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Structural Features of $[(CpPPh_2AuCl)_2ZrCl_2]$: Exploring the Limits of Aurophilic Interactions

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Abstract: The reaction of $[(CpPPh_2)_2ZrCl_2]$ (**1a**) with two molar equivalents of $(Me_2S)AuCl$ gave the trimetallic complex $[(CpPPh_2AuCl)_2ZrCl_2]$ (**6**). Crystalline complex **6** shows a conformational structure that features both P–Au–Cl vectors oriented toward the open front side of the bent metallocene wedge. Quantum-chemical calculations rationalized the absence of an aurophilic Au···Au interaction in **6** by showing that a combination of noncovalent forces overcompensates any possible attractive Au···Au interaction.

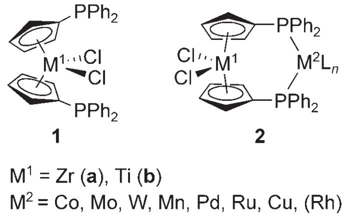
Keywords: conformation analysis · gold · metallocenes · metal–metal interactions · zirconium

Introduction

The importance of noncovalent interactions as structural construction motifs is increasingly demonstrated by intra- as well as intermolecular examples.[1] Attractive closed-shell interactions between d^{10}–d^{10} metal pairs have received increasing attention, especially those between pairs or arrays of gold atoms.[2] Examples of aurophilic interaction have become very common in situations in which these heavy-metal atoms come close to each other so that the formation of the attractive Au···Au interaction seems to be the rule rather than the exception.[3–5] However, some caution is advised as the magnitude of the inter- or intramolecular Au···Au interaction is usually in a similar energy range to, for example, H bonding.[6] Bonding features in this energy range are known to be adversely affected by a variety of competing effects. Because of the relatively low bonding energies involved with single Au···Au pairs, the positive interaction between two gold atoms can be readily overcome by other structurally determining factors, such as steric hindrance, dipole interactions, charge effects, or electrostatics.[7] We present herein a case whereby, in a competitive situation, such effects overrule a possible pathway that is a priori favorable for the formation of structurally determining intramolecular Au···Au interactions.

Results and Discussion

We selected $[(CpPPh_2)_2ZrCl_2]$ (**1a**; Cp = cyclopentadienyl)[8] as the starting material for our study. Complex **1a** and/or its titanium analogue **1b** was previously used for the synthesis of $CpPPh_2$-bridged early/middle- and early/late-transition-metal complexes (Scheme 1). Systems containing the metal combinations Zr (or Ti) with Cr, Mo, W, Mn, Pd, Pt, Ru, or Cu were synthesized.[9–11] We recently prepared and described closely related $Zr(\mu\text{-}CpPR_2)_2Rh$ complexes that were very active hydroformylation catalysts.[12,13] To the best of our knowledge, related $Zr(\mu\text{-}CpPPh_2)Au$ complexes have not been described previously.



Scheme 1. Examples of complexes **1** and **2**.

Group 4 metallocenes exhibit a pair of rapidly rotating η^5-cyclopentadienyl ligands bonded at a characteristic angle at the central metal atom.[14,15] This arrangement is very well-suited to bringing pairs of substituents attached at the Cp rings into close proximity to each other. We recently used this effect successfully to carry out reactions under “dynamic topochemical control”.[16–18] As a characteristic example, the bringing of alkenyl groups into close proximity to each

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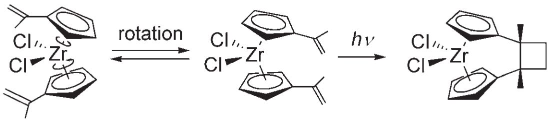
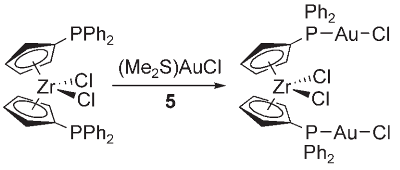
other by means of the dynamic rotation of the typically bent metallocene arrangement was used to achieve a novel synthetic method for the formation of *ansa*-metallocenes by intramolecular photochemical [2+2] cycloaddition at the functionalized bent metallocene framework (Scheme 2).[17]



3 **4**

Scheme 2. *ansa*-Metallocene formation by a dynamic topochemical reaction.

It might be envisaged with this favorable general situation to attempt the utilization of such dynamic features to induce aurophilic Au···Au interactions between pairs of gold centers attached at the periphery of the bent metallocene framework while keeping in mind potential adverse repulsive effects.



1a **6**

Scheme 3. Reaction of complex **1a** with $(Me_2S)AuCl$ (**5**) to give complex **6**.

For this purpose, we treated $[(CpPPh_2)_2ZrCl_2]$ (**1a**) with $(Me_2S)AuCl$ (**5**) (Scheme 3). The addition reaction was carried out in dichloromethane at room temperature. It furnished the bis(AuCl) adduct **6** in 76% yield after workup with pentane. In CD_2Cl_2, complex **6** features two broad ^{1}H NMR signals of the Cp protons at 6.75 and 6.76 ppm and a multiplet system of the phenyl resonances at 7.7–7.4 ppm. More characteristic is the ^{13}C NMR spectrum, which features well-resolved Cp resonances at 124.0 ($^2J_{P,C}=10.5$ Hz, C2), 119.1 ($^3J_{P,C}=8.3$ Hz, C3), and 116.8 ppm ($^1J_{P,C}=63.8$ Hz, *ipso*-C of Cp). The ^{13}C NMR signals of the phenyl groups at the phosphorus atom are equally well-resolved, with signals at 134.5 ($^2J_{P,C}=14.5$ Hz), 132.7 ($^4J_{P,C}=2.6$ Hz), 129.6 ($^3J_{P,C}=12.2$ Hz), and 129.3 ppm ($^1J_{P,C}=64.2$ Hz) for the *o*-, *p*-, *m*-, and *ipso*-C(phenyl) atoms. The increase in the absolute values of $^1J_{ipso\text{-Ph}}$ from 12 Hz for **1a** to 64.2 Hz for **6** and of $^1J_{ipso\text{-Cp}}$ from 17 Hz for **1a** to 63.8 Hz for **6** is a clear indication of the P–Au coordination, as the ^{31}P NMR resonance at 21.8 ppm (compare with starting material **1a**: −17.3 ppm[12b]) also suggests.

Abstract in German: Die Umsetzung von $[(CpPPh_2)_2\,ZrCl_2]$ (**1a**) mit zwei Moläquivalenten $(Me_2S)AuCl$ lieferte den trimetallischen Komplex $[(CpPPh_2AuCl)_2ZrCl_2]$ (**6**). Die Verbindung **6** nimmt im Kristall eine Metallocen-Konformation ein, bei der beide P–Au–Cl Vektoren an der offenen Vorderseite des gewinkelten Metallocens angeordnet sind. Die Abwesenheit einer aurophilen Au···Au Wechselwirkung in **6** wurde nach quantenchemischen Rechnungen als Resultat einer Kombination nicht-kovalenter Kräfte erklärt, die hier eine mögliche attraktive Gold–Gold Interaktion überkompensieren.

Colorless single crystals of complex **6** were obtained by slow diffusion of diethyl ether into a solution of **6** in chloroform at room temperature. The bent metallocene core features a typical pseudotetrahedral arrangement of a pair of chloride ligands and a pair of mono-substituted Cp ligands around the central zirconium atom. The Cp rings are quite uniformly η^5-coordinated to zirconium, with C(Cp)−Zr bond lengths ranging from 2.497(6) (Zr−C14) to 2.557(6) Å (Zr−C25). The Zr−Cl bond lengths were found to be 2.403(2) (Zr−Cl12) and 2.415(2) Å (Zr−Cl11). The Cl11−Zr−Cl12 angle is 100.58(6)°. Each of the Cp ligands bears a phosphorus-based substituent bonded to it (C11−P1: 1.803(6); C21−P2: 1.811(6) Å). Each of the phosphorus atoms carries a pair of phenyl groups (P1−C31: 1.822(6); P1−C41: 1.809(6); P2−C51: 1.820(5); P2−C61: 1.804(5) Å). Furthermore, an Au–Cl unit is coordinated to each of the phosphorus atoms. This makes the coordination geometry at the P atoms pseudotetrahedral (typical bond angles at P1: 108.8(3) (C11−P1−C41), 104.3(3) (C11−P1−C31), 104.7(3) (C41−P1−C31), 111.6(2) (C11−P1−Au1), 113.7(2) (C41−P1−Au1), and 113.1(2)° (C31−P1−Au1); at P2: 109.5(3) (C61−P2−C21), 105.4(3) (C61−P2−C51), 103.2(3) (C21−P2−C51), 113.8(2) (C61−P2−Au2), 112.7(2) (C21−P2−Au2), and 111.5(2)° (C51−P2−Au2); Figure 1). We noticed a systematic deviation of the C−P−C and C−P−Au angles toward smaller and larger values, respectively, relative to the 109° tetrahedral angle (see above).

The P−Au bond lengths (P1−Au1 2.231(2), P2−Au2 2.233(2) Å) and angles (P1−Au1−Cl1 179.19(6), P2−Au2−Cl2 175.98(6)°) are in the typical range (compare Ph_3P−Au−Cl:[19] P−Au 2.235(3), Au−Cl 2.279(3) Å, P−Au−Cl

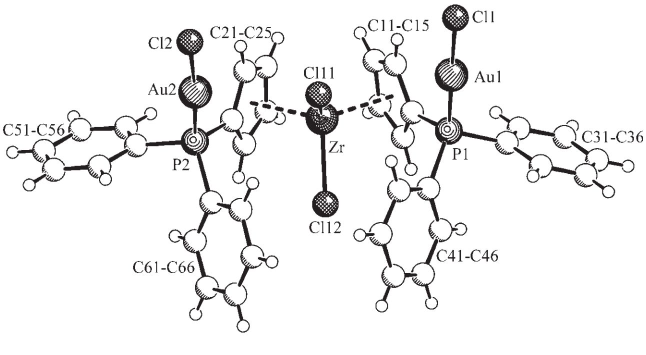


Figure 1. Projection of the molecular geometry of complex **6** in the crystal.

179.68(8)°). The corresponding Au–Cl bond lengths in complex **6** amount to 2.282(2) (Au1–Cl1) and 2.285(2) Å, respectively.

Most remarkable is the conformation of the bent metallocene unit in complex **6**. It adopts a rotameric orientation in which both the C(Cp)–P vectors are oriented toward the open front sector of the bent metallocene wedge (Figure 1). The attached Au–Cl units are both oriented close to parallel with the Cp-ring planes (C12–C11–P1–Au1 11.4(5), C22–C21–P2–Au2 −21.4(5)°). Both Au–Cl units are oriented to the same side. This means that the pair of gold atoms are almost ideally positioned above and below the chloride ligand Cl1. In this arrangement, the Au1–Au2 distance (7.211 Å) is far beyond any range for aurophilic interaction. The Au1–Cl11 separation is 3.869 Å, that of Au2–Cl11 is 3.572 Å, and the Au1···Cl11···Au2 angle amounts to 151.4°.

Complex **6** could in principle have energetically favorable rotational isomers that would have brought the pair of gold atoms into reasonably close proximity to each other to allow the buildup of a bonding aurophilic interaction. Instead, a specific rotamer that placed the gold atoms at an almost-maximum distance from each other was observed. Furthermore, a separating chloride ligand is present in this isomer, and a high dipole moment results from this specific conformational arrangement. Our attempts to achieve some rationale for this unexpected and at first sight obscure rotational behavior were aided by a DFT analysis of complex **6**.

Computational Study

Initially, we performed a full structural optimization of the mixed Zr–Au complex **6** at the dispersion-corrected DFT/PBE-D level (for details, see Experimental Section) with the experimental X-ray structure as the starting point. The optimization converged rather quickly to the same conformation. The final bond lengths, bond angles, and characteristic dihedral angles are in excellent agreement with the experimental data, thus confirming the reliability of our theoretical approach. For example, the C–Zr distances were found experimentally to be in the range 2.50–2.54 Å, which is comparable to the computed values of 2.53–2.57 Å. The bond lengths that involve the gold atoms were also described rather accurately (theory: P–Au 2.24, Au–Cl 2.28 Å; exp.: 2.23, 2.28 Å, respectively). Although the gold atoms are located on the same side of the molecule, their spatial separation is rather large (theory: 7.30 Å; exp.: 7.21 Å), thus indicating no apparent bonding interaction. Notably, conformer A (Figure 2), in which the almost-linear P–Au–Cl units are oriented in a parallel manner, has a huge computed dipole moment of 17.7 D. It is not surprising to find this structure in the solid state because long-range electrostatic interactions between the very polar molecules yield large stabilizing contributions to the lattice energy. We also considered PH_3–Au–Cl as a model system and computed its dipole moment. The dipole moment of 6.9 D obtained at the PBE-D level is almost half that of **6**, which indicates that the orientation of the P–Au–Cl groups (and the cumulation of their effect) is mainly responsible for the large dipole moment.

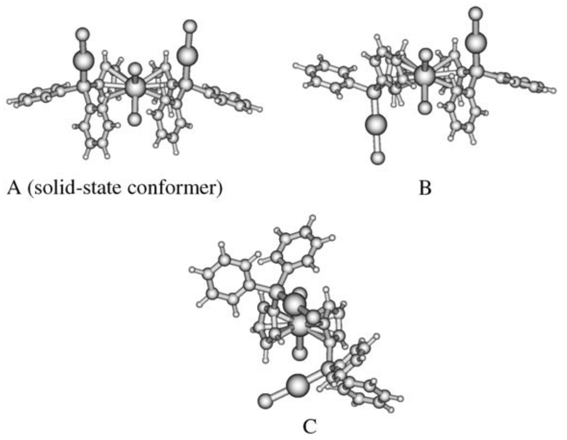

A (solid-state conformer) B C

Figure 2. PBE-D/def2-TZVP′-optimized structures of the conformers of **6** considered herein.

As a next step, we conducted a systematic search for energetically low-lying conformations based on the X-ray structure by rotating the Zr–Cp vectors and P–C(Cp) bonds. Particular emphasis was paid to find structures with short Au···Au contacts, which should be theoretically possible owing to the rotational flexibility of the various functional groups in the molecule. Figure 2 displays two other stable energy-minimum structures (B and C) that were found in full geometry optimizations.

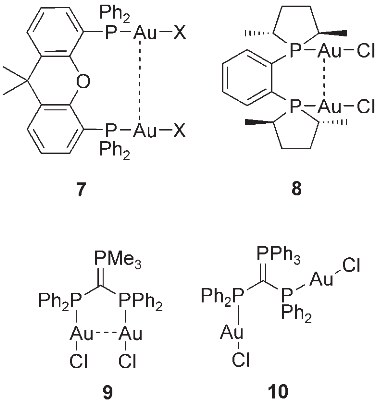
Conformers B and C were computed to be lower in energy than A by 3.2 and 6.2 kcal mol^{-1}, respectively. This is attributed to the more favorable antiparallel orientations of the two P–Au–Cl units, which lead to relatively small overall molecular dipole moments of 6.5 and 8.0 D, respectively. Notably, this does not contradict the experimental findings as our calculations refer to an isolated molecule in the gas phase in which the intermolecular dipole–dipole interactions that lead to conformer A in the solid state are not present. Despite significant effort, we were not able to locate other stable structures with short Au···Au distances. The value of 5.92 Å found for conformer C is (although shorter than for A and B) still far from that expected for typical "aurophilic" interactions (≈3 Å[2,20]).

To check the DFT-GGA results for the conformational energies, we applied the SCS-MP2[21] wavefunction-based method (with the same basis set), which yields much better (but not completely satisfying) results than MP2 for such transition-metal systems.[22] At this level, we obtained relative energies for B and C of 13.8 and −8.8 kcal mol^{-1}, respectively, as opposed to the PBE-D values of −3.2 and −6.2 kcal mol^{-1}, respectively. Thus, also at the SCS-MP2 level, conformer C appears as the global-energy-minimum structure. However, SCS-MP2 still suffers from an inappropriate description of transition-metal complexes by the Hartree–Fock reference (which is the basis for the perturbation theory); thus, we investigated the relative energies further. At the very reliable B2-PLYP theoretical level[23] (hybrid

GGA with orbital-dependent, nonlocal correlation terms), we obtained values of -2.1 and $-7.9\ \mathrm{kcal\,mol^{-1}}$, respectively, which are in very good agreement with the PBE-D data.

Conclusions

It is commonly assumed that it is sufficient to allow two $\mathrm{Au^{I}}$–X centers to come together to within 3.5 Å to induce the formation of a bonding aurophilic Au···Au interaction. Many examples, such as complexes **7**–**9** (Scheme 4), may serve to support this notion.[2,7,24,25] In this regard, one would have expected complex **6** to be an ideal candidate to rotate its Cp–$\mathrm{PPh_2}$–Au–Cl units to the narrow backside of the bent metallocene wedge and form an Au···Au bonded trimetallic *ansa*-metallocene. However, this system behaves quite to the contrary: its $\mathrm{PPh_2}$–Au–Cl units were found to be rotated straight toward the open front side of the bent metallocene, a conformation that leads to an almost-maximal separation of the gold atoms. Futhermore, this rotameric isomer has one of the highest molecular dipole moments that such a system can have. A close inspection of the crystal lattice (Figure 3), however, revealed a perfect compensation of the dipole moments in the solid state, a situation that has turned a seemingly unfavorable molecular feature into an energetically most favorable characteristic of the bulk material of **6**.



Scheme 4. Structural formulae of complexes **7**–**10**.

In this situation, it is not unexpected that different rotational isomers of complex **6** were found as structures with local minima or even as that with the global energy minimum in the gas phase calculated by the applied DFT method. In a structural evaluation and energetic characterization, the compensating dipolar forces that apparently govern the overall structural features of **6** in the crystal are, of course, absent in the individual, arbitrarily isolated molecules of **6** and, thus, do not show up in the calculation. Nevertheless, the DFT calculation did not identify any rotational isomer of **6** with a reasonably favorable energy content to show any aurophilic Au···Au interaction. Following earlier related observations by Schmidbaur et al.[7] on the structurally different but conceptually remotely related pair of dimetallic chelate phosphane$\mathrm{(AuCl)_2}$ complexes **9** and **10** (Scheme 4), one must keep in mind that aurophilic interactions represent rather weak noncovalent binding forces that can easily be disturbed or overcompensated by cumulative adverse effects, in particular, Pauli repulsion within sterically encumbered systems or unfavorable electrostatic effects. Our trimetallic complex **6** seems to fall into this category (as does **10**), which reminds us that consideration of aurophilic interaction as structural building units should be used with care in the synthetic planning of complex dynamic organic or organometallic systems.

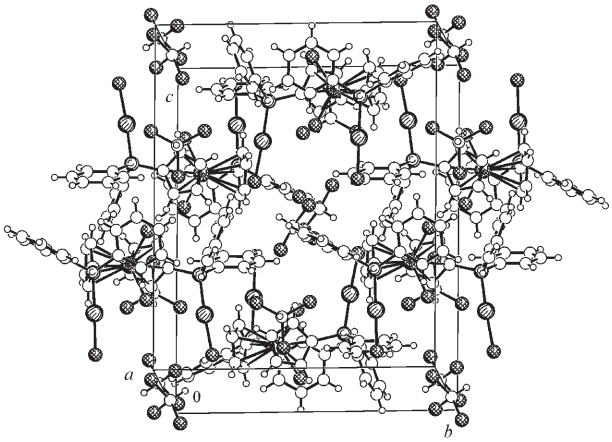


Figure 3. View of the packing of the polar monomers of **6** in the crystal.

Experimental Section

General Procedure

All air- and moisture-sensitive compounds were manipulated by using standard Schlenk and vacuum-line techniques under argon atmosphere or inside a glovebox. Argon was dried over $\mathrm{P_4O_{10}}$ prior to use. $\mathrm{CD_2Cl_2}$ was dried over $\mathrm{CaH_2}$ and distilled prior to use. Toluene was distilled from sodium benzophenone ketyl and stored under argon atmosphere. ^{1}H, ^{11}B, ^{13}C, ^{19}F, and ^{31}P NMR spectra were recorded on a Bruker AV 300-MHz, Varian Inova 500-MHz, or Varian Inova 600-MHz unity plus spectrometer with residual $\mathrm{CDHCl_2}$ (5.32 ppm) as internal standard. In some cases, assignment of the signals was also confirmed by ^{13}C DEPT, ^{1}H–^{1}H COSY, ^{1}H-^{13}C gHSQC, and ^{1}H-^{13}C gHMBC. IR spectra were recorded on a Varian 3100 FTIR spectrometer. Elemental analysis was performed by a Foss-Heraeus CHN-Rapid elemental analyzer. $\mathrm{(Me_2S)AuCl}$ (Aldrich) was used as received without further purification. X-ray crystal-structure analysis: Data were collected with a Nonius Kappa CCD diffractometer equipped with a rotating anode generator. Programs used: data collection COLLECT (Nonius B.V., 1998), data reduction Denzo-SMN,[26] absorption correction SORTAV,[27] structure solution SHELXS-97,[28] structure refinement SHELXL-97,[29] graphics SCHAKAL.[30]

Theoretical Methods and Technical Details of the Computations

Quantum-chemical calculations were performed with slightly modified versions of the TURBOMOLE suite of programs.[31] The large triple-zeta (denoted def2-TZVP′) sets of Ahlrichs and co-workers[32] were employed as Gaussian atomic-orbital basis sets. In standard notation, these are [5s3p2d] for C, [5s5p2d1f] for P and Cl, and [3s1p] for H. For the zirconium and gold atoms, the basis sets are of comparable quality (i.e., [6s4p3d1f]). For these atoms, scalar relativistic pseudopotentials[33] were used to describe the 28 and 60 core electrons, respectively. All geometries were fully optimized at the DFT level by using the PBE density functional,[34] which also includes an empirical correction for intramolecular dispersion (also called van der Waals) interactions[35] (dubbed PBE-D in the following). For a detailed description of this dispersion correction that is of great importance in studies of large molecules, which includes many illustrative examples, see reference [36]; for the most recent chemical application of this method, see reference [37]. In all DFT treatments, the RI approximation was used[38] for the Coulomb integrals, which speeds up the computations considerably without any significant loss of accuracy.

Synthesis

6: A reaction flask was charged with (Me$_2$S)AuCl (100 mg, 0.34 mmol) and CH$_2$Cl$_2$ (15 mL). After dropwise addition of a solution of [(CpPPh$_2$)$_2$ZrCl$_2$] (110 mg, 0.17 mmol) in CH$_2$Cl$_2$ (20 mL), the solution was stirred for 30 min at room temperature. The solution turned colorless immediately. The solvent was then reduced to 5 mL in vacuo. After the addition of pentane (30 mL), the resulting white precipitate was collected by filtration, washed with pentane (3×10 mL), and dried in vacuo. [(CpPPh$_2$AuCl)$_2$ZrCl$_2$] (**6**; 146 mg, 0.13 mmol, 76 %) was afforded as a white powder. Colorless single crystals were obtained by slow diffusion of diethyl ether into a solution of **6** in CHCl$_3$ at room temperature. IR (KBr): $\tilde{\nu}=482$, 521, 554, 632, 691, 735, 767, 829, 996, 1037, 1069, 1101, 1185, 1263, 1435, 1481, 2964, 3091 cm^{-1}; ^{1}H NMR (300 MHz, 298 K, CD$_2$Cl$_2$): $\delta=7.7$–7.4 (m, 20 H, Ph), 6.76 (br, 4 H, C$_5$$H_4PPh_2$), 6.75 ppm (br, 4 H, C$_5$$H_4PPh_2$); ^{13}C{^{1}H} NMR (75 MHz, 298 K, CD$_2$Cl$_2$): $\delta=134.5$ (d, $^2J_{\mathrm{C,P}}=14.5$ Hz, *o*-Ph), 132.7 (d, $^4J_{\mathrm{C,P}}=2.6$ Hz, *p*-Ph), 129.6 (d, $^3J_{\mathrm{C,P}}=12.2$ Hz, *m*-Ph), 129.3 (d, $^1J_{\mathrm{C,P}}=64.2$ Hz, *ipso*-Ph), 124.0 (d, $^2J_{\mathrm{P,C}}=10.5$ Hz, C2), 119.1 (d, $^3J_{\mathrm{P,C}}=8.3$ Hz, C3), 116.8 ppm (d, $^1J_{\mathrm{P,C}}=63.8$ Hz, C1); ^{31}P{^{1}H} NMR (121 MHz, 298 K, CD$_2$Cl$_2$) $\delta=21.8$ ppm; elemental analysis: calcd (%) for C$_{34}$H$_{28}$Au$_2$Cl$_4$P$_2$Zr: C 36.28, H 2.51; found: C 36.51, H 2.80.

X-ray Crystal-Structure Analysis

6: C$_{34}$H$_{28}$Au$_2$Cl$_4$P$_2$Zr·2CHCl$_3$, $M_r=1364.19$, colorless crystals, 0.30×0.30×0.15 mm^3, monoclinic, space group $P2_1/c$ (No. 14), $a=14.7207(2)$, $b=15.1426(2)$, $c=19.0498(1)$ Å, $\beta=93.573(1)°$, $V=4238.13(12)$ Å^3, $\rho_{\mathrm{calcd}}=2.138$ g cm^{-3}, $\mu=7.881$ mm^{-1}, empirical absorption correction ($0.201\leq T\leq 0.384$), $Z=4$, $\lambda=0.71073$ Å, $T=198$ K, ω and ϕ scans, 36799 reflections collected ($\pm h$, $\pm k$, $\pm l$), $((\sin\theta)/\lambda)=0.67$ Å^{-1}, 10460 independent ($R_{\mathrm{int}}=0.055$) and 7636 observed reflections ($I\geq 2\sigma(I)$), 460 refined parameters, $R=0.040$, $wR2=0.104$, maximum (minimum) residual electron density $=1.67$ (-1.34) e Å^{-3}, hydrogen atoms calculated and refined with a riding model. CCDC-658484 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk) or at www.ccdc.cam.ac.uk/conts/retrieving.html.

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