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Gold Complexes with Difunctional Perfluoroalkyl Chains: Quantifying the Energy of Auophilic Interactions in Flexible Open-Chain Complexes

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Abstract: The first dinuclear Au(I) compounds containing bridging (CF₂)_n chains (n = 4, 6, 8) and Au(III) metallaperfluorocyclopentanes have been obtained by photoinitiated reactions of LAuMe (L = PPh₃, PMe₃, PCy₃ or IPr) with α,ω-diodoperfluorocarbons. Complexes LAu(CF₂)₄AuL present an unusual looped structure stabilized by an auophilic interaction for L = PMe₃, PPh₃ and PCy₃. The study of their dynamic behaviour has provided new insights about the strength of auophilic interactions in solution, allowing quantification of the energy of a single Au⋯Au interaction.

The development of metal-mediated or -catalyzed reactions that allow the introduction of fluorinated alkyl groups onto organic substrates is a main goal in synthetic chemistry, justified by the important applications of organofluorine compounds^[1–3] and the demand for selective and atom-efficient fluoroalkylation methodologies.^[4–8] One of the fundamental issues in this research field is to find metal complexes capable of promoting C–perfluoroalkyl coupling. Notable progress toward this target has been made for metal trifluoromethyl complexes. In contrast, complexes containing longer perfluoroalkyl chains have been much less explored.^[9–18]

Particularly, complexes containing difunctional perfluoroalkyl chains (Figure 1) have received very little attention. Thus, a few binuclear complexes with bridging (CF₂)₂ chains have been prepared by insertion of C₂F₄ into metal-metal bonds (**A**)^[19–22] or by reaction of C₂F₄ with low oxidation-state metal complexes (**B**, **C**).^[23–25] M(CF₂)_nM complexes with n > 2 (**D**, **E**) are very rare.^[26–30] Recently, Zn(II) complexes (**E**) have been used to transfer the (CF₂)₄ moiety to other metals or to organic substrates.^[31]

Fluorinated metallacyclopentanes have been obtained by cyclodimerization of fluorinated ethenes (**F**),^[22,32–38] or co-cyclodimerization of C₂F₄ and C₂H₄ (**G**),^[39,40] on electron-rich metal centers. Their unusual reactivity^[41–44] illustrates the potential of C₂F₄ in the synthesis of valuable fluoroorganic compounds.^[37,39,40] Only a few perfluorometallacycles with n ≠ 4 have been reported.^[45–47] Remarkably, fluorinated metallacyclobutanes (**H**) have been proposed as intermediates in metathesis reactions of fluoroolefins.^[48–50]

Herein we report the first gold complexes containing bridging or chelating (CF₂)_n chains. Remarkably, complexes LAu(CF₂)_nAuL adopt different structures depending on n and L, and show an interesting dynamic behaviour in solution, which is mainly dictated by the presence and strength of an intramolecular auophilic interaction.

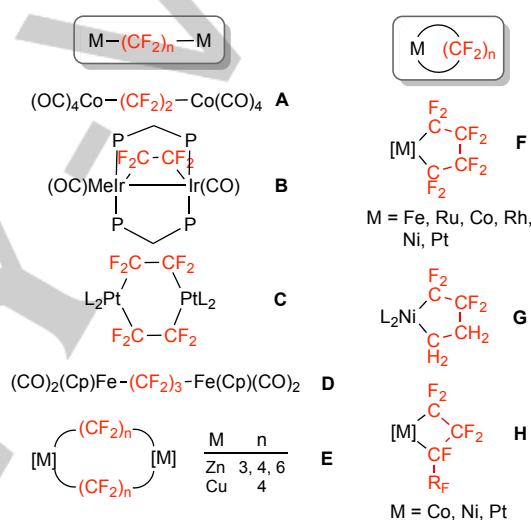


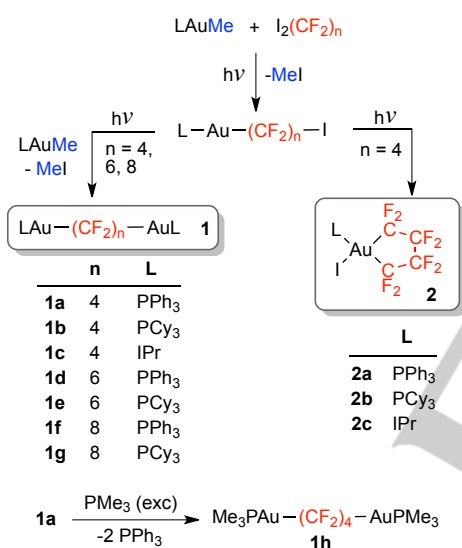
Figure 1. Representative reported complexes containing (CF₂)_n ligands.

Attractive interactions between closed-shell Au centers are frequently observed in the crystal structures of gold compounds, exerting a significant influence in their molecular and supramolecular structures and properties.^[51–56] Despite the wealth of reported experimental and computational studies about auophilic interactions, there is still debate about their origin and associated energy.^[57–60] Indeed, separating the contribution of the Au⋯Au interaction from other contributions to the observed overall interaction energy in a given molecule has proved problematic.^[60,61] The most reliable estimations of the energy of a single Au⋯Au interaction have been carried out in binuclear complexes of the type (Y(PPh₂)₂)(AuX)₂ (Y = organic linker), where the obtained values (20–50 KJ mol⁻¹)^[51,55,62,63] may comprise significant contributions of attractive or repulsive interactions between the mutually approaching PPh₂ groups.^[61] A gas-phase experimental and theoretical study on dimers of charged Au-carbene complexes also afforded energies within this range.^[59] In contrast, recent ligand exchange and self-assembly studies in Au(I) carbene complexes, combined with computational studies, suggested that Au⋯Au interactions could be much weaker than supposed, being surpassed by interactions involving the ligands or solvent.^{[60][64]} In this context,

the singular characteristics of the $\text{LAu}(\text{CF}_2)_n\text{AuL}$ complexes reported herein have allowed to assess the effect of n and L on the auriphilic interactions and to provide a reliable estimation of the associated energy.

The perfluoroalkyl gold complexes **1** and **2** were prepared by photoactivated reactions between Au(I) methyl complexes and $\text{I}(\text{CF}_2)_n\text{I}$ (Scheme 1). Thus, irradiation of a solution of LAuMe ($L = \text{Ph}_3\text{P}$, Cy_3P , N,N -bis(2,6-diisopropylphenyl)imidazol-2-ylidene (IPr)) and 1,4-diiodoperfluorobutane in CH_2Cl_2 at 402 nm gave mixtures containing MeI, binuclear Au(I) complexes **1** and auracyclopentanes **2**. The selectivity toward formation of **1** or $\mathbf{2}$ depended upon the initial LAuMe to $\text{I}(\text{CF}_2)_n\text{I}$ ratio (2 or 1, respectively).^[65]

In contrast, the analogous reactions of LAuMe ($L = \text{Ph}_3\text{P}$, Cy_3P) with $\text{I}(\text{CF}_2)_6\text{I}$ or $\text{I}(\text{CF}_2)_8\text{I}$ did not produce detectable amounts of perfluoroauracycles $[\text{Au}(\kappa^2\text{-C}_n\text{F}_{2n})\text{I}(\text{PR}_3)]$ ($n = 6$ or 8). Instead, binuclear Au(I) complexes $\text{LAu}(\text{CF}_2)_n\text{AuL}$ (**1d–g**), or mixtures of these complexes with $\text{LAu}(\text{CF}_2)_n\text{I}$, were formed depending on whether the initial Au to $\text{I}(\text{CF}_2)_n\text{I}$ molar ratio was 2 or 1, respectively (Scheme 1).



Scheme 1. Synthesis of binuclear Au(I) complexes and Au(III) auracycles.

LAuI and minor amounts of unidentified fluorinated products were detected as byproducts in all cases. Complexes **1** and **2** were isolated and structurally characterized. The reactions likely proceed through the initial formation of $\text{LAu}(\text{CF}_2)_n\text{I}$ (Scheme 1), which reacts with another molecule of LAuMe to give **1** or alternatively, undergoes intramolecular photooxidative addition to give **2** ($n = 4$). The intermediates $\text{LAu}(\text{CF}_2)_n\text{I}$ ($L = \text{PPh}_3$ or IPr) were detected by NMR spectroscopy using short irradiation times (Supporting Information).

The sluggish reactions observed in the dark or in the presence of TEMPO (Supporting Information) suggest a photoinitiated radical mechanism analogous to that proposed for the reactions of LAuMe with $\text{IC}_n\text{F}_{2n+1}$.^[18] It is noteworthy that, whereas the Au(I) complexes $\text{LAu}(\kappa^2\text{C}_4\text{F}_9)$ ($L = \text{PPh}_3$ or IPr) are unreactive toward $\text{I}^{\kappa^2}\text{C}_4\text{F}_9$,^[18] complexes $\text{LAu}(\text{CF}_2)_n\text{I}$ undergo intramolecular oxidative addition when n is 4, but not when n is 6 or 8. Since the reaction of 2 equivalents of Me_3PAuMe with $\text{I}(\text{CF}_2)_4\text{I}$ gave a complex mixture where the expected binuclear

complex **1h** was a minor component, we synthesized it by a phosphine substitution reaction on **1a** (Scheme 1).

The crystal structures of **1a** and **1h** show intramolecular $\text{Au}\cdots\text{Au}$ interactions, with similar Au-Au distances (Figure 2). In both cases, the close approach of the Au atoms is facilitated by a skew disposition of the C-Au-P axes (Figures S1 and S8), which originates chiral looped structures. The crystals of both **1a** and **1h** are racemic mixtures of Δ and Λ enantiomers. Whereas the molecule of **1a** presents a crystallographic C_2 axis, in **1h** there are slight differences between both halves of the molecule. The folded conformation of **1a** is further stabilized by intramolecular $\text{C-H}\cdots\text{F}$ and $\text{C-H}\cdots\pi(\text{Ar})$ interactions between atoms from opposite sides of the molecule (Figures S2 and S3). In contrast, the crystal structure of **1h** does not show any significant intramolecular contact other than the $\text{Au}\cdots\text{Au}$ one, but it shows intermolecular auriphilic contacts, which give rise to auriphilic chains disposed along the crystallographic b axis (Figure 2).

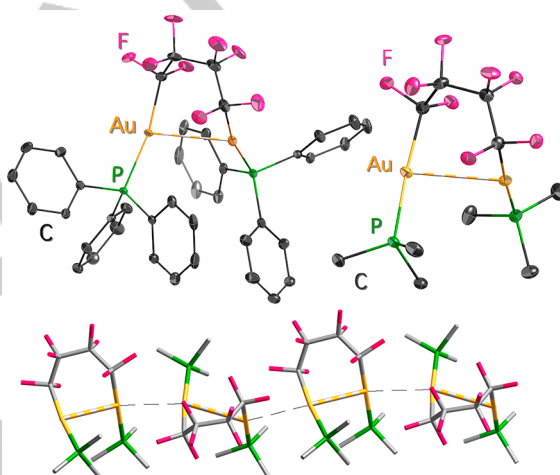


Figure 2. Top: ORTEP diagrams (50% probability ellipsoids, H atoms omitted) showing the molecular structures of **1a** (left) and **1h** (right). Bottom: Chains of molecules of **1h** connected by intermolecular auriphilic interactions. $\text{Au}\cdots\text{Au}$ distances (Å): **1a**, 3.0394(3); **1h**, 3.0782(5) (intramolecular), 3.2324(6) (intermolecular).^[66]

In the crystal structures of $\text{IPrAu}(\text{CF}_2)_4\text{Au}(\text{IPr})$ (**1c**) and $(\text{R}_3\text{P})\text{Au}(\text{CF}_2)_6\text{Au}(\text{PR}_3)$ ($\text{R} = \text{Ph}$ (**1d**), Cy (**1e**)), the $(\text{CF}_2)_n$ chains adopt an extended conformation (Figures 3 and S6). No intra- or inter-molecular auriphilic interactions were observed. Complex **2a** shows an octafluoroauracyclopentane ring and a distorted square planar coordination geometry (Figures 4 and S9).

The NMR data of **1a** and **1h** suggest that the folded structures observed in their X-ray structures persist in solution (Figures 5, S10 and S13). Thus, at low temperatures, the ^{19}F NMR spectra of both complexes show four doublets with large F-F coupling constants ($^2J_{\text{FF}} = 257\text{--}311$ Hz), which agree with the averaged C_2 symmetry of the folded structures, where the CF_2 couples are diastereotopic (F_{1a}/F_{1b} or F_{2a}/F_{2b} in Figure 5). On increasing T , fast exchange between Δ and Λ enantiomers renders the diastereotopic CF_2 couples isochronous, giving only two signals. In principle, the Δ/Λ interconversion could take place through an extended chain intermediate, or by a ring-flip process without breaking the $\text{Au}\cdots\text{Au}$ interaction. However, the second possibility is expected to show a much higher energy-

barrier, because at some point it would require a parallel arrangement of the C-Au-P axes, which would force a very close approach of the PR₃ ligands.

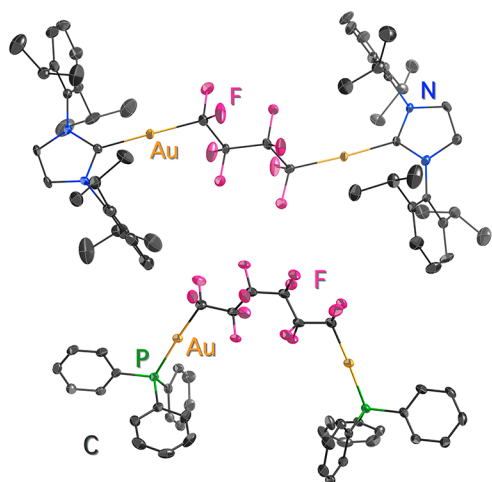


Figure 3. ORTEP diagrams (50% probability ellipsoids, H atoms omitted) showing the molecular structures of **1c** (top) and **1d** (bottom).^[66]

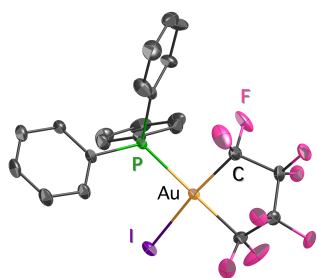


Figure 4. ORTEP diagram (50% probability, H atoms omitted) showing the molecular structure of **2a**.^[66]

The ¹⁹F NMR spectra of the IPr analogue (**1c**) and those of complexes containing a longer (CF₂)_n chain (**1d–g**) show homotopic CF₂ couples even at low temperatures, which suggests that the conformational mobility of the Au(CF₂)_nAu chain is not significantly restricted. This is in agreement with the extended conformations observed in the crystal structures of **1c**, **1d** and **1e**. In the following, we will denote extended or folded conformers as *ext-1* or *fold-1*, respectively.

Compound **1b** deserves special attention, because both *fold-1b* and *ext-1b* were observed in its NMR spectra at low temperature (Figure 6). In the ¹⁹F spectrum, *fold-1b* gave four doublets, with δ and J_{FF} values similar to those of **1a** and **1h**, whereas *ext-1b* gave two very broad signals. In the ³¹P{¹H} spectrum they gave a broad multiplet and a triplet, respectively (Supporting Information). The *ext-1b* to *fold-1b* molar ratio was 3.4, as determined by integration. Coalescence of the ¹⁹F signals of *ext-* and *fold-1b* into two broad singlets occurs between 203 and 214 K, which suggests a low exchange barrier.

Closer inspection of the low-temperature ¹⁹F NMR spectrum of **1h** revealed the presence of two broad signals at δ values similar to those of *ext-1b* (Figure 5), which were assigned to a small amount of *ext-1h*,^[67] while in the low temperature spectra of **1a** only the folded conformer was observed.

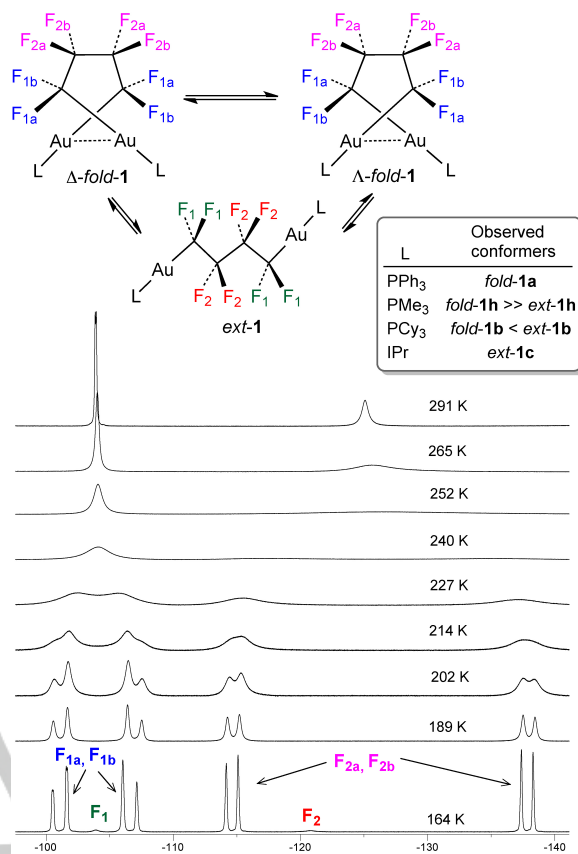


Figure 5. Exchange processes of complexes LAu(CF₂)₄AuL. The observed conformers are indicated in the table. ¹⁹F NMR spectra of **1h** at selected representative temperatures (CD₂Cl₂, 282.4 MHz).

Table 1. Activation enthalpies for the Δ/Δ exchange and thermodynamic parameters for the *extended* - *folded* equilibrium in **1a** and **1h**.

	L	ΔH^\ddagger (KJ mol ⁻¹)	ΔH° (KJ mol ⁻¹)	ΔS° (KJ mol ⁻¹ K ⁻¹)
1a	PPh ₃	35.8 ± 0.9	-17 ± 2	-52 ± 9
1h	PMe ₃	30.4 ± 1.8	-11.7 ± 0.2	-29.1 ± 0.5

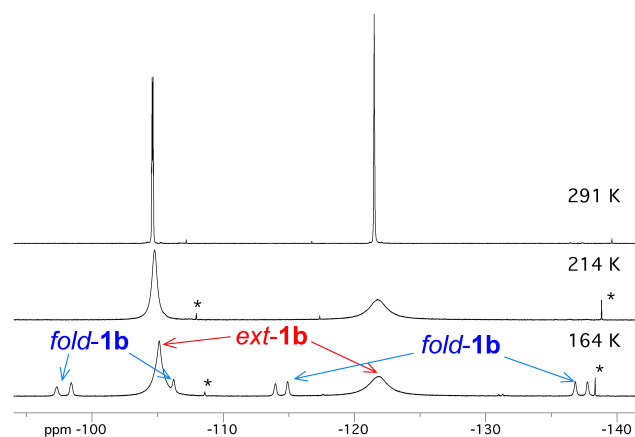


Figure 6. ¹⁹F NMR spectra of **1b** at selected representative temperatures. Signals of impurities are marked with an asterisk (CD₂Cl₂, 282.4 MHz).

It is noteworthy that the ^{19}F NMR signals of *ext-1b,c* and *ext-1d* become broader on decreasing the temperature, whereas those of *fold-1a,b* and *fold-1h* become sharper (Figures 5, 6 and Supporting Information). This can be understood if we consider that in *ext-1* the rotation of the $\text{CF}_2\text{-CF}_2$ bonds will become slower on decreasing the temperature, whereas in *fold-1* the conformational mobility of the $(\text{CF}_2)_4$ chain is already restricted.

The different behaviour of complexes **1a–c**, and **1h** is in agreement with the steric properties of the ligands. Thus, the size of PPh_3 or PMe_3 does not impede the mutual approach of the gold atoms. Consequently, at low temperatures **1a** and **1h** are almost exclusively in the folded conformation. In contrast, the bulkier IPr ligand^[68] hinders the approach of the gold centers, and hence only the extended structure was observed for **1c**. PCy_3 has an intermediate steric volume between PPh_3 and IPr ,^[68] which destabilizes *fold-1b* but does not prevent its formation. Therefore, both conformers were observed at low temperature, being *ext-1b* the dominant one.

The Δ/Λ exchange rates of **1a** and **1h** were estimated by line shape analysis of their ^{19}F NMR spectra at different temperatures. Activation enthalpies were derived by Eyring analyses (Table 1 and Supporting Information).

At temperatures above the coalescence, the ^{19}F resonances of **1h** move toward those of *ext-1h* on increasing T , indicating a shift of the equilibrium toward *ext-1h*. A similar behaviour was observed for **1a** (see Supporting Information). From the observed $\delta(^{19}\text{F})$ changes, the value of the equilibrium constant (K) was determined for **1a** and **1h** at several temperatures. ΔH° and ΔS° were obtained from a plot of ΔG° against T (Table 1 and Supporting Information). For **1b**, a reliable estimation of the equilibrium constants at different temperatures was not possible due to an additional drift of the NMR signals produced by other causes.

The determined ΔH° values suggest that the folded structure is more stable than the extended one by 17 or 11.7 KJ mol^{-1} for **1a** or **1h**, respectively. The higher value of **1a** is in line with the shorter $\text{Au}\cdots\text{Au}$ distance and the presence of $\text{C-H}\cdots\text{F}$ and $\text{C-H}\cdots\pi(\text{Ar})$ interactions in its crystal structure.^[69] The negative ΔS° values are consistent with the lower conformational freedom of the $\text{Au}(\text{CF}_2)_4\text{Au}$ chain in the folded structures. The more negative entropy value of **1a** is attributed to the restricted rotation of the phenyl groups produced by the close approach of the AuPPH_3 units, which does not occur in **1h**.

The Δ/Λ interconversion should involve the breakage of the intramolecular $\text{Au}\cdots\text{Au}$ interaction in one enantiomer of *fold-1* to give a transition state, which further relaxes to the other enantiomer or to *ext-1*. Then, the obtained ΔH^\ddagger values represent the energy difference between the folded structure and this transition state.^[61] Therefore, the higher value of **1a** respect to **1h** could be the consequence of: (i) a lower energy of the folded structure due to the additional stabilizing $\text{Ar-H}\cdots\text{X}$ interactions, (ii) a higher steric repulsion between the AuPR_3 units in the transition state of **1a** ($\text{R} = \text{Ph}$) respect to **1h** ($\text{R} = \text{Me}$). Owing to the low steric hindrance of the PMe_3 ligands and the absence of other significant interactions in the X-ray structure of **1h**, the ΔH^\ddagger value of **1h** should be close to the true energy of the aurophilic interaction. The calculated amount (30.4 KJ mol^{-1}) is within the reported range of estimated values for binuclear $\text{Au}(\text{I})$ complexes containing bridging diphosphine ligands (25–33 Kcal mol^{-1}),^[51,55,62] but smaller than those determined for $1,1'$ -(AuPPH_3)₂[2,2'-bis-(*o*-carboranyl)]^[61] and $[\text{Au}_2(\mu\text{-Xantphos})_2]^{2+}$

(46 and 48.1 KJ mol^{-1} , respectively).^[63] In all these systems, as in **1a**, the observed energies may include a significant contribution from interactions between the closely approaching phenyl rings. The observed value for **1h** is close to that reported for complexes of the type $[(\text{NHC})\text{AuCl}]^+$ (NHC = cationic nitrogen heterocyclic carbene) in the gas phase (25–30 KJ mol^{-1}).^[59]

In conclusion, the photoinitiated reactions of α,ω -diiodoperfluorocarbons with $\text{Au}(\text{I})$ methyl complexes gave rise to the first perfluorinated auracycles and binuclear complexes of the type $\text{LAu}(\text{CF}_2)_n\text{AuL}$. Depending on the value of n and the steric properties of L, these binuclear complexes show a high conformational freedom, or adopt a folded conformation stabilized by an aurophilic interaction. The study of their dynamic behaviour in solution has allowed to experimentally obtain a good approximation to the energy associated to a single $\text{Au}\cdots\text{Au}$ interaction.

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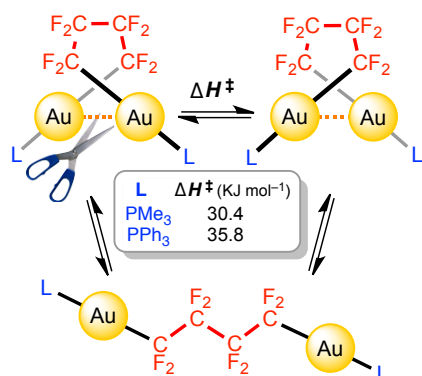
Keywords: Aurophilicity • fluorinated ligands • gold • metallocycles

- [1] E. P. Gillis, K. J. Eastman, M. D. Hill, D. J. Donnelly, N. A. Meanwell, *J. Med. Chem.* **2015**, *58*, 8315–8359.
- [2] M. Hird, *Chem. Soc. Rev.* **2007**, *36*, 2070–2095.
- [3] T. Fujiwara, D. O'Hagan, *J. Fluorine Chem.* **2014**, *167*, 16–29.
- [4] S. Barata-Vallejo, A. Postigo, *Coord. Chem. Rev.* **2013**, *257*, 3051–3069.
- [5] T. Liang, C. N. Neumann, T. Ritter, *Angew. Chem. Int. Ed.* **2013**, *52*, 8214–8264; *Angew. Chem.* **2015**, *54*, 3216–3221.
- [6] C. Alonso, E. Martínez de Marigorta, G. Rubiales, F. Palacios, *Chem. Rev.* **2015**, *115*, 1847–1935.
- [7] B. Lantaño, M. R. Torviso, S. M. Bonesi, S. Barata-Vallejo, A. Postigo, *Coord. Chem. Rev.* **2015**, *285*, 76–108.
- [8] T. Koike, M. Akita, *Acc. Chem. Res.* **2016**, *49*, 1937–1945.
- [9] N. D. Ball, J. B. Gary, Y. Ye, M. S. Sanford, *J. Am. Chem. Soc.* **2011**, *133*, 7577–7584.
- [10] V. I. Bakhmutov, F. Bozoglian, K. Gómez, G. González, V. V. Grushin, S. A. Macgregor, E. Martin, F. M. Miloserdov, M. A. Novikov, J. A. Panetier, L. V. Romashov, *Organometallics* **2012**, *31*, 1315–1328.
- [11] M. S. Winston, W. J. Wolf, F. D. Toste, *J. Am. Chem. Soc.* **2014**, *136*, 7777–7782.
- [12] J. R. Bour, N. M. Camasso, E. A. Meucci, J. W. Kampf, A. J. Canty, M. S. Sanford, *J. Am. Chem. Soc.* **2016**, *138*, 16105–16111.
- [13] D. M. Ferguson, J. R. Bour, A. J. Canty, J. W. Kampf, M. S. Sanford, *J. Am. Chem. Soc.* **2017**, *139*, 11662–11665.
- [14] M. Rovira, S. Roldán-Gómez, V. Martín-Diaconescu, C. J. Whiteoak, A. Company, J. M. Luis, X. Ribas, *Chem. Eur. J.* **2017**, *23*, 11662–11668.
- [15] S. Liu, K. Kang, S. Liu, D. Wang, P. Wei, Y. Lan, Q. Shen, *Organometallics* **2018**, *37*, 3901–3908.
- [16] M. Paeth, S. B. Tyndall, L.-Y. Chen, J.-C. Hong, W. P. Carson, X. Liu, X. Sun, J. Liu, K. Yang, E. M. Hale, D. L. Tierney, B. Liu, Z. Cao, M.-J. Cheng, W. A. Goddard, W. Liu, *J. Am. Chem. Soc.* **2019**, *141*, 3153–3159.
- [17] D. M. Ferguson, J. R. Bour, A. J. Canty, J. W. Kampf, M. S. Sanford, *Organometallics* **2019**, *38*, 519–526.

- [18] A. Portugués, I. López-García, J. Jiménez-Bernad, D. Bautista, J. Gil-Rubio, *Chem. Eur. J.* **2019**, *25*, 15535–15547.
- [19] A. D. Beveridge, H. C. Clark, *J. Organomet. Chem.* **1968**, *11*, 601–614.
- [20] B. L. Booth, R. N. Haszeldine, P. R. Mitchell, J. J. Cox, *J. Chem. Soc. A* **1969**, 691–698.
- [21] J. J. Bonnet, R. Mathieu, R. Poilblanc, J. A. Ibers, *J. Am. Chem. Soc.* **1979**, *101*, 7487–7496.
- [22] H. H. Hoehn, L. Pratt, K. F. Watterson, G. Wilkinson, *J. Chem. Soc.* **1961**, 2738–2745.
- [23] J. Forniés, M. Green, A. Laguna, M. Murray, J. L. Spencer, F. G. A. Stone, *J. Chem. Soc., Dalton Trans.* **1977**, 1515–1518.
- [24] M. Green, A. Laguna, J. L. Spencer, F. G. A. Stone, *J. Chem. Soc., Dalton Trans.* **1977**, 1010–1016.
- [25] D. Ristic-Petrovic, D. J. Anderson, J. R. Torkelson, R. McDonald, M. Cowie, *Organometallics* **2003**, *22*, 4647–4657.
- [26] R. B. King, M. B. Bisnette, *J. Organomet. Chem.* **1964**, *2*, 15–37.
- [27] R. B. King, *J. Am. Chem. Soc.* **1963**, *85*, 1922–1926.
- [28] B. L. Booth, R. N. Haszeldine, T. Inglis, *J. Chem. Soc., Dalton Trans.* **1975**, 1449–1455.
- [29] C. G. Krespan, *J. Fluorine Chem.* **1988**, *40*, 129–137.
- [30] B. Chen, D. A. Vicic, *J. Fluorine Chem.* **2014**, *167*, 139–142.
- [31] P. T. Kaplan, L. Xu, B. Chen, K. R. McGarry, S. Yu, H. Wang, D. A. Vicic, *Organometallics* **2013**, *32*, 7552–7558.
- [32] T. A. Manuel, S. L. Stafford, F. G. A. Stone, *J. Am. Chem. Soc.* **1961**, *83*, 249–250.
- [33] T. D. Coyle, R. B. Kings, E. Pitcher, S. L. Stafford, P. Teichel, F. G. A. Stone, *J. Inorg. Nucl. Chem.* **1961**, *20*, 172–173.
- [34] R. Kuwae, K. Kawakami, T. Tanaka, *Inorg. Chim. Acta* **1977**, *22*, 39–42.
- [35] A. J. Mukhedkar, V. A. Mukhedkar, M. Green, F. G. A. Stone, *J. Chem. Soc. A* **1970**, 3166–3171.
- [36] J. Ashley-Smith, M. Green, F. G. A. Stone, *J. Chem. Soc. A* **1969**, 3019–3023.
- [37] K. A. Giffin, L. A. Pua, S. Piotrkowski, B. M. Gabidullin, I. Korobkov, R. P. Hughes, R. T. Baker, *J. Am. Chem. Soc.* **2017**, *139*, 4075–4086.
- [38] J. Browning, H. D. Empsall, M. Green, F. G. A. Stone, *J. Chem. Soc., Dalton Trans.* **1973**, 381–387.
- [39] M. Ohashi, T. Kawashima, T. Taniguchi, K. Kikushima, S. Ogoshi, *Organometallics* **2015**, *34*, 1604–1607.
- [40] M. Ohashi, H. Shirataki, K. Kikushima, S. Ogoshi, *J. Am. Chem. Soc.* **2015**, *137*, 6496–6499.
- [41] R. R. Burch, J. C. Calabrese, S. D. Ittel, *Organometallics* **1988**, *7*, 1642–1648.
- [42] K. A. Giffin, D. J. Harrison, I. Korobkov, R. T. Baker, *Organometallics* **2013**, *32*, 7424–7430.
- [43] K. A. Giffin, I. Korobkov, R. T. Baker, *Dalton Trans.* **2015**, *44*, 19587–19596.
- [44] N. O. Andrella, A. J. Sicard, S. I. Gorelsky, I. Korobkov, R. T. Baker, *Chem. Sci.* **2015**, *6*, 6392–6397.
- [45] K. J. Karel, T. H. Tulip, S. D. Ittel, *Organometallics* **1990**, *9*, 1276–1282.
- [46] L. Xu, D. P. Solowey, D. A. Vicic, *Organometallics* **2015**, *34*, 3474–3479.
- [47] K. R. McGarry, D. A. Vicic, *J. Fluorine Chem.* **2017**, *203*, 206–209.
- [48] D. J. Harrison, G. M. Lee, M. C. Leclerc, I. Korobkov, R. T. Baker, *J. Am. Chem. Soc.* **2013**, *135*, 18296–18299.
- [49] J. T. Fuller, D. J. Harrison, M. C. Leclerc, R. T. Baker, D. H. Ess, R. P. Hughes, *Organometallics* **2015**, *34*, 5210–5213.
- [50] D. J. Harrison, A. L. Daniels, J. Guan, B. M. Gabidullin, M. B. Hall, R. T. Baker, *Angew. Chem. Int. Ed.* **2018**, *57*, 5772–5776; *Angew. Chem.* **2018**, *130*, 5874–5878.
- [51] H. Schmidbaur, A. Schier, *Chem. Soc. Rev.* **2008**, *37*, 1931–1951.
- [52] J. Gil-Rubio, J. Vicente, *Chem. Eur. J.* **2018**, *24*, 32–46.
- [53] S. Han, Y. Y. Yoon, O.-S. Jung, Y.-A. Lee, *Chem. Commun.* **2011**, *47*, 10689–10691.
- [54] M. E. S. Moussa, H. Chen, Z. Wang, M. Srebro-Hooper, N. Vanthuyne, S. Chevance, C. Roussel, J. A. G. Williams, J. Autschbach, R. Réau, Z. Duan, C. Lescop, J. Crassous, *Chem. Eur. J.* **2016**, *22*, 6075–6086.
- [55] H. Schmidbaur, A. Schier, *Chem. Soc. Rev.* **2012**, *41*, 370–412.
- [56] N. B. Jayaratna, M. M. Olmstead, B. I. Kharisov, H. V. R. Dias, *Inorg. Chem.* **2016**, *55*, 8277–8280.
- [57] P. Pyykkö, *Angew. Chem. Int. Ed.* **2004**, *43*, 4412–4456.
- [58] M. B. Brands, J. Nitsch, C. F. Guerra, *Inorg. Chem.* **2018**, *57*, 2603–2608.
- [59] E. Andris, P. C. Andrikopoulos, J. Schulz, J. Turek, A. Růžička, J. Roithová, L. Rulišek, *J. Am. Chem. Soc.* **2018**, *140*, 2316–2325.
- [60] Q. Zheng, S. Borsley, G. S. Nichol, F. Duarte, S. L. Cockcroft, *Angew. Chem. Int. Ed.* **2019**, *58*, 12617–12623; *Angew. Chem.* **2019**, *131*, 12439–12455.
- [61] D. E. Harwell, M. D. Mortimer, C. B. Knobler, F. A. L. Anet, M. F. Hawthorne, *J. Am. Chem. Soc.* **1996**, *118*, 2679–2685.
- [62] J. Zank, A. Schier, H. Schmidbaur, *J. Chem. Soc., Dalton Trans.* **1998**, 323–324.
- [63] A. Deák, T. Megyes, G. Tárkányi, P. Király, L. Biczók, G. Pálinkás, P. J. Stang, *J. Am. Chem. Soc.* **2006**, *128*, 12668–12670.
- [64] A. Wuttke, M. Feldt, R. A. Mata, *J. Phys. Chem. A* **2018**, *122*, 6918–6925.
- [65] When the initial molar ratio was 2, the observed 1:2 ratio was in the range 3–4. when the initial molar ratio was 1, complex **2** was the main reaction product and only traces of **1** were observed.
- [66] CCDC 1995517, 1995518, 1995513, 1995514, 1995515, and 1995516 (**1a**, **1c**, **1d**, **1e**, **1h** and **2a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre.
- [67] A ca. 2% of ext-**1h** was estimated by integration of the ¹⁹F NMR spectrum.
- [68] H. Clavier, S. P. Nolan, *Chem. Commun.* **2010**, *46*, 841–861.
- [69] No unusual shifts of the phenylic protons were found in its ¹H NMR spectrum at low temperature.

Entry for the Table of Contents

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The first perfluorinated auracycles and complexes containing Au(CF₂)_nAu chains are presented. LAu(CF₂)₄AuL complexes adopt a folded conformation stabilized by an aurophilic interaction depending on the auxiliary ligand L. The study of their dynamic behaviour in solution has allowed to determine the energy associated to an aurophilic interaction

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