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Bis(1,2,3-triazol-5-ylidenes) (i-bitz) as Stable 1,4-Bidentate Ligands Based on Mesoionic Carbenes (MICs)

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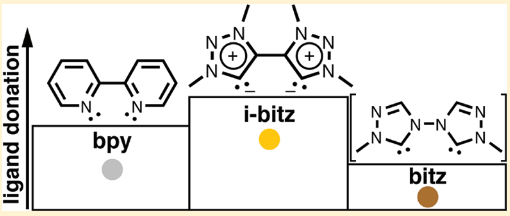
S *Supporting Information*

ABSTRACT: Direct metalation of bis(1,2,3-triazolium) salts affords mononuclear rhodium(I) complexes, which feature a 1,4-bidentate bis(1,2,3-triazol-5-ylidene) (i-bitz) ligand. The topology of the ligand is similar to that of 2,2′-bipyridines (bpy) and their congeners, as well as bis(1,2,4-triazol-5-ylidenes) (bitz). As the former, but in contrast to the latter, the free i-bitz can be isolated, which paves the way for various applications.



INTRODUCTION

2,2′-Bipyridines (bpy) and their congeners (Figure 1), such as phenanthrolines, are privileged 1,4-bidentate ligands[1] in structural inorganic chemistry, in catalysis, and more recently in light-emitting devices and solar cells.[2] Their electronic properties, and the strength of the resulting metal−ligand bonds, can be tuned, but only to a limited extent, by the introduction of substituents on the heterocyclic ring. Therefore, readily accessible ligands, featuring the same topology but with strikingly different electronic properties, are highly desirable. In this regard, neutral ligands bearing a lone pair at carbon are attractive candidates.[3] Peris, Crabtree, et al.[4] introduced 4,4′-bis(1,2,4-triazol-5-ylidenes) (bitz) as N-heterocyclic carbene (NHC) equivalents of 2,2′-bipyridines. Here we report the preparation of rhodium(I) complexes bearing a bis(1,2,3-triazol-5-ylidene) ligand (i-bitz) and show that, in contrast with their bitz isomers, the metal-free bidentate ligand can be isolated and structurally characterized.

RESULTS AND DISCUSSION

Recently, the coordination chemistry of 1,2,3-triazol-5-ylidenes, which are mesoionic carbenes (MICs),[5] has attracted considerable interest.[6,7] They feature electron-donor properties stronger than those of their 1,2,4-triazolylidene isomers,[8] as well as of any other five-membered NHCs.[9] Importantly, ligands can only find numerous applications if they are readily available in large quantities. This is the case for 1,2,3-triazol-5-ylidenes, as well as bis(1,2,3-triazoles),[10] which prompted us to tackle the synthesis of metal complexes featuring bidentate 4,4′-bis(1,2,3-triazol-5-ylidenes) (i-bitz). The protonated precursors **2a**−**c** are rapidly prepared on a multigram scale following the route shown in Scheme 1. Bis(triazoles) **1a**−**c** are obtained in a single pot in 51−84% yield from the corresponding aniline and 1,4-bis(trimethylsilyl)butadiyne. Alkylation with methyl trifluoromethanesulfonate affords the bis(triazolium) salts **2a**−**c** in 42−70% yield.

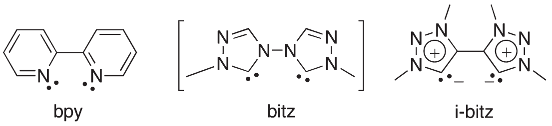
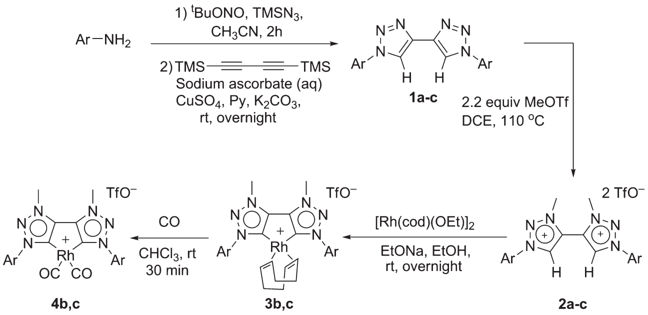


Figure 1. Schematic representation of bpy, bitz, and i-bitz, showing the topological analogy.

Scheme 1. Synthesis of Bis(triazoles) 1a−c, Bis(triazolium) Salts 2a−c, and i-bitz−Rhodium Complexes 3b,c and 4b,c



Ar = Ph (**a**); 2,4,6-trimethylphenyl (**b**); 2,6-diisopropylphenyl (**c**)

The direct metalation of bis(triazolium) salts **2a**−**c** with [Rh(cod)(OEt)]$_2$, following the approach described for the formation of bitz−Rh complexes,[4b] was first explored. In the case of bitz, attempts to chelate Rh(I) were unsuccessful: only dinuclear Rh(I) and pseudo-octahedral mononuclear Rh(III) species were obtained, depending on the conditions employed. In contrast, when [Rh(cod)(OEt)]$_2$ was reacted with

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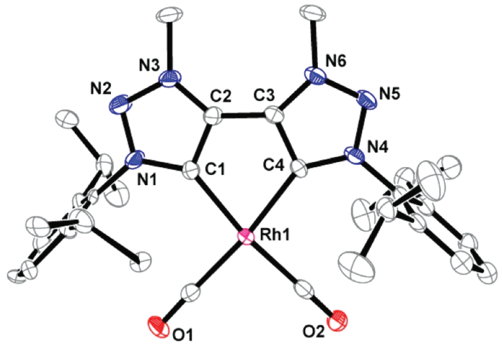
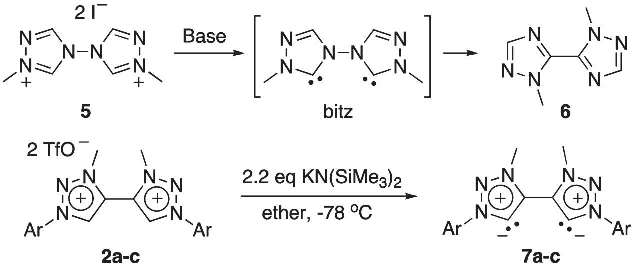


Figure 2. Solid-state structure of **4c** with 50% probability ellipsoids. Hydrogens and the triflate anion are omitted for clarity. Selected bond lengths (Å) and angles (deg): C1−Rh1 = 2.071(4), C4−Rh1 = 2.068(4), C1−C2 = 1.399(5), C2−C3 = 1.446(6), C3−C4 = 1.391(5), C2−N3 = 1.3501(5), C3−N6 = 1.349(5), N3−N2 = 1.324(5), N6−N5 = 1.315(6), N2−N1 = 1.350(4), N5−N4 = 1.343(5), N1−C1 = 1.353(5), N4−C4 = 1.353(5); C1−Rh1−C4 = 77.01(15), N1−C1−C2 = 101.9(3), N4−C4−C3 = 101.8(3), C1−C2−N3 = 108.3(3), C4−C3−N6 = 108.2 (4), C2−N3−N2 = 111.4(3), C3−N6−N5 = 111.6(3), N3−N2−N1 = 103.7(3), N6−N5−N4 = 103.6(3), N2−N1−C1 = 114.7(3), N5−N4−C4 = 114.7(4).

Scheme 2. Rearrangement of Transient bitz and Preparation of Stable i-bitz 7a−c



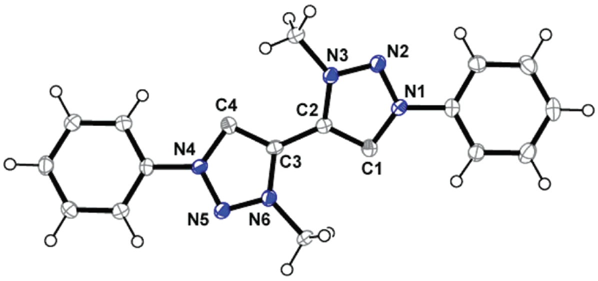


Figure 3. Crystal structure of bis(1,2,3-triazol-5-ylidene) **7a** with ellipsoids shown at the 50% probability level. Selected bond lengths (Å) and angles (deg): C1−C2 = 1.395(2), C2−C3 = 1.467(2), C3−C4 = 1.400(2), N1−C1 = 1.3791(19), N4−C4 = 1.376(2), N1−N2 = 1.3443(18), N4−N5 = 1.3463(18), N2−N3 = 1.3185(18), N5−N6 = 1.3205(18), N3−C2 = 1.378(2), N6−C4 = 1.379(2); N1−C1−C2 = 99.59(14), N4−C4−C3 = 99.35(14), N3−C2−C1 = 109.16(13), N6−C3−C4 = 109(13), N2−N3−C2 = 111.62(13), N5−N6−C3 = 111.39(13), N3−N2−N1 = 102.56(12), N4−N5−N6 = 102.58(12), N2−N1−C1 = 117.06(13), N5−N4−C4 = 117.33(13).

bis(triazolium) salts **2b**,**c**, i-bitz-chelated Rh(I) complexes **3b**,**c** were obtained in 77−86% yield (Scheme 1).[11] Addition of carbon monoxide to **3b**,**c** displaces the cycloctadiene ligand to give complexes **4b**,**c**.

According to a single-crystal X-ray diffraction study, complex **4c** adopts a square-planar geometry (Figure 2). The Rh−C bonds (2.07 Å) are rather long, and the bite angle of 77.0° is very similar to those found in bitz− and bpy−Rh complexes (78.6−79.9° and 75.6−77.1°, respectively).[4a,b,12]

The donor properties of i-bitz were evaluated by measuring the IR CO stretching frequencies of rhodium complexes **4b**,**c** in dichloromethane (ν_{av}(CO) = 2047 and 2048 cm^{-1}, respectively). These values indicate that they are stronger electron donors than bis(dicyclohexylphosphinoethane) (ν_{av}(CO) = 2059 cm^{-1}) and phenantrolines (ν_{av}(CO) = 2069−2073 cm^{-1}).[13] Note that, in contrast, bitz has been calculated to be a weaker donor than bpy and diphosphines.[4b]

Direct metalation of protic carbene precursors offers a practical and expeditious synthesis of metal complexes but lacks generality beyond some late transition metals, such as Rh. Ligand substitution with the free carbenes offers a much broader scope but requires carbenes that are sufficiently robust to show prolonged lifetimes. Despite the excellent stability of 1,2,4-triazolylidenes,[8] the bitz ligand spontaneously rearranges into bitriazole **6** upon attempted deprotonation of the bis(triazolium) salt **5** (Scheme 2), limiting further applicability.[4b] Given the excellent stability of MICs,[14,15] we hypothesized that i-bitz **7a**−**c**, linked by a strong C−C bond, would not suffer from the fragility of the N−N linker found in bitz. Gratifyingly, deprotonation of triazolium salts **2a**−**c** with KHMDS in diethyl ether or tetrahydrofuran at −78 °C allows for the isolation of the free species **7a**−**c** in 63−90% yield. The ^{1}H NMR spectra show the absence of the triazolium acidic proton, located in the 9.3−10.2 ppm region, and in the ^{13}C NMR spectra there is a low-field signal (**7a**, 196.3 ppm; **7b**, 200.9 ppm; **7c**, 201.4 ppm) within the expected range for 1,2,3-triazol-5-ylidenes.[14]

Metal-free i-bitz **7a**−**c** are stable in the solid state in the absence of oxygen and moisture (mp: **7a**, 134 °C; **7b**, 129 °C; **7c**, 139 °C). Single crystals of **7a** suitable for X-ray analysis were obtained from a toluene solution at −30 °C (Figure 3). The two carbene centers adopt an antiperiplanar geometry with a torsion angle (C1−C2−C3−C4) of 166.1°. Both heterocycles are planar, presenting bond lengths between those of single and double bonds, and the carbene bond angles N(1)−C(1)−C(2) and N(4)−C(4)−C(3) (99.59 and 99.35°, respectively) are comparable to those previously observed for 1,2,3-triazol-5-ylidenes.[14]

CONCLUSIONS

In summary, bis(1,2,3-triazol-5-ylidenes) (i-bitz) are readily available and can be isolated even with small flanking aryl groups such as phenyl. They behave as 1,4-bidentate ligands, and the IR CO stretching frequencies of the cationic (i-bitz)(CO)$_2$Rh^{I} complexes indicate that these novel chelating ligands are strong electron donors. Research in our laboratory is currently underway to extend the scope of bis(mesoionic) carbenes and to explore the properties of the corresponding complexes.

EXPERIMENTAL SECTION

Materials. Unless otherwise noted, all reagents including solvents were obtained from commercial suppliers and used directly without further purification. Anhydrous Et$_2$O and THF were obtained after distillation over sodium−benzophenone ketyl under an argon atmosphere. Anhydrous toluene was obtained after distillation over sodium under an argon atmosphere. Anhydrous benzene and hexane were obtained after distillation over potassium. Anhydrous CH_2Cl_2 and CH_3CN were obtained after distillation over calcium hydride under an argon atmosphere. Column chromatography was performed with silica gel (32−63 μM).

General Methods, Instrumentation, and Measurements. Synthetic manipulations that required an inert atmosphere (unless otherwise noted) were carried out in flame-dried glassware equipped with magnetic agitators under argon using standard Schlenk techniques or in an inert-atmosphere glovebox. NMR (^1H, ^{13}C, and ^{19}F) spectra were recorded on 300, 400, and 500 MHz spectrometers. The chemical shift data for each signal are given in units of δ (ppm) relative to tetramethylsilane (TMS), where δ(TMS) = 0, and are referenced to the residual solvent resonances. Splitting patterns are denoted as s (singlet), d (doublet), t (triplet), q (quartet), sept (septet), m (multiplet), and br (broad). IR spectra were recorded on a Bruker Equinox 55 FTIR spectrometer. High-resolution mass spectra (HR-MS) were acquired on an LC-TOF instrument using electrospray ionization mode (ESI). Melting points (open or sealed capillaries) are reported without correction.

*Synthesis of 1,1′-Diphenyl-1H,1′H-4,4′-bis(1,2,3-triazole) (**1a**).* The title compound was prepared by combining two reported methods.[16,10a] To a stirred solution of aniline (6.34 g, 68.2 mmol) in CH_3CN (40 mL) at 0 °C, were added first *tert*-butyl nitrite (10.2 g, 99.0 mmol), then trimethylsilyl azide (9.28 g, 80.6 mmol). The reaction mixture was warmed to room temperature, while stirring was maintained for 2 h. Afterward, 1,4-bis(trimethylsilyl)buta-1,3-diyne (6.27 g, 31.0 mmol), pyridine (24.5 g, 310 mmol), potassium carbonate (8.5 g, 62.0 mmol), and an aqueous solution containing $CuSO_4 \cdot 5H_2O$ (3.10 g, 1.24 mmol) and sodium ascorbate (4.90 g, 2.48 mmol) in H_2O (40 mL) were added. The mixture was stirred overnight at room temperature. The solution was concentrated. A 9/1 DCM/NH_4OH solution mixture was added to the concentrate, and this mixture was stirred overnight. The organic phase was extracted with dichloromethane, dried over magnesium sulfate, and the solvent was evaporated to yield **1a** as an off-white solid (4.58 g, 51.3%). Mp: 251 °C, ^1H NMR ($CDCl_3$, 25 °C, 300 MHz): δ 8.57 (s, 2 H, H_{tr}), 7.83 (d, 4H, J = 7.95 MHz), 7.57 (m, 4H), 7.48 (m, 2H). ^{13}C NMR ($CDCl_3$, 25 °C, 75 MHz): δ 140.6, 137.1, 130.1, 129.2, 120.7, 119.0. HR-MS (ESI, CH_2Cl_2): m/z calcd for $C_{16}H_{12}N_6$ 289.1196, found 289.1200.

*Synthesis of 1,1′-Dimesityl-1H,1′H-4,4′-bis(1,2,3-triazole) (**1b**).* The title compound was prepared by following the reported method.[10a] In a 250 mL flask containing 60 mL of a 1/1 *tert*-butyl alcohol/water mixture were added 2-azido-1,3,5-trimethylbenzene (5.0 g, 31.0 mmol),[17,18] 1,4-bis(trimethylsilyl)buta-1,3-diyne (3.01, 15.5 mmol), pyridine (12.26 g, 15.5 mmol), potassium carbonate (4 g, 28.9 mmol), $CuSO_4 \cdot 5H_2O$ (1.44 g, 6.21 mmol), and sodium ascorbate (2.45 g, 12.4 mmol) at 0 °C. The mixture was stirred overnight at room temperature. A 9/1 DCM/NH_4OH solution mixture was added, and this mixture was stirred overnight. The organic phase was extracted with dichloromethane, dried over magnesium sulfate, and the solvent was evaporated to yield **1b** as a yellowish solid (4.88 g, 84.5%). Mp: 314 °C. ^1H NMR ($CDCl_3$, 25 °C, 300 MHz): δ 8.20 (s, 2 H, H_{tr}), 7.04 (s, 4 H, H_{ar}), 2.38 (s, 6 H, CH_3), 2.05 (s, 12 H, CH_3). ^{13}C NMR ($CDCl_3$, 25 °C, 75 MHz): δ 140.4, 140.2, 135.3, 133.5, 129.4, 122.8, 21.3, 17.5. HR-MS (ESI, CH_2Cl_2): m/z calcd for ($C_{22}H_{24}N_6$ [M + Na] 395.1955, found 395.1974.

*Synthesis of 1,1′-Bis(2,6-diisopropylphenyl)-1H,1′H-4,4′-bis(1,2,3-triazole) (**1c**).* The title compound was prepared by combining two reported methods.[16,10a] To a stirred solution of diisopropylaniline (12.08 g, 68.2 mmol) in CH_3CN (40 mL) at 0 °C, were added first *tert*-butyl nitrite (10.2 g, 99.0 mmol), then trimethylsilyl azide (9.28 g, 80.6 mmol). The reaction mixture was warmed to room temperature, while stirring was maintained for 2 h. Afterward, 1,4-bis(trimethylsilyl)buta-1,3-diyne (6.03 g, 31.0 mmol), pyridine (24.5 g, 310 mmol), potassium carbonate (8.5 g, 62 mmol), and an aqueous solution containing $CuSO_4 \cdot 5H_2O$ (3.1 g, 12.4 mmol) and sodium ascorbate (4.9 g, 24.8 mmol) in H_2O (40 mL) was added. The mixture was stirred overnight at room temperature. The solution was concentrated; a 9/1 DCM/NH_4OH solution mixture was added, and this mixture was stirred overnight. The organic phase was extracted with dichloromethane, dried over magnesium sulfate, and the solvent was evaporated to yield **1c** as a yellowish solid (11.6 g, 82%). Mp: 289 °C. ^1H NMR ($CDCl_3$, 25 °C, 300 MHz): δ 8.26 (s, 2 H, H_{tr}), 7.55 (t, 2 H, H_{dipp}, J = 7.8 Hz), 7.34 (t, 4 H, H_{dipp}, J = 7.8 Hz), 2.38 (s, 4 H, CH, J = 6.7 Hz), 1.20 (d, 24 H, CH_3, J = 6.81 Hz). ^{13}C NMR ($CDCl_3$, 25 °C, 75 MHz): δ 146.3, 140.0, 133.1, 131.2, 124.1, 123.8, 28.6, 24.4, 24.2. HR-MS (ESI, CH_2Cl_2): m/z calcd for $C_{28}H_{36}N_6$ [M + H] 457.3074, found 457.3096.

*Synthesis of 3,3′-Dimethyl-1,1′-diphenyl-1H,1′H-4,4′-bis(1,2,3-triazolium) Trifluoromethanesulfonate (**2a**).* 3,3′-Dimethyl-1,1′-diphenyl-1*H*,1′*H*-4,4′-bis(1,2,3-triazolium) trifluoromethanesulfonate **2a** was prepared by an adaptation of a reported method.[14] To a stirred solution of 1,1′-diphenyl-1*H*,1′*H*-4,4′-bis(1,2,3-triazole) **1a** (0.45 g, 1.57 mmol) in 1,2-dichloroethane (20 mL), previously cooled to −78 °C, was added methyl trifluoromethanesulfonate (0.57 g, 3.54 mmol). The reaction mixture was warmed to room temperature, and then heated to 100 °C in a sealed Schlenk flask for 48 h. The solvent was evaporated; addition of diethyl ether prompted the precipitation of a white solid after stirring the crude solution for 30 min. Afterward, the precipitate was washed with hexane and diethyl ether. Crystals suitable for X-ray study were obtained by slow solvent evaporation of a solution of **2a** in acetone. Yield: 0.75 g (97.6%). Mp: 251 °C. ^1H NMR (d_6-DMSO, 25 °C, 400 MHz): δ 10.18 (s, 2 H, H_{tr}), 8.08 (s, 4 H, H_{ar}), 7.81 (s, 6 H, H_{ar}), 4.57 (s, 6 H, CH_3). ^{13}C NMR (d_6-DMSO, 25 °C, 100 MHz): δ 134.5, 132.4, 131.25, 130.6, 127.4, 121.9, 39.8. HR-MS (ESI, acetone): m/z calcd for $C_{19}H_{18}F_3N_6O_3S^+$ 467.1108 [M − OTf], found 467.1102.

*Synthesis of 1,1′-Dimesityl-3,3′-dimethyl-1H,1′H-4,4′-bis(1,2,3-triazolium) Trifluoromethanesulfonate (**2b**).* 1,1′-Dimesityl-3,3′-dimethyl-1*H*,1′*H*-4,4′-bis(1,2,3-triazolium) trifluoromethanesulfonate **2b** was prepared by an adaptation of a reported method.[14] To a stirred solution of 1,1′-dimesityl-1*H*,1′*H*-4,4′-bis(1,2,3-triazole) **1b** (4.7 g, 12.6 mmol) in DCE (20 mL), previously cooled to −78 °C, was added methyl trifluoromethanesulfonate (4.58 g, 27.7 mmol). The reaction mixture was warmed to room temperature, then heated to 100 °C in a sealed Schlenk flask for 48 h. The solvent was evaporated; addition of diethyl ether prompted the precipitation of a white solid after stirring the crude solution for 30 min. Afterward, the precipitate was washed with hexane and diethyl ether. Yield: 6.11 g (70%). Mp: 274 °C. ^1H NMR (CD_3CN, 25 °C, 400 MHz): δ 9.33 (s, 2 H, H_{tr}), 7.35 (s, 4 H, H_{ar}), 4.58 (s, 6 H, CH_3), 2.52 (s, 6 H, CH_3), 2.04 (m, 6 H, CH_3). ^{13}C NMR (CD_3CN, 25 °C, 75 MHz): δ 144.3, 135.6, 131.1, 130.8, 128.5, 117.0, 41.4, 21.2, 17.4. HR-MS (ESI, acetone): m/z calcd for $C_{25}H_{30}F_3N_6O_3S^+$ 551.2047 (M − OTf), found 551.2060.

*Synthesis of 1,1′-Bis(2,6-diisopropylphenyl)-3,3′-dimethyl-1H,1′H-4,4′-bis(1,2,3-triazolium) Trifluoromethanesulfonate (**2c**).* 1,1′-Bis(2,6-diisopropylphenyl)-3,3′-dimethyl-1*H*,1′*H*-4,4′-bis(1,2,3-triazolium) trifluoromethanesulfonate **2c** was prepared by following the reported method.[14] To a stirred solution of 1,1′-bis(2,6-diisopropylphenyl)-1*H*,1′*H*-4,4′-bis(1,2,3-triazole) **1c** (5.0 g, 10.9 mmol) in DCM (20 mL), previously cooled to −78 °C, was added methyl trifluoromethanesulfonate (3.97 g, 24.1 mmol). The reaction mixture was warmed to room temperature, and stirring was maintained overnight. The solvent was evaporated; addition of diethyl ether prompted the precipitation of a white solid after stirring the crude mixture for 30 min, which was filtered and washed with hexane. The title compound **2c** was obtained as a white solid after column chromatography (DCM/MeOH 95/5). Yield: 5.72 g (66.7%). Mp: 265 °C. ^1H NMR ($CDCl_3$, 25 °C, 300 MHz): δ 9.61 (s, 2 H, H_{tr}) 7.67 (t, 2 H, H_{dipp}, J = 7.8 Hz), 7.36 (t, 4 H, H_{dipp}, J = 7.9 Hz), 4.54 (s, 6 H, CH_3), 2.29 (s, 4 H, CH, J = 6.7 Hz), 1.10 (m, 24 H, CH_3, J = 6.63 Hz). ^{13}C NMR ($CDCl_3$, 25 °C, 75 MHz): δ 145.9, 135.0, 133.5, 130.4, 128.0, 126.8, 124.9, 40.6, 23.9, 23.8. HR-MS (ESI, CH_2Cl_2): *m/z* calcd for $C_{31}H_{42}F_3N_6O_3S^+$ [M − OTf] 635.2986, found 635.2678.

*Synthesis of [Rh^I(cod)(**7b**)]$^+$OTf$^-$ (**3b**).* The metal complex [Rh^I(cod)(**7b**)]$^+$OTf$^-$ **3b** was prepared by following slight modifications of the reported methods.[19,20] NaH (24.32 mg, 1.02 mmol) was dissolved in EtOH (5 mL), and the resulting solution was transferred via cannula to a supension of [RhCl(cod)]$_2$ (100 mg, 0.20 mmol) in EtOH (5 mL). The reaction mixture was stirred for 30 min at room temperature. 1,1′-Dimesityl-3,3′-dimethyl-1*H*,1′*H*-4,4′-bis-(1,2,3-triazolium) trifluoromethanesulfonate **2b** (294.2 mg, 0.42 mmol) was added to the reaction mixture at −78 °C, warmed to room temperature after 10 min, and then stirred for another 12 h. Solvent was evaporated; dichloromethane was added to dissolve the product, and the mixture was filtered. After removal of the solvent, **3b** was obtained as an orange solid (256.5 mg, 77.3%). Mp: 223 °C. ^{1}H NMR ($CDCl_3$, 25 °C, 500 MHz): δ 6.98 (s, 2H, H$_{ar}$), 4.68 (s, 6 H, CH_3), 4.09 (s, 4H, CH$_{cod}$), 2.37 (s, 6H, CH_3), 2.11 (s, 12H, CH_3), 2.00 (m, 4 H, CH$_{2\ cod}$), 1.73 (m, 4 H, CH$_{2\ cod}$), 1.13 (d, 12 H, CH_3, *J* = 6.5 Hz). ^{13}C NMR ($CDCl_3$, 25 °C, 125 MHz): δ 172.9 (d, $^1J_{Rh,C}$ = 40 Hz, NCC), 143.4, 141.2, 134.7, 134.4, 129.6, 88.0, 40.5, 31.0, 21.5, 17.6. ^{19}F NMR ($CDCl_3$, 25 °C, 376 MHz) δ −78.8. HR-MS (ESI, CH_2Cl_2): *m/z* calcd for $C_{32}H_{40}N_6Rh^+$ [M$^+$] 611.2364, found 611.2383.

*Synthesis of [Rh^I((cod)(**7c**)]$^+$OTf$^-$ (**3c**).* The metal complex [Rh^I(cod)(**7c**)]$^+$OTf$^-$ was prepared by following slight modifications of the reported methods.[19,20] NaH (12.16 mg, 0.51 mmol) was dissolved in EtOH (5 mL), and the resulting solution was transferred via cannula to a suspension of [RhCl(cod)]$_2$ (50 mg, 0.10 mmol) in EtOH (5 mL). The reaction mixture was stirred for 30 min at room temperature. 1,1′-Bis(2,6-diisopropylphenyl)-3,3′-dimethyl-1*H*,1′*H*-4,4′-bis(1,2,3-triazolium) trifluoromethanesulfonate **2c** (164 mg, 0.21 mmol) was added to the reaction mixture at −78 °C, warmed to room temperature after 10 min, and then stirred overnight for 12 h. Solvent was evaporated, dichloromethane was added to dissolve the product, and the mixture was filtered. After removal of the solvent, **3c** was obtained as an orange solid (158 mg, 86%). Mp: 239 °C. ^{1}H NMR ($CDCl_3$, 25 °C, 500 MHz): δ 7.50 (t, 2H, H$_{dipp}$, *J* = 7.5 Hz), 7.28 (d, 4H, H$_{dipp}$, *J* = 8.0 Hz), 4.71 (s, 6 H, CH_3), 4.02 (s, 4 H, CH$_{cod}$), 2.49 (4 H, CH$_{dipp}$, *J* = 7.0 Hz), 1.87 (m, 4 H, CH$_{2\ cod}$), 1.72 (m, 4 H, CH$_{2\ cod}$), 1.33 (d, 12 H, CH_3, *J* = 6.5 Hz), 1.13 (d, 12 H, CH_3, *J* = 6.5 Hz). ^{13}C NMR ($CDCl_3$, 25 °C, 125 MHz): δ 172.1 (d, $^1J_{Rh,C}$ = 41.2 Hz, NCC), 145.4, 142.9, 134.3, 131.8, 124.2, 87.9, 55.6, 30.7, 28.8, 25.7, 22.4. HR-MS (ESI, CH_2Cl_2): *m/z* calcd for $C_{40}H_{58}N_6Rh^+$ 695.3303 [M$^+$], found 695.3354.

*Synthesis of [Rh(CO)$_2$(**7b**)]$^+$OTf$^-$ (**4b**).* The preparation of [Rh(CO)$_2$(**7b**)]$^+$OTf$^-$ was carried out by following a procedure similar to the reported method.[14] In a solution of [Rh(cod)(**7b**)]$^+$OTf$^-$ (256 mg, 0.32 mmol) in chloroform (5 mL) was bubbled CO over 30 min. Evaporation of the solvent afforded **4b** as a yellow solid (230 mg, 99%). Mp: 199 °C. ^{1}H NMR ($CDCl_3$, 25 °C, 300 MHz): δ 7.02 (s, 4, H$_{ar}$), 4.73 (s, 6 H, CH_3), 2.36 (6 H, CH_3), 2.07 (s, 12 H, CH_3). ^{13}C NMR ($CDCl_3$, 25 °C, 75 MHz): δ 187.3 (s, CO), 173.6 (d, $^1J_{Rh,C}$ = 44.0 Hz, NCC), 144.3, 141.6, 135.0, 134.2, 128.8, 128.2, 40.5, 28.2, 21.4, 17.6, ^{19}F NMR ($CDCl_3$, 25 °C, 282 MHz): δ −78.8. MS (ESI, CH_2Cl_2): *m/z* calcd for $C_{26}H_{28}N_6O_2Rh^+$ [M$^+$] 559.1323, found 559.1392. IR (CH_2Cl_2, cm^{-1}): ν 2076 (ν(CO)), 2019 (ν(CO)).

*Synthesis of [Rh(CO)$_2$(**7c**)]$^+$OTf$^-$ (**4c**).* The preparation of [Rh(CO)$_2$(**7c**)]$^+$OTf$^-$ was carried out by following an adaptation of a reported method.[14] The red powder [Rh(cod)(**7c**)]$^+$OTf$^-$ **3c** (159 mg, 0.18 mmol) was suspended in chloroform (5 mL). The solution was bubbled with CO over 30 min. Evaporation of the solvent yielded **4c** as a yellow solid (55 mg, 60%). Crystals suitable for X-ray diffraction were obtained in a glovebox by slow evaporation of the solvent of a solution of **4c** in $CDCl_3$. Mp: 233 °C. ^{1}H NMR ($CDCl_3$, 25 °C, 400 MHz): δ 7.47 (t, 2H, H$_{dipp}$, *J* = 7.6 MHz), 7.27 (d, 4H, H$_{dipp}$, *J* = 7.6 MHz), 4.74 (s, 6 H, CH_3), 2.32 (4 H, CH, *J* = 6.8 Hz), 1.14 (dd, 24 H, CH_3, *J* = 6.4 Hz). ^{13}C NMR ($CDCl_3$, 25 °C, 100 MHz): δ 187.1 (d, $^1J_{Rh,C}$ = 57.1 Hz, CO), 174.8 (d, $^1J_{Rh,C}$ = 45.3 Hz, NCC), 145.8, 143.9, 132.1, 128.5, 124.4, 40.8, 28.6, 24.5, 23.8. ^{19}F NMR ($CDCl_3$, 25 °C, 376 MHz): δ −79.2; MS (ESI, CH_2Cl_2): *m/z* calcd for $C_{32}H_{40}N_6O_2Rh^+$ (M$^+$) 643.2262, found 643.2333. IR (CH_2Cl_2, cm^{-1}): ν 2076 (ν(CO)), 2020 (ν(CO)).

*Synthesis of 4,4′-Bis(1-phenyl-3-methyl-1H-1,2,3-triazol-5-ylidene) (**7a**).* In a flame-dried Schlenk flask were added 1,1′-diphenyl-3,3′-dimethyl-1*H*,1′*H*-4,4′-bis(1,2,3-triazolium) trifluoromethanesulfonate **2b** (0.400 g, 0.65 mmol) and potassium bis(trimethylsilyl)amide (0.280 g, 1.43 mmol). The Schlenk flask was cooled to −78 °C, and then tetrahydrofuran (15 mL) was added. After 10 min, the cold bath was removed; the reaction mixture was warmed to room temperature. After 1 h the solvent was removed under vacuum. The metal-free **7a** was extracted by trituration in dry benzene (2 × 10 mL) and the extract filtered via cannula. Solvent was evaporated to yield **7a** as a purple-white solid (0.184 g, 90%). Note: colorless crystals suitable for X-ray analysis were obtained after dissolving the title compound in toluene at room temperature and slowly cooling the solution to −30 °C under an argon atmosphere. Mp: 134 °C. ^{1}H NMR (C_6D_6, 25 °C, 300 MHz): δ 8.71 (d, 4 H, *J* = 7.86 Hz, H$_{ar}$), 7.34 (m, 4 H, H$_{ar}$), 7.21 (t, 2 H, *J* = 7.29 Hz, H$_{ar}$), 4.6 (s, 6 H, CH_3). ^{13}C NMR (C_6D_6, 25 °C, 75 MHz): δ 196.0, 142.8, 129.5, 128.7, 121.7, 39.1.

*Synthesis of 4,4′-Bis(1-mesityl-3-methyl-1H-1,2,3-triazol-5-ylidene) (**7b**).* In a flame-dried Schlenk flask were added 1,1′-dimesityl-3,3′-dimethyl-1*H*,1′*H*-4,4′-bis(1,2,3-triazolium) trifluoromethanesulfonate **2b** (0.4 g, 0.57 mmol) and potassium bis(trimethylsilyl)amide (0.250 g, 1.25 mmol). The Schlenk was cooled to −78 °C, and then diethyl ether (7 mL) was added. After 10 min the cold bath was removed, and the reaction mixture was warmed to room temperature. After 1 h the solvent was removed under vacuum. Dry benzene (15 mL) was added to the crude mixture, and the free carbene was extracted by filtration via cannula. Afterward, solvent was removed under vacuum to yield **7b** as an off-white solid (0.186 g, 81%). Mp: 129 °C. ^{1}H NMR (C_6D_6, 25 °C, 300 MHz): δ 6.88 (s, 4 H, H$_{ar}$), 4.71 (s, 6 H, CH_3), 2.26 (s, 12 H, CH_3), 2.22 (d, 12 H, CH_3). ^{13}C NMR (C_6D_6, 25 °C, 75 MHz): δ 200.9, 141.8, 140.2, 139.0, 135.3, 129.7, 39.5, 21.6, 18.4.

*Synthesis of 4,4′-Bis(1-(2,6-diisopropylphenyl)-3-methyl-1H-1,2,3-triazol-5-ylidene) (**7c**).* In a flame-dried Schlenk flask were added 1,1′-bis(2,6-diisopropylphenyl)-3,3′-dimethyl-1*H*,1′*H*-4,4′-bis(1,2,3-triazolium) trifluoromethanesulfonate **2c** (0.3 g, 0.38 mmol) and potassium bis-(trimethylsilyl)amide (0.161 g, 0.84 mmol). The Schlenk flask was cooled to −78 °C, and then diethyl ether (7 mL) was added. After 10 min the dry ice−acetone bath was removed. The reaction mixture was warmed to room temperature and stirred for 1 h. Volatiles were removed under vacuum. The free carbene was extracted by filtration via cannula. Afterward, solvent was removed under vacuum to afford **7c** as an off-white solid (115 mg, 62%). Mp: 139 °C. ^{1}H NMR (C_6D_6, 25 °C, 300 MHz): δ 7.39 (m, 2 H, H$_{dipp}$), 7.29 (t, 4 H, H$_{dipp}$, *J* = 8.5 Hz), 4.70 (s, 6 H, CH_3), 2.85 (s, 4 H, CH, *J* = 6.8 Hz), 1.32 (d, 12 H, CH_3, *J* = 6.6 Hz), 1.25 (d, 12 H, CH_3, *J* = 6.7 Hz). ^{13}C NMR (C_6D_6, 25 °C, 100 MHz): δ 201.4, 145.5, 140.4, 139.3, 129.7. 129.3, 124.7, 39.3, 29.2, 24.6, 24.5.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. NMR spectra for all new compounds, and X-ray crystallographic data for **2a**, **4c**, and **7a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ REFERENCES

(1) (a) Smith, A. P.; Fraser, C. L. Bipyridine Ligands. In *Comprehensive Coordination Chemistry II*; McCleverty, J. A., Meyer, T. J., Eds.; Elsevier: Oxford, U.K., 2004; pp 1−23. (b) Kaes, C.; Katz, A.; Hosseini, M. W. *Chem. Rev.* **2000**, *100*, 3553. (c) Accorsi, G.; Listorti, A.; Yoosaf., K.; Armaroli, N. *Chem. Soc. Rev.* **2009**, *38*, 1690.

(2) (a) Hagfeldt, A.; Boschloo, G.; Sun, L.; Kloo, L.; Pettersson, H. *Chem. Rev.* **2010**, *110*, 6595. (b) Nazeeruddin, M. K.; Grätzel, M. Transition Metal Complexes for Photovoltaic and Light Emitting Applications. In *Photofunctional Transition Metal Complexes*; Yam, V. W. W., Ed.; Springer-Verlag: Berlin, 2007; Structure and Bonding Series 123; pp 113−175. (c) Dixon, I. M.; Lebon, E.; Sutra, P.; Igau, A. *Chem. Soc. Rev.* **2009**, *38*, 1621.

(3) For recent books and reviews, see for example: (a) *N-Heterocyclic Carbenes, From Laboratory Curiosities to Efficient Synthetic Tools*; Díez-González, S., Ed.; Royal Society of Chemistry: London, 2011. (b) *N-Heterocyclic Carbenes in Transition Metal Catalysis*; Glorius, F. A., Ed.; Springer-Verlag: Berlin, 2007. (c) *N-Heterocyclic Carbenes in Synthesis*; Nolan, S. P., Ed.; Wiley-VCH: Weinheim, Germany, 2006. (d) Melaimi, M.; Soleilhavoup, M.; Bertrand, G. *Angew. Chem., Int. Ed.* **2010**, *49*, 8810. (e) Hahn, F. E.; Jahnke, M. C. *Angew. Chem., Int. Ed.* **2008**, *47*, 3122.

(4) (a) Poyatos, M.; McNamara, W.; Incarvito, C.; Peris, E.; Crabtree, R. H. *Chem. Commun.* **2007**, 2267. (b) Poyatos, M.; McNamara, W.; Incarvito, C.; Clot, E.; Peris, E.; Crabtree, R. H. *Organometallics* **2008**, *27*, 2128. (c) Corberán, R.; Mas-Marzá, E.; Peris, E. *Eur. J. Inorg. Chem.* **2009**, 1700. (d) Poyatos, M.; Mata, J. A.; Peris, E. *Chem. Rev.* **2009**, *109*, 3677.

(5) For the origin of the acronym MIC, see: Araki, S.; Wanibe, Y.; Uno, F; Morikawa, A.; Yamamoto, K.; Chiba, K.; Butsugan, Y. *Chem. Ber* **1993**, *12*, 1149.

(6) For reviews on MICs and related species, see: (a) Schuster, O.; Yang, L.; Raubenheimer, H. G.; Albrecht, M. *Chem. Rev.* **2009**, *109*, 3445. (b) Albrecht, M. *Chem. Commun.* **2008**, *31*, 3601. (c) Arnold, P. L.; Pearson, S. *Coord. Chem. Rev.* **2007**, *251*, 596. (d) Albrecht, M. *Chimia* **2009**, *63*, 105.

(7) For recent reports on the coordination chemistry of 1,2,3-triazol-5-ylidenes, see: (a) Mathew, P.; Neels, A.; Albrecht, M. *J. Am. Chem. Soc.* **2008**, *130*, 13534. (b) Karthikeyan, T.; Sankararaman, S. *Tetrahedron Lett.* **2009**, *50*, 5834. (c) Nakamura, T.; Ogata, K.; Fukuzawa, S.-i. *Chem. Lett.* **2010**, *39*, 920. (d) Lalrempuia, R.; McDaniel., N. D.; Müller-Bunz, H.; Bernhard, S.; Albrecht, M. *Angew. Chem., Int. Ed.* **2010**, *49*, 9765. (e) Kilpin, K. J.; Paul, U. S. D.; Lee, A.-L.; Crowley, J. D. *Chem. Commun.* **2011**, *47*, 328. (f) Nakamura, T.; Terashima, T.; Ogata, K.; Fukuzawa, S.-i. *Org. Lett.* **2011**, *13*, 620. (g) Prades, A.; Peris, E.; Albrecht, M. *Organometallics* **2011**, *30*, 1162. (h) Bouffard, J.; Keitz, B. K.; Tonner, R.; Guisado-Barrios, G.; Frenking, G.; Grubbs, R. H.; Bertrand, G. *Organometallics* **2011**, *30*, 2617. (i) Keitz, B. K; Bouffard, J.; Bertrand, G.; Grubbs, R. H. *J. Am. Chem. Soc.* **2011**, *133*, 8498. (j) Saravanakumar, R.; Ramkumar, V.; Sankararaman, S. *Organometallics* **2011**, *30*, 1689. (k) Schulze, B.; Escudero, D.; Friebe, C.; Siebert, R.; Görls, H.; Köhn, U.; Altunas, E.; Baumgaertel, A.; Hager, M. D.; Winter, A.; Dietzek, B.; Popp, J.; González, L.; Schubert, U. S. *Chem. Eur. J.* **2011**, *17*, 5494. (l) Bernet, L.; Lalrempuia, R.; Ghattas, W.; Mueller-Bunz, H.; Vigara, L.; Llobet, A.; Albrecht, M. *Chem. Commun.* **2011**, *47*, 8058. (m) Poulain, A.; Canseco-Gonzalez, D.; Hynes-Roche, R.; Müller-Bunz, H.; Schuster, O.; Stoeckli-Evans, H.; Neels, A.; Albrecht, M. *Organometallics* **2011**, *30*, 1021.

(8) Enders, D.; Breuer, K.; Raabe, G.; Runsink, J.; Teles, J. H.; Melder, J. P.; Ebel, K.; Brode, S. *Angew. Chem., Int. Ed.* **1995**, *34*, 1021.

(9) Dröge, T.; Glorius, F. *Angew. Chem., Int. Ed.* **2010**, *49*, 6940.

(10) (a) Fletcher, J. T.; Bumgarner, B. J.; Engels, N. D.; Skoglund, D. A. *Organometallics* **2008**, *27*, 5430. (b) Aizpurua, J. M.; Azcune, I.; Fratila, R. M.; Balentova, E.; Sagartzazu-Aizpurua, M.; Miranda, J. I. *Org. Lett.* **2010**, *12*, 1584.

(11) Direct metalation of bis(triazolium) **2a** gave rise to complex mixtures.

(12) (a) Dadci, L.; Elian, H.; Frey, U.; Hörnig, A.; Koelle, U.; Merbach, A. E.; Paulus, H.; Schneider, J. S. *Inorg. Chem.* **1995**, *34*, 306. (b) Ogo, S.; Hayashi, H.; Uehara, K.; Fukuzumi, S. *Appl. Organomet. Chem.* **2005**, *19*, 639. (c) Riis-Johannessen, T.; Schenk, K.; Severin, K. *Inorg. Chem.* **2010**, *49*, 9546.

(13) (a) Del Zotto, A.; Costella, L.; Mezzetti, A.; Rigo, P. *J. Organomet. Chem.* **1991**, *414*, 109. (b) Clauti, G.; Zassinovich, G.; Mestroni, G. *Inorg. Chim. Acta* **1986**, *112*, 103.

(14) 1,2,3-Triazol-5-ylidenes have recently been isolated: Guisado-Barrios, G.; Bouffard, J.; Donnadieu, B.; Bertrand, G. *Angew. Chem., Int. Ed.* **2010**, *49*, 4759.

(15) Other types of MICs have been isolated: (a) Lavallo, V.; Dyker, C. A; Donnadieu, B.; Bertrand, G. *Angew. Chem., Int. Ed.* **2008**, *47*, 5411. (b) Fernández, I.; Dyker, C. A.; DeHope, A.; Donnadieu, B.; Frenking, G.; Bertrand, G. *J. Am. Chem. Soc.* **2009**, *131*, 11875. (c) Aldeco-Perez, E.; Rosenthal, A. J.; Donnadieu, B.; Parameswaran, P.; Frenking, G.; Bertrand, G. *Science* **2009**, *326*, 556. (d) Ung, G.; Bertrand, G. *Chem. Eur. J.* **2011**, *17*, 8269.

(16) Barral, K.; Moorhouse, A. D.; Moses, J. E. *Org. Lett.* **2007**, *9*, 1809. Note: the reaction leading to the formation of 2,6-diisopropylphenyl azide is highly exothermic following a variable induction period, which can lead to a runaway reaction and pose a safety hazard (explosion). Consequently, we advise caution in performing this reaction, especially on a large scale. In particular, even when the reaction is performed at room temperature, it should be conducted with a large heat sink (e.g. flask immerged in a water bath at room temperature) and with efficient heat transfer (e.g. rapid and efficient stirring, oversized glassware).

(17) Ugi, I.; Perlinger, H.; Behringer, L. *Chem. Ber.* **1958**, *91*, 2330.

(18) Bochmann, M.; Sarsfield, M. J. (BP Chemicals Limited, U.K.) Application: WO 2000047592 A1.

(19) Riederer, S. U.; Gigler, P.; Hoegerl, M.; Herdtweck, E. B.; Bechlars, B.; Herrmann, W. A.; Kuehn, F. E. *Organometallics* **2010**, *29*, 5681.

(20) Koecher, C.; Herrmann, W. A. *J. Organomet. Chem.* **1997**, *532*, 261.