DOI: 10.1002/ejic.201000691

The First Cyanomethyl Complex of Gold, Synthesized by Reaction of a Au^I Complex with Acetonitrile in the Presence of a New Guanidine N-Superbase

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Keywords: Gold / C–H acidity / C–H activation / Guanidine / Superbase

Herein we report on the synthesis of the new strong N-base and electron donor tdmegb [1,2,4,5-tetrakis(*N*,*N*′-dimethylethyleneguanidino)benzene]. Compared to the previously synthesized ttmgb [1,2,4,5-tetrakis(tetramethylguanidino)-benzene], this compound turned out to be a slightly better electron donor and a slightly weaker base. In experiments in which [AuCl(PPH_3)] was dissolved in CH_3CN together with tdmegb, we observed the formation of the first cyanomethyl complex of Au, namely [Au(CH_2CN)(PPh_3)] in good yield. This reaction does not take place for ttmgb. Moreover, in CH_2Cl_2 solutions containing the three components [AuCl(PPh_3)], tdmegb and a nitrile (in large excess), only Au^I reduction leading to a [$Au_{11}Cl_3(PPh_3)_7$] cluster is observed. Possible reaction mechanisms for this unusual reaction are discussed.

Introduction

Deprotonation of an alkyl group is facilitated by resonance and/or inductive effects leading to the stabilization of the deprotonated species. Prominent examples of such C–H acidic molecules include cyclopentadiene (C_5H_6) and β-diketones (acetylacetone in its keto form). The C–H acidity of compounds of the general formula CH_3X was shown to decrease in the order X = NO_2 > CHO > CN > CCH > $CHCH_2$.[1] The cyanomethylene anion, $(CH_2CN)^-$, was already subject of a number of experimental and theoretical studies, evaluating in detail the inductive and resonance effects of the cyano moiety.[2] The C–H acidity of CH_3CN in H_2O was determined recently by isotopic experiments.[3] In these experiments, deprotonation of cyanomethyl by deuteriooxide ions (OD^-) in D_2O was followed by tracing the appearance of deuterium-labeled cyanomethyl in the NMR spectra, leading to a pK_a value of 28.9.

Two ways have been established allowing the deprotonation of acetonitrile and generation of $(CH_2CN)^-$ in quantities sufficient for synthetic chemistry in organic solutions. The first one includes reaction of *n*BuLi with CH_3CN leading to $LiCH_2CN$.[4] Metal complexes can then be synthesized by reaction with metal halide complexes such as [$NiCl_2(Ph_3P)_2$].[5] The cyanomethyl anion can also be generated in larger quantities by galvanostatic electrolysis of CH_3CN/Et_4NPF_6, and was in this form applied in organic synthesis,[6] e. g. for the synthesis of carbamates under mild and safe conditions.[7] Metal complexes featuring cyanomethyl ligands are also accessible via oxidative addition reactions. Hence oxidative addition of $ClCH_2CN$ to Pd^0 or Pt^0 complexes such as $Pt(PPh_3)_4$ was previously shown to give the cyanoalkyl Pd^{II} or Pt^{II} complexes [e. g. Pt(Cl)-(CH_2CN)($Ph_3P)_2$].[8] Stoichiometric oxidative addition of CH_3CN occurs when [$Ir(PPh_3)_4$]Cl is dissolved in neat CH_3CN at room temperature.[9,10] On the other hand, oxidative addition reactions of XCH_2CN species (e. g., X = hydrogen or halide) to Au^I complexes were up to date not observed. Moreover, no cyanomethyl complex of Cu, Ag or Au was previously structurally characterized, although (cyanomethyl)copper(I), $CuCH_2CN$, can be synthesized by decarboxylation of Cu^I or Cu^{II} cyanoacetates,[11] or in situ from a CuI/(MeCN + *n*BuLi) mixture.[12] Its insolubility in common organic solvents suggests a high degree of association. Catalytic reactions involving nitriles and Au^I catalysts were recently described, but lead to transformation of the cyano group into amides under mild conditions (a very important process, but not involving the methyl group).[13]

We recently developed a new class of strong electron donors and N-bases consisting of aromatic systems to which at least four guanidino groups are attached, and denoted such compounds GFAs (guanidino-functionalized aromatic donors).[14–17] Two representatives are ttmgb [1,2,4,5-tetrakis(tetramethylguanidino)benzene] and the superbase[18] ttmgn [1,4,5,8-tetrakis(tetramethylguanidino)naphthalene], see Scheme 1. In the last years, we studied a number of transition metal (Ni^{II}, Co^{II}, Cu^I, Ag^I and Zn^{II}) and main group element (especially Al^{III}) complexes of the guanidines ttmgb and ttmgn and related guanidine ligands.[19] The re-

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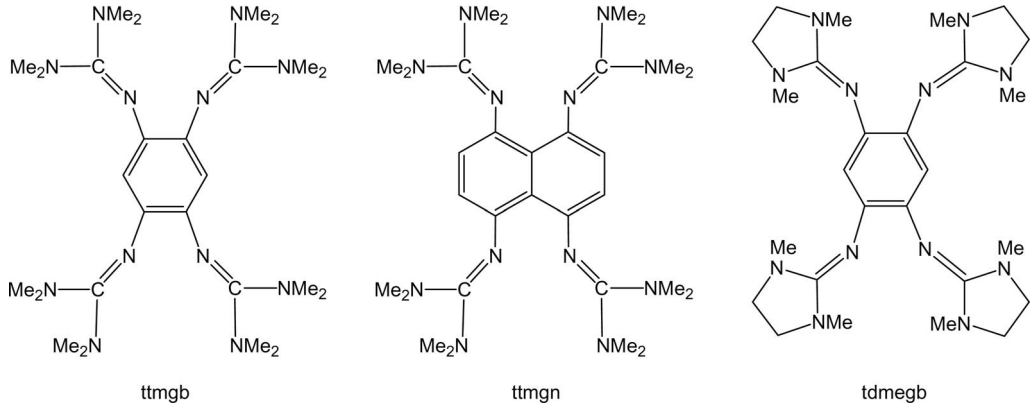


Scheme 1. Lewis structures of the N-superbase ttmgb as well as ttmgn and tdmegb.

sults show that the GFA compounds are nucleophilic, and in their properties different to for instance Schwesinger's P2 phosphazene bases.[20]

Results and Discussion

Synthesis and Characterization of 1,2,4,5-Tetrakis(*N*,*N*′-dimethylethyleneguanidino)benzene (tdmegb)

The new GFA compound tdmegb (see Scheme 1) can be obtained in good yield as the product of reaction between 1,2,4,5-tetraaminobenzene and activated 1,3-dimethyl-2-imidazolidinone. The molecular structure as derived from X-ray diffraction is visualized in Figure 1 (a). The C=N double bond lengths measure 128.66(16)/129.03(15) pm, and compare with values of 128.77(16)/129.10(16) pm for ttmgb.[14] All guanidines of Scheme 1 have in common a high N-basicity. The pK_a value of the superbase btmgn [1,8-bis(tetramethylguanidino)naphthalene] in CH_3CN was estimated to be 25.1 (experimentally derived estimate)[21] or 25.4 (calculated with the help of IPCM-B3LYP/6-311+G**//HF/6-31G* calculations and an empirical formula, IPCM = isodensity polarized continuum model), being thus higher than that of guanidine (24.1 in CH_3CN according to the calculations).[22,23] The calculated pK_a value in CH_3CN is lower for the related 1,8-bis(*N*,*N*′-dimethylethyleneguanidino)naphthalene. We expect pK_a values in a similar range for the three GFA molecules. We carried out quantum chemical (B3LYP/6-311+G**) calculations to estimate the pK_a values of ttmgb and tdmegb [employing the conductor-like polarisable continuum model (CPCM) to estimate the solvent effect]. With the empirical formula provided by Maksić et al.,[24] we arrived at pK_a values of 25.3 and 23.8 for ttmgb and tdmegb, respectively, in CH_3CN solutions. For the reference guanidines $HNC(NMe_2)_2$ and $MeNC(NMe_2)_2$, our calculated values (23.2 and 24.8, respectively, also in CH_3CN) are in pleasing agreement with the experimental values in CH_3CN (23.3 and 25.0, respectively [25]). We also measured titration curves for tdmegb (see Supporting Information). However, the individual protonation steps turned out to be difficult to separate. In addition to their high basicity, ttmgb and tdmegb are characterized by their electron donor capacity. In Figure 1 (b) the CV curves in CH_3CN recorded for ttmgb and tdmegb are compared. The two-electron wave observed at $E_{1/2}(CH_3CN)$ = –0.32 V vs. SCE for ttmgb [14] shifts to –0.36 V for tdmegb, indicating that the latter is (under the conditions of the experiment) a slightly superior electron donor. To further compare the electron donor capacities we carried out quantum chemical calculations on the *gas-phase* reaction between $(ttmgb)^{2+}$ and tdmegb to give ttmgb and $(tdmegb)^{2+}$. According to B3LYP/6-311G**, this reaction is associated with a negative ΔE value of –28 kJ mol^{-1}. The

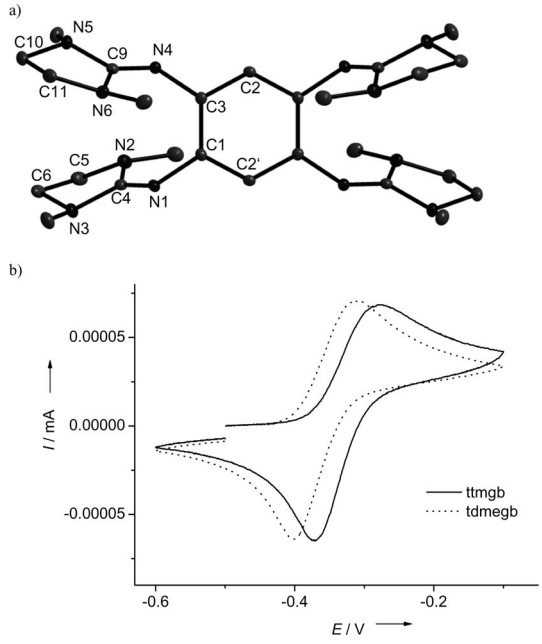


Figure 1. a) Molecular structure of tdmegb as derived from X-ray diffraction (hydrogen atoms omitted for sake of clarity). Ellipsoids are drawn at the 50% probability level. Selected structural parameters (distances in pm, angles in deg.): N1–C1 141.57(15), N1–C4 128.66(16), N2–C4 138.12(16), N3–C4 139.24(16), N4–C3 141.60(15), N4–C9 129.03(15), N5–C9 138.71(15), N6–C9 137.32(15), C1–C2′ 139.45(16), C1–C3 141.34(16), C2–C3 139.23(16), C1–N1–C4 123.76(10), C3–N4–C9 122.81(10), N2–C4–N3 107.95(10), N5–C9–N6 108.42(10); b) CV curves recorded for ttmgb and tdmegb (in CH_3CN, electrode: SCE, scan speed 100 mV s^{-1}).

$\Delta H^{\ominus}$ and $\Delta G^{\ominus}$ values (at 298 K, 1 bar) are –27 and –33 kJ mol^{-1}, respectively. In summary it can be concluded that tdmegb is a slightly weaker Brønsted base than ttmgb in CH_3CN. It is, on the other hand, a slightly better electron donor.

Reactions Involving Au^{I}

In a series of experiments we heated mixtures of one of the GFAs shown in Scheme 1 and [AuCl(PPh_3)] in neat CH_3CN to reflux for a period of 2 h. Interestingly, no reaction was observed when [AuCl(PPh_3)] and ttmgb (in a 2:1 stoichiometric ratio) were dissolved in acetonitrile and the reaction mixture heated to 80 °C.

The guanidine ttmgn also showed no signs of reaction, and only huge, bar-shaped crystals of the [AuCl(PPh_3)] reactant precipitated from the reaction mixture. We only observed a colouring of the solution, which we explain by the formation of small amounts of Au nanoparticles. In contrast, the tdmegb/[AuClPPh$_3$]/CH_3CN reaction mixture adopted a bright yellow colour, and upon cooling of the mixture to room temperature yellow crystals precipitated. Spectroscopic data in alliance with an XRD analysis of the crystalline material revealed the formation of the new Au^{I} complex [Au(CH_2CN)(PPh_3)], crystallizing together with 0.5 equiv. of the neutral tdmegb molecules. Figure 2 illustrates the molecular structure. The tdmegb units separate the Au^{I} molecules from each other. The Au–C14 bond length measures 208.5(2) pm. For comparison, in the complex [Au{CH($SiMe_3$)$_2$}(PPh_3)], a Au–C bond length of 204.1(6) pm is realized,[26] being close to the values in [AuPh(PPh_3)] and related molecules in which an sp^2 hybridized carbon is bound to Au^{I} (around 205 pm).[27,28] A significantly longer Au–C bond [208.7(3) pm] is found in the Au complex arising from coordination of 1,3-dimethyl-2-methylene-imidazoline to the [Ph_3PAu] fragment (see Scheme 2).[29] The Au–C bond in [Au(CH_2CN)(PPh_3)] is in the same range. The C14–C15 bond [143.7(4) pm] is slightly shorter, and the C15–N7 bond [115.1(3) pm] slightly longer than in CH_3CN. For comparison, in [PtH(CH_2CN)(PPh_3)$_2$], the methyl cyano group exhibits C–C and C–N bond lengths of 143(2) and 112(3) pm.[30] In the ^{1}H NMR spectrum, the methylene group of the cyanomethyl ligand shows at δ = 1.64 ppm.

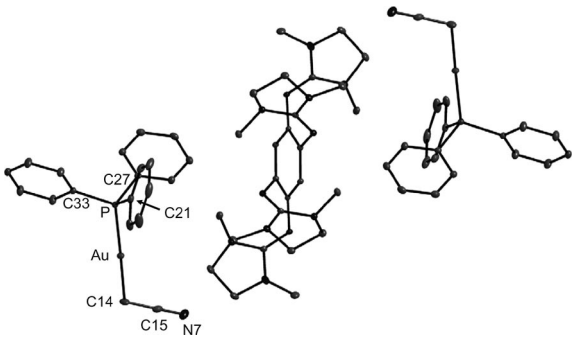
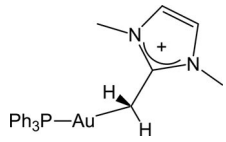


Figure 2. Molecular structure of 2[Au(CH_2CN)PPh_3]/tdmegb (hydrogen atoms omitted for sake of clarity). Thermal ellipsoids are drawn at the 50% probability level. Selected structural parameters (bond lengths in pm, angles in deg.): Au–C14 208.5(2), C14-C15 143.7(4), C15–N7 115.1(3), Au–P 227.22(8), P–C21 182.11(12), P–C27 182.71(12), P–C33 182.88(11), P–Au–C14 177.25(9), Au–C14–C15 111.86(18), C14–C15–N7 179.0(3).



Scheme 2. Product of the reaction between 1,3-dimethyl-2-methyleneimidazoline and [AuCl(PPh_3)] in THF.

The thermal stability of the 2[Au(CH_2CN)(PPh_3)]/tdmegb crystals was assessed in TG and DSC experiments. Figure 3 displays the DSC and TG curves for temperatures up to 300 °C. The DSC curve contains two peaks; the first one corresponds to an endothermal process (peak around 170 °C, 68 kJ mol^{-1}) and is caused by melting of the solid material. (The melting point was determined to be 162 °C.) For comparison, the melting points of [AuCl(PPh_3)] and [Au($OCOCHCl_2$)(PPh_3)] are 233–234 °C and 232 °C, respectively.[31] From the TG curve it can be seen that there is no mass loss at this point. However, the material already changes its colour at this temperature indicating the formation of Au nanoparticles. It follows a peak due to an exothermal process (peak around 207 °C, ca. –33 kJ mol^{-1}). This peak is clearly associated with a mass loss (maximum of the first derivative of the TG curve at ca. 215 °C) of ca. 36%. We explain this exothermal process with the elimination of all the PPh_3 units (accounting in total for 34.5% of the mass) and the formation of Au nanoparticles in an irreversible exothermic process. This interpretation finds support by the dark-red colour of the material after the heat treatment (see Supporting Information) and by the ^{1}H and ^{31}P NMR spectra recorded after dissolving the heated material, which show no more sign of any aromatic protons or P nuclei after heating. Interestingly, all attempts to sepa-

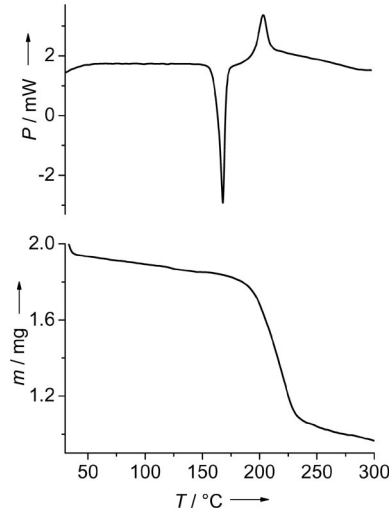


Figure 3. DSC (top) and TG curves (N_2 atmosphere, scan speed 5 K min^{-1}) measured for crystalline 2[Au(CH_2CN)PPh_3]/tdmegb.

rate the [Au(CH_2CN)(PPh_3)] complex from the tdmegb molecules by column chromatography (silica, MeOH/CH_2Cl_2, 1:4) were not successful. We observed decomposition of the Au^I complex under these conditions.

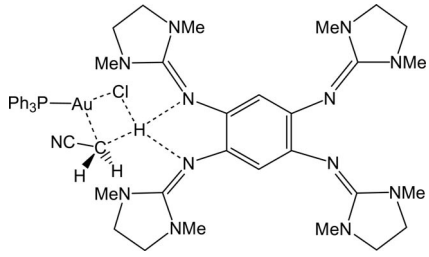
No electron transfer from the tdmegb electron donor units to the Au^I acceptors takes place. However, in solution conditions can be found under which redox chemistry is observed. Hence when [AuCl(PPh_3)] is dissolved in CH_2Cl_2 solutions together with tdmegb and valeronitrile (C_4H_9CN), and the reaction mixture heated to a temperature of 60 °C for a period of 5 h, we observed no nitrile deprotonation but instead formation of the Au cluster [$Au_{11}Cl_3(PPh_3)_7$]. Similar clusters [$Au_{11}X_3(P(aryl)_3)_7$] (e. g., X = SCN, I, or CN) and [$Au_{11}(PMePh_2)_{10}$]$^{3+}$ were already structurally characterized, and were synthesized by reduction of the triarylphosphane gold(I) complexes with $NaBH_4$.[32] These Au_{11} clusters are of interest for several applications.[33]

In preliminary experiments we also analysed with the help of NMR spectroscopy the reaction between 2 [Au(CH_2CN)(PPh_3)]/tdmegb and PhC(O)Cl, in the hope to regain [AuCl(PPh_3)] by transfer of the CH_2CN group and formation of 3-oxo-3-phenylpropanenitrile, PhC(O)-CH_2CN. A characteristic signal at δ = 4.1 ppm (due to the methylene group) in the ^1H NMR spectra indeed indicates the formation of PhC(O)CH_2CN already at –20 °C (see the spectra in the Supporting Information).[34] However, the reaction does not stop at this stage. The C–H acidity of the product is larger than that of CH_3CN, and therefore further deprotonation reactions occur leading to a product mixture. More work in this direction is on the way.

Possible Reaction Pathway/Mechanism

How can the formation of the cyanomethyl Au^I complex be explained? The first idea is that the guanidine base tdmegb simply deprotonates the CH_3CN and then the CH_2CN^- anions (being present in small concentrations) react with the Au^I complex in a ligand-substitution reaction (replacement of chloride by cyanomethyl). However, the experimental results do not support this simple picture. First of all the basicity of the tdmegb base is not high enough to generate significant amounts of the cyanomethyl anion. Deprotonation of CH_3CN by the organometallic base MeLi can be detected directly, for instance by NMR spectroscopy. In contrast, the NMR spectrum of a CH_3CN solution of the guanidine tdmegb showed no signal due to a reaction product of any sort. Of course, it could be argued that only small concentrations of the cyanomethyl anion are sufficient. However, even more difficult to explain is the fact that the weaker base, tdmegb, promotes the reaction while the stronger base, ttmgb, does not. One possibility would be that the equilibrium is shifted to the product side through precipitation of the Au complex [Au(CH_2CN)-(PPh_3)] for reactions with tdmegb, but not ttmgb. On the other hand, the product can clearly be observed with NMR already in the reaction mixture in the case of tdmegb, but not at all in the case of ttmgb (even for prolonged reaction times). The reaction exhibits at least two channels, the first leading to formation of the cyanomethyl complex (basicity of the guanidine) and the second to reduction of Au^I (electron donor properties of the guanidine) to give Au clusters. The cyanomethyl complex is only formed if CH_3CN is used in extremely large excess (as solvent). An Au_{11} cluster is formed if tdmegb and Au^I are dissolved in CH_2Cl_2 solutions together with a nitrile excess. This poses the question if the reduction channel is relatively fast in comparison to deprotonation in the case of ttmgb but not tdmegb, even if the nitrile is used as solvent. However, our experiments indicated that Au cluster formation occurs slowly in the ttmgb/[AuCl(PPh_3)]/CH_3CN reaction mixture, and in fact the only indication for it is the colouring of the solution. It is therefore unlikely that the reduction channel is much faster for ttmgb compared to tdmegb.

In the light of these experimental findings, we think that it is plausible to suggest C–H activation by the Au^I complex.[35] The energy of a possible transition state is lowered by interaction with the guanidine base as sketched in Scheme 3 (leading finally to HCl abstraction). Steric effects are then responsible for the differences between tdmegb and ttmgb. The tetramethylguanidino groups of ttmgb are sterically more demanding, so that the transition state cannot be stabilized sufficiently. Interestingly, a similar transition state was very recently suggested for arene-H activation by Au^I.[36] It is clear that at the present stage we cannot prove this proposed mechanism. However, this is in line with the experimental findings.



Scheme 3. Possible transition state of the reaction.

Conclusions

With 1,2,4,5-tetrakis(*N*,*N*′-dimethylethyleneguanidino)-benzene (tdmegb), we prepared a new strong N-base and electron donor. This molecule is related to the previously reported molecule 1,2,4,5-tetrakis(tetramethylguanidino)-benzene (ttmgb). The guanidine tdmegb is a slightly weaker base and a slightly better electron donor than ttmgb. Surprisingly, if tdmegb is dissolved together with the Au^I complex [AuCl(PPh_3)] in CH_3CN, the complex [Au(CH_2CN)-(PPh_3)] is formed in good yield. On the other hand, the guanidine ttmgb, although slightly more basic than tdmegb, shows no sign of reaction. Several experiments were carried out to obtain more information about this reaction, and a possible approach to the reaction mechanism is presented

which is in line with these results. More experiments and also quantum chemical calculations will be carried out in the future to support or disprove this idea for the mechanism. We will extend the analysis to other LAuCl complexes. In addition similar reactions of other alkyl compounds (e. g., CH_3NO_2, CH_3CHO or $PhCH_2CCH$) will be studied. Finally, the new synthetic method might open up the possibility of designing catalytic C–H activation reactions.

Experimental Section

General: All synthetic work was carried out under inert gas atmosphere using standard Schlenk techniques. [AuCl(PPh$_3$)] was purchased from ChemPur. The guanidines ttmgb and ttmgn were prepared as described in the literature.[14,16] NMR spectra were measured on a Bruker AVII-400 or a Bruker AVIII-600 spectrometer at a temperature of 23 °C and referenced to known standards, and IR spectra were recorded with a BIORAD Excalibur FTS 3000. A Perkin–Elmer Lambda 19 spectrometer was used for UV/Vis measurements.

tdmegb: To a solution of 1,3-dimethylimidazolidin-2-one (2.0 mL, 18.7 mmol) in anhydrous CH_3Cl (15 mL) was slowly added via syringe oxalyl chloride (7.9 mL, 92.0 mmol, 4.9 equiv.). The mixture was refluxed for 20 h at 80 °C. After solvent removal in vacuo, the residue was washed with dry Et_2O. The remaining pale yellow salt was dissolved in CH_3CN (12 mL) and added dropwise to a CH_3CN solution (25 mL) containing 1,2,4,5-tetraaminobenzene (0.83 g, 2.9 mmol) and triethylamine (3.5 mL, 43.0 mmol) at a temperature of 0 °C. Subsequently the reaction mixture was stirred for 1.5 h at 0 °C. Removal of the solvent in vacuo led to a brown-greenish precipitate which was then redissolved in water. After addition of NaOH (20%) a white precipitate was formed. The precipitate was filtered and washed three times with cold water and dried under vacuum to afford tdmegb (1.14 g, 2.2 mmol, 74%) as a white powder. $C_{26}H_{42}N_{12}$ (522.70): calcd. C 59.74, H 8.10, N 32.16; found C 58.08, H 8.09, N 31.21. ^{1}H NMR (600.13 MHz, CD_3CN): δ = 5.95 (s, 2 H, CH_{Ar}), 3.13 (s, 16 H, -CH_2-), 2.58 (s, 24 H, -CH_3). ^{13}C NMR (150.92 MHz, CD_3CN): δ = 154.13, 136.19, 116.76 (C_{Ar}), 49.21 (-CH_2-), 35.12 (-CH_3). IR (CsI): $\tilde{\nu}$ = 2932 (w), 2834 (w), 1644 (vs), 1483 (s), 1443 (m), 1391 (m), 1274 (m), 1244 (m), 1152 (w), 1037 (m), 973 (w), 897 (w), 804 (w), 718 (w), 633 (w) cm^{-1}. UV/Vis (CH_3CN, $c = 1.80\times10^{-5}$ mol L^{-1}): λ_{max} (ε, dm^3 mol^{-1} cm^{-1}): 253 (2.99×10^4), 345 (1.08×10^4) nm. CV (CH_3CN, $c = 1.80\times10^{-3}$ mol L^{-1}, vs. SCE). $E_{1/2}$ = –0.36 V. MS (FAB$^+$): *m*/*z* (%) = 523 (100) [tdmegb(H)]$^+$. Crystal data for $C_{26}H_{42}N_{12}\cdot4H_2O$, *M*r = 594.78, $0.40\times0.40\times0.35$ mm^3, monoclinic, space group *C*2/*c*, *a* = 20.994(4), *b* = 10.119(2), *c* = 16.139(3) Å, β = 113.97(3)°, *V* = 3132.9(13) Å^3, *Z* = 4, d_{calc} = 1.261 Mg m^{-3}, Mo-K_α radiation (graphite-monochromated, λ = 0.71073 Å), *T* = 100 K, θ_{range} 2.12 to 30.04°. Reflections measd. 9118, indep. 4591, R_{int} = 0.0299. Final *R* indices [$I>2\sigma(I)$]: R_1 = 0.0455, wR_2 = 0.1313.

2[Au(CH$_2$CN)(PPh$_3$)]/tdmegb: To a solution of 200 mg (362 μmol) tdmegb in 18 mL acetonitrile 358 mg (724 μmol) [AuClPPh$_3$] were added. The reaction mixture was stirred for a period of 2 h at 80 °C. Subsequently it was allowed to cool to room temp. and filtered. Half of the solvent was removed from the solvent, and the appearing precipitate re-dissolved by mild heating. Over night crystals were formed. After filtration and drying under vacuum 303 mg (199 μmol) 2[Au(CH$_2$CN)(PPh$_3$)]/tdmegb were obtained as yellow-golden shining crystals (52% yield). M. p. 162 °C. $C_{66}H_{76}Au_2N_{14}P_2$ (1521.28): calcd. C 52.11, H 5.04, N 12.89; found C 51.91, H 5.04, N 12.82. ^{1}H NMR (600 MHz, CD_2Cl_2): δ = 1.64 (s, 4 H, -CH_2-), 2.63 (s, 24 H, -CH_3), 3.15 (s, 16 H, -CH_2-), 6.06 (s, 2 H, Ar-H), 7.52 (m, 30 H, P-Ar-H). ^{13}C NMR (150 MHz, CD_2Cl_2): δ = 5.59 (s, -*C*H$_2$-CN) 35.28 (s, -CH_3), 49.18 (s, -CH_2-), 116.41 (s, C_{Ar}), 127.97, 129.71 (d, $^{2/3}J_{C,P}$ = 11.06 Hz), 130.63 (d, $^1J_{C,P}$ = 52.89 Hz), 132.04 (d, ^4J = 2.40), 134.75 (d, $^{2/3}J_{C,P}$ = 13.72), 135.82, 154.01. ^{31}P NMR (242 MHz, CD_2Cl_2): δ = 41.96. IR (Nujol): $\tilde{\nu}$ = 2193 (m), 1626 (s), 1273 (w), 1091 (w), 1036 (w) cm^{-1}. IR (CsI): $\tilde{\nu}$ = 2858 (s), 2201 (s), 1618 (s), 1388 (s), 1288 (s), 1143 (m), 1036 (s), 972 (s), 757 (s), 638 (w), 538 (s) cm^{-1}. UV/Vis (CH_3CN, $c = 4.94\times10^{-4}$): λ_{max}(ε, dm^3 mol^{-1} cm^{-1}) = 340 (9898), 423 (155) nm. MS (FAB$^+$): *m*/*z* (%) = 459.0 (80) [AuPPh$_3$]$^+$, 500.1 (40) [Au(CH$_2$CN)PPh$_3$ + H]$^+$, 523.3 (100) [tdmegb + H]$^+$, 721.2 (10) [tdmegb + 2H + Au]$^+$, 1022.3 (2) [tdmegb + H + Au(CH$_2$CN)PPh$_3$]$^+$. MS (ESI$^-$): *m*/*z* (%) = 249.29 (100) [Au(CH$_2$CN)PPh$_3$]$^{2-}$, 521.59 (45) [tdmegb-H]$^-$. Crystal data for $C_{66}H_{76}Au_2N_{14}P_2$, *M*r = 1521.28, $0.30\times0.30\times0.27$ mm^3, monoclinic, space group $P\bar{1}$, *a* = 9.3030(19), *b* = 10.893(2), *c* = 15.311(3) Å, α = 85.28(3), β = 89.43(3)°, γ = 89.72(3), *V* = 1546.2(5) Å^3, *Z* = 1, d_{calc} = 1.634 Mg m^{-3}, Mo-K_α radiation (graphite-monochromated, λ = 0.71073 Å), *T* = 100 K, θ_{range} 2.19 to 29.99°. Reflections measd. 16331, indep. 8942, R_{int} = 0.0187. Final *R* indices [$I>2\sigma(I)$]: R_1 = 0.0223, wR_2 = 0.0537.

[Au$_{11}$Cl$_3$(PPh$_3$)$_7$]: The guanidine tdmegb (52.8 mg, 101 μmol) was dissolved in 6 mL CH_2Cl_2. Then 100 mg (202 μmol) [AuCl(PPh$_3$)] and a large excess of valeronitrile (83.9 mg, 1010 μmol) were added, and the reaction mixture stirred for a period of 5 h at a temperature of 60 °C. Subsequently the solvent was partially removed leaving ca. ca. 1 mL. The crude product was purified by column chromatography (silica gel, EtOH/CH_2Cl_2, 1:4). After removal of the solvent, one obtains 100 mg solid. NMR spectra show that this solid consists of a 1:1 mixture of the cluster [Au$_{11}$Cl$_3$(PPh$_3$)$_7$] and [AuCl(PPh$_3$)]. The yield of [Au$_{11}$Cl$_3$(PPh$_3$)$_7$] can thus be estimated to be 12 μmol (65.2%). NMR spectra measured at several stages of the reaction show that the valeronitrile is not deprotonated. Moreover, the NMR spectra signal decomposition of the [Au$_{11}$Cl$_3$(PPh$_3$)$_7$] cluster for prolonged reaction times at 60 °C. ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 6.69 (2 H, Ar-H), 6.94 (1 H, Ar-H), 7.32 (2 H, Ar-H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 129.08, 130.39, 134.81. ^{31}P NMR (161 MHz, CD_2Cl_2): δ = 52.32. $RF_{Cluster}$ (EtOH/CH_2Cl_2, 1:4): 0.42.

X-ray Crystallographic Study: Suitable crystals were taken directly out of the mother liquor, immersed in perfluorinated polyether oil, and fixed on top of a glass capillary. Measurements were made on a Nonius-Kappa CCD diffractometer with low-temperature unit using graphite-monochromated Mo-K_α radiation. The temperature was set to 100 K. The data collected were processed using the standard Nonius software.[37] All calculations were performed using the SHELXT-PLUS software package. Structures were solved by direct methods with the SHELXS-97 program and refined with the SHELXL-97 program.[38,39] Graphical handling of the structural data during solution and refinement was performed with XPMA.[40] Atomic coordinates and anisotropic thermal parameters of non-hydrogen atoms were refined by full-matrix least-squares calculations.

CCDC-770432 (for tdmegb) and -779106 (for 2[Au(CH$_2$CN)PPh$_3$]/tdmegb) 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.

Supporting Information (see also the footnote on the first page of this article): It includes a titration curve for tdmegb in water, pho-

tos before and after heating **5** to a temperature of 300 °C, ^{1}H NMR spectra (200 MHz, CD_2Cl_2) for the reaction between **5** and PhC(O)Cl and the results of the quantum chemical calculations on the basicity and electron donor capacity of ttmgb and tdmegb

Acknowledgments

The authors gratefully acknowledge continuous financial support by the Deutsche Forschungsgemeinschaft (DFG).

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Received: June 24, 2010
Published Online: August 26, 2010

