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PAPER

1,3-Dipolar cycloaddition between a metal–azide (Ph_3PAuN_3) and a metal–acetylide ($Ph_3PAuC{\equiv}CPh$): an inorganic version of a click reaction†

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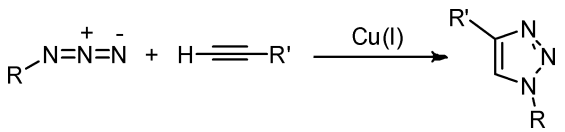
This report describes the synthesis and characterization of 1,5-bis-triphenylphosphinegold(I) 1,2,3-triazolate ($\mathbf{3}_{(1,5)}$). The synthesis of the dinuclear complex $\mathbf{3}_{(1,5)}$ is achieved *via* an unprecedented inorganic click (iClick) reaction between the metal–azide PPh_3AuN_3 (**1**) and the metal–acetylide $PPh_3Au{-}C{\equiv}CPh$ (**2**). Characterization of $\mathbf{3}_{(1,5)}$ includes multinuclear NMR spectroscopy, combustion analysis, and single crystal X-ray crystallography. Experimental characterization is complemented with density-functional-theory (DFT) calculations which indicate the 1,4-isomer $\mathbf{3}_{(1,4)}$ is less stable by 3.3 kcal mol^{-1}. The energetic difference lies primarily in the ability of the phenyl group in the 4-position of $\mathbf{3}_{(1,5)}$ to lie coplanar with the triazolate to create a delocalized π-bonding HOMO orbital.

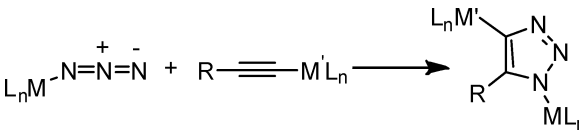
Introduction

Click reactions, first outlined by Sharpless in 2001,[1] are synthetically powerful tools that use small molecular building blocks to assemble complex molecules and materials in a myriad of ways *via* carbon–heteroatom bonds. Of the reactions that are classified as "Click", by far the most well recognized and prolific in application is the Cu(I)-catalyzed Huisgen 1,3-dipolar cycloaddition[2–4] of alkynes and azides to yield 1,4-disubstituted 1,2,3-triazoles (eqn (1), CuAAC).[5,6] This reaction is particularly powerful and accessible due to the ease of synthesis of the alkyne and azide functional groups, the nearly quantitative yields, the tolerance of a wide variety of solvents including water, and the stereoselective nature of the reaction that allows synthesis of 1,4-triazoles.



(1)

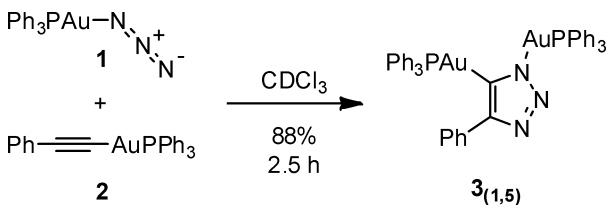
Despite the growing applications[7–12] of Click chemistry, and Huisgen cycloadditions, there are considerably fewer examples of these ideas in the field of inorganic or organometallic chemistry. Within a metal coordination sphere,[13,14] cycloadditions exist[14–17] in which an organoazide adds to a metal-bound acetylide[18–20] and *vice versa*;[20–25] and in which isocyanides,[26] isonitriles,[27–30] nitriles,[14,22,31–34] and carbon disulfide[35] add to a metal azide. Undocumented however, is the reaction between a metal–azide and a metal–acetylide (eqn (2)). Described within is the first inorganic version of a 1,3-dipolar Huisgen cycloaddition reaction, given the moniker inorganic click (iClick).



(2)

Results and discussion

Gold(I), chosen to provide diamagnetic products and mimic the Huisgen cycloaddition, is isolobal with a proton and both the azide[20,36,37] and acetylide[38,39] derivatives are known. Treating triphenylphosphinegold(I) azide (**1**) with triphenylphosphinegold(I) phenylacetylide (**2**) results in the formation of colorless 4-phenyl-1,5-bis-triphenylphosphinegold(I) 1,2,3-triazolate ($\mathbf{3}_{(1,5)}$) in excellent yield (eqn (3), quantitative by NMR, 88% isolated).



(3)

The reaction is amendable to different solvents including benchtop synthesis in wet benzene, chloroform and dimethyl sulfoxide. In benzene the product precipitates as large colorless crystals, allowing easy isolation. Performed in $CDCl_3$, it is possible to monitor the reaction progress by ^1H NMR spectroscopy. Within five minutes a downfield doublet (J = 9.0 Hz) resonance attributable to the *o*-protons of the triazolate 4-phenyl appears at 8.43 ppm. Monitoring the reaction by $^{31}P\{^1H\}$ NMR spectroscopy indicates the resonances for the phosphine ligands on **1** (30.33 ppm) and **2** (41.76 ppm) disappear, concomitant with the appearance of two

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† Electronic supplementary information (ESI) available: NMR spectra, X-ray crystallographic data, calculated coordinates and experimental details. CCDC reference number 820816. For ESI and crystallographic data in CIF or other electronic format, see DOI: 10.1039/c1dt10787a

new signals at 43.93 (PAuC) and 31.45 ppm (PAuN) attributable to $\mathbf{3}_{(1,5)}$.

Crystals deposit from a benzene solution of $\mathbf{3}_{(1,5)}$, and Fig. 1 depicts the results of a single crystal X-ray diffraction experiment. Apparent from the molecular structure is the formation of the 1,5-digold substituted product, instead of the corresponding 1,4-digold isomer. The complex is C_s-symmetric and crystallizes in the *Pbca* space group along with two molecules of benzene, one being disordered. Additional disorder exists within two of the PPh_3 rings and the 4-phenyl of the triazolate. The geometry of each Au(I) ion is nearly linear; P1–Au1–N1 = 176.9(1) and P2–Au2–C1 = 177.99(12)°. Au(I) coordination to the heterocycle produces similar bond lengths for each connection (Au1–N1 = 2.032(3) Å and Au2–C1 = 2.035(4) Å).

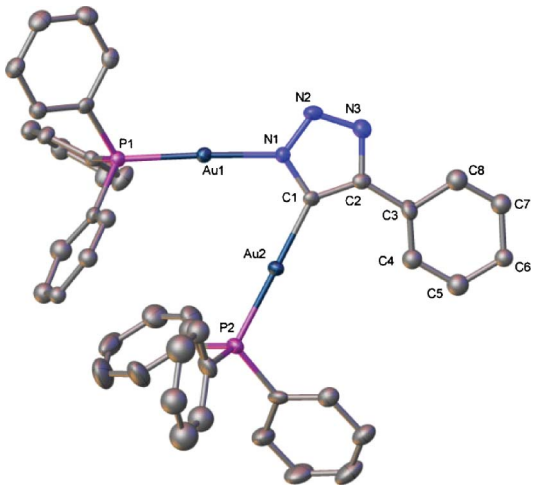

Fig. 1 Molecular structure of $\mathbf{3}_{(1,5)}$ with ellipsoids drawn at the 50% probability level. Two lattice molecules of benzene, disordered atoms, and hydrogen atoms are removed for clarity. Selected bond lengths (Å) and angles (°): Au1–N1 = 2.032(3), Au2–C1 = 2.035(4), Au1–P1 = 2.2416(12), Au2–P2 = 2.2846(12), N1–N2 = 1.346(5), N2–N3 = 1.332(5), N3–C2 = 1.365(5), C1–C2 = 1.383(6), C1–N1 = 1.368(5); P1–Au1–N1 = 176.9(1), P2–Au2–C1 = 177.99(12), N1–N2–N3 = 108.0(4), N2–N3–C2 = 107.9(4), C1–N1–N2 = 110.7(3), N3–C2–C3 = 109.3(4), C2–C1–N1 = 104.1(4).

Most structurally similar to $\mathbf{3}_{(1,5)}$, mononuclear (NHC)Au[I]- and R_3PAu^I-triazolates, derived from the addition of organoazides to Au–acetylides and alkynes to Au–azides,[18,19] exhibit 0.02 Å shorter Au–$C_{triazolate}$ bonds. Relatively rare, crystallographically characterized gold(I)–vinyl complexes contain similar Au–C bond lengths that range between 2.002(9) to 2.0573(18) Å.[18,19,40–46]

The most salient structural feature within $\mathbf{3}_{(1,5)}$ is that the 4-phenyl ring aligns nearly coplanar with the triazolate. The phenyl ring disorders over two positions with equal occupancy. The planes comprised of the non-H atoms from the disordered rings bisect the triazolate plane at 7.2 and 18°. Near coplanarity implies electronic delocalization across the two rings because, spatially, a perpendicular orientation is more favorable.

Support for electronic delocalization comes from spin restricted geometry optimization and density-functional-theory (DFT) calculations of $\mathbf{3}_{(1,5)}$ by employing the atomic coordinates from the crystal structure as the initial input (see ESI†). Fig. 2 depicts the optimized geometry structure $\mathbf{3}_{(1,5)}'$ and lists some calculated bond lengths and experimental values for comparison. Overall the

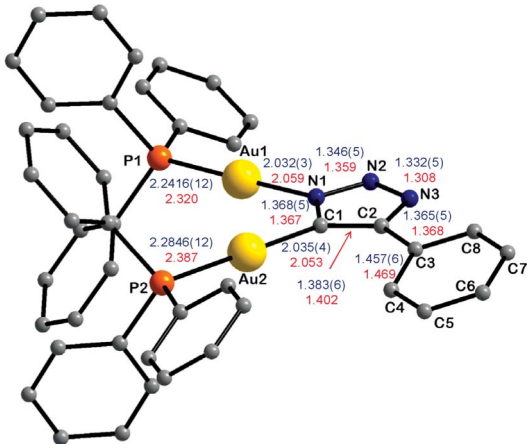

Fig. 2 Optimized geometry of $\mathbf{3}_{(1,5)}'$. Selected bond distances (in Å) for $\mathbf{3}_{(1,5)}$ are blue and for $\mathbf{3}_{(1,5)}'$ are red.

simulated bond lengths compare well with experimental values, including important bonds such as the Au1–N1 = 2.059 (2.032(3) Å) and Au2–C1 = 2.053 (2.035(4) Å). The calculation generates a twist angle of 16° between the ring planes of the triazolate and 4-phenyl, which agrees well with the solid state characterization.

Thermal cycloaddition of organic azides and terminal alkynes typically results in a mixture of 1,4 and 1,5-triazoles.[2] Curious as to why the 1,5-isomer forms selectively in this case, we investigated the geometry optimized structure of the 1,4-derivative as well. Fig. 3 depicts the optimized structure of the 1,4-digold triazolate complex $\mathbf{3}_{(1,4)}'$. Again, the bond length metrics compare well with the experimental values of $\mathbf{3}_{(1,5)}$, but the main difference occurs within the relative disposition of the triazolate and 4-phenyl ring. Now planes comprised of the non-H atoms bisect at 43°, which is clearly of steric origin. The two adjacent Au(I) ions prevent coplanarity of the rings. Comparing the total energy of the two calculated isomers reveals the 1,5-isomer $\mathbf{3}_{(1,5)}'$ is more stable than the 1,4-isomer $\mathbf{3}_{(1,4)}'$ by 3.3 kcal mol^{-1}.

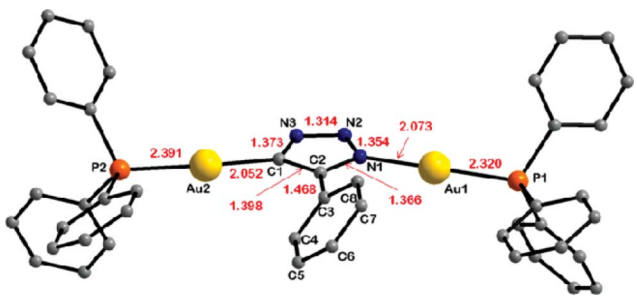

Fig. 3 Optimized geometry of $\mathbf{3}_{(1,4)}'$ and selected bond lengths (Å).

Closer inspection of the ^1H NMR spectrum of the product reveals a doublet (J = 9 Hz) at 8.62 ppm attributable to the 1,4-isomer $\mathbf{3}_{(1,4)}$, which integrates to <3% of the peak area of the corresponding doublet at 8.42 ppm for $\mathbf{3}_{(1,5)}$. At 24 °C, the $^{31}P\{^1H\}$ NMR spectrum ($CDCl_3$) only exhibits two broad intense resonances for $\mathbf{3}_{(1,5)}$. However, upon lowering the temperature to –40 °C the phosphorus resonances sharpen revealing a second set of two minor (<3%) resonances for $\mathbf{3}_{(1,4)}$ at 42.50 (PAuC) and 31.66 ppm (PAuN) (Fig. 4). Variable temperature NMR spectroscopy performed on the mixture of $\mathbf{3}_{(1,5)}$ and $\mathbf{3}_{(1,4)}$ are

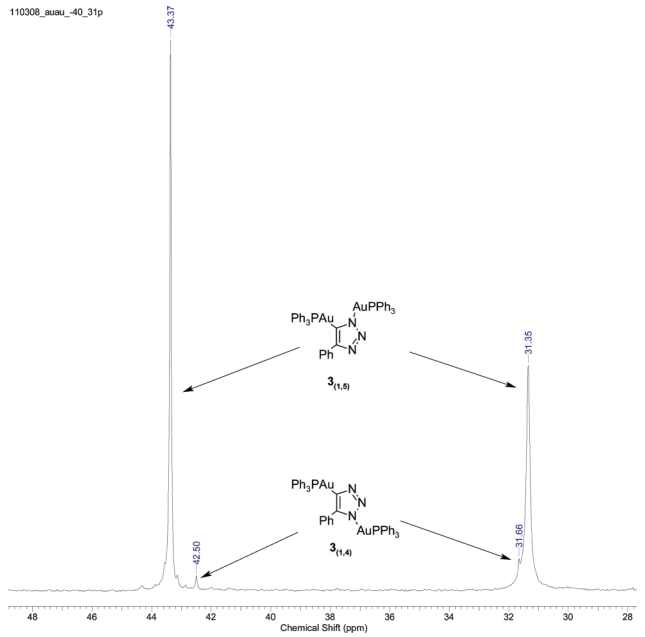

Fig. 4 $^{31}P\{^{1}H\}$ NMR spectrum of $\mathbf{3}_{(1,5)}$ (major) and $\mathbf{3}_{(1,4)}$ (minor) in $CDCl_3$ at −40 °C.

unable to conclusively establish whether the two isomers are in equilibrium due to the low concentration of $\mathbf{3}_{(1,4)}$. Over a 90 °C temperature range, no change occurs in their relative concentrations.

The energy difference is a result of the broken electronic delocalization within the 1,4-isomer. Supporting this observation, the highest occupied molecular orbital (HOMO) of the 1,5-isomer consists of a π-bonding orbital delocalized over the two rings (Fig. 5, top). In contrast, the perpendicular rings in the 1,4-derivative localize the HOMO π-orbital on the triazolate, thus elevating its energy (Fig. 5, bottom). The lowest unoccupied molecular orbital (LUMO) for both isomers comprises high lying π* orbitals of the P–aryl moiety and results in a HOMO–LUMO gap of 2.98 eV and 3.38 eV for $\mathbf{3}_{(1,5)}'$ and $\mathbf{3}_{(1,4)}'$, respectively. Consistent with the calculation, $\mathbf{3}_{(1,5)}$ is colorless and the UV-Vis spectrum of $\mathbf{3}_{(1,5)}$ reveals only an absorption in the UV region centered at 290 nm.

Conclusions

In summary, these results demonstrate for the first time an iClick reaction between a metal–azide (Ph_3PAuN_3) and a metal–acetylide ($Ph_3PAu–C{\equiv}CPh$), which represents a new direction for 1,3-dipolar cycloadditions. Work remains to elucidate the generality of this reaction across different metal ions and reaction conditions. Considering the expansive repertoire of M–azide and M–acetylide complexes known across the transition metals and main group elements featuring different oxidation states, valence electron counts, and ancillary ligands; an infinite combination of homo- and heterodinuclear triazolate complexes are feasible. Further extension to more complex structures and materials is possible by linking multiple metal ions together *via* cycloaddition between complexes featuring di and triacetylide/azide groups.

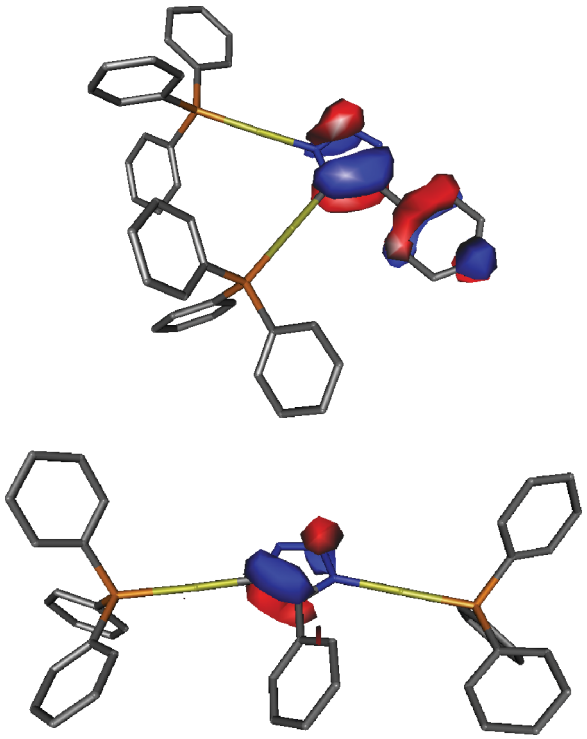

Fig. 5 Highest occupied molecular orbital (HOMO) for $\mathbf{3}_{(1,5)}'$ (top) and $\mathbf{3}_{(1,4)}'$ (bottom).

Experimental

Glassware was oven dried before use. Pentane, toluene, and diethyl ether (Et_2O) were dried using a Glass Contours drying column. Benzene-d_6 and chloroform-d_1 (Cambridge Isotopes) were dried over sodium-benzophenone ketyl and distilled or vacuum transferred and stored over 4 Å molecular sieves. Commercially available PPh_3AuCl and $TMSN_3$ were used without further purification. Commercially available phenylacetylene was distilled before use. Ph_3PAuN_3[20,36,37] and $PPh_3Au–C{\equiv}CPh$[38,39] were prepared according to literature procedures. NMR spectra were obtained on Varian Mercury Broad Band 300 MHz, Varian Mercury 300 MHz, or on Varian Inova 500 MHz spectrometers. Chemical shifts are reported in δ (ppm). For ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra the solvent resonance was referenced as an internal reference, and for $^{31}P\{^{1}H\}$ NMR spectrum the 85% H_3PO_4 resonance was referenced as an external standard. Elemental analyses were performed at Complete Analysis Laboratory Inc., Parsippany, New Jersey. FT-IR spectra were recorded on a Thermo Scientific instrument.

Synthesis of $\mathbf{3}_{(1,5)}$ (major) and $\mathbf{3}_{(1,4)}$ (minor)

A sealable NMR tube was charged with $Ph_3PAuCCPh$ (10 mg, 0.018 mmol), Ph_3PAuN_3 (9 mg, 0.018 mmol), and benzene-d_6 (0.6 mL). After 24 h clear colorless crystals deposit along the sides of the NMR tube. Crystals were collected and washed with pentane to give the major product $\mathbf{3}_{(1,5)}$ and <3% minor product $\mathbf{3}_{(1,4)}$ (17 mg, 89% yield). $\mathbf{3}_{(1,5)}$: ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 8.43 (d, J = 9 Hz), 7.1–7.6 (m, aromatic). $^{31}P\{^{1}H\}$ NMR (121.16 MHz, $CDCl_3$, 25 °C), δ (ppm): 43.93 (bs, *P*AuC), 31.45 (bs, *P*AuN). $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$), δ (ppm): 136.6 (s,

Table 1 Crystallographic data for $\mathbf{3}_{(1,5)}$

Compound code	CCDC 820816
Empirical formula	$C_{56}H_{47}N_2P_2Au_2$
Formula weight	1217.84
T/K	100(2)
λ/Å	0.71073
Crystal system	Orthorhombic
Space group	*Pbca*
a/Å	15.4234(3)
b/Å	17.1790(3)
c/Å	35.8699(7)
α (°)	90
β (°)	90
γ (°)	90
V/Å^3	9504.0(3)
Z	16
ρ_{calcd} (Mg mm^{-3})	1.702
Crystal size/mm	0.15 × 0.12 × 0.04
μ/mm^{-1}	6.275
F(000)	4736
θ range for data collection (°)	1.74 to 27.50
Limiting indices	$-17 \le h \le 20$, $-22 \le k \le 19$, $-46 \le l \le 46$
No. of reflns collcd	85 533
No. of ind reflns (R_{int})	10 916 (0.0949)
Completeness to $\theta = 27.50°$	100.0%
Absorption corr	Numerical
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	10 916/24/515
$R1$,[a] w$R2$[b] [$I > 2\sigma(I)$]	0.0333, 0.0600 [7820]
$R1$,[a] w$R2$[b] (all data)	0.0570, 0.0640
GOF[c] on F^2	0.932
Largest diff. peak and hole	1.646 and −1.395 e Å^{-3}

[a] $R1 = \sum \| F_o - \| F_c \| / \sum | F_o |$. [b] $wR2 = (\sum(w(F_o^2 - F_c^2)^2)/\sum(w(F_o^2)^2))^{1/2}$. [c] GOF = $(\sum w(F_o^2 - F_c^2)^2/(n-p))^{1/2}$ where n is the number of data and p is the number of parameters refined.

$C_{aromatic}$, triazolate), 134.2 (d, J_{PC} = 14 Hz, *o*-C, overlapping, C–Au–P(C_6H_5)$_3$ and N–Au–P(C_6H_5)$_3$)), 131.5 (bs, *i*-C, overlapping, C–Au–P(C_6H_5)$_3$ and N–Au–P(C_6H_5)$_3$), 129.1 (d, J_{PC} = 11 Hz, *m*-C and *p*-C, overlapping, C–Au–P(C_6H_5)$_3$ and N–Au–P(C_6H_5)$_3$), 127.9 (s, $C_{aromatic}$, triazolate), 126.4 (s, $C_{aromatic}$, triazolate), 125.4 (s, $C_{aromatic}$, triazolate). $\mathbf{3}_{(1,4)}$: ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 8.6 (d, J = 9 Hz), aromatic resonances overlapping with $\mathbf{3}_{(1,5)}$ between 7.1–7.6. $^{31}P\{^1H\}$ NMR (121.16 MHz, $CDCl_3$, –40 °C), δ (ppm): 42.50 (s, *P*AuC), 31.66 (s, *P*AuN). Anal. Calcd. for $C_{44}H_{35}N_3P_2Au_2$: C, 49.78; H, 3.32; N, 3.96. Found: C, 49.86; H, 3.41; N, 3.88.

X-Ray crystallography

X-Ray intensity data were collected at 100 K on a Bruker SMART diffractometer using Mo-Kα radiation (λ = 0.71073 Å) and an APEXII CCD area detector (Table 1). Raw data frames were read by the program SAINT[47] and integrated using 3D profiling algorithms. The resulting data were reduced to produce *hkl* reflections and their intensities and estimated standard deviations. The data were corrected for Lorentz and polarization effects and numerical absorption corrections were applied based on indexed and measured faces.

The structure was solved and refined in SHELXTL6.1, using full-matrix least-squares refinement. The non-H atoms were refined with anisotropic thermal parameters and all of the H atoms were calculated in idealized positions and refined riding on their parent atoms. The asymmetric unit consists of the digold complex and two benzene solvent molecules. The complex has three disordered aryl rings. They were refined in two parts each with their site occupation factors dependently refined. One of the benzene solvent molecules is disordered and was also refined in two parts. In the final cycle of refinement, 10 916 reflections (of which 7820 are observed with $I > 2\sigma(I)$) were used to refine 515 parameters (and 24 restraints) and the resulting R_1, wR_2 and S (goodness of fit) were 3.33%, 6.00% and 0.932, respectively. The refinement was carried out by minimizing the wR_2 function using F^2 rather than F values. R_1 is calculated to provide a reference to the conventional R value but its function is not minimized.

Computational details

Spin-restricted density-functional theory computations were executed in the Gaussian 09 program suite.[48] All calculations employed the B3LYP functional[49,50] along with the standard 6-31G(d,p) basis set on all non-metal atoms.[51–53] Gold orbitals were described with the Stuttgart effective core potential and the associated basis set.[54] Geometries were optimized without imposed symmetry and harmonic frequency calculations find all structures to be potential minima. Molecular orbital pictures with isovalues of 0.05 were generated using the Gabedit visualization program.[55] Computational resources and support were provided by the University of Florida High-Performance Computing Center.

Acknowledgements

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