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Journal of Organometallic Chemistry 690 (2005) 5979–5988
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

# Synthesis, structure and electronic properties of *N*-dialkylamino- and *N*-alkoxy-1,2,4-triazol-3-ylidene ligands

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Received 31 May 2005; received in revised form 25 July 2005; accepted 26 July 2005
Available online 25 October 2005

**Abstract**

4-Amino- and 4-alkoxy-1,2,4-triazoles **4a–d** and **6** were readily obtained from the reaction of *N*,*N*-dimethylformamidazin dihydrochloride **3** with hydrazines **2** and hydroxylamine **5**. Alkylation of compounds **4a–d** and **6** by MeOTf or MeI afforded azolium salts **9–11**, which in turn were transformed into Rh(I) carbene complexes **13–15**, Ag carbenes **16**, and cationic Rh(I) bis-carbenes **17**. Additionally, complexes **13** and **15** were transformed into dicarbonyl derivatives **18** and **19**, and the carbonyl stretching frequencies of these compounds were used to evaluate the effect of the amino and alkoxy groups in the σ-donor ability of these 1,2,4-triazol-3-ylidenes.


*Keywords:* Heterocycles; Carbenes; Rhodium

## 1. Introduction

Since the isolation of the first stable *N*-heterocyclic carbene (NHC) by Arduengo and co-workers,[1] the chemistry of these compounds has developed rapidly [2], fueled mainly by their application as C-ligands [3]. Late transition metal complexes containing NHC ligands are usually air stable and kinetically robust compounds, which are particularly promising in the field of catalysis in general and in asymmetric catalysis in particular. Nevertheless, there are still some limitations that reduce the scope of application of these ligands. Thus, although steric demand is easily tuned using different substitution patterns, the electron donor ability of NHCs can only be modified slightly, mainly by the choice of the formal parent heterocyclic precursor between imidazol, dihydroimidazol and triazole, while the effect of the substituents at the heterocyclic nitrogen atoms seems to be negligible [4].

Since the pioneering work of Enders and co-workers [5], relatively little attention has been devoted to the chemistry of 1,2,4-triazol-5-ylidene metal complexes [6], a phenomenon that is surprising considering that there are relatively simple routes to access these compounds, and that the catalytic activity has been demonstrated [7], even though 1,2,4-triazol-3-ylidenes are weaker σ donors than other NHCs as imidazol-2-ylidenes or imidazolin-2-ylidene [2]. Additionally, chiral triazol-5-ylidenes have been successfully used as organocatalysts in the benzoin condensation [8] and the intramolecular Stetter reaction [9].

Very recently we have reported the synthesis of 1,3-bis(*N*,*N*-dialkylamino)imidazolin-2-ylidenes [10] and we found out that substitution by *N*-dialkylamino groups slightly increases the donor ability of these ligands with respect to alkyl or aryl analogues in a way that these compounds appear as the best known donors in the imidazolin-2-ylidene series [11]. In this paper we wish to report on the first efficient synthesis of 4-dialkylamino- and 4-alkoxy-1,2,4-triazoles (**A**), their transformation into the corresponding triazolium salts (**B**) and triazol-5-ylidene metal complexes (**C**) (Fig. 1), and the comparative analysis of the carbene ligand donor ability in the latter.

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doi:10.1016/j.jorganchem.2005.07.120

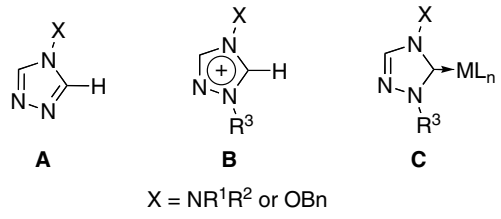



Fig. 1. Target compounds in this study.

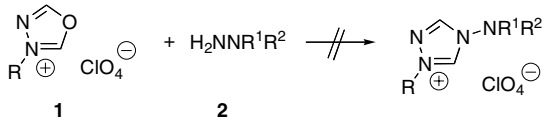
## 2. Results and discussion

For the synthesis of the target 1-alkyl-4-dialkylamino-1,2,4-triazol-5-ylidene complexes **C**, we decided to use the corresponding triazolium salts **B** as the most common type of precursors. In turn, these compounds can be obtained by a direct cyclisation from a suitable precursor or by a simple alkylation of 4-dialkylamino triazoles **A**. Surprisingly, a search of the pertinent literature sources revealed that, in spite of the simplicity of their structures, there are no efficient methods reported for the synthesis of such heterocycles.

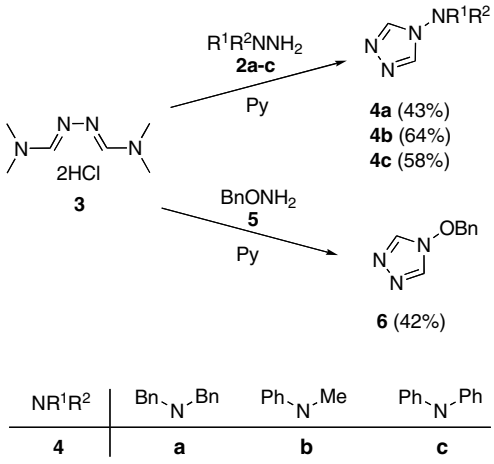
Initially, we tried to apply the method used by Boyd [12] for the direct synthesis of triazolium salts. Unfortunately, reaction of 1,3,4-oxadiazolium salts **1** with *N*,*N*-dialkylhydrazines **2** did not take place, even under forcing conditions (Scheme 1).

Comparing with Boyd's [12a] and Enders' [12b] results using primary aryl amines, the lack of reactivity in our case suggests that the strong acidic medium required results in eliminate the nucleophilicity of the more basic hydrazines **2** by protonation. Therefore, we concluded that less acidic conditions are required, and, consequently, *N*,*N*-dimethylformamidazin dihydrochloride **3** was made to react with hydrazines **2** in pyridine as the solvent to afford, as for anilines [13], the corresponding 4-amino-1,2,4-triazoles **4a**–**c** in moderate yields. Moreover, this method proved to be also suitable for the synthesis of the 4-benzyloxy-1,2,4-triazole **6**, readily obtained by reaction of *O*-benzyl hydroxylamine **5** with the same reagent in 42% yield (Scheme 2).

Finally, 4-[2,5-dimethylpyrrol-1-yl]-1,2,4-triazole **4d** was also considered as an interesting substrate in order to further increase the structural diversity of the study. This compound had been previously synthesized by reaction of a methanolic solution of commercially available 4-amino-1,2,4-triazole **7** with 2,5-hexanedione **8**, but a very poor 7% yield was reported [14]. Fortunately, a modification of the reaction conditions allowed the synthesis of the target heterocycle **4d** in 86% yield from the same starting materials (Scheme 3).




Scheme 1.



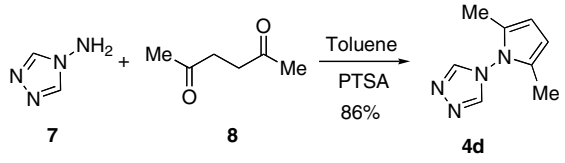




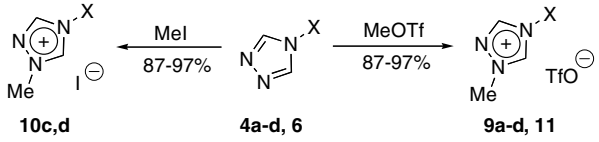
Scheme 2.

With the heterocycles **4a**–**d** and **6** in hand, the synthesis of the required azolium salts **B** was easily accomplished. Thus, alkylation of the new *N*-dialkylamino and *N*-alkoxy heterocycles **4a**–**d**, **6** with MeOTf or MeI proceeds cleanly to afford the 1,2,4-triazolium salts **9a**–**d**, **10c**,**d**, and **11** in good-to-excellent yields (Scheme 4 and Table 1).

The reactivity of the salts **9**–**11** was then explored in different contexts. The synthesis of the corresponding free carbenes was attempted by deprotonation with NaH in

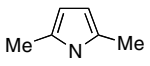
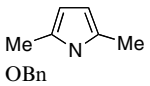


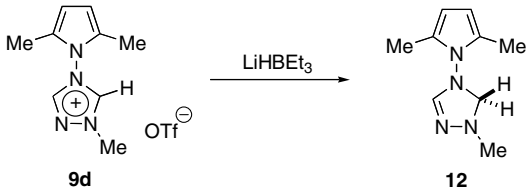

Scheme 3.




Scheme 4.

Table 1
Synthesis of 4-(amino- or alkoxy)-1,2,4-triazolium salts **9**–**11**

| Starting material | X | Anion | Product | *T* | *t* (h) | Yield (%) |
|---|---|---|---|---|---|---|
| **4a** | $NBn_2$ | OTf | **9a** | rt | 1 | 87 |
| **4b** | N(Me)Ph | OTf | **9b** | rt | 1 | 97 |
| **4c** | $NPh_2$ | OTf | **9c** | rt | 1 | 94 |
| **4c** | $NPh_2$ | I | **10c** | 60 °C | 48 | 81 |
| **4d** |  | OTf | **9d** | rt | 1 | 96 |
| **4d** |  | I | **10d** | 60 °C | 48 | 79 |
| **6** | OBn | OTf | **11** | rt | 1 | 89 |




Scheme 5.

THF at low temperature (−78 to −30 °C), followed by removal of the solvent and extraction with toluene, but, unfortunately, this procedure led to a complex mixture, presumably resulting from the decomposition of the free carbenes. Alternatively, the reaction of **9d** with $LiHBEt_3$ was investigated. This reagent has been recently used to prepare the $BEt_3$ adducts of imidazol-2-ylidenes from the corresponding imidazolium salts [15]. In our case, however, the conditions described afforded the reduction 1*H*-triazoline product **12** instead, which was isolated in 71% yield (Scheme 5).

Much better results were observed for the direct synthesis of some transition metal complexes. First, both triflates **9a**–**d**, **11** and iodides **10c**,**d** were reacted with $[RhCl(COD)]_2$ in the presence of $Et_3N$ to afford Rh(NHC)Z(COD) complexes **13a**–**d** (Z = Cl) (Scheme 6, Table 2), **14c**,**d** (Z = I) and **15**, which proved to be air and moisture-tolerant products that even resisted chromatographic purification on silica-gel to isolate high yields of pure products.

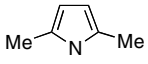
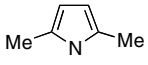
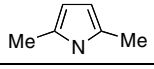
The existence of diastereotopic signals for benzylic protons in **13a** and **15** and for methyl groups in the pyrrol moiety in **13d** and**14d** indicates a high rotation barrier of the carbene carbon–rhodium bond and, therefore, the existence of a configurationally stable chiral axis can be postulated in these complexes as a result of steric interactions [16].

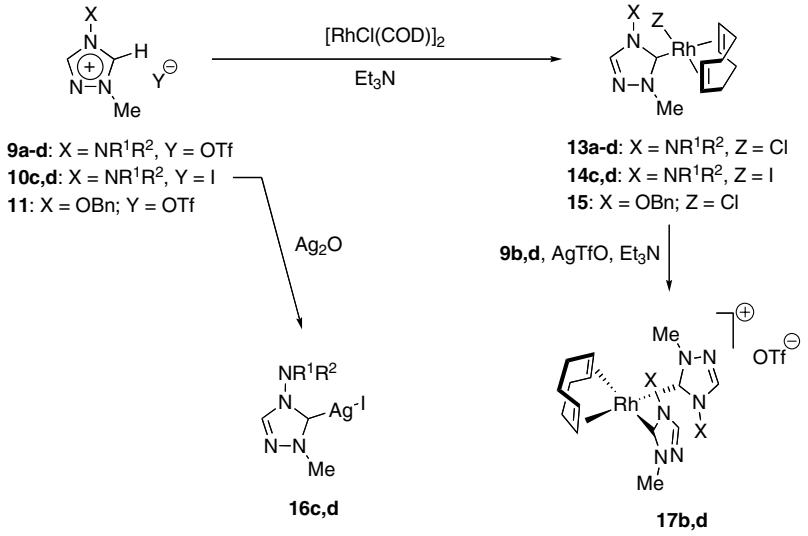
The X-ray structures of **14c** and **14d** (Fig. 2) show the expected square-planar geometry around the rhodium atom with the carbene ligand perpendicular to this plane. The carbene carbon-rhodium bond lengths of 201.6 and 201.1 pm, respectively, are similar to those observed in other NHC-rhodium(I) complexes [17]. In **14d**, the 2,5-dimethylpyrrol-1-yl substituent on the 1,2,4-triazol-3-ylidene ring also adopts a relative perpendicular orientation that minimizes steric interactions.

Starting from iodides **10c**,**d**, a simple reaction with $Ag_2O$ led to the silver carbenes **16c**,**d** in good yields (Table 2, entries 8 and 9). These compounds are particularly useful as a potential source for other transition metal complexes via the efficient transmetalation procedures recently reported [18].

Finally, a reaction of the carbene complexes **13b** and **13d** with their parent salts **9b** and **9d** in the presence of AgOTf as a halide scavenger was performed to obtain the cationic bis-carbene complexes **17b** and **17d** in 69% and 57% yield, respectively (Scheme 6). Considering that the starting material possesses a stable chiral axis and that the reaction generates a second one, the product of this reaction could in

Table 2
Synthesis of Rh and Ag triazolylidene complexes **13–16**

| Entry | Starting material | X | Y | Z | Product | Yield (%) |
|---|---|---|---|---|---|---|
| 1 | **9a** | $NBn_2$ | OTf | Cl | **13a** | 64 |
| 2 | **9b** | N(Me)Ph | OTf | Cl | **13b** | 86 |
| 3 | **9c** | $NPh_2$ | OTf | Cl | **13c** | 91 |
| 4 | **10c** | $NPh_2$ | I | I | **14c** | 81 |
| 5 | **9d** |  | OTf | Cl | **13d** | 93 |
| 6 | **10d** |  | I | I | **14d** | 68 |
| 7 | **11** | OBn | OTf | Cl | **15** | 89 |
| 8 | **10c** | $NPh_2$ | I | – | **16c** | 91 |
| 9 | **10d** |  | I | – | **16d** | 88 |




Scheme 6.

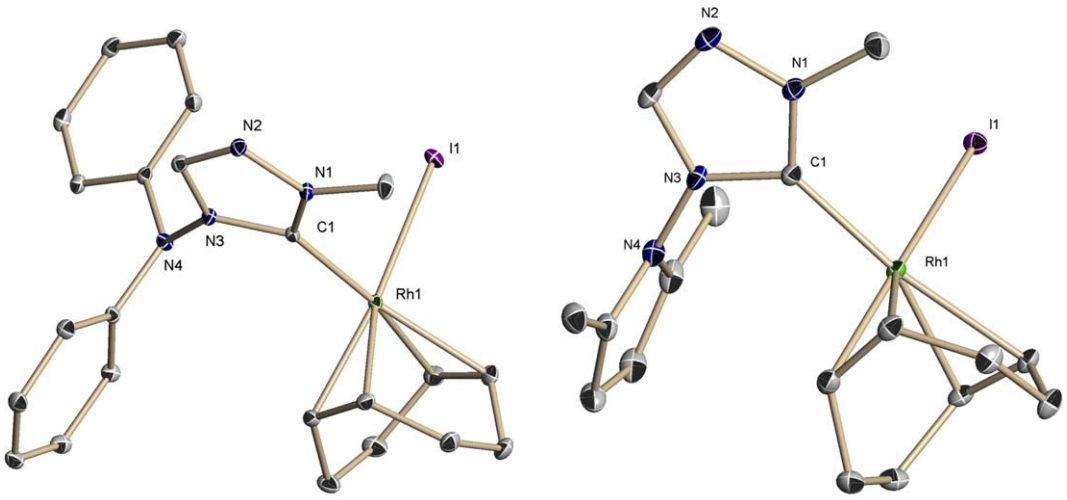



Fig. 2. X-ray structures of **14c** and **14d**. H atoms are omitted for clarity. A single enantiomer is shown for each complex, though both compounds crystallized as racemate.

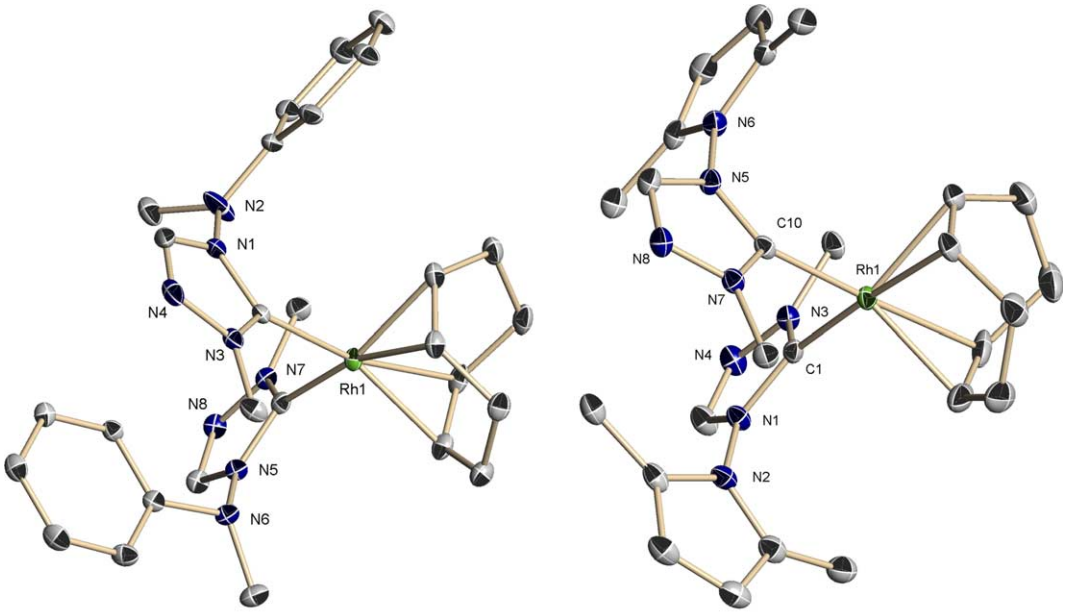
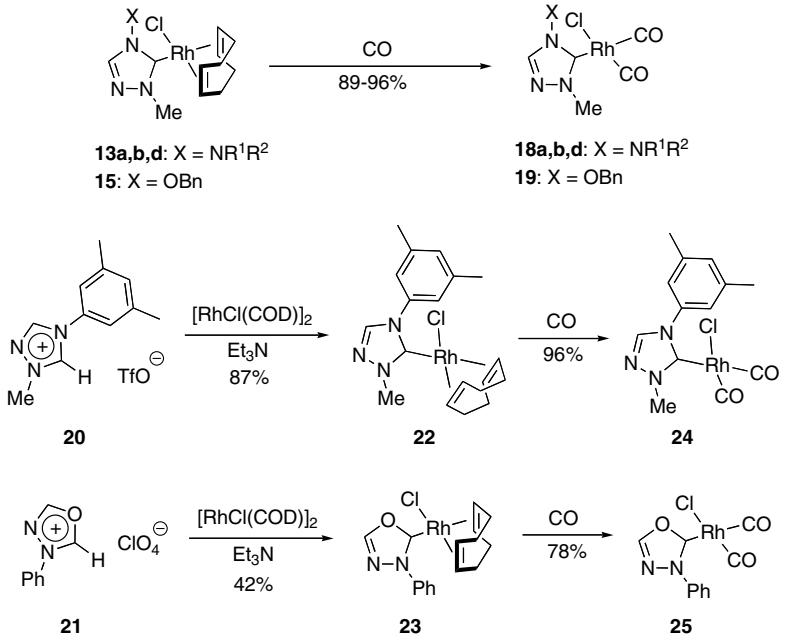



Fig. 3. X-ray structures of the cations of **17b** and **17d**. H atoms and and counteranions are omitted for clarity. A single enantiomer of each structure is represented, although both salts crystallized as racemate.

theory be a mixture of *meso* and racemic compounds [19], associated to a 'parallel' or 'antiparallel' arrangement of the triazol-5-ylidene ligands, respectively. As was already observed in the recently reported bis-imidazo[1,5-a]pyridine-3-ylidene Rh(I) cationic complexes [20], these reactions exclusively afforded the chiral racemic compounds, a fact attributed to the higher steric interactions expected for the 'parallel' arrangement of the carbene ligands. The structures of compounds **17b** and **17d** were unambiguously determined by single-crystal X-ray diffractometry (Fig. 3), showing again the characteristic square-planar geometry with CRhC angles of 91.6° and 91.3°, respectively.

In order to gain some information about the electronic properties of these carbene complexes, compounds **13a**,**b**,**d** and **15** were reacted with carbon monoxide to afford dicarbonyl complexes **18a**,**b**,**d** and **19** in excellent yields (Scheme 7), and their carbonyl stretching frequencies were used to evaluate the σ donor ability of the ligands. For comparative purposes and in order to acquire a better overview of the effect of the substituent at N(4), triazolium **20** [21] and oxadiazolium **21** [22] salts were also transformed into the corresponding Rh(NHC)Cl(COD) complexes **22** and **23** and the dicarbonyl derivatives Rh(NHC)Cl$(CO)_2$ **24** and **25** following standard procedures.




Scheme 7.

Table 3
Carbonyl stretching frequencies for Rh(NHC)Cl(CO)$_2$ complexes **18**, **19**, **24** and **25**

| IR frequency | Compound | | | | | |
|---|---|---|---|---|---|---|
| | **18a** | **18b** | **18d** | **19** | **24** | **25** |
| $\nu_{CO}$(*trans*) | 2010 | 2011 | 2013 | 2012 | 2010 | 2020 |
| $\nu_{CO}$(*cis*) | 2092 | 2088 | 2095 | 2090 | 2090 | 2098 |
| $\nu_{CO}$(average) | 2051 | 2050 | 2054 | 2051 | 2050 | 2059 |

The analysis of the $\nu_{CO}$ stretching frequencies collected in Table 3 suggests that the introduction of amino (data for **18a**,**b**) or alkoxy (data for **19**) groups at N(4) does not significantly modify the σ-donor ability exhibited by 4-alkyl(aryl) analogues.

Probably the expected inductive effect that should reduce the donor ability is waged by a conjugative $n \rightarrow \pi$ interaction in solution, also observed in imidazolin-2-ylidenes,[10] between the dialkylamino group and the triazolylidene system. Supporting this hypothesis, the data collected for **18d** indicate a clear loss of σ donor ability; a negligible $n \rightarrow \pi$ interaction is expected, as the N lone pair is involved in the pyrrole aromaticity, and, therefore, only the inductive effect is observed. Thus, the average $\nu_{CO}$ frequency for **18d** falls between that of the triazol-3-ylidene derivatives **18a**–**b**, **19**, and **24** and the 1,3,4-oxadiazol-2-ylidene complex **25**, which, due to the poorer π-donor and higher electronegativity of the oxygen atom, exhibits the poorer σ-donor ability in this series (Fig. 4).

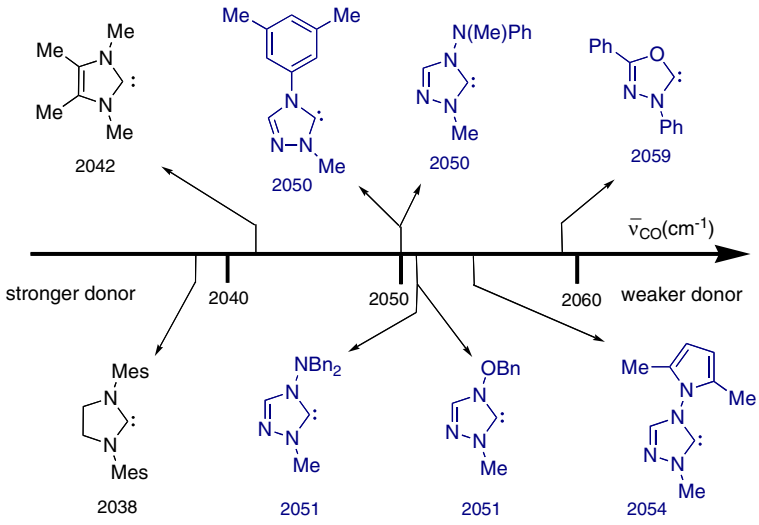



Fig. 4. Scale of σ-donor ability of various carbene ligands, as correlated with the average $\nu_{CO}$ frequencies in their corresponding Rh(I)(carbene)(CO)$_2$ complexes.

In conclusion we have developed a new procedure for the synthesis of *N*,*N*-dialkylamino- and alkoxy-1,2,4-triazoles and for some transition metal complexes containing the triazolylidenes derived from them. A study of the effect of the amino or alkoxy groups on the σ-donor ability of these ligands points to the existence of opposite mesomeric and inductive effects.

The synthesis of analogues of the products described in this paper containing chiral dialkylamino moieties and their application in asymmetric catalysis is the current object of study in our laboratory.

## 3. Experimental

### 3.1. Synthesis of 4-(dialkylamino or alkoxy)-1,2,4-triazoles *1a–c*

To a solution of hydrazine **2a–c** or *O*-benzylhydroxylamine **5** (1 mmol) in pyridine (2 mL) was added *N*,*N*-dimethylformamidazin dihydrochloride **3** (325 mg, 1.5 mmol) and the reaction mixture was stirred for 4 h at 100 °C. The solvent was then removed in vacuo, and the residue was dissolved in a 1:1 $H_2O$: satd. $NaHCO_3$ mixture and extracted with $CH_2Cl_2$($3 \times 5$ mL). The organic layer was dried ($MgSO_4$), concentrated, and the residue was purified by flash chromatography (AcOEt). Starting materials, yields, and characterization data for compounds **4a–c** and **6** are as follows:

**4a**: From **2a**, the above general procedure yielded 114 mg (43%) of **4a** as a colorless oil. $^1$H NMR (300 MHz, $CDCl_3$): δ 8.30 (s, 2H), 7.28–7.04 (m, 10H), 3.81 (s, 4H). $^{13}$C NMR (75 MHz, $CDCl_3$): δ 143.6, 136.4, 128.6, 128.1, 127.4, 57.8. Anal. Calc. for $C_{16}H_{16}N_4$: C, 72.70; H, 6.10; N, 21.20. Found: C, 72.53; H, 5.97; N, 21.01%.

**4b**: From **2b**, the above general procedure yielded 111 mg (64%) of **4b** as a white solid. $^1$H NMR (300 MHz, $CDCl_3$): δ 8.31 (s, 2H), 7.24 (dd, $J = 8.7$, 7.5 Hz, 2H), 6.97 (t, $J = 7.5$ Hz, 1H), 6.54 (d, $J = 8.7$ Hz, 2H), 3.37 (s, 3H). $^{13}$C NMR (75 MHz, $CDCl_3$): δ 148.7, 142.7, 129.9, 122.8, 114.3, 43.6. Anal. Calc. for $C_9H_{10}N_4$: C, 62.05; H, 5.79; N, 32.16. Found: C, 62.11; H, 5.69; N, 32.04%.

**4c**: From **4c**, the above general procedure yielded 137 mg (58%) of **4c** as a light pink solid. $^1$H NMR (500 MHz, $CDCl_3$): δ 8.40 (s, 2H), 7.31 (dd, $J = 8.0$, 7.5 Hz, 4H), 7.14 (t, $J = 8.0$ Hz, 2H), 6.91 (d, $J = 7.5$ Hz, 4H). $^{13}$C NMR (150 MHz, $CDCl_3$): δ 145.1, 143.2, 129.9, 125.2, 120.0. Anal. Calc. for $C_{14}H_{12}N_4$: C, 71.17; H, 5.12; N, 23.21. Found: C, 71.24; H, 5.13; N, 23.20%.

**6**: From **5**, the above general procedure yielded 74 mg (42%) of **6** as a colorless oil. $^1$H NMR (400 MHz, $CDCl_3$): δ 8.00 (s, 2H), 7.43–7.35 (m, 3H), 7.24 (d, $J = 6.4$ Hz, 2H), 5.11 (s, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 138.9, 132.5, 130.3, 129.9, 129.2, 83.5. Anal. Calc. for $C_9H_9N_3O$: C, 61.70; H, 5.18; N, 23.99. Found: C, 61.52; H, 5.01; N, 23.78%.

### 3.2. Synthesis of *4d*

To a solution of 2,5-hexanedione **8** (3.42 g, 30 mmol) and 4-amino-1,2,4-triazole **7** (2.52 g, 30 mmol) in toluene was added a catalytic amount of *p*-toluenesulfonic acid (few crystals), and the mixture was heated to reflux for 3 h with azeotropic removal of water. The solvent was then removed in vacuo and resulting residue was washed with *n*-hexane to yield crude **4d** (4.1 g, 86%), which had characterization data identical to those previously reported [23]. Colorless crystals were obtained by crystallization from toluene.

### 3.3. Synthesis of 4-(dialkylamino or alkoxy)-1-methyl-1,2,4-triazolium triflates *9a–d*, *11*, and iodides *10c*, and *10d*

To a solution of triazole **4a–d** or **6** (1 mmol) in dry $CH_2Cl_2$ (1 mL) was added MeOTf (164 mg, 1 mmol) and the mixture was stirred for 1 h at room temperature. The supernatant was decanted and the remaining solid was washed with $Et_2O$ ($2 \times 10$ mL) to afford pure products **9a–d** and **11**. Alternatively, MeI (6 mmol) was added to a solution of triazole **4c** or **4d** (1 mmol) in THF (1 mL) and the mixture was stirred for 48 h at 60 °C. The supernatant was decanted and the solid was treated as described above to afford **10c** and **10d**. Starting materials, yields, and characterization data for these compounds are as follows:

**9a**: From **4a** and MeOTf, the above general procedure yielded **9a** (372 mg, 87%) as a colorless syrup. $^1$H NMR (500 MHz, $CDCl_3$): δ 10.70 (s, 1H), 7.85 (s, 1H), 7.22–7.40 (m, 10H), 4.44 (s, 4H), 4.01 (s, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$): δ 143.9, 143.5, 133.8, 129.8, 129.5, 128.5, 62.7, 40.3. Anal. Calc. for $C_{18}H_{19}N_4F_3O_3S$: C, 50.46; H, 4.47; N, 13.08. Found: C, 50.81; H, 4.87; N, 12.86%.

**9b**: From **4b** and MeOTf, the above general procedure yielded **9b** (328 mg, 97%) as a white solid. $^1$H NMR (300 MHz, acetone-$d_6$): δ 10.48 (s, 1H), 9.49 (s, 1H), 7.37 (dd, $J = 8.7$, 7.5 Hz, 2H), 7.13 (t, $J = 7.5$ Hz, 1H), 7.02 (d, $J = 8.7$ Hz, 2H), 4.31 (s, 3H), 3.63 (s, 3H). $^{13}$C NMR (75 MHz, $CDCl_3$): δ 147.9, 145.0, 144.5, 129.9, 124.2, 116.2, 43.2, 39.9. Anal. Calc. for $C_{11}H_{13}N_4F_3O_3S$: C, 39.05; H, 3.87; N, 16.56. Found: C, 39.14; H, 3.93; N, 16.60%.

**9c**: From **4c** and MeOTf, the above general procedure yielded **9c** (376 mg, 94%) as a light-yellow solid. M.p. 128–130 °C (dec.); $^1$H NMR (300 MHz, acetone-$d_6$): δ 10.70 (s, 1H), 9.70 (s, 1H), 7.46 (t, $J = 7.8$ Hz, 4H), 7.30 (t, $J = 7.5$ Hz, 2H), 7.21 (d, $J = 7.8$ Hz, 4H), 4.32 (s, 3H). $^{13}$C NMR (75 MHz, acetone-$d_6$): δ 146.3, 145.9, 145.3, 130.9, 127.2, 122.2, 40.8. Anal. Calc. for $C_{16}H_{15}N_4F_3O_3S$: C, 48.00; H, 3.78; N, 13.99. Found: C, 47.87; H, 3.68; N, 13.78%.

**10c**: From **4c** and MeI, the above general procedure yielded crystalline **10c** (303 mg, 81%). M.p. 120–121 °C (dec.); $^1$H NMR (300 MHz, acetone-$d_6$): δ 11.31 (s, 1H), 9.72 (s, 1H), 7.43 (t, $J = 7.8$ Hz, 4H), 7.28 (t, $J = 7.5$ Hz,

2H), 7.23 (d, $J = 7.8$ Hz, 4H), 4.29 (s, 3H). $^{13}$C NMR (75 MHz, acetone-$d_6$): $\delta$ 146.7, 145.8, 145.1, 140.0, 127.1, 122.2, 40.7. Anal. Calc. for $C_{15}H_{15}N_4I$: C, 47.64; H, 4.00; N, 14.81. Found: C, 47.39; H, 3.91; N, 14.72%.

**9d**: From **4d** and MeOTf, the above general procedure yielded **9d** (3.1 g, 96%) as a white solid. $^1$H NMR (300 MHz, acetone-$d_6$): $\delta$ 10.68 (s, 1H), 9.61 (s, 1H), 5.94 (s, 2H), 4.41 (s, 3H), 2.10 (s, 6H). $^{13}$C NMR (75 MHz, acetone-$d_6$): $\delta$ 145.7, 145.6, 129.6, 107.3, 41.1, 10.6. Anal. Calc. for $C_{10}H_{13}N_4F_3O_3S$: C, 36.81; H, 4.02; N, 17.17. Found: C, 36.70; H, 3.90; N, 16.89%.

**10d**: From **4d** and MeI, the above general procedure yielded crystalline **10d** (241 mg, 79%). M.p. 230–130 °C (dec.); $^1$H NMR (500 MHz, acetone-$d_6$): $\delta$ 11.25 (s, 1H), 9.61 (s, 1H), 5.91 (s, 2H), 4.39 (s, 3H), 2.13 (s, 6H). $^{13}$C NMR (75 MHz, acetone-$d_6$): $\delta$ 146.3, 145.6, 129.4, 107.3, 40.2, 10.7. Anal. Calc. for $C_9H_{13}N_4I$: C, 35.54; H, 4.31; N, 18.42. Found: C, 35.42; H, 4.58; N, 18.22%.

**11**: From **6** and MeOTf, the above general procedure yielded **11** (302 mg, 89%) as a colorless syrup. $^1$H NMR (500 MHz, acetone-$d_6$): $\delta$ 10.45 (s, 1H), 9.29 (s, 1H), 7.57 (d, $J = 6.5$ Hz, 2H), 7.47 (m, 3H), 5.68 (s, 2H), 4.23 (s, 3H). $^{13}$C NMR (125 MHz, acetone-$d_6$): $\delta$ 142.0, 141.9, 132.7, 131.4, 131.2, 129.9, 86.1, 40.6. Anal. Calc. for $C_{11}H_{12}N_3OF_3S$: C, 38.94; H, 3.56; N, 12.38. Found: C, 38.64; H, 3.22; N, 12.47%.

### 3.4. Synthesis of *12*

Triazolium salt **4d** (1 mmol) was treated with $LiBEt_3H$ as described in the literature [15] to afford triazoline **12** (127 mg, 71%) as a colorless syrup. $^1$H-RMN (300 MHz, $CDCl_3$): $\delta$ 6.84 (s, 1H), 5.72 (s, 2H), 4.43 (s, 2H), 2.83 (s, 3H), 2.21 (s, 6H). $^{13}$C-RMN (75 MHz, $CDCl_3$): $\delta$ 143.1, 128.6, 105.1, 77.6, 43.6, 12.7. HRMS *m/z* Calc. for $C_9H_{14}N_4$: 178.1219, found: 178.1224.

### 3.5. Synthesis of RhCl(COD)[4-(dialkylamino or alkoxy)-1-methyl-1,2,4-triazol-5-ylidenes] *13a–d, 14c,d and 15*: General procedure

To a suspension of 4-(dialkylamino or alkoxy)-1-methyl-1,2,4-triazolium salt **9a–d**, **10c,d** or **11** (0.5 mmol) and $[RhCl(COD)]_2$ (123 mg, 0.25 mmol) in THF (5 mL) was added $Et_3N$ (76 μL, 0.55 mmol) and the mixture was stirred for 1 h at room temperature. The solvent was removed in vacuo and the residue was purified by flash chromatography (AcOEt-Hex 1:4) to afford products **13a–d**, **14c**, **d** and **15**. Starting materials, yields, and characterization data for these compounds are as follows:

**13a**: From **9a**, the above general procedure yielded 179 mg (64%) of **13a** as a yellow solid. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 7.48–7.21 (m, 11H), 5.32–5.16 (m, 1H), 5.12–5.00 (m, 1H), 4.72 (d, $J = 13.2$ Hz, 2H), 4.52 (d, $J = 13.2$ Hz, 2H), 4.27 (s, 3H), 3.50–3.36 (m, 1H), 3.35–3.20 (m, 1H), 2.70–2.60 (m, 1H), 2.60–2.40 (m, 1H), 2.40–2.20 (m, 2H), 2.20–2.10 (m, 1H), 2.10–2.00 (m, 1H), 1.90–1.70 (m, 2H). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 184.9 (d, $J_{C-Rh} = 50.3$ Hz), 142.4, 135.9, 129.8, 128.9, 128.5, 98.9 (d,$J_{C-Rh} = 7.2$ Hz), 98.6 (d, $J_{C-Rh} = 7.0$ Hz), 71.2 (d,$J_{C-Rh} = 14.5$ Hz), 68.2 (d, $J_{C-Rh} = 14.1$ Hz), 60.7, 41.6, 34.3, 31.9, 30.5, 28.2. HRMS *m/z* Calc. for $C_{25}H_{30}N_4ClRh$524.1214, found 524.1206. Anal. Calc. for $C_{25}H_{30}N_4ClRh$: C, 57.21; H, 5.76; N, 10.67. Found: C, 57.09; H, 5.84; N, 10.88%.

**13b**: From **9b**, the above general procedure yielded 188 mg (86%) of **13b** as a yellow solid. M.p. 182–184 °C (dec.); $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 8.02 (s, 1H), 7.28 (t, $J = 7.8$ Hz, 2H), 6.97 (t, $J = 7.2$ Hz, 1H), 6.64 (d, $J = 8.4$ Hz, 2H), 5.01 (br s, 2H), 4.34 (s, 3H), 3.78 (s, 3H), 3.41 (br s, 1H), 2.76 (br s, 1H), 2.41 (br s, 1H), 2.32–2–20 (m, 2H), 1.93 (br s, 2H), 1.62 (br s, 2H), 1.51 (br s, 1H).$^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 187.6 (d, $J_{C-Rh} = 50.9$ Hz), 149.1, 143.9, 129.8, 126.5, 122.0, 114.1, 99.2 (d, $J_{C-Rh} = 7.1$ Hz), 70.2 (br s), 68.2 (br s), 44.0, 41.5, 34.2 (br s), 31.9 (br s), 30.0 (br s), 28.2 (br s). HRMS *m/z* Calc. for $C_{18}H_{28}N_4ClRh$ 434.0745, found 434.0736. Anal. Calc. for $C_{18}H_{24}N_4ClRh$: C, 49.73; H, 5.56; N, 12.89. Found: C, 49.81; H, 5.50; N, 13.00%.

**13c**: From **9c**, the above general procedure yielded 226 mg (91%) of **13c** as a yellow solid. M.p. 188–190 °C (dec.); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 8.03 (s, 1H), 7.31 (t, $J = 7.6$ Hz, 4H), 7.20–7.05 (m, 6H), 4.97 (br s, 2H), 4.35 (br s, 3H), 3.43 (br s, 1H), 2.85 (br s, 1H), 2.50–2.40 (m, 1H), 2.34–2.22 (m, 1H), 2.20–2.10 (br s, 1H) 1.94 (br s, 2H), 1.71 (br s, 2H), 1.48 (br s, 1H).$^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 188.3 (d,$J_{C-Rh} = 50.1$ Hz), 145.3, 143.4, 129.6, 124.7, 120.6, 99.0 (d, $J_{C-Rh} = 12.1$ Hz), 69.9 (d,$J_{C-Rh} = 13.7$ Hz), 67.4 (d, $J_{C-Rh} = 13.1$ Hz), 41.1, 34.4, 31.4, 29.7, 27.7. HRMS Calc. for $C_{23}H_{26}N_4ClRh$ 496.0901, found 496.0904. Anal. Calc. for $C_{23}H_{26}N_4ClRh$: C, 55.60; H, 5.27; N, 11.28. Found: C, 55.82; H, 5.43; N, 11.09%.

**14c**: From **10c**, the above general procedure yielded 238 mg (81%) of **14c** as a yellow solid. M.p. 216–218 °C (dec.); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 8.08 (s, 1H), 7.31 (t, $J = 8.0$ Hz, 4H), 7.20–7.05 (m, 6H), 5.20 (br s, 2H), 4.25 (s, 3H), 3.62–3.54 (m, 1H), 2.95–2.85 (m, 1H), 2.50–2.20 (m, 2H), 2.15–2.03 (m, 1H), 2.00–1.90 (m, 1H), 1.85–1.53 (m, 2H), 1.62–1.50 (m, 4H), 1.42–1.30 (m, 1H).$^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 188.4 (d,$J_{C-Rh} = 49.3$ Hz), 145.2, 143.5, 129.6, 124.9, 121.0, 96.9 (d, $J_{C-Rh} = 9.4$ Hz), 96.8 (d, $J_{C-Rh} = 10.0$ Hz), 73.1 (d, $J_{C-Rh} = 14.0$ Hz), 71.0 (d, $J_{C-Rh} = 13.5$ Hz), 41.7, 34.3, 30.8, 30.4, 28.0. Anal. Calc. for $C_{23}H_{26}N_4IRh$: C, 46.96; H, 4.45; N, 9.52. Found: C, 47.12; H, 4.49; N, 9.31%.

**13d**: From **9d**, the above general procedure yielded 197 mg (93%) of **13d** as a yellow solid. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 7.99 (s, 1H), 5.91 (br s, 2H), 4.98 (br s, 2H), 4.37 (s, 3H), 3.47 (br s, 1H), 3.00 (br s, 1H), 2.40 (br s, 4H), 2.28–2.10 (m, 2H), 1.67 (br s, 8H). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 187.3 (d, $J_{C-Rh} = 51.8$ Hz), 142.7, 130.9, 127.2, 106.3, 105.7, 99.9 (br s), 69.6 (d,

$J_{C-Rh} = 14.4$ Hz), 68.3 (d, $J_{C-Rh} = 13.5$ Hz), 47.0, 34.4, 32.1, 29.5, 28.4, 12.9, 11.3. Anal. Calc. for $C_{17}H_{24}N_4ClRh$: C, 48.30; H, 5.72; N, 13.25. Found: C, 48.06; H, 5.65; N, 13.08%.

**14d**: From **10d**, the above general procedure yielded 175 mg (68%) of **14d** as a yellow solid. M.p. 178–180 °C (dec.); $^1$H-RMN (400 MHz, $CDCl_3$): $\delta$ 7.99 (s, 1H), 5.91 (s, 2H), 5.32–5.27 (m, 1H), 5.31–5.14 (m, 1H), 4.31 (s, 3H), 3.72–3.62 (m, 1H), 3.33–3.25 (m, 1H), 2.46 (s, 3H), 2.40–2.25 (m, 1H), 2.25–2.05 (m, 2H), 1.95–1.85 (m, 1H), 1.85–1.65 (m, 6H), 1.55–1.45 (m, 1H).$^{13}$C-RMN (100 MHz, $CDCl_3$): $\delta$ 187.48 (d,$J_{C-Rh} = 50.1$ Hz), 143.1, 130.5, 127.0, 106.2, 105.6, 97.5 (d, $J_{C-Rh} = 6.4$ Hz), 97.4 (d, $J_{C-Rh} = 6.0$ Hz), 72.6 (d, $J_{C-Rh} = 13.2$ Hz), 71.3 (d, $J_{C-Rh} = 13.3$ Hz), 43.0, 33.9, 31.0, 30.2, 28.6, 14.4, 11.1. Anal. Calc. for $C_{17}H_{24}N_4IRh$: C, 39.71; H, 4.70; N, 10.90. Found: C, 39.52; H, 4.51; N, 10.81.

**15**: From **11**, the above general procedure yielded 167 mg (77%) of **15** as a yellow solid. $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ 7.60–7.50 (m, 2H), 7.45–7.30 (m, 4H), 5.85 (br s, 1H), 5.77 (br s, 1H), 5.15 (br s, 2H), 4.22 (s, 3H), 3.87 (br s, 1H), 3.43 (br s, 1H), 2.41 (br s, 4H), 2.00 (br s, 4H). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 181.1 (d, $J_{C-Rh} = 50.3$ Hz), 139.2, 133.4, 130.8, 130.0, 129.2, 99.7 (br s), 99.4 (br s), 83.0, 69.9 (br s), 41.5, 33.2 (br s), 29.4 (br s). Anal. Calc. for $C_{18}H_{23}N_3ClORh$: C, 49.61; H, 5.32; N, 9.64. Found: C, 49.82; H, 5.21; N, 9.87%.

### 3.6. Synthesis of *22*

To a solution of 1-methyl-4-(3,5-dimethylphenyl)-1,2,4-triazolium triflate **20** [21] (101 mg, 0.3 mmol) in THF (10 mL) was added $[RhCl(COD)]_2$ (74 mg, 0.15 mmol) and $Et_3N$ (38 μL, 0.3 mmol) and the mixture was stirred at room temperature for 30 min. The solvent was removed in vacuo an the residue was purified by flash chromatography (AcOEt-hexane 1:3) to yield **22** (114 mg, 87%) as a yellow powder. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 8.09 (s, 1H), 7.76 (s, 2H), 7.11 (s, 1H), 5.17–5.10 (m, 1H), 5.05–4.97 (m, 1H), 4.32 (s, 3H), 3.32 (s, 1H), 2.68–2.48 (m, 1H), 2.43 (s, 6H), 2.38–2.25 (m, 2H), 2.15–2.05 (m, 1H), 1.93–1.78 (m, 3H), 1.64–1.50 (m, 2H).$^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 185.6 (d, $J_{C-Rh} = 51.1$ Hz), 141.3, 139.5, 136.5, 130.7, 122.4, 99.2 (t, $J_{C-Rh} = 6.0$ Hz), 69.0 (t, $J_{C-Rh} = 15.8$ Hz), 40.6, 33.7, 32.0, 29.5, 28.7, 21.6. Anal. Calc. for $C_{19}H_{25}N_3ClRh$: C, 52.49; H, 6.03; N, 9.66. Found: C, 52.31; H, 5.89; N, 9.73%.

### 3.7. Synthesis of *23*

To a solution of 2-methyl-4-phenyl-1-oxa-3,4-diazolium perchlorate **21** [22] (78 mg, 0.3 mmol) in THF (10 ml) was added $[RhCl(COD)]_2$ (74 mg, 0.15 mmol) and $Et_3N$ (38 μL, 0.3 mmol) and the mixture was stirred for 30 min at room temperature. The solvent was then removed in vacuo and the residue was purified by flash chromatography (AcOEt/hexane 1:3) to afford 51 mg (42%) of RhCl(COD)-(2-methyl-4-phenyl-1-oxa-3,4-diazol-5-ylidene) **23**: $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.60–7.40 (m, 5H), 5.27 (br s, 2H), 3.30 (br s, 2H), 2.57 (s, 3H), 2.30–2.45 (m, 2H), 2.30–2.15 (m, 2H), 2.05–1.90 (m, 2H), 1.90–1.80 (m, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 204.8 (d, $J_{C-Rh} = 56.5$ Hz), 166.6, 136.6, 129.4, 129.0, 123.3, 102.4 (t,$J_{C-Rh} = 6.6$ Hz), 70.3 (t, $J_{C-Rh} = 13.9$ Hz), 32.6, 28.7, 11.1. Anal. Calc. for $C_{17}H_{20}N_2ClRhO$: C, 50.20; H, 4.96; N, 6.89. Found: C, 50.02; H, 5.14; N, 6.72%.

### 3.8. Synthesis of silver carbenes *16c,d*: General procedure

To a solution of **10c** or **10d** (1 mmol) in $CH_2Cl_2$ (20 mL) was added $Ag_2O$ (128 mg, 0.55 mmol) and the mixture was stirred in the darkness at room temperature for 3 h. The mixture was then filtered through a celite pad and concentrated to yield the products **16c** and **16d** as white foams. Starting materials, yields, and characterization data for these compounds are as follows:

**16c**: From **10c**, the above general procedure yielded 440 mg (91%) of **16c** as a white foam. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 8.15 (s, 1H), 7.23 (t, $J = 7.8$ Hz, 4H), 7.06 (t, $J = 7.2$ Hz, 2H), 6.94 (d, $J = 7.2$ Hz, 4H), 3.98 (s, 3H).$^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 145.1, 143.2, 130.0, 125.2, 121.0, 42.3. Anal. Calc. for $C_{15}H_{14}N_4IAg$: C, 37.14; H, 2.91; N, 11.55. Found: C, 37.25; H, 2.99; N, 11.78%.

**16d**: From **10d**, the above general procedure yielded 361 mg (88%) of **16d** as a white foam. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 8.21 (s, 1H), 5.88 (s, 2H), 3.96 (s, 3H), 2.08 (s, 6H). $^{13}$C NMR (75 MHz, acetone-$d_6$): $\delta$ 145.3, 129.1, 107.2, 42.1, 10.6. Anal. Calc. for $C_9H_{12}N_4IAg$: C, 26.30; H, 2.94; N, 13.63. Found: C, 25.98; H, 3.13; N, 13.79%.

### 3.9. Synthesis of cationic rhodium complexes *17b,d*: General procedure

To a solution of RhCl(1,2,4-triazol-5-ylidene)(COD) **13b** or **13d** (0.2 mmol) in dry THF (4 mL) was added the corresponding azolium triflate **9b** or **9d**, AgOTf (51 mg, 0.2 mmol) and $Et_3N$ (22 μL, 0.2 mmol). The mixture was stirred in the darkness for 2 h, the solvent was removed in vacuo and the residue was purified by flash chromatography (AcOEt/$CH_2Cl_2$ 1:1) to yield **17b** or **17d**. Crystals suitable for X-ray diffraction analysis were grown by slow diffusion of diethyl ether in a solution of the complex in dichloromethane. Starting materials, yields, and characterization data for these compounds are as follows:

**17b**: From **13b** and **9b**, the above general procedure yielded 102 mg (69%) of **17b** as a yellow solid. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 8.20 (s, 2H), 7.23 (t, $J =$ 8.0 Hz, 4H), 7.01 (t, $J = 7.2$ Hz, 2H), 6.32 (d, $J = 8.0$ Hz, 4H), 4.56 (br s, 2H), 4.18 (br s, 2H), 3.74 (br s, 6H), 3.52 (s, 6H), 2.45–2.20 (m, 6H), 2.10–2.00 (m, 2H).$^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 185.1 (d, $J_{C-Rh} = 52.2$ Hz), 148.1, 142.9, 129.9, 122.8, 113.5, 92.7 (d, $J_{C-Rh} = 7.4$ Hz), 90.0

(d,$J_{C-Rh}$ = 6.5 Hz), 43.7, 40.3, 31.9, 29.0. Anal. Calc. for $C_{29}H_{36}N_8F_3O_3SRh$: C, 47.16; H, 5.06; N, 15.17. Found: C, 47.21; H, 5.21; N, 15.01%.

**17d**: From **13d** and **9d**, the above general procedure yielded 82 mg (57%) of crystalline **17d**. M.p. 252–253 °C (dec.); $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 8.22 (s, 2H), 6.00 (d, $J$ = 6.9 Hz, 4H), 4.81 (br s, 2H), 4.25–4.15 (m, 2H), 3.98 (s, 6H), 2.40–2.10 (m, 8H), 2.02 (s, 6H), 1.37 (s, 6H). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 185.4 (d, $J_{C-Rh}$ = 52.9 Hz), 145.2, 128.9, 127.9, 108.0, 107.8, 94.1 (d, $J_{C-Rh}$ = 8.0 Hz), 90.0 (d, $J_{C-Rh}$ = 7.2 Hz), 41.8, 31.6, 29.7, 11.9, 11.1. Anal. Calc. for $C_{27}H_{36}N_8F_3O_3SRh$: C, 45.38; H, 5.30; N, 15.68. Found: C, 45.28; H, 5.42; N, 15.47%.

### 3.10. Synthesis of rhodium dicarbonyl complexes *18a,b,d*, *19*, *24*, and *25*: General procedure

CO was bubbled through a solution of Rhodium cyclooctadiene complexes **13a**,**b**,**d**, **15**, **22** or **23** (0.1 mmol) in THF (3 mL) for 10 min. The solvent was then removed in vacuo and the residue was washed several times with *n*-pentane and dried in high vacuum. Starting materials, yields, and characterization data for these compounds are as follows:

**18a**: From **13a**, the above general procedure yielded 42 mg (89%) of **18a** as a yellow syrup. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 7.44 (s, 1H), 7.40–7.20 (m, 10H), 4.59 (s, 4H), 4.08 (s, 3H). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 185.0 (d,$J_{C-Rh}$ = 55.1 Hz), 182.4 (d, $J_{C-Rh}$ = 74.8 Hz), 176.8 (d,$J_{C-Rh}$ = 43.5 Hz), 144.3, 135.6, 129.9, 129.0, 128.9, 61.9, 42.6. FTIR: $\nu_{CO}$ = 2092, 2010 cm$^{-1}$. Anal. Calc. for $C_{19}H_{18}N_4ClO_2Rh$: C, 48.27; H, 3.84; N, 11.85. Found: C, 48.60; H, 3.51; N, 11.89.

**18b**: From **13b**, the above general procedure yielded 37 mg (96%) of **18b** as a yellow powder. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 8.20 (s, 1H), 7.31 (t, $J$ = 7.8 Hz, 2H), 7.03 (t, $J$ = 7.5 Hz, 1H), 6.70 (d, $J$ = 8.1 Hz, 2H), 4.17 (s, 3H), 3.55 (s, 3H). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 184.9 (d, $J_{C-Rh}$ = 55.4 Hz), 181.4 (d, $J_{C-Rh}$ = 71.3 Hz), 148.0, 143.7, 129.4, 123.2, 115.4, 43.8, 42.1. FTIR: $\nu_{CO}$ = 2088, 2010 cm$^{-1}$. Anal. Calc. for $C_{12}H_{12}N_4ClO_2Rh$: C, 37.57; H, 3.42; N, 14.60. Found: C, 37.45; H, 3.22; N, 14.94%.

**18d**: From **13d**, the above general procedure yielded 33 mg (93%) of **18b** as a yellow powder. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 8.20 (s, 1H), 5.92 (s, 2H), 4.23 (s, 3H), 2.06 (s, 6H). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 184.1 (d, $J_{C-Rh}$ = 55.7 Hz), 181.2 (br s), 181.1 (d,$J_{C-Rh}$ = 47.6 Hz), 142.8, 128.5, 106.2, 41.8, 11.6. FTIR: $\nu_{CO}$ = 2095, 2013 cm$^{-1}$. Anal. Calc. for $C_{11}H_{12}N_4ClO_2Rh$: C, 35.65; H, 3.26; N, 15.12. Found: C, 35.39; H, 3.03; N, 15.01%.

**19**: From **15**, the above general procedure yielded 35 mg (91%) of **19** as a yellow syrup. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 7.51–7.30 (m, 6H), 5.56 (s, 2H), 4.09 (s, 3H).$^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 184.6 (d,$J_{C-Rh}$ = 55.7 Hz), 181.6 (d, $J_{C-Rh}$ = 72.2 Hz), 173.8 (d,$J_{C-Rh}$ = 43.5 Hz), 139.3, 132.3, 130.5, 130.2, 129.2, 83.3, 42.7. FTIR: $\nu_{CO}$ = 2090, 2012 cm$^{-1}$. Anal. Calc. for $C_{12}H_{11}N_3ClO_3Rh$: C, 37.47; H, 3.14; N, 10.93. Found: C, 37.23; H, 3.02; N, 11.21%.

**24**: From **22**, the above general procedure yielded 36 mg (96%) of **24** as a yellow powder. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 8.18 (s, 1H), 7.27 (s, 2H), 7.14 (s, 1H), 4.22 (s, 3H), 2.40 (s, 6H). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 184.8 (d,$J_{C-Rh}$ = 55.2 Hz), 181.8 (d, $J_{C-Rh}$ = 68.4 Hz), 177.6 (d,$J_{C-Rh}$ = 44.1 Hz), 142.0, 139.8, 135.4, 131.6, 123.0, 40.9, 21.3. FTIR: $\nu_{CO}$ = 2090, 2010 cm$^{-1}$. Anal. Calc. for $C_{13}H_{13}N_3ClO_2Rh$: C, 40.91; H, 3.43; N, 11.01. Found: C, 41.12; H, 3.23; N, 11.15%.

**25**: From **23**, the above general procedure yielded 28 mg (78%) of **25** as a yellow solid. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 8.10–8.00 (m, 2H), 7.65–7.45 (m, 3H), 2.59 (s, 3H).$^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 196.3 (d, $J_{C-Rh}$ = 65.2 Hz), 184.4 (d, $J_{C-Rh}$ = 74.2 Hz), 181.5 (br s), 168.0, 135.8, 130.9, 129.7, 124.7, 11.4. FTIR: $\nu_{CO}$ = 2098, 2020 cm$^{-1}$. Anal. Calc. for $C_{11}H_8N_2ClO_3Rh$: C, 37.26; H, 2.27; N, 7.90. Found: C, 37.31; H, 2.44; N, 7.98%.

### 3.11. X-ray crystallography

A single crystal of suitable size was mounted on glass fiber with perfluoropolyether oil (FOMBLIN® 140/13, Aldrich) and attached to the goniometer head on a Bruker-Nonius X8Apex-II CCD diffractometer using graphite monochromator $\lambda$ (Mo K$\alpha$1) = 0.71073 Å, and equipped with a Bruker-Nonius Kryo-Flex low temperature device cooled at 100 K. Data collection was performed using $\omega$ and $\phi$ scans with a width of 0.30° and exposure times of 10 s (in the range $5.70 < 2\theta < 61.12°$, **14c**), 15 s (in the range $5.90 < 2\theta < 61.16°$, **14d**), 10 s (in the range $2.66 < 2\theta < 61.14°$, **17b**) or 30 s (in the range $4.68 < 2\theta < 55.60°$, **17d**) with a detector distance of 37.5 mm. The data were reduced (SAINT) [24] and corrected for Lorentz polarization effects and absorption (SADABS [25]. The structure was solved by direct methods (SIR-2002) [26] and refined against all $F^2$ data by full-matrix least-squares techniques (SHELXTL-6.12) [27]. All the non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were included from calculated positions and refined riding on their respective carbon atoms with isotropic displacement parameters.

### 3.12. Crystallographic data for *14c*

$C_{23}H_{26}IN_4Rh$, $M_r$ = 588.29, yellow prism crystal (0.34 × 0.33 × 0.31 mm$^3$) from hexane– $CH_2Cl_2$; monoclinic, space group $P2_1/n$ (no.14), $a$ = 9.8051(2) Å, $b$ = 13.1029(3) Å, $c$ = 17.4440(4) Å, $\beta$ = 101.8510(10)°, $V$ = 2193.35(8) Å$^3$, $Z$ = 4, $\rho_{calc}$ = 1.782 g cm$^{-3}$, $F(000)$ = 1160, $\mu$ = 2.203 mm$^{-1}$, 30,946 measured reflections, of which 6692 were unique ($R_{int}$ = 0.0225); 264 refined parameters, $R_1$ = 0.0176 for reflections with $I > 2\sigma(I)$ and $wR_2$ = 0.0456 for all data (GOF = 1.079).

### 3.13. Crystallographic data for **14d**

$C_{17}H_{24}IN_4Rh$, $M_r = 514.21$, orange prism crystal ($0.28 \times 0.26 \times 0.25$ mm$^3$) from hexane– $CH_2Cl_2$; monoclinic, space group $C2/c$ (no. 15), $a = 24.2857(8)$ Å, $b = 12.1154(4)$ Å, $c = 16.1964(5)$ Å, $\beta = 128.5620(10)°$, $V = 3726.3(2)$ Å$^3$, $Z = 8$, $\rho_{calc} = 1.833$ g cm$^{-3}$, $F(000) = 2016$, $\mu = 2.578$ mm$^{-1}$, 21,308 measured reflections, of which 5643 were unique ($R_{int} = 0.0240$); 212 refined parameters, $R_1 = 0.0282$ for reflections with $I > 2\sigma(I)$ and $wR_2 = 0.0768$ for all data (GOF = 1.049).

### 3.14. Crystallographic data for **17b**

$C_{29}H_{36}F\ N_8O_3RhS$, $M_r = 736.63$, yellow prism crystal ($0.48 \times 0.45 \times 0.43$ mm$^3$) from ethyl ether–$CH_2Cl_2$; monoclinic, space group $P2_1/n$ (no. 14), $a = 17.6377(5)$ Å, $b = 9.5102(2)$ Å, $c = 20.3236(6)$ Å, $\beta = 108.7710(10)°$, $V = 3227.72(15)$ Å$^3$, $Z = 4$, $\rho_{calc} = 1.516$ g cm$^{-3}$, $F(000) = 1512$, $\mu = 0.655$ mm$^{-1}$, 36,959 measured reflections, of which 9471 were unique ($R_{int} = 0.0248$); 410 refined parameters, $R_1 = 0.0571$ for reflections with $I > 2\sigma(I)$ and $wR_2 = 0.1532$ for all data (GOF = 1.032).

### 3.15. Crystallographic data for **17d**

$C_{27}H_{36}F_3N_8O_3RhS$, $M_r = 712.61$, yellow block crystal ($0.20 \times 0.17 \times 0.07$ mm$^3$) from ethyl ether–$CH_2Cl_2$; monoclinic, space group $P2_1/c$ (no. 14), $a = 16.8666(5)$ Å, $b = 21.0129(6)$ Å, $c = 17.4842(4)$ Å, $\beta = 96.1430(10)°$, $V = 6161.1(3)$ Å$^3$, $Z = 8$, $\rho_{calc} = 1.536$ g cm$^{-3}$, $F(000) = 2928$, $\mu = 0.683$ mm$^{-1}$, 57,059 measured reflections, of which 14,522 were unique ($R_{int} = 0.0835$); 775 refined parameters, $R_1 = 0.0585$ for reflections with $I > 2\sigma(I)$ and $wR_2 = 0.1670$ for all data (GOF = 1.018).

## 4. Supplementary material

Full crystallographic data (CIF files) for **14c**, **14d**, **17b** and **17d** have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 273322–273325. Copies of this information may be obtained free of charge from The Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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