS AND DISCUSSION**

Synthesis of Complexes and Their Interaction with Small Molecules. The transmetalation reaction of silver-NHC complexes is a well-known synthetic procedure for the introduction of NHC ligands into a system.12,13,22 We have successfully used this methodology for the preparation of Ru19,21,23 and Ni24 complexes. In particular, we prepared the complex [TpRuCl(L)] by reaction of [TpRuCl(COD)] with L·AgCl in dichloroethane at 120 °C over 20 h.21 In an attempt to synthesize the homologous bis carbene bearing Cp* instead of Tp, we carried out the reaction of [Cp*RuCl(COD)] with L·AgCl in dichloroethane at 130 °C over 18 h. A cherry red microcrystalline product was obtained from this reaction. NMR spectroscopy showed that the compound was paramagnetic. Recrystallization from dichloromethane/petroleum ether yielded dark cherry red crystals. The X-ray structure analysis identified this product as the RuIII derivative [Cp*RuCl(L)]Cl (1). An ORTEP view of the complex cation [Cp*RuCl(L)]+ in 1 is shown in Figure 1, together with the most relevant bond distances and angles.

The complex cation has a typical three-legged piano stool structure in which the ruthenium atom adopts a distorted pseudo-octahedral geometry. The bis-carbene chelating bite angle C(11)−Ru(1)−C(16) of 81.9(1)° is slightly smaller than the typical values reported for this ligand, usually in the range 83.2−87.8°.21,23−27 although values as small as 79.4° have been reported. The average dihedral angle between the plane defined by the atoms C(11)−Ru(1)−C(16) and the imidazol rings of 35.65° is slightly higher than the same angle observed for other pseudo-octahedral complexes containing the same ligand L (range 19.7−32.1°).21,25−27 The Ru−C distances for the NHC ligand are 2.038(3) and 2.045(2) Å, typical for Ru−C σ-bonds, and indicative of an essentially symmetrical arrangement of the imidazolylidene rings. The Ru(1)−Cl bond distance of 2.3766(9) Å is slightly shorter than the Ru−Cl separations of 2.4436(11) and 2.389(2) Å reported for the chloro complexes [TpRuCl(k2-C,N-picolyl-1,3-p)] (picolyl49,50 = 3-isopropyl-1-(2-picolyl)imidazol-2-ylidene)23 and [(p-cymene)RuCl(k2-C,N-picolyl-Me)] [PF6−] (picolyl-Me = 3-methyl-1-(2-picolyl)imidazol-2-ylidene),18 but in the range of 2.340−2.376 Å observed for Ru−Cl bond lengths in the complexes [Cp*RuCl(NHC)] (NHC = 1,3-bis(2,6-diisopropylphenyl)-4,5-imidazol-2-ylidene, 1,3-bis(mesityl)-4,5-imidazol-2-ylidene, 1,3-bis(mesityl)-4,5-dihydropyrimidazol-2-ylidene, 1,3-bis(2,6-diisopropylphenyl)-4,5-dihydropyrimidazol-2-ylidene).28

Since the transmetalation reaction of [Cp*RuCl(COD)] with the silver bis-carbene in 1,2-dichloroethane takes place with oxidation of the metal center to RuIV14 to yield 1, it was not possible to use this synthetic approach for the preparation of the RuIII target compound [Cp*RuCl(L)]. Alternatively, we used the direct reaction of [Cp*RuCl(COD)] with the bis-carbene L generated in situ by deprotonation of the bis(imidazolium) salt [LiH2]Cl with an excess of LiBu4 in tetrahydrofuran. In this fashion, the complex [Cp*RuCl(L)] (2) (Chart 1) was isolated in the form of an extremely air-sensitive yellow microcrystalline material.

**Chart 1. Preparation of Complexes 1 and 2**

![Compound 2 is extremely air-sensitive and turns cherry red immediately upon exposure to atmospheric oxygen. This color is consistent with the oxidation to the RuIII cation [Cp*RuCl(L)]. It is very sparingly soluble in C6D6 and it reacts with chlorinated solvents yielding oxidation products. Its 1H NMR spectrum in THF-d8 at room temperature consists of very broad features. The resonances become sharper when the temperature is raised. At 65 °C, the spectrum is reasonably well-resolved, and shows one broad singlet for the Cp* ring protons, one singlet for the protons of the methyl substituents of the imidazolylidene rings, and two characteristic AB doublet...](https://dx.doi.org/10.1021/acs.organomet.1c00045)
signals with a coupling constant of 11.6 Hz corresponding to the methylene bridge protons, which become diastereotopic upon bidentate coordination of the ligand to the Ru atom. The protons of the double bond of the imidazolylidene rings appear as two broad singlets near 7 ppm. Similar NMR features have been observed on the complex [TpRuCl(L)₂]. The ¹³C(¹H) NMR signal of the equivalent carbene carbon atoms of 2 was not observed. It is assumed that it is too broad even at high temperature and it merges with the baseline. All the resonances for the other carbon atoms of the ligands L and Cp* appear in the expected positions. We found nitromethane as the best solvent to be used in this system due to its polarity and poor coordinating abilities. Thus, complex 3 reacts with acetonitrile and NaBH₄ in MeOH at room temperature furnishing complex [Cp*Ru(MeCN)(L)]⁺[BPh₄]⁻ (3). Recrystallization from acetonitrile/methanol yielded amber crystals suitable for X-ray structure analysis.

The complex cation in 3 has a three-legged piano stool structure. The bis-carbene chelating bite angle C(11)−Ru(1)−C(12) of 85.3(2)° is within the expected range. The average dihedral angle between the plane defined by the atoms C(10)−Ru(1)−C(15) and the imidazol rings is 35.3°, still above the average values for the same angle in other complexes containing the same ligand L, but very similar to the value found for compound 1. The Ru−C distances for the NHC ligand of 2.029(4) and 2.035(4) Å are both of the same order and consistent with Ru−C separations expected for σ-bonds. The acetonitrile ligand is almost linearly assembled to ruthenium. The Ru(1)−N(5) and N(5)−C(20) bond lengths of 2.051(3) and 1.134(4) Å respectively compare well with the values of 2.043(5) and 1.128(7) Å found in [Cp*Ru(MeCN)(N₂)][BAr₄⁻] (2). All other dimensions in the structure are in the expected ranges and are unexceptional.

Complex 3 is far more stable toward atmospheric oxygen than 2. It can be handled as a solid in the air without visible decomposition or oxidation. It shows a medium intensity IR band at 2252 cm⁻¹ corresponding to ν(C=O) in the acetonitrile ligand. Its ¹H NMR spectrum in acetonitrile-d₃ shows the two characteristic AB doublet signals for the methylene bridge protons as expected. In this case, the ¹³C(¹H) NMR signal of the equivalent carbene carbon atoms of 3 appear clearly on the spectrum at 193.0 ppm, i.e., in the expected range for Ru−NHC compounds. Compound 3 is a convenient and efficient catalyst precursor for hydrogen transfer reactions to ketones, as discussed below.

Complex 2 reacts with NaBH₄ in methanol under N₂ yielding a yellow microcrystalline precipitate which exhibits a strong band at 2050 cm⁻¹ in its Raman spectrum, attributable to ν(N≡N) in a bridging dinitrogen ligand attached to two Ru atoms. As expected, this band is inactive and does not show on the IR spectrum. This observation is consistent with the formation of the binuclear complex [{TpRu(L)₂(μ-N₂)]−[BPh₄]⁻ (4). The value for the Raman ν(N≡N) band compare well with data in the literature for bridging dinitrogen complexes of ruthenium. The position of this band in 4 appears shifted ca. 50 cm⁻¹ to lower wavenumbers with respect to the ν(N≡N) in the homologous complex [{TpRu(L)₂(μ-N₂)]−[BAr₄⁻] (2106 cm⁻¹) consistent with a slight increase of the relaxation of the coordinated N≡N in 4 in comparison with the latter. At variance with [{TpRu(L)₂(μ-N₂)]−[BAr₄⁻]₂, which contains a dinitrogen ligand strongly bound to ruthenium, compound 4 is very labile and the compound is very reactive. Whereas the reaction of [{TpRu(L)₂(μ-N₂)]−[BAr₄⁻], with CO or acetonitrile is very sluggish, 4 reacts readily with MeCN furnishing complex 3. It also reacts with chlorinated solvents such as dichloromethane and chloroform yielding dark red solutions with display complex NMR spectra. We found nitromethane as the best solvent to be used in this system due to its polarity and poor coordinating abilities. Thus, clean ¹H and ¹³C(¹H) NMR spectra were obtained in nitromethane-d₃. One singlet for Cp* and two AB doublet signals for the methylene bridge protons are the most characteristic features of the ¹H NMR spectrum. The equivalent carbene carbon atoms appear as one singlet at 185.1 ppm on the ¹³C(¹H) NMR spectrum. We attempted recrystallization of 4 in a mixture nitromethane/ethanol. Dark orange crystals were obtained. These crystals showed a strong band at 1813 cm⁻¹ on the IR spectrum. This band was absent in the compound prior to recrystallization. X-ray structure

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**Chart 2. Proposed Exchange in Solution of Chloride Ligand with THF-d₆**

In fact, the chloride ligand in 2 is easily replaced by a range of donor molecules in the presence of a suitable chloride scavenger. Thus, 2 reacts with acetonitrile and NaBH₄ in MeOH at room temperature furnishing the complex [Cp*Ru(MeCN)(L)]⁺[BPh₄]⁻ (3). Recrystallization from acetonitrile/methanol yielded amber crystals suitable for X-ray structure analysis.

![Chart 2](https://example.com/chart2)

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**Figure 2. ORTEP drawing (30% displacement ellipsoids, hydrogen atoms omitted) of [Cp*Ru(MeCN)(L)]⁺ in 3.** Selected bond lengths (Å) and angles (deg): Ru(1)−C(11) 2.029(4), Ru(1)−C(17) 2.035(4), Ru(1)−N(5) 2.051(3), Ru(1)−C(1) 2.224(5), Ru(1)−C(2) 2.194(5), Ru(1)−C(3) 2.166(4), Ru(1)−C(4) 2.206(4), Ru(1)−C(5) 2.204(4), C(20)−N(5) 1.134(4), C(20)−C(21) 1.464(5), C(11)−Ru(1)−C(17) 83.3(1), Ru(1)−N(5)−C(20) 179.4(3), N(5)−C(20)−C(21) 177.7(4), N(2)−C(14)−N(3) 110.6(3).
Organometallics

Figure 3. ORTEP drawing (30% displacement ellipsoids, hydrogen atoms omitted) of one of the two identical molecules [Cp*Ru(NO)(L)]^2+ in 5. Selected bond lengths (Å) and angles (deg): Ru(1)−C(11) 2.056(4), Ru(1)−C(17) 2.057(3), Ru(1)−N(1) 1.769(3), Ru(1)−C(2) 2.251(3), Ru(1)−C(2) 2.205(4), Ru(1)−C(3) 2.260(5), Ru(1)−C(4) 2.271(4), Ru(1)−C(5) 2.270(3), N(1)−O(3) 1.140(4); C(11)−Ru(1)−C(17) 83.2(1), C(11)−Ru(1)−N(1)−O(3) 169.6(3).

The crystal structure of 5 consists of two virtually identical molecules [Cp*Ru(NO)(L)]^2+ and two [BPh_4]^− anions per metal cation. The crystal also contains one nitromethane solvate molecule per ruthenium. The [Cp*Ru(NO)(L)]^2+ ion adopts a three-legged piano stool geometry, with almost identical Ru(1)−C(11) and Ru(1)−C(17) distances for the NHC ligand of 2.056(4) and 2.057(3) Å. The average dihedral angle between the plane defined by the atoms C(11)−Ru(1)−C(17) and the imidazol rings is 29.6°, smaller than the values found for compounds 1 and 3, but within the range observed for other complexes containing the L ligand. The nitrosyl ligand is very slightly bent, with a Ru(1)−N(1)−O(3) angle of 169.6(3) Å. The Ru(1)−N(1) and N(1)−O(3) separations of 1.769(3) and 1.140(4) Å respectively compare well with the values found for the nitrosyl complex [Ru(L^2)(NO)Cl_2] (L^2 = (N’-phenyl-N’-(pyridin-2-yl)picolinohydrazide)), and in the Ru^II nitrosyl complexes with pyridine-functionalized N-heterocyclic carbene ligands [Ru(L^2)(NO)Cl_2] (L^2 = 3-tert-butyl-1-(2-pyridyl)imidazol-2-ylidine, 3-n-butyl-1-(2-pyridyl)imidazol-2-ylidine, 3-tert-butyl-1-picolylimidazol-2-ylidine). The formation of the nitrosyl complex 5 at the expense of the dihydrogen derivative 4 is completely unexpected. The crystals of 5 were isolated in low yield based on ruthenium, and the origin of the nitrosyl ligand is unclear. We can only speculate that it comes from nitromethane, but we are unsure about the chemical reactions leading to the ultimate products, as there are no precedents for this. One reviewer tentatively suggested the possibility of formation of the nitrosyl complex 5 by the transfer hydrogenation between nitromethane and EtOH during recrystallization. In fact, we assume that other metal-containing products must be formed in the process, but we failed to identify any other species. We monitored by NMR a solution of 4 in nitromethane-d_4 under dinitrogen over several days. We were able to detect gradually increasing signals for the nitrosyl compound 5, mixed with many other resonances and broad features corresponding to unidentified species. We did not detect the formation of any hydride containing species in the overall process, which is not clean nor simple, and the nitrosyl species 5 was the only fully characterized compound in this most intriguing reaction sequence.

Compound 4 also acts as a catalyst precursor for ketone hydrogen transfer reactions (vide infra). The dihydrogen ligand in 4 is readily replaced by a number of donor molecules furnishing the corresponding complexes. These reactions are summarized in Scheme 1.

Scheme 1. Reactivity of the Bridging Dinitrogen Complexes 4

Thus, 4 reacts with H_2 in nitromethane affording the labile dihydrogen complex [Cp*Ru(H_2)(L)][BPh_4]^− (6). This compound was isolated by reaction of 2 with NaBPh_4 in methanol under a dihydrogen atmosphere in the form of an off white solid. All subsequent manipulations were performed under an atmosphere of argon unless otherwise stated. The ^1H NMR spectrum of 6 in nitromethane-d_4 under dihydrogen shows a broad resonance at −7.81 ppm attributable to the protons of the coordinated dihydrogen. As it is characteristic of dihydrogen ligands, this resonance exhibits a short longitudinal relaxation time T_1 of 21.4 ms at 248 K (500 MHz). This was the shortest measured T_1, as the minimum value could not be determined due to freezing of the solvent. In any case, the value is fully consistent with the presence of a coordinated dihydrogen molecule. In general, dihydrogen complexes stabilized with NHC-ligands are not very common. We were not able to prepare the homologous complex [TpRu(H_2)(L)]^+, an observation that emphasizes the difference between the {Cp*Ru(L)} and {TpRu(L)} moieties. The dihydrogen complex 6 has also been successfully used as catalyst precursor for ketone hydrogen transfer.
reactions. The dihydrogen ligand in 6 is readily deprotonated by strong bases yielding the corresponding neutral monohydrate complex. Thus, the reaction of 6 with KOBu' in tetrahydrofuran under dihydrogen afforded [Cp*RuH(L)] (7) in high yield as a yellow microcrystalline, air-sensitive solid (Chart 3).

Chart 3. Deprotonation of the Dihydrogen Complex 6

A medium band at 1780 cm⁻¹ in the IR spectrum is attributable to ν(RuH), whereas one singlet at -11.65 ppm in the ¹H NMR spectrum corresponds to the hydride proton. Since 7 it is formed in strongly basic conditions, it is assumed that this compound must be involved in the catalytic keto hydro transfer reactions described below, and it possibly represents a key intermediate in the overall catalytic cycle.

Compound 4 also reacts with olefins CH2=CHR (R = H, COOMe) to yield the corresponding η²-adducts [Cp*Ru(η²-CH2=CHR)L][BPh4] (R = H 8a, COOMe 8b) (Scheme 1). These compounds were not isolated. They were generated in solution either by bubbling ethylene or adding an excess of methyl acrylate to a nitromethane-d₃ solution of 4 under argon, and were characterized in solution by NMR spectroscopy. The resonances for the proton and carbon atoms of coordinated ethylene in 8a appear at 2.14 and 47.2 ppm on the respective ¹H and ¹³C[¹H] NMR spectra. In the case of 8b, only one diastereoisomer is observed as indicated by one single C¹H signals in the ¹H NMR spectrum, but the presence of the COOME substituent on the η²-alkene ligand is evident. Thus, two resonances are observed for the methyl substituents at the nitrogen, and four separate resonances for the H and C atoms in the positions 3 and 4 of the NHC rings. Most notably, two carbene carbon atom signals at 180.8 and 183.9 ppm are present on the η¹-carbene ligand.21 At variance with 8a, the C¹H resonance for the carbene atom of the allenylidene ligand is shifted ca. 30 ppm compared to its position in 8a on the 13C[¹H] NMR spectrum. The two AB doublet signals for the methylene bridge protons are maintained.

Compound 4 reacts with freshly prepared solutions of phenylidazomethane in tetrahydrofuran under argon yielding the carbene complex [Cp*Ru≡CHPh(L)][BPh4] (9) (Scheme 1). This compound can be also prepared starting from the dihydrogen derivative 6 in a similar fashion. We have used a similar synthetic approach in the preparation of the carbene complexes [Cp*Ru≡CHPh(x²-P,N-Pr₂PPh₂)] [BAr₄] (Py = C₆H₄N) [19] and [TpRu≡CHPh(Cl)(PMesPr₂)].21 The ¹H NMR spectrum of compound 9 is characterized by the presence of the carbene proton resonance at 15.7 ppm. This resonance is correlated with a strongly coupled ¹H resonance at 15.7 ppm. The coupling constant is 1780 cm⁻¹ in the IR spectrum is attributable to ν(RuH), whereas one singlet at -11.65 ppm in the ¹H NMR spectrum corresponds to the hydride proton. Since 7 it is formed in strongly basic conditions, it is assumed that this compound must be involved in the catalytic keto hydro transfer reactions described below, and it possibly represents a key intermediate in the overall catalytic cycle.

The allenylidene complex 10 shows a strong ν(C≡C=C) band in the IR spectrum at 1880 cm⁻¹. The signals observed at 157.3, 147.7, and 139.8 ppm in the ¹³C[¹H] NMR spectrum are respectively characteristic for the CpNu and C₉ atoms of the allenylidene ligand, whereas the resonance for the carbene carbon atom of the L ligand appears at 178.0 ppm. The signal for the C₉ atom in 10 is shifted upfield ca. 30 ppm compared to the value observed for the homologous complex [TpRu=C≡C=CP₈(L)][BPh₄] (305.0 ppm).21 Likewise, the IR ν(C≡C=C) band for the allenylidene ligand in 10 appears at 1820 cm⁻¹ in the IR spectrum. The latter exhibits a rich reactivity toward a variety of N- and S-donor nucleophiles such as pyrazole, piperedine, 2-pyrindinethiol or 1,3-benzenedithiol leading to vinylcarbene complexes resulting from the addition to the C₉ atom of the allenylidene ligand.21 At variance with this, complex 10 is apparently much less reactive toward nucleophiles, and did not show any visible reaction with pyrazole at 55 °C in acetone-d₆ after 18 h.

Ketone Transfer Hydrogenation. The transfer hydrogenation of ketones was explored using acetophenone (11) as
model substrate, with 2-propanol as the hydrogen source in the presence of 0.5 mol % of ruthenium complexes 3, 4, and 6 at 80 °C. A catalytic amount of KOiPr was initially used as base. The results given in Table 1 showed that catalysts 3 and 4 led to the desired product (±)-11a in low yields and TOF values after 2 h (Table 1, entries 1 and 3). With longer reaction times (16 h), yields increased to 75% and 79%, respectively (Table 1, entries 2 and 4). In contrast, complex 6 was found to be the best catalyst toward transfer hydrogenation under the same reaction conditions affording compound (±)-11a in 75% yield after 2 h (Table 1, entry 5). When KOH was used as base instead of KOiPr, the yield increased up to 94% in the presence of complex 6 (Table 1, entry 6). Reduction of the amount of KOH to 5 mol % gave an identical result (Table 1, entry 7). These new conditions led to a higher catalytic activity after 1 h affording (±)-11a in 81% yield with TOF value of 162 h⁻¹ (Table 1, entry 8). However, the reaction did not take place in the absence of base (Table 1, entry 9). Interestingly, when the catalyst loading of complex 6 was reduced to 0.1 mol %, compound (±)-11a was formed in a similar yield with a TOF value of 455 h⁻¹ after 2 h (Table 1, entry 10). Finally, we confirmed that compound (±)-11a was only obtained in 10% yield in the absence of catalyst (Table 1, entry 11).

With the optimized conditions in hand, the scope of the transfer hydrogenation of ketones and aldehydes was investigated. A variety of ketones were suitable for this procedure giving the desired alcohols in high to good yields. The bulkier 2-acetonaphthone (12) underwent transfer hydrogenation to give alcohol (±)-12a in 88% yield (Table 2, entry 1). Para-substituted phenylketones or benzophenones 13–15 bearing electron-withdrawing groups such as trifluoromethyl or chloro groups were well tolerated to afford the corresponding alcohols (±)-13a–15a in 71–99% yields (Table 2, entries 2–4), whereas electron-donating substituents on aryl group such as p-methoxy group led to alcohol (±)-16a in 72% yield (Table 2, entry 5). Similarly, the transfer hydrogenation was compatible with benzoazepin-5-one (17) bearing 7-chloro substituent, providing the corresponding alcohol (±)-17a in 66% yield (Table 2, entry 6). However, the reaction was not compatible with the presence of a free

Table 1. Optimization of Reaction Conditions for Transfer Hydrogenation of Acetophenone (11) with Ruthenium Complexes

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<th>entry</th>
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<th>base (mol %)</th>
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<th>yield (%)</th>
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<td>10</td>
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“Unless noted otherwise, reactions were carried out with 2 mmol of acetophenone in 2 mL of 2-propanol at 80 °C. bDetermined by GC-MS. cTurnover frequency (moles of ketone converted to alcohol per mole of catalyst per hour). d4 mmol of acetophenone in 4 mL of 2-propanol.

Table 2. Screening of Substrates for Transfer Hydrogenation of Carbonyl Groups Catalyzed by Complex 6

<table>
<thead>
<tr>
<th>entry</th>
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<th>yield (%)</th>
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<td>&gt;99%</td>
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“Unless noted otherwise, reactions were carried out with 2 mmol of substrate in 2 mL of 2-propanol at 80 °C for 2 h. bDetermined by GC-MS.
unsaturated ketones corresponding alkanols (reduction products. The Guerbet-type alcohol unfortunately, the reaction failed to give the corresponding obtained in 83% yield from octanal (Chart 5, a). The Guerbet reaction involves homocoupling of the new C−C bond is generated by an aldol condensation.37 Aliphatic ketones were also well tolerated. Hex-4-en-2-one (19) was transformed into alcohol (±)-19a in 75% yield whereas (+)-dihydrocarvone (20) afforded stereoselectively compound 20a in quantitative yield (Table 2, entries 8−9). The absolute configuration of 20a was determined by NOE effects. On the other hand, the transfer hydrogenation of α,β-ununsaturated ketones 21−22 was performed to produce the corresponding alkanols (±)-21a and 20a with both C==C and C≡O reduced in 90% and 99%, respectively (Table 2, entries 10−11). We further extended our study to aldehydes 23−25. Unfortunately, the reaction failed to give the corresponding reduction products. The Guerbet-type alcohol 23a was obtained in 83% yield from octanal (23) (Table 2, entry 12) (Chart 5, a). The Guerbet reaction involves homocoupling of primary alcohols to obtain β-alkylated dimer alcohols where the new C−C bond is generated by an aldol condensation.37 Recently, Ir, Rh, and Ru complexes have been reported to catalyze the Guerbet reaction and produce higher-order alcohols in a more economical and environmentally friendly manner.38 In most cases, these catalytic systems required temperature higher than 100 °C. Compound 23a was also prepared starting from octanal in 80% yield in a similar fashion. Moreover, benzaldehyde derivative 24 performed a cross-coupling with 2-propanol to afford the saturated dimer 24a in 56% yield, whereas 2-furfural (25) gave the unsaturated dimer 25a as major product (Table 2, entries 13−14). These findings indicate that complex 6 could be an efficient catalyst precursor for β-alkylation of secondary alcohols and α-alkylation of ketones by borrowing hydrogen reaction (Chart 5, b).39 In comparison with previously reported ruthenium(II) complexes bearing chelating NHCs, our catalytic system based on methylene-linked bis(NHC) ligands exhibits similar efficiency in a wide scope of substrates even with lower catalyst loadings allowing significant shortening of reaction times.17,18 In this sense, compound 6 seems to perform in ketone hydrogen transfer somewhat less efficiently than the picolylcarbene complex [Cp*Ru(MeCN)(κ²-C,N-

**Chart 5. Formation of Products Derived from Guerbet-Type Reactions**

![Chart 5](image-url)

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primary alcohols to obtain β-alkylated dimer alcohols where the new C−C bond is generated by an aldol condensation.37 Recently, Ir, Rh, and Ru complexes have been reported to catalyze the Guerbet reaction and produce higher-order alcohols in a more economical and environmentally friendly manner.38 In most cases, these catalytic systems required temperature higher than 100 °C. Compound 23a was also prepared starting from octanal in 80% yield in a similar fashion. Moreover, benzaldehyde derivative 24 performed a cross-coupling with 2-propanol to afford the saturated dimer 24a in 56% yield, whereas 2-furfural (25) gave the unsaturated dimer 25a as major product (Table 2, entries 13−14). These findings indicate that complex 6 could be an efficient catalyst precursor for β-alkylation of secondary alcohols and α-alkylation of ketones by borrowing hydrogen reaction (Chart 5, b).39 In comparison with previously reported ruthenium(II) complexes bearing chelating NHCs, our catalytic system based on methylene-linked bis(NHC) ligands exhibits similar efficiency in a wide scope of substrates even with lower catalyst loadings allowing significant shortening of reaction times.17,18 In this sense, compound 6 seems to perform in ketone hydrogen transfer somewhat less efficiently than the picolylcarbene complex [Cp*Ru(MeCN)(κ²-C,N-

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**CONCLUSION**

We have hereby reported the synthesis and characterization of a series of novel pentamethylcyclopentadienylruthenium(II) complexes bearing the methylene linked bis(NHC) ligand bis(3-methylimidazol-2-ylidene)methane. The binuclear dinitro-bridge product 4 displays a rich reactivity toward a range of small molecules. Compound 4 undergoes an unprecedented degradation in nitromethane solution leading to the nitrosyl derivative 5, which has been structurally characterized. Compounds 3, 4, and 6 act as catalyst precursors for the transfer hydrogenation of acetophenone. In particular, the dihydrogen complex 6 has proven to be a very efficient catalyst precursor, reaching a TOF of up to 455 h⁻¹ at catalyst loadings of 0.1% mol. Moreover, 6 exhibits high tolerance of functional groups on the reduction of a broad scope of ary1 and aliphatic ketones giving rise the corresponding alcohols in high yields. Additionally, the transfer hydrogenation of aldehydes using 6 act as catalyst afforded Guerbet-type reaction products and the β-alkylation of 2-propanol under mild conditions. The study of further organic transformations mediated by these novel complexes is currently in progress in our laboratory, and will be reported in due course.

**EXPERIMENTAL SECTION**

All synthetic operations were performed under a dry dinitrogen or argon atmosphere following conventional Schlenk techniques. Tetrahydrofuran, diethyl ether, and petroleum ether (boiling point range 40−60 °C) were obtained oxygen- and water-free from a solvent purification apparatus. All other solvents (acetonitrile, dichloromethane, toluene, nitromethane, methanol, 2-propanol) were of anhydrous quality and used as received. All solvents were degassed immediately before use. [Cp*RuCl(COD)] was prepared according to the literature.25 The imidazolium salt bis(3-methylimidazolium)methane dichloride ([Li][Cl]) was prepared following suitable adaptations of published procedures.25 IR spectra were taken in Nujol mulls on a FTIR spectrophotometer. Raman spectrum was recorded at the Instituto de Ciencia de Materiales-CSIC on a dispersive Raman microscope equipped with a He−Ne laser (λ = 532.14 nm) using a working power of 0.2 mW in order to avoid overheating and alteration of the sample. Optical rotations were determined with a digital polarimeter. NMR spectra were taken on a dispersive Raman microscope equipped with a He−Ne laser (λ = 532.14 nm) using a working power of 0.2 mW in order to avoid overheating and alteration of the sample. Optical rotations were determined with a digital polarimeter. NMR spectra were taken on spectrometers operating at 400 or 500 MHz (1H frequency). Chemical shifts are given in ppm from SiMe₄ (1H and 13C{1H}) experiments. As a general feature, in the spectra of cationic compounds the signals for the [BPh₄]⁻ anion are omitted. High resolution mass spectroscopy (HRMS) was performed in a Q-TOF mass spectrometer in the positive ion ESI mode. Silica gel (Merck) was used for column chromatography. TLC was performed on Merck Kieselgel 60 F254, 0.25 mm thick. GC-MS analyses were recorded on a Bruker Scion GC-TQ gas chromatograph coupled to a Bruker TQ mass spectrometer. Microanalyses were performed at the Servicio Central de Ciencia y Tecnología, Universidad de Cádiz.

[Cp*RuCl(COD)][PF₆] (picolyl-MeI = 3-methyl-1-(2-picolyl)-imidazol-2-ylidene) previously reported by our research group.17 This compound had already shown an excellent catalytic activity and wider scope compared to other previously reported ruthenium40 or even iridium41 pyridyl−NHC complexes. The hydride transfer is a key step in many catalytic transformations, and further studies are in progress aimed to extend the use of these new complexes as catalysts for reactions of N-alkylation of amines with alcohols.
mmol) and AgO (0.28 g, 1.2 mmol). It was protected from light by wrapping with aluminum foil. Then, 1,2-dichloroethane (15 mL) was added, and the mixture stirred at room temperature for 18 h. After this time, a solution of [Cp*RuCl(COD)] (0.38 g, 1 mmol) in 1,2-dichloroethane (15 mL) was added. The resulting mixture was stirred for further 18 h at 130 °C. A purple suspension was obtained. It was filtered through Celite, and the Celite was washed with two portions of dichloromethane. The solvent of the filtered solution was removed in vacuo. The resulting yellow-purple microcrystalline product was washed with petroleum ether and dried in vacuo. Recrystallization from dichloromethane/petroleum ether afforded crystals suitable for X-ray structure analysis. Yield (based upon Ru): 0.21 g, 43%. Calculated for C5H32N4RuCl: C, 47.21; H, 5.63; N, 11.59. Found: C, 47.29; H, 5.71, N, 11.30. The product is paramagnetic.

[Cp*RuCl(COD)] 2. A Schlenk tube was charged with bis(3-methylimidazolium)methane dichloride (1.5 g, 6 mmol), degassed and placed under dinitrogen. Deoxygenated tetrahydrofuran (30 mL) was added. It was cooled to −80 °C and LiBu* (7.5 mL of a 1.6 M solution, 12 mmol) was added via syringe. The mixture was warmed to room temperature and stirred for 2 h. At the end of this time, a solution of [Cp*RuCl(COD)] (1.77 g, 4.66 mmol) in tetrahydrofuran (25 mL) was added. The resulting mixture was stirred overnight at 65 °C. A brown-orange solution with a finely divided white precipitate was obtained. The suspension was filtered through Celite. The solvent was removed in vacuo, and the resulting yellow-brown, very air-sensitive microcrystalline product was washed with two portions of petroleum ether and dried in vacuo. Yield: 1.77 g, 85%. Calculated for C6H32N4RuCl4: C, 50.94; H, 6.08; N, 12.51. Found: C, 50.85; H, 5.99, N, 12.10. NMR: 1H NMR (500 MHz, THF-d8, 333 K) δ 1.77 (s, 15 H, C(CH3)3), 3.93 (s, 6 H, NCH3), 5.26, 5.76 (d, J$_{HH}$ = 1.16 Hz, 1 H each, CH2), 6.95, 6.99 (s, 2 H, CH2, CHH = CHH), 13C{1H} NMR (125.7 MHz, THF-d8, 333 K) δ 10.3 (C(CH3)3), 36.8 (NCH3), 61.8 (CH3), 83.3 (C(CH3)3), 118.5, 121.4 (CH = CH), Ru unobserved.

[Cp*Ru(MeCN)(L)][BPh4] 3. Compound 2 (0.45 g, ca. 1 mmol) was dissolved in MeOH (15 mL) under dinitrogen. Acetonitrile (1 mL) and solid NaBP3a (0.45 g, 1.3 mmol) was added. A yellow precipitate was formed. The mixture was stirred at room temperature for 1 h. The mixture was filtered, and the yellow solids washed with ethanol and petroleum ether and dried in vacuo. The crude product was dissolved in acetonitrile, and the solution filtered through Celite. The solution was layered with MeOH. Slow diffusion afforded well-formed amber crystals, suitable for X-ray analysis. Yield: 0.59 g, 77%. Calculated for C5H32N4Ru: C, 69.94; H, 6.52; N, 9.06. Found: C, 70.02; H, 6.54, N, 9.00. IR ν(CN) 2252 cm$^{-1}$. NMR: 1H NMR (500 MHz, CD2Cl2, 298 K) δ 1.57 (s, 15 H, C(CH3)3), 2.15 (s, 3 H, CH2), 3.77 (s, 6 H, NCH3), 5.31, 5.80 (d, J$_{HH}$ = 13.5 Hz, 1 H each, CH2), 7.10, 7.19 (d, J$_{HH}$ = 2.1 Hz, 2 H each, CHH = CHH); 13C{1H} NMR (125.7 MHz, CD2Cl2, 298 K) δ 10.8 (C(CH3)3), 37.1 (NCH3), 62.3 (CH3), 86.93 (C(CH3)3), 121.6, 126.6 (CH = CH), 193.0 (Ru).

[[Cp*Ru(L)][(μ−N$_2$)][BPh4]] 4. To a mixture of 2 (1.77 g, 3.96 mmol) and NaBP3a (1.9 g, 5.66 mmol), MeOH (20 mL) was added under dinitrogen. A yellow precipitate was formed. The mixture was stirred at room temperature for 12 h. At the end of this time, the suspension was filtered, and the yellow product was washed thoroughly with ethanol and petroleum ether and dried in vacuo. Yield: 2 g, 68%. Calculated for C6H32N4RuBP3a: C, 69.25; H, 6.35; N, 9.39. Found: C, 69.11; H, 6.25, N, 9.10. Raman: ν(N≡N) 2050 cm$^{-1}$. NMR: 1H NMR (500 MHz, CD2Cl2, 298 K) δ 1.71 (s, 15 H, C(CH3)3), 3.52 (s, 12 H, NCH3), 5.99, 5.52 (d, J$_{HH}$ = 13.0 Hz, 2 H each, CH2), 7.05, 7.31 (d, J$_{HH}$ = 2.0 Hz, 4 H each, CHH = CHH); 13C{1H} NMR (125.7 MHz, CD2Cl2, 298 K) δ 11.0 (C(CH3)3), 37.1 (NCH3), 63.1 (CH3), 92.1 (C(CH3)3), 122.9, 124.2 (CH = CH), 185.1 (Ru).

[Cp*Ru(NO)(μ−N$_2$)][BPh4] 5. Compound 4 (0.3 g 0.2 mmol) was dissolved in MeOH and the solution filtered through Celite. The solution was layered with EtOH. On standing at room temperature for several days, well-formed dark orange crystals were obtained. The crystals were filtered off, rinsed with petroleum ether and dried in vacuo. Yield: 0.085 g, 37%. Calculated for C5H32N4RuNO: C, 71.52; H, 6.18; N, 7.36. Found: C, 71.50; H, 6.16, N, 7.27. IR ν(NO) 1813 cm$^{-1}$. NMR: 1H NMR (400 MHz, CD2NO2, 233 K) δ 2.12 (s, 15 H, C(CH3)3), 2.89 (s, 6 H, NCH3), 5.74, 6.42 (d, J$_{HH}$ = 13.8 Hz, 1 H each, CH2), 7.53, 7.64 (s, 1 H each, CH = CH); 13C{1H} NMR (101 MHz, CD2NO2, 233 K) δ 10.6 (C(CH3)3), 39.0 (NCH3), 63.9 (CH3), 113.2 (C(CH3)3), 127.0, 127.5 (CH = CH), 186.3 (CH2).
6.29, 5.63 (d, \(J_{HH} = 12.7\) Hz, 1 H each, \(CH,H_2\)), 7.39, 7.42 (d, \(J_{HH} = 2.0\) Hz, 2 H each, \(CH=CH\)), 7.61, 7.41 (m, 5 H, \(CH,H_2\)), 15.7 (s, 1 H, Ru=CHPh); \(^{13}C(\text{H})\) NMR (125.7 MHz, CD\(_2\)NO\(_2\)) 298 K 10.5 (C\(_5\)C\(_\text{Ph}_2\)), 37.2 (N\(HCH_3\)), 63.9 (CH\(_3\)), 102.9 (C\(_\text{Ph}C\)), 122.6, 125.9 (CH=CH), 127.8, 129.6, 130.4, 135.9 (C\(_\text{Ph}\)), 184.0 (Ru\(C\)).

Crystal Structure Analysis. Crystals suitable for X-ray structural determination were mounted on glass fibers and then transferred to a Bruker Smart CCD three-circle diffractometer with a sealed-tube source and graphite-monochromated Mo K\(\alpha\) radiation (\(\lambda = 0.7073\) Å) at the Servicio Central de Ciencia y Tecnología de la Universidad de Cádiz (1) or Servicios Técnicos de Investigación de la Universidad de Alicante (3 and 5). In each case, three (3 and 5) at 298 K or four at 100 K (1) sets of frames were recorded over a hemisphere of the reciprocal space by \(\omega\) scans with \(\Delta(\omega) = 0.30^\circ\) and exposure of 10 to 20 s per frame. In the case of 3 and 5, an additional run at \(\theta = 0^\circ\) of 100 frames was collected to improve redundancy. The diffraction frames were integrated using the program SAINT\(^{43}\) and the integrated intensities were corrected for Lorentz-polarization effects with SADABS.\(^{44}\) An insignificant crystal decay correction was also applied. The structure of 1 was solved by Patterson method, and direct methods were used for 3 and 5. All structures were refined on \(F^2\) by full-matrix least-squares (SHELX97)\(^{45}\) using all unique data. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed at idealized positions and refined as rigid atoms. ORTEP was used for plotting.\(^{46}\) CCDC 1483010, 2056271−2056272 contain supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/ac500045.

General procedure for the catalytic transfer hydrogenation of carbonyl compounds and characterization data for compounds 11a−25a; \(\text{H}\) and \(^{13}C(\text{H})\) NMR spectra for compounds 2−10 (Figures S1−S10) and 11a−25a (Figures S1−S23); Crystal data and experimental details for the crystal structure determination (Table S1) (PDF)

Accession Codes

CCDC 1483010 and 2056271−2056272 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 366033.

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Notes

The authors declare no competing financial interest.

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