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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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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 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.

Keywords

Mesoionic Carbenes; N-heterocyclic carbenes; bidentate ligands; Rhodium complexes

Introduction

2,2'-Bipyridines (bpy) and their congeners (Figure 1), such as phenanthrolines, are privileged 1,4-bidentate ligands¹ in structural inorganic chemistry, catalysis, and more recently in light-emitting devices and solar cells.² Their electronic properties, and 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.

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 stronger electron-donor properties than their 1,2,4-triazolylidenes isomers,⁸ as well as 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 of 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.

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Supporting Information **Available**. Full experimental details; X-ray crystallographic data for **2a**, **4c** and **7a** in CIF format. This material is available free of charge via the internet at <http://pubs.acs.org>.

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 bis(triazolium) salts **2a-c** in 42-70% yield.

The direct metalation of bis(triazolium) salts **2a-c** with $[\text{Rh}(\text{cod})(\text{OEt})]_2$, 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. By contrast, when $[\text{Rh}(\text{cod})(\text{OEt})]_2$ is reacted with 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 cyclooctadiene ligand to give complexes **4b,c**.

According to a single crystal X-ray diffraction study, complex **4c** adopts a square planar geometry. 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 to 79.9° and 75.6 to 77.1°, respectively).^{4a,4b,12}

The donor properties of i-bitz were evaluated by measuring the IR CO stretching frequencies of rhodium complexes **4b,c** in dichloromethane [$\nu_{\text{av}}(\text{CO}) = 2047$ and 2048 cm^{-1} , respectively]. These values indicate that they are stronger electron-donors than bis(dicyclohexylphosphinoethane) [$\nu_{\text{av}}(\text{CO}) = 2059 \text{ cm}^{-1}$] and phenantrolines [$\nu_{\text{av}}(\text{CO}) = 2069\text{-}2073 \text{ cm}^{-1}$].¹³ Note that in contrast bitz have been calculated to be weaker donors 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 to 90% yield. The ¹H NMR spectra show the absence of the triazolium acidic proton, located in the 9.3-10.2 ppm region, and in the ¹³C NMR spectra there is a low field signal (**7a** = 196.3, **7b** = 200.9 and **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 (C1C2C3C4) 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

Experimental section

Materials

Unless otherwise noted, all reagents including solvents were obtained from commercial suppliers and used directly without further purification. Anhydrous Et₂O 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 or 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 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 Bruker Equinox 55 FTIR spectrometer. High-resolution mass spectra (HR-MS) were acquired on LC-TOF instrument using electrospray ionization mode (ESI). Melting points (open or sealed capillaries) are reported without correction.

Synthesis of 1,1'-Diphenyl-1*H*,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) and *tert*-butylnitrite (10.2 g, 99.0 mmol) in CH_3CN (40 mL), was added, at 0° C, trimethylsilylazide (9.28 g, 80.6 mmol). The reaction mixture was allowed to warm to room temperature, while stirring was maintained for two hours. Afterwards, 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), an aqueous solution containing copper sulfate (3.10 g, 1.24 mmol) and sodium ascorbate (4.90 g, 2.48 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 to the concentrate, and 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 $\text{C}_{16}\text{H}_{12}\text{N}_6$ = 289.1196, found 289.1200).

Synthesis of 1,1'-Dimesityl-1*H*,1'-*H*-4,4'-bis(1,2,3-triazole) (1b)—The title compound was prepared by following the reported method.^{10a} To a 250 mL flask containing 60 mL of a 1:1 mixture of (*tert*-butanol/water) was added at 0° C, 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), copper sulfate (1.44 g, 6.21 mmol) and sodium ascorbate (2.45, 12.4 mmol). The mixture was stirred overnight at room temperature. A (9:1 DCM/ NH_4OH solution) mixture was added, and 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 = 140.40, 140.18, 135.26, 133.45, 129.35, 122.81, 21.31, 17.50 HR-MS (ESI, CH_2Cl_2): m/z calcd for ($\text{C}_{22}\text{H}_{24}\text{N}_6 + \text{H}^+$) 395.1955 [M+H], value found 395.1974.

Synthesis of 1,1'-Bis(2,6-diisopropylphenyl)-1*H*,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) and *tert*-butylnitrite (10.2 g, 99.2 mmol) in CH_3CN (40 mL), was added, at 0° C, trimethylsilylazide (9.28 g, 80.6 mmol). The reaction mixture was allowed to warm to room temperature, while stirring was maintained for two hours. Afterwards, 1,4-bis(trimethylsilyl)buta-1,3-diyne (6.03g, 31.0 mmol),

pyridine (24.5g, 310 mmol), potassium carbonate (8.5g, 62 mmol), an aqueous solution containing copper sulfate (3.1 g, 12.4 mmol) and sodium ascorbate (4.9 g, 24.8 mmol) in H₂O (40 mL) was added. The mixture was stirred overnight at room temperature. The solution was concentrated; a (9:1 DCM/ NH₄OH solution) mixture was added and stirred overnight. The organic phase was extracted with dichloromethane, dried over magnesium sulfate, and the solvent was evaporated to yield a **1c** as yellowish solid. (11.6 g, 82%) mp = 289 °C, ¹H NMR (CDCl₃, 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, CH₃, *J* = 6.81 Hz), ¹³C-NMR, (CDCl₃, 25° C, 75 MHz): δ = 146.25, 140.00, 133.05, 131.15, 124.07, 123.77, 28.59, 24.42, 24.21 HR-MS (ESI, CH₂Cl₂): *m/z* calcd for C₂₈H₃₆N₆ 457.3074 [M+H], value found 457.3096.

Synthesis of 3,3'-Dimethyl-1,1'-diphenyl-1*H*,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 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) (0.45 g, 1.57 mmol) in 1,2-dichloroethane (20 mL), previously cooled at -78°C, was added methyl trifluoromethanesulfonate (0.57g, 3.54 mmol). The reaction mixture was allowed to warm to room temperature, and then heated at 100 °C in a sealed Schlenk for 48 h. The solvent was evaporated; addition of diethylether prompted the precipitation of a white solid after stirring the crude solution for 30 min, afterwards the precipitate was washed with hexane and diethyl ether. Crystals suitable for X-ray were obtained by slow solvent evaporation of a solution of **2a** in acetone. Yield (0.75 g, 97.6%) mp = 251 °C, ¹H NMR (d₆-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, CH₃). ¹³C-NMR, d₆-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 C₁₉H₁₈F₃N₆O₃S⁺ 467.1108 [M-OTf], value found 467.1102.

Synthesis of 1,1'-Dimesityl-3,3'-dimethyl-1*H*,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 was prepared by an adaptation of a reported method.¹⁴ To a stirred solution of 1,1'-dimesityl-1*H*,1'*H*-4,4'-bi(1,2,3-triazole) (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 allowed to warm to room temperature and heated at 100 °C in a sealed Schlenk 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, afterwards the precipitate was washed with hexane and diethyl ether. Yield (6.11 g, 70%) mp = 274 °C, ¹H NMR (CD₃CN, 25° C, 400 MHz): δ = 9.33 (s, 2 H, H_{tr}), 7.35 (s, 4 H, H_{ar}), 4.58 (s, 6 H, CH₃), 2.52 (s, 6 H, CH₃), 2.04 (m, 6 H, CH₃). ¹³C-NMR, (CD₃CN, 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 C₂₅H₃₀F₃N₆O₃S⁺ 551.2047 (M-OTF), value found 551.2060.

Synthesis of 1,1'-Bis(2,6-diisopropylphenyl)-3,3'-dimethyl-1*H*,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 was prepared 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) (5.0 g, 10.9 mmol) in DCM (20 mL), previously cooled at -78°C, was added methyl trifluoromethanesulfonate (3.97g, 24.1 mmol). The reaction mixture was allowed to warm up to room temperature and stirring was maintained overnight. The solvent was evaporated; addition of diethylether prompted the precipitation of a white solid after stirring the crude for 30 min, which was filtered and washed with hexane. The title compound was obtained as a white solid after column chromatography (DCM/MeOH 95:5 %). Yield (5.72 g, 66.7%) mp = 265 °C, ¹H NMR

(CDCl₃, 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, CH₃), 2.29 (s, 4 H, CH, J = 6.7 Hz), 1.10 (m, 24 H, CH₃, J = 6.63 Hz), ¹³C-NMR, (CDCl₃, 25° C, 75 MHz): δ = 145.91, 135.03, 133, 54, 130.43, 127.99, 126.76, 124.94, 40.55, 23.94, 23.76 HR-MS (ESI, CH₂Cl₂): m/z calcd for (C₃₁H₄₂F₃N₆O₃S⁺) 485.3376 [M-OTf], value found 485.3412

Synthesis of [Rh(I)((cod)(7b)]⁺OTf⁻ (3b)—The metal complex [Rh(I)((cod)(7b)]⁺OTf⁻ was prepared 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 suspension of [RhCl(cod)]₂ (100.0 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 (294.2 mg, 0.42 mmol) was added to the reaction mixture at -78 °C, allowed to warm to RT after 10 min, then stirred for another 12 hours. 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, ¹H NMR (CDCl₃, 25°C, 500 MHz): δ = 6.98 (s, 2H, H_{ar}), 4.68 (s, 6 H, CH₃), 4.09 (s, 4H, CH_{cod}), 2.37 (s, 6H, CH₃), 2.11 (s, 12H, CH₃), 2.00 (m, 4 H, CH_{2cod}), 1.73 (m, 4 H, CH_{2cod}), 1.13 (d, 12 H, CH₃, J = 6.5).¹³ C-NMR, (CDCl₃, 25° C, 125 MHz): δ = 172.9 (d, ¹J_{Rh,C} = 40. Hz, NCC), 143.4, 141.2, 134.7, 134.4, 129.6, 88.01, 40.48, 31.0, 21.5, 17.6; ¹⁹F NMR (CDCl₃, 25°C, 376.36 MHz) δ = -78.78; HR-MS (ESI, CH₂Cl₂) m/z = calculated 611.2364 [C₃₂H₄₀N₆Rh]⁺ 611.2383.

Synthesis of [Rh(I)((cod)(7c)]⁺OTf⁻ (3c)—The metal complex [Rh(I)((cod)(7c)]⁺OTf⁻ was prepared 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 (50.0 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 (164 mg, 0.21 mmol) was added to the reaction mixture at -78 °C, allowed to warm to RT after 10 min, then stirred overnight for 12 hours. 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 (158.7 mg, 86%). mp = 239 °C, ¹H NMR (CDCl₃, 25°C, 500 MHz): δ = 7.50 (t, 2H, H_{dipp}, J = 7.5 MHz), 7.28 (d, 4H, H_{dipp}, J = 8.0 MHz), 4.71 (s, 6 H, CH₃), 4.02 (s, 4 H, CH_{cod}), 2.49 (4 H, CH_{dipp}, J = 7.0 MHz), 1.87 (m, 4 H, CH_{2cod}), 1.72 (m, 4 H, CH_{2cod}), 1.33 (d, 12 H, CH₃, J = 6.5), 1.13 (d, 12 H, CH₃, J = 6.5) ppm. ¹³C-NMR, (CDCl₃, 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 ppm. HR-MS (ESI, CH₂Cl₂): m/z = calculated 695.3303 [C₄₀H₅₈N₆Rh]⁺ [M⁺], value found 695.3354.

Synthesis of Complex [Rh((CO)₂(7b)]⁺OTf⁻ (4b)—The preparation of [Rh(CO)₂(7b)]⁺ OTf⁻ was carried out following a procedure similar to the reported method.¹⁴ To a solution of [Rh(cod)(7b)]⁺OTf⁻ (158.7 mg, 0.18 mmol) in chloroform (5 mL), was bubbled CO during 30 min. Evaporation of the solvent affords **4b** as a yellow solid (230 mg, 77.3 %). mp = 199 °C, ¹H NMR (CDCl₃, 25°C, 300 MHz): δ = 7.02 (s, 4, H_{ar}), 4.73 (s, 6 H, CH₃), 2.36 (6 H, CH₃), 2.07 (s, 12 H, CH₃). ¹³C-NMR, (CDCl₃, 25° C, 75 MHz): δ = 187.29 (s, CO), 173.62 (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, 17.6¹⁹ F-NMR, (CDCl₃, 25° C, 282 MHz): δ = -78.79; MS (ESI, CH₂Cl₂): (M⁺): m/z = calculated 642.2184 value found 642.2173 [C₃₂H₃₉N₆O₂Rh]⁺ IR (CH₂Cl₂, cm⁻¹): ν = 2076 (ν CO), 2019 (ν CO).

Synthesis of Complex [Rh((CO)₂(7c)]⁺OTf⁻ (4c)—The preparation of [Rh(CO)₂(7c)]⁺ OTf⁻ was carried out following an adaptation of a reported method.¹⁴ The red powder

[Rh(cod)(**7c**)]⁺OTf⁻ (158.7 mg, 0.18 mmol) was suspended in benzene (5 mL). The solution was bubbled with CO during 30 min. Evaporation of the solvent yields **4c** as a yellow solid (55 mg, 60%). Crystals suitable for X-ray diffraction were obtained into a glovebox by slow evaporation of the solvent of a solution of **4c** in CDCl₃. mp = 233 °C, ¹H NMR (CDCl₃, 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, CH₃), 2.32 (4 H, CH, *J* = 6.8 MHz), 1.138 (dd, 24 H, CH₃, *J* = 6.4) ppm, ¹³C-NMR, (CDCl₃, 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; ¹⁹F NMR (CDCl₃, 25 °C, 376.36 MHz) δ = -79.19; MS (ESI, CH₂Cl₂): (M⁺): *m/z* = 643.2262 calculated, 643.2333 value found [C₃₂H₄₀N₆O₂Rh]⁺ IR (CH₂Cl₂, cm⁻¹) ν = 2076 (νCO), 2020 (νCO).

Synthesis of 4,4'-Bis(1-phenyl-3-methyl-1*H*-1,2,3-triazol-5-ylidene) (7a)—In a flamed dried Schlenk were added 1,1'-diphenyl-3,3'-dimethyl-1*H*,1'*H*-4,4'-bis(1,2,3-triazolium) trifluoromethanesulfonate (0.4 g, 0.65 mmol) and potassium bis(trimethylsilyl)amide (0.28 g, 1.43 mmol). The Schlenk was cooled to -78 °C, and then tetrahydrofuran (15 mL) was added. After 10 min, the cold bath was removed; the reaction mixture was allowed to warm to room temperature. After one hour the solvent was removed under vacuum. The metal-free **7a** was extracted by trituration in dry benzene (2 × 10 mL) and 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 RT, and slowly cooling the solution to -30 °C under an argon atmosphere. mp = 134 °C, ¹H NMR (C₆D₆, 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, CH₃). ¹³C-NMR, (C₆D₆, 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-1*H*-1,2,3-triazol-5-ylidene) (7b)—In a flamed dried Schlenk were added 1,1'-dimesityl-3,3'-dimethyl-1*H*,1'*H*-4,4'-bis(1,2,3-triazolium) trifluoromethanesulfonate (0.4 g, 0.57 mmol) and potassium bis(trimethylsilyl)amide (0.25 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 allowed to warm to room temperature. After one hour 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. Afterwards, solvent was removed under vacuum to yield **7b** as an off-white solid (0.186 g, 81%). mp = 129 °C, ¹H NMR (C₆D₆, 25 °C, 300 MHz): δ = 6.88 (s, 4 H, H_{ar}), 4.71 (s, 6 H, CH₃), 2.26 (s, 12 H, CH₃), 2.22 (d, 12 H, CH₃). ¹³C NMR, (C₆D₆, 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-1*H*-1,2,3-triazol-5-ylidene) (7c)—In a flamed dried Schlenk were added 1,1'-bis(2,6-diisopropylphenyl)-3,3'-dimethyl-1*H*, 1'*H*-4,4'-bis(1,2,3-triazolium) trifluoromethanesulfonate (0.3 g, 0.38 mmol) and potassium bis(trimethylsilyl)amide (0.161 g, 0.84 mmol). The Schlenk 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 allowed to warm to room temperature and stirred for one hour. Volatiles were removed under vacuum. The free carbene was extracted by filtration via cannula. Afterwards, solvent was removed under vacuum to afford **7c** as an off-white solid (115 mg, 62%). mp = 139 °C, ¹H NMR (C₆D₆, 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, CH₃), 2.85 (s, 4 H, CH, *J* = 6.8 Hz), 1.32 (d, 12 H, CH₃, *J* = 6.6 Hz), 1.25 (d, 12 H, CH₃, *J* = 6.7 Hz) ¹³C-NMR, (C₆D₆, 25 °C, 100 MHz): δ = 201.37, 145.50, 140.38, 139.30, 129.74, 129.32, 124.72, 39.29, 29.21, 24.55, 24.45.

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)₂rhodium(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.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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

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 (°): 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).

Figure 3.

Crystal structure of bis(1,2,3-triazol-5-ylidene) **7a** with ellipsoids shown at 50% probability. Selected bond lengths (Å) and angles (°): 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).

Scheme 1.

Synthesis of bis(triazoles) **1a-c**, bis(triazolium) salts **2a-c** and i-bitz-rhodium complexes **3b,c** and **4b,c**

Scheme 2. Rearrangement of transient bitz, and preparation of stable i-bitz **7a-c**.