Metallostructures

DOI: 10.1002/anie.201309493

Preparation of an Organometallic Molecular Square by Self-Assembly of Phosphorus-Containing Building Blocks**

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Abstract: *Molecular squares are among the most common supramolecular architectures, but phospha-organometallic complexes have not been used as building blocks for this type of structure. Herein we describe the formation of the molecular square $[Au\{Co(P_2C_2tBu_2)_2\}]_4$ (**1**) by the self-assembly of anionic 1,3-diphosphacyclobutadiene cobalt complexes and gold(I) cations. The X-ray crystallographic determination of the molecular structure of **1** is complemented by solid-state ^{31}P and ^{13}C NMR investigations. High-level DFT calculations confirm the assignment of the ^{31}P and ^{13}C NMR resonances.*

Since Lehn and co-workers first illustrated the concept of coordination-driven self-assembly in their seminal work on the spontaneous formation of multinuclear double- and triple-helical metal complexes,[1] metallosupramolecular compounds have attracted much attention.[2] A diverse range of structures has become accessible which increasingly find application in diverse areas such as host–guest chemistry and catalysis.[2,3] The search for new functional building blocks for such supramolecular assemblies is a timely challenge.

Molecular squares are among the most extensively investigated supramolecular architectures. They may be rationally designed by self-assembly of linear building units and rectangular corner pieces. Impressive square-like compounds have been prepared by combining metal cations capable of octahedral or square-planar coordination, for example, Fe^{2+}, Co^{2+}, Ni^{2+}, Pd^{2+}, and Pt^{2+}, with bidentate ligands such as cyanide, nitrogen-based heterocycles, ditopic N-heterocyclic carbenes, isonitriles, and phosphanes.[4] The further diversification of square-type architectures requires novel synthetic strategies. Herein, we describe for the first time the rational synthesis of a molecular square by using phospha-organometallic building blocks.[5]

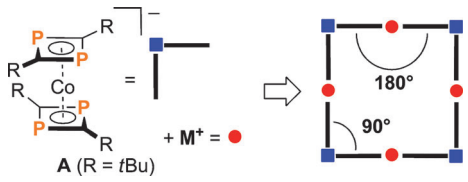
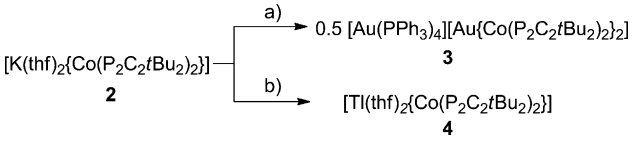


Figure 1. Design principle for the construction of new phospha-organometallic molecular squares.

As illustrated in Figure 1, our synthetic approach utilizes the recently reported anionic complex **A**, which shows a D_{2d} symmetrical sandwich structure.[6] Anion **A** is readily accessible by the metal-mediated dimerization of *tert*-butyl phosphaalkyne with a low-valent anthracene cobaltate complex.[7] The molecular structure of **A** features two coplanar 1,3-diphosphacyclobutadiene rings in a staggered orientation, that is, the two P_2C_2 rings are rotated by 90° with respect to one another. We hypothesized that this structural detail might allow the construction of a completely new type of molecular square by coordination of suitable metal cations that require a linear coordination geometry. Considering the established ability of 1,3-diphosphacyclobutadiene complexes to coordinate univalent coinage metal ions,[8] we decided to focus on gold(I) complexes. Herein, we report the synthesis and structural characterization of the new octanuclear Au_4Co_4 compound $[Au\{Co(P_2C_2tBu_2)_2\}]_4$ (**1**), which is formed by the self-assembly of four Au^+ cations and four $[Co(P_2C_2tBu_2)_2]^-$ anions.

Initial attempts to access **1** by straightforward salt metathesis of the potassium salt $[K(thf)_2\{Co(P_2C_2tBu_2)_2\}]$ (**2**) with gold(I) halides were unsuccessful. Instead, the reaction of **2** with $[AuCl(PPh_3)]$ (Scheme 1a) afforded the ionic ate compound $[Au(PPh_3)_4][Au\{Co\text{-}P_2C_2tBu_2)_2\}_2]$ (**3**) as deep red crystals in 32% yield. A single-crystal X-ray structure determination revealed an ionic structure (Figure 2a) that consists of the linear $[Au\{Co(P_2C_2tBu_2)_2\}_2]^-$ anion (Au1-P1,P5 2.2786(10) and 2.2786(11) Å) and the $[Au(PPh_3)_4]^+$ cation.[9]



Scheme 1. Synthesis of complexes **3** and **4**. Reagents: a) + [AuCl(PPh$_3$)]/−KCl and by-products, b) + $TlPF_6$/−KPF_6.

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[**] Funding from the DFG (WO1496/4-1 and EC168/10-2) is gratefully acknowledged. We also thank Prof. Stefan Grimme (University of Bonn) for supporting the DFT calculations.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201309493.

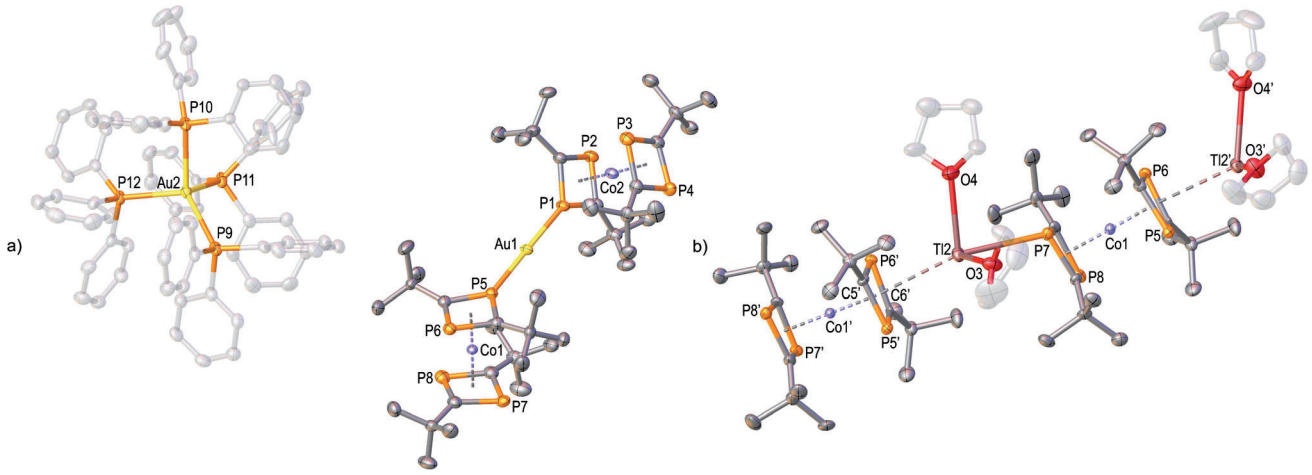


Figure 2. Solid-state molecular structures of $[Au(PPh_3)_4][Au\{Co(P_2C_2tBu_2)_2\}_2]$ (**3**, left) and $[Tl(thf)_2\{Co(P_2C_2tBu_2)_2\}]$ (**4**, right). Thermal ellipsoids are set at 40% probability. Hydrogen atoms, the site disorder of Au2 in **3**, and the disorder of one THF molecule of **4** are omitted for clarity. Selected bond lengths [Å] and angles [°] of **3**: Au1–P1 2.2786(10), Au1–P5 2.2786(11), P1-Au1-P5 177.93(4), Au2–P9 2.4035(11), Au2–P10 2.3821(11), Au2–P11 2.3592(11), Au2–P12 3.366(13); P9-Au2-P10 100.01(4), P9-Au2-P11 101.81(5), P10-Au2-P11 99.69(5), P9-Au2-P12 118.05(5), P10-Au2-P12 118.71(5), P11-Au2-P12 115.44(5); Selected bond lengths [Å] of **4**: Tl2–P7 3.1606(15), Tl2–P6′ 3.4268(15), Tl2–P5′ 3.1810(15), Tl2–O3 2.770(6), Tl2–O4 2.703(6), Tl2–C5′ 3.296(6), Tl2–C6′ 3.327(6), symmetry operation to generate the equivalent atoms of **4**: ′ $+x$, $0.5-y$, $0.5+z$.

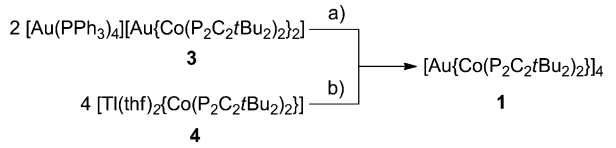
The cation shows a distorted trigonal pyramidal structure similar to that reported for $[Au(PPh_3)_4]BPh_4$.[10]

The ^{1}H NMR and $^{31}P\{^1H\}$ NMR spectra of **3** are temperature-dependent as a result of the labile coordination of the gold(I) cations.[11] Two very broad $^{31}P\{^1H\}$ NMR signals at $\delta = +10.4$ ppm ($\nu_{FWHM} = 1000$ Hz) and $\delta = +26.1$ ppm ($\nu_{FWHM} = 1000$ Hz) were observed in the spectrum recorded in $[D_8]$THF at room temperature. The $^{31}P\{^1H\}$ NMR spectrum recorded at −80 °C displays three signals for the $[Au\{Co(P_2C_2tBu_2)_2\}_2]^-$ anion at $\delta = -27.0$, $+14.3$, and $+37.4$ ppm and an extremely broad peak $\delta = +41.1$ ppm ($\nu_{FWHM} = 1100$ Hz) assigned to the coordinated PPh_3 ligand. The large line width of the signal for the coordinated PPh_3 ligand shows that the solution equilibria are not fully resolved even at low temperature. Careful integration of the ^{1}H NMR spectra of the aromatic and the *tert*-butyl signals revealed a ratio Ph:*t*Bu of 52:72, whereas a ratio of 60:72 would be expected for pure **3**. This observation is presumably explained by the presence of approximately 20% of tris(triphenylphosphane) complex $[Au(PPh_3)_3][Au\{Co(P_2C_2tBu_2)_2\}_2]$ as a minor component in the isolated bulk solid.[12]

To facilitate the transmetalation reaction, we subsequently synthesized the new thallium(I) complex $[Tl(thf)_2\{Co(P_2C_2tBu_2)_2\}]$ (**4**) in 81% yield by treating **2** with one equivalent of $TlPF_6$ (Scheme 1b). Dark-brown **4** is the first structurally characterized p-block metal complex of a sandwich anion of type **A**. Single-crystal X-ray diffraction revealed a polymeric arrangement (Figure 2) with two similar, crystallographically independent $[Tl(thf)_2\{Co(P_2C_2tBu_2)_2\}]$ moieties in the asymmetric unit.[9] The Tl^+ ions are coordinated by two THF molecules and three phosphorus atoms from two different $[Co(P_2C_2tBu_2)_2]^-$ anions with comparatively long Tl–P distances in the range 3.1606(15)–3.4268(15) Å.[13,14]

Complex **4** gives rise to one ^{1}H NMR signal (C_7D_8/$[D_8]$THF) for the *t*Bu groups at $\delta = +1.18$ ppm and one $^{31}P\{^1H\}$ NMR singlet at $\delta = +30.0$ ppm. The $^{31}P\{^1H\}$ resonance is shifted to higher frequency by approximately 25 ppm compared to the starting compound **2** ($\delta = +5.1$ ppm in $[D_8]$THF). No decoalescence was observed for these signals on cooling the sample to −80 °C. The observation of symmetrical NMR spectra is presumably either caused by the formation of an ionic structure $[Tl(thf)_x]^+[Co(P_2C_2tBu_2)_2]^-$ in solution or by the rapid exchange of the coordinated Tl^+ cation between different P_2C_2 rings by intra- or intermolecular pathways with low kinetic barriers.

Having the new complexes **3** and **4** in hand, we were gratified to discover that both compounds can be successfully employed for the preparation of our targeted Au_4Co_4 square $[Au\{Co(P_2C_2tBu_2)_2\}]_4$ (**1**): Complex **1** is formed in 46% yield by heating **3** with four equivalents of $[AuCl(PPh_3)]$ in THF at 70 °C for 2 h (Scheme 2a).[15,16] Furthermore, **1** can be synthesized in 20% yield by slow addition of **4** to a dilute THF suspension of [AuCl(tht)] (tht = tetrahydrothiophene, Scheme 2b).



Scheme 2. Synthesis of molecular square **1**. Reagents: a) $+8$ [AuCl(PPh$_3$)]/-8 [AuCl(PPh$_3$)$_2$], b) $+4$ [AuCl(tht)]/-4 TlCl, -4 THT.

Compound **1** crystallizes as deep red blocks from *n*-hexane in the space group *I*4/*mmm* with two formula units per unit cell.[9] The solid-state molecular structure (Figure 3) shows four $[Co(P_2C_2tBu_2)_2]^-$ units connected by four Au^+ cations with a linear coordination environment (Au1–P1 2.276(3) Å, P1-Au1-P1a 179.6(2)°). This connectivity pattern results in the formation of a strictly D_{4d} symmetrical square

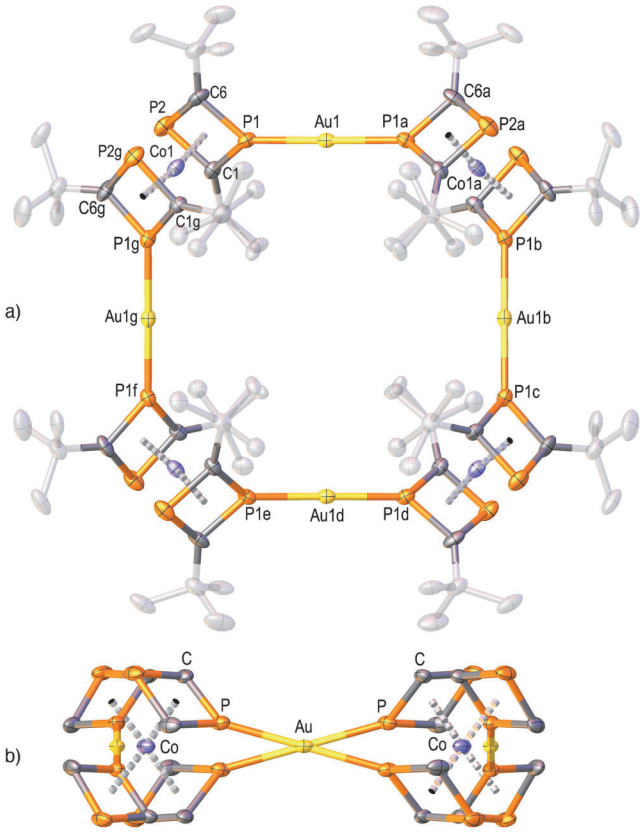


Figure 3. Solid-state molecular structure of $[Au\{Co(P_2C_2tBu_2)_2\}]_4$ (**1**); a) view along the crystallographic *b* axis; b) view along the crystallographic *c* axis. The thermal ellipsoids are set at the 20% level, H atoms and the disorder of the $[Co(P_2C_2tBu_2)_2]^-$ ions are omitted, the *t*Bu groups have been made transparent for clarity. Selected bond lengths [Å] and angles [°]: Au1–P1 2.276(3), Co1–P1 2.193(3), Co1–P2 2.266(3), Co1–C1 2.108(11), P1–C1 1.756(12), P2–C1 1.806(12); P1–Au1–P1a 179.6(2), angle between vectors P1,Au1,P1a/P1d,Au1d,P1e 31.2°; symmetry operations to generate equivalent atoms: a) *x*, 1−*y*, *z*; b) *y*, 1−*x*, −*z*; c) 1−*y*, 1−*x*, *z*; d) 1−*x*, 1−*y*, −*z*; e) 1−*x*, *y*, *z*; f) 1−*y*, *x*, −*z*; g) *y*, *x*, *z*.

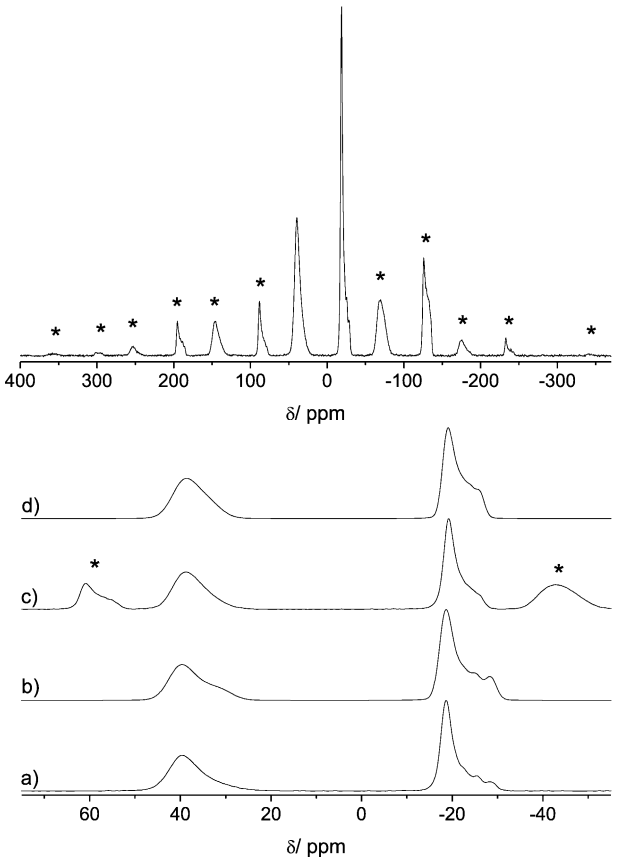


Figure 4. Top: $^{31}P\{^1H\}$ CPMAS-NMR spectrum of **1** acquired at 7.05 T with a spinning frequency of 13.0 kHz. Bottom: central band region of the $^{31}P\{^1H\}$ CPMAS-NMR spectrum of **1** acquired at 7.05 T (a), with the corresponding line-shape simulation (b), the spectrum measured at 9.4 T (c), with the corresponding line-shape simulation (d). * marks spinning sidebands.

with edge dimensions of nearly 10 Å (Au1–Au1d 9.8248(10) Å, Co1–Co1d 11.748(4) Å). The gold and cobalt atoms are each located on a crystallographic mirror plane, while the phosphorus, carbon, and hydrogen atoms reside above or below that plane, which results in a puckered structure. The puckering of the $[Au\{Co(P_2C_2tBu_2)_2\}]_4$ molecule is evident from the twisted P-Au-P vectors, which form an angle P1,Au1,P1a/P1d,Au1d,P1e of 31.2° (Figure 3b). The structure contains a cavity, which is free of any solvent molecules, in the center of the molecule with an approximate diameter of 1.5 to 6.6 Å.[17]

The solid-state and solution NMR spectra of **1** fully agree with its highly symmetrical molecular structure. The $^{31}P\{^1H\}$ CPMAS-NMR spectrum of **1**, shown in Figure 4, displays two resonance signals at $\delta = -21.4$ and $\delta = +37.5$ ppm with sizeable magnetic shielding anisotropies $\Delta\sigma = -297 \pm 30$ ppm for each resonance and asymmetry parameters, η_σ, of 0.3 and 0.7, respectively. The solution $^{31}P\{^1H\}$ NMR spectrum of **1** recorded in $[D_8]$THF (Supporting Information Figure S2) corresponds very well to the spectrum of the solid, showing two singlets at $\delta = -19.5$ ppm and $\delta = +38.9$ ppm. The solid-state NMR spectrum displays significant broadening of the resonances. The dependence of the linewidth (in Hz) on the magnetic field strength indicates the influence of heteronuclear spin–spin couplings to the quadrupolar nucleus ^{59}Co ($I = 7/2$) on the MAS-NMR line shape. This effect produces an asymmetric splitting within the *J*-multiplet pattern and is described by the "residual dipolar coupling parameter", *d*.[18–20] It is reasonable to assume that the structured multiplet at low frequency arises from ^{31}P–^{59}Co spin–spin couplings ($^1J(^{31}P–^{59}Co) = 175$ Hz, $d(^{31}P–^{59}Co) = 250$ Hz at 7.05 T) while the high-frequency resonance is additionally affected by the interaction with the ^{197}Au ($I = 3/2$) nuclei, leading to a loss in hyperfine structure resolution.[21,22] The $^{13}C\{^1H\}$ CPMAS-NMR spectrum reveals one single resonance for the C_2P_2 species (C1 and C6) at $\delta = 103.8$ ppm which is also influenced by ^{31}P–^{59}Co spin–spin couplings.[15]

In summary, an unprecedented Au_4Co_4 square $[Au\{Co(P_2C_2tBu)_2\}]_4$ (**1**) is formed through the self-assembly of gold(I) cations and anions sandwiched by 1,3-diphosphacyclobutadiene moieties. The synthesis of **1** illustrates a new strategy for the preparation of organometallic molecular squares, and possibly other types of supramolecular aggre-

gates, which capitalizes on the coordination ability of phosphorus-containing building blocks.[5,8] The synthesis of analogous molecular squares with copper(I) and silver(I) cations is currently under investigation. A further extension of this work to metals beyond Group 11 should provide diverse new metallostructures with interesting structural, electronic, and magnetic properties.

Received: October 31, 2013
Published online: February 4, 2014

Keywords: cobalt · gold · metallomacrocycles · sandwich complexes · self-assembly

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[9] CCDC 969295 (**1**), 969296 (**3**), and 969297 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. For details of the X-ray crystal structure determinations see the supporting information.

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[16] The colorless bis(phosphane)complex $[AuCl(PPh_3)_2]$ was identified as the by-product by its $^{31}P\{^{1}H\}$ NMR singlet at $\delta = +29.7$ ppm in $[D_8]$THF and by a unit cell determination. This complex is conveniently separated during work-up through to its lack of solubility in *n*-hexane: a) G. H. Woehrle, L. O. Brown, J. E. Hutchinson, *J. Am. Chem. Soc.* **2005**, *127*, 2172; b) T. J. Harrison, J. A. Kozak, M. Corbella-Pane, G. R. Dake, *J. Org. Chem.* **2006**, *71*, 4525.

[17] See Figure S15 of the supporting information for a van der Waals plot. The dimensions of the cavity were estimated by subtracting the corresponding van der Waals radii from the interatomic distances across the cavity. A minimum diameter of 1.5 Å is obtained by subtracting twice the van der Waals radius of a CH_3 group (2×2.0 Å) from the C–C distance (5.48(2) Å) of two CH_3 groups which are located diagonally across the cavity. The maximum value of 6.6 Å is obtained by subtracting twice the van

der Waals radius of a gold(I) atom (2.1 Å) from the Au–Au distance of 9.82 Å. Van der Waals radii were obtained from: a) L. Pauling, *The Nature of the Chemical Bond*, 3rd ed., Cornell University Press, Ithaca, NY, **1960**; b) S. S. Batsanov, *Inorg. Mater.* **2001**, *37*, 871.

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[22] The unambiguous assignment of the high-frequency signal to the gold-coordinated species P1 and the resonance at low frequencies to P2 is confirmed by relativistic zeroth order regular approximation (ZORA) DFT calculations (Table S1),[23] which are also in line with previous assignments made for related complexes.[8c,d]

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