

1,2,4-Triazole-3,5-diylidene: A Building Block for Organometallic Polymer Synthesis

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Coordination polymers, especially those containing rigid π -conjugated chains, are currently attracting considerable interest.¹ Transition metal carbene complexes have been widely studied,² but carbene–metal-type polymers have never been explored. In contrast to the stable phosphinocarbenes,³ the stable imidazol-2-ylidenes⁴ have proved to be excellent ligands for transition metals.⁵ Thus, it was of interest to try using 1,2,4-triazole-3,5-diylidene (**1**) as a building block for organometallic polymer synthesis, and here, we report the solid state structure of a bis(carbene)–silver(I) polymer.

To check that bis(carbenes) of type **1** are rigid π -conjugated systems, we first performed *ab initio* calculations.⁶ The parent compound **1** is a true minimum on the potential surface, although as expected higher in energy than the triazole isomers **2–4** and

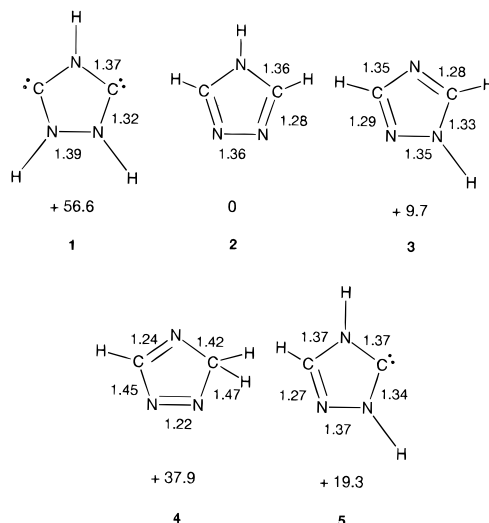
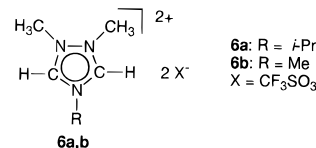


Figure 1. Calculated bond length (Å) and relative energies (kcal mol⁻¹) for **1–5**.

1,2,4-triazol-3-ylidene (**5**) recently reported by Enders⁷ (Figure 1). Due to the interaction between the vacant carbene p-orbital and the nitrogen lone pairs, bis(carbene) **1** is indeed calculated to be planar. It presents some aromatic character,⁸ as shown by comparing the geometry of **1** with those of the conjugated triazoles **2–3** and nonconjugated triazole **4**. Consequently, the carbene lone pairs are in the plane of the ring, which is particularly interesting when considering the construction of π -conjugated organometallic polymers.

The obvious potential precursors for bis(carbenes) **1a,b** are the dicationic heterocycles **6a,b**.⁹ A single-crystal X-ray



diffraction study¹⁰ of **6b** (Figure 2) reveals that the carbon–nitrogen and nitrogen–nitrogen bond lengths are half way between those for single and double bonds, and all the substituents are in the plane of the ring (maximum deviation 0.13 Å).

By analogy with Wanzlick's synthetic strategy,⁵ⁿ 2 equiv of silver(I) acetate was treated with **6a** in refluxing thf for 2 h (Scheme 1). After filtration, an extremely light-sensitive white powder was obtained. Single crystals of **7a** suitable for an X-ray diffraction study¹⁰ were obtained at –30 °C from an acetonitrile/ether solution. The view of the solid-state structure (Figure 3) shows the polymeric nature of **7a**. There is no interaction between the metal and the anion (nearest distance: Ag(2)F(2) = 3.18 Å). The silver atoms are essentially linearly coordinated with C–Ag–C bond angles of 175–180°. The Ag–C bond lengths [2.086(4)–2.090(4) Å] and the N–C–N angles [103.9–(3)°] are very similar to those observed for the imidazol-2-

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(9) The synthesis of **6b** has already been reported: Curphey, T. J.; Prasad, K. S. *J. Org. Chem.* **1972**, *37*, 2259. Selected physical data for **6a**: mp 170–172 °C. ¹H NMR (CD₃CN, 298 K): δ 1.65 (d, ³J_{H-H} = 6.6 Hz, 6H, CH(CH₃)₂), 4.34 (s, 6H, NCH₃), 5.03 (sept, ³J_{H-H} = 6.6 Hz, 1H, NCH(CH₃)₂), 10.22 (s, 2H, CH); ¹³C{¹H} NMR (CD₃CN): δ 21.5 (CH(CH₃)₂), 38.7 (NCH₃), 58.9 (NCH(CH₃)₂), 121.1 (q, ¹J_{C-F} = 320.1 Hz, CF₃), 145.2 (CH).

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(6) Calculations were performed at the RHF-SCF-DZP level for the geometry optimizations. On each minimum, correlation effects were estimated through MP4 calculations (HONDO8 program from the MO-TECC89 package¹⁶).

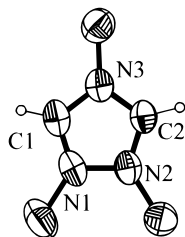


Figure 2. Crystal structure of **6b** and anisotropic displacement parameters depicting 50% probability. The triflate anions have been omitted for clarity. Selected bond lengths (Å) and angles (deg) N1–C1, 1.296(7); N1–N2, 1.370(5); N2–C2, 1.305(6); C1–N3, 1.326(6); C2–N3, 1.337(6); C1–N1–N2, 107.5(4); C2–N2–N1, 107.3(4); N1–C1–N3, 109.1(5); N2–C2–N3, 108.4(4); C1–N3–C2, 107.7(5).

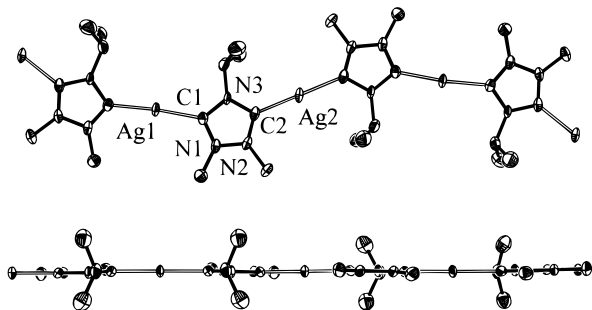
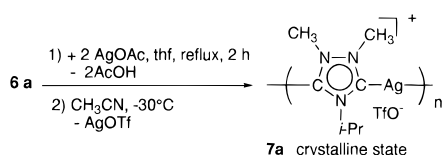


Figure 3. Crystal structure of **7a** and anisotropic displacement parameters depicting 50% probability. The uncoordinated triflate anions and acetonitrile molecules have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Ag1–C1, 2.086(4); Ag2–C2, 2.090(4); N1–C1, 1.320(5); C1–N3, 1.370(5); N1–N2, 1.373(5); N2–N3, 1.368(5); C2–N2, 1.318(5); C1–Ag1–C1A, 174.7(2); C2–Ag2–C2A, 180.0(1); N1–C1–Ag1, 126.0(3); N3–C1–Ag1, 130.1(3); N2–C2–Ag2, 126.8(3); N3–C2–Ag2, 129.1(3); N1–C1–N3, 103.9(3); C1–N1–N2, 109.9(3); N2–C2–N3, 104.0(3); C2–N2–N1, 110.0(3); C2–N3–C1, 112.2(3).

Scheme 1



ylidene–silver complex [2.067(4)–2.078(4) Å; 103.6(4)–104.8(4)°].^{5b} The five-membered rings are planar (maximum deviation: 0.07 Å), and all the bond lengths in the ring are very close to those of the calculated free bis(carbene) **1**. Due

(10) Crystal data for **6b**: C₇H₁₁F₆N₃O₆S₂, *M* = 411.31, triclinic, *P* $\bar{1}$, *a* = 6.373(2) Å, *b* = 10.385(3) Å, *c* = 13.158(4) Å, α = 76.44(2)°, β = 76.18(2)°, γ = 82.04(3)°, *V* = 819.0(4) Å³, *Z* = 2, ρ_c = 1.668 Mg m⁻³, *F*(000) = 416, λ = 0.710 73 Å, *T* = 293(2) K, μ (Mo K α) = 0.419 mm⁻¹, crystal size 0.2 × 0.1 × 0.1 mm, 4.6° < 2 θ < 48.5°, 4796 reflections collected, 2441 independent (*R*_{int} = 0.044), refinements of 312 parameters using 151 restraints, largest electron density residue: 0.429 e Å⁻³, *R*₁ (for *F* > 2 σ (*F*)) = 0.057 and *wR*₂ = 0.166 (all data) with *R*₁ = $\sum||F_o| - |F_c|| / \sum|F_o|$ and *wR*₂ = $(\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2)^{0.5}$. The data were collected on a STOE-IPDS diffractometer. The structure was solved by direct methods (SHELXS-96)¹⁷ and refined using the least-squares method on *F*².¹⁸ Crystal data for **7a**: C₈H₁₃AgF₃N₃O₃S (CH₃CN), *M* = 437.20, orthorhombic, *Pnma*, *a* = 16.737(3) Å, *b* = 24.393(4) Å, *c* = 7.911(1) Å, *V* = 3229.8(9) Å³, *Z* = 8, ρ_c = 1.798 Mg m⁻³, *F*(000) = 1744, λ = 0.710 73 Å, *T* = 133(2) K, μ (Mo K α) = 1.424 mm⁻¹, crystal size 0.25 × 0.25 × 0.15 mm, 4.8° < 2 θ < 50.5°, 30 981 reflections collected, 2931 independent (*R*_{int} = 0.051), refinements of 215 parameters using 33 restraints, largest electron density residue: 1.433 e Å⁻³, *R*₁ (for *F* > 2 σ (*F*)) = 0.039 and *wR*₂ = 0.103 (all data) with *R*₁ = $\sum||F_o| - |F_c|| / \sum|F_o|$ and *wR*₂ = $(\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2)^{0.5}$. The data were collected on a STOE-SIEMENS-HUBER four-circle diffractometer. The intensities of a cooled crystal in an oil drop were measured with a SIEMENS-CCD area detector. The structure was solved by direct methods (SHELXS-96)¹⁷ and refined using the least-squares method on *F*².¹⁸

to the alternation in the orientation of the rings (two rings with the *i*-Pr group on one side of the chain and two rings with the *i*-Pr group on the other side), **7a** is a one-dimensional polymer, in which all the rings are coplanar.

The crystals of **7a** analyzed by X-ray diffraction study appeared to be totally insoluble. However, addition of a small amount of silver triflate to the suspension of **7a** in acetonitrile gave an homogeneous solution. Interestingly, the bulk material is soluble in acetonitrile and according to NMR spectroscopy both solutions are identical. Note that in contrast to the 1/1 silver triflate/bis(carbene) ratio found in the X-ray analysis of **7a**, elemental analyses of the bulk material showed a 2/1 ratio, in agreement with the ratio of the reagents used.¹¹ The ¹H and ¹³C NMR spectra of the solution¹² revealed the presence of an isopropyl group bound to nitrogen and two equivalent N–Me groups, which suggested the presence of the bis(carbene) fragment. The signal for the carbenic carbon appeared at $\delta^{13}\text{C}$ = 182.9 ppm, very close to that observed for the imidazol-2-ylidene–silver complex reported by Arduengo (183.6, ¹*J*_{AgC} = 188.0 and ¹*J*_{AgC} = 208.6 Hz),^{5b,k} but no silver–carbon coupling constant was observed, even at low temperatures. However, when the ¹³C NMR spectrum was performed in acetone-*d*₆ at 193 K, in the presence Cl⁻ (from KCl),¹³ the signal of the quaternary carbon was split into two broad signals (¹*J*_{AgC} = 200 Hz), while the other signals remained unchanged. These results as a whole suggest that the silver–bis(carbene)–silver unit is present in solution, but as already observed for other silver complexes,¹⁴ rapid metal exchange occurs. The exchange process is slowed down in the presence of a coordinating anion such as Cl⁻.

As expected for such ionic organometallic polymers,^{1ac,15} **7a** only exists in the solid state. The synthesis and electronic properties of polymers featuring coplanar 1,2,4-triazole-2,5-diylidene fragments and various transition metals are being investigated. The synthesis of a stable free bis(carbene) of type **1**, which would considerably broaden the choice of potential metal fragments for complexation, is still a challenging but reasonable project.

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Supporting Information Available: Tables of crystal and intensity collection data, position and thermal parameters, and interatomic distances and angles (12 pages). See any current masthead page for ordering and Internet access instructions.

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(11) The bulk material either is a 1/1 mixture of **7a** and silver triflate or, alternatively, has a structure such as TfO–Ag–bis(carbene)–Ag–OTf as suggested by one of the reviewers.

(12) Selected physical data for **7a**: mp 154 °C (dec); **7a** + AgOSO₂CF₃ (CD₃CN, 298 K): ¹H NMR: δ 1.60 (d, ³*J*_{H–H} = 6.85 Hz, 6H, CH(CH₃)₂), 4.14 (s, 6H, NCH₃), 4.83 (sept, ³*J*_{H–H} = 6.6 Hz, 1H, NCH(CH₃)₂); ¹³C NMR: δ 24.1 (CH(CH₃)₂), 38.9 (NCH₃), 56.8 (NCH(CH₃)₂), 121.1 (q, ¹*J*_{C–F} = 320.1 Hz, CF₃), 182.9 (C_{Ag}); no signals were detected by ¹⁰⁹Ag NMR. Anal. Calcd (found): C, 16.55 (16.72); H, 2.01 (1.80); N, 6.43 (6.15).

(13) A 1/1 ratio of AgOTf and KCl was added to an acetonitrile suspension of **7a**.

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