CHEMISTRY A European Journal



Accepted Article

Title: Gold Sulfonium Benzylide Complexes Undergo Efficient Benzylidene Transfer to Alkenes

Authors: Ross Widenhoefer and Robert Carden

This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: Chem. Eur. J. 10.1002/chem.201902845

Link to VoR: http://dx.doi.org/10.1002/chem.201902845

Supported by ACES



COMMUNICATION

Gold Sulfonium Benzylide Complexes Undergo Efficient Benzylidene Transfer to Alkenes

Robert G. Carden and Ross A. Widenhoefer*

gold sulfonium Abstract: The benzvlide complexes $[(\textbf{P1})AuCHPh(SR^{1}R^{2})]^{+} \ \{B[3,5\text{-}CF_{3}C_{6}H_{3}]_{4}\}^{-} \ [\textbf{P1} = P(\textit{t-Bu})_{2}\textit{o-biphenyl};$ R^{1} , $R^{2} = -(CH_{2})_{4} - (1a)$; $R^{1} = Et$, $R^{2} = Ph (1b)$; $R^{1} = R^{2} = Ph (1c)$] were synthesized via reaction of the gold α -chloro benzyl complex (P1)AuCHCIPh with sodium tetrakis[3,5bis(trifluoromethyl)phenyl]borate and excess sulfide. Complexes 1 undergo efficient benzylidene transfer to alkenes and DMSO under mild conditions without external activation. Kinetic analysis of the reaction of 1c with styrene was consistent with the intermediacy of the cationic gold benzylidene complex [(P1)AuCHPh]⁺ (I).

Of the myriad transformations attributed to reactive gold carbene intermediates, perhaps none is more important or more prevelant than is gold to alkene carbene transfer.^[1-4] Although carbene transfer to alkenes is certainly not unique to gold,[5-10] the particular properties of gold including high d-electron count and electronegativity,^[11] poor d \rightarrow π back bonding,^[12] and the formation of stable π -complexes^[13] likely render the mechanisms of gold to alkene carbene transfer distinct from other transition metals.^[5-10] However, our understanding of the mechanisms of gold(I) to alkene carbene transfer is largely restricted to information gleaned from indirect experimental observations, such as the product ratios and stereoselectivity of catalytic reactions,^[14,15] from gas-phase reactions,^[16-19] and from computational analyses.^[14-18] As such, many gaps remain in our understanding of the mechanisms of the carbene transfer processes of gold including control of stereoselectivity, the nature of C-C bond formation, and the involvement of carbocationic and/or metallacyclobutane intermediates.[4,14-19]

Largely absent from the discussion of the mechanisms of gold to alkene carbene transfer are the potential insights gained from analysis of carbene transfer from well-defined carbene complexes in the condensed phase.^[2,3] Recent efforts in this area have led to identification of a small number of well-defined gold carbene complexes that undergo carbene transfer to alkenes (A - C).^[20-22] However, extracting detailed mechanistic information relevant to catalysis from these stoichiometric carbene transfer processes is complicated by the (1) excessive stabilization of the carbene complex, (2) *in situ* generation of the carbene complex with strong Lewis acids under cryogenic conditions, and/or (3) the extreme facility of carbene transfer.^[20-22]

[a] Robert G. Carden, Prof. R. A. Widenhoefer
 French Family Science Center, Duke University
 Durham, NC 27708–0346 (USA)
 E-mail: rwidenho@chem.duke.edu

Supporting information for this article is given via a link at the end of the document.



Figure 1. Well defined gold carbene (A - C) and carbenoid (D - F) complexes that undergo carbene transfer to alkenes [Ar = $4-C_6H_4OMe$; P1 = P(¹Bu₂)o-biphenyl; IPr = 1,3-bis(2,6-bis-(diisopropylphenyl)imidazol-2-ylidene].

As an alternative to free gold carbene complexes, we sought to identify gold carbenoid complexes that would spontaneously and reversibly generate reactive gold carbene complexes in solution under mild conditions,^[23] thereby allowing kinetic and mechanistic analysis of carbene transfer processes from otherwise inaccessible gold carbene complexes. Although a small number of gold(I) carbenoid complexes that undergo carbene transfer to alkenes have been identified (e.g. D-F; Figure 1),^[1719,24] only imidazolium sulfonyl complex **F** does so in solution without Lewis acid activation.^[18,25,26] However carbene transfer from F requires forcing conditions and a stabilizing C1 anisyl group for spontaneous activation and undergoes irreversible carbene formation, all of which would complicate kinetic and mechanistic analysis of carbene transfer. Here we report the synthesis of thermally stable gold sulfonium benzylide complexes that undergo benzylidene transfer to alkenes under mild conditions without activation via the intermediacy of an unstabilized gold benzylidene complex.

Inspired by the facile alkylidene transfer reactions of iron sulfonium ylide complexes,^[27] and the generation of well-defined Rh, Os, and Ru benzylidene complexes from sulfonium benzylides,^[28] we targeted gold sulfonium benzylide complexes of the form $[(L)AuCHPh(SR^1R^2)]^+$ as potential carbone transfer reagents.^[29-32] Initial efforts to synthesize gold sulfonium benzylide complexes via S-alkylation of gold a-thiobenzyl complexes^[26,27] or through ligand displacement with sulfonium benzylides^[28] proved unsuccessful. However, a third approach involving nucleophilic substitution of a gold *a*-chlorobenzyl carbenoid complex with sulfide, which was modelled after similar transformations reported by Steinborn^[26] and Echavarren,^[24] proved effective. In an optimized procedure, treatment of (P1)AuCHClPh^[24] [P1 = P(^tBu)₂o-biphenyl] with sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (NaBAr^F₄; 1.1 equiv) and excess tetrahydrothiophene (THT; 10 equiv) in

COMMUNICATION

toluene at room temperature led to isolation of the gold (tetramethylene)sulfonium benzylide complex $[(P1)AuCHPh(THT)]^+ BAr^{F_4-}(1a)$ in 68% yield after crystallization (Scheme 1). The ethylphenylsulfonium benzylide complex **1b** and diphenylsulfonium benzylide complex **1c** were isolated employing similar procedures. Complexes **1** were stable indefinitely in the solid state at room temperature and complexes **1a** and **1b** displayed no detectable decomposition in solution after 24 h at room temperature, whereas **1c** decomposed slowly ($t_{1/2} = ~7$ h) under these conditions.



Scheme 1. Synthesis of gold sulfonium benzylide complexes 1.

Gold sulfonium benzylide complexes 1 were characterized by NMR spectroscopy and X-ray crystallography (Figure 2, Table 1). Complexes 1 displayed diagnostic phosphorous-coupled doublets in both the ¹H (δ 2.28 - δ 3.75, J_{PH} \approx 6 Hz) and ¹³C (δ 62.7 - δ 66.6, J_{PH} \approx 85 Hz) NMR spectra assigned to the benzylic proton and carbon atom, respectively. In the solid state, complexes 1 adopt slightly distorted linear conformations with P-Au-C angles ranging from 171 - 175° (Figure 2, Table 1). The benzylic carbon atom adopts a distorted sp³ geometry with a larger Au-C1-C2 angle (113-117°) and a smaller Au-C1-S angle (101-106°). Complex 1b, which contains a stereogenic sulfur atom, crystallized exclusively as the S*, R* diastereomer [(S*, R*)-**1b**] (Figure 2), but isomerized in [D₈]toluene at 25 °C ($t_{1/2}$ = 25 min) to form an equilibrium 2.5:1 mixture of (S^*, R^*) -1b and (S^*, S^*) -1b (eq 1). Kinetic analysis of the conversion of (S^*, R^*) -1b to (S*,S*)-1b established first-order approach to equilibrium with forward and reverse rate constants $k_{\rm f} = 1.33 \pm 0.15 \times 10^{-4} \, {\rm s}^{-1}$ ¹ and $k_r = 3.3 \pm 0.4 \times 10^{-4} \text{ s}^{-1}$. Periodic analysis of an equimolar solution of (S*,R*)-1b and THT (13 mM) revealed that isomerization of (S*,R*)-1b was not significantly inhibited by THT $(k_{\rm f}$ = 1.4 ± 0.20 × 10⁻⁴ s⁻¹) and was ~5 times faster than was conversion of **1b** to **1a** ($k_{obs} = 2.8 \pm 0.5 \times 10^{-5} \text{ s}^{-1}$). These observations argue against isomerization of (S*,R*)-1b via a dissociation/reassociation pathway and instead point to isomerization via inversion at sulfur.[33]

Table 1. Selected bond lengths (Å) and angles (deg) for 1a, (S^*, R^*) -1b, and 1c.

	1a	(S*,R*)- 1b	1c
P–Au	2.2920(6)	2.294(1)	2.298(1)
Au–C1	2.096(2)	2.095(4)	2.125(2)
C1–S	1.796(2)	1.787(4)	1.813(3)
C1–C2	1.507(3)	1.513(4)	1.513(3)
P–Au–C1	174.63(6)	171.9(1)	171.37(8)
Au–C1–S	105.3(1)	106.3(2)	101.5(1)
Au–C1–C2	116.6(1)	113.3(2)	116.5(2)
SC1C2	114.6(2)	108.0(2)	104.1(2)



Figure 2. ORTEP diagrams of complexes **1a** (upper left), (S^*,R^*) -**1b** (middle right), and **1c**-**C**₇H₈ (lower right) with ellipsoids shown at the 50% probability level and with counterion, solvent, and hydrogen atoms omitted for clarity.



Table 2. Reactions of gold carbenoid sulfonium benzylide complexes 1 (12 -32 mM) with alkenes and DMSO (10 equiv) in [D_8]toluene.

_					
entry	benzylide complex	nucleophile	organic product ^[a]	temp (°C)/ t _{1/2} (min)	yield (%)/dr
1 ^[b] 2 ^[e] 3 ^[f]	1a 1b 1c	2 2 2	Ar 3 Ph	75/51 ^[c] 40/29 ^[c] 25/0.7 ^[c]	96/6:1 ^[d] 95/6:1 ^[d] 87/6:1 ^[d]
4 ^[b] 5 ^[e] 6 ^[g]	1a 1b 1c	DMSO DMSO DMSO	H Ph	75/95 ^[c] 40/29 ^[c] 25/≤2 ^[h]	78/— ^[d] 65/— ^[d] 65/— ^[d]
7 ^[f]	1c	Ph	Ph	25/0.7 ^[c]	82/2:1 ^[d]
8 ^[g]	1c		Ph	25/≤2 ^[h]	67/2:1 ^[d]
9 ^[f]	1c	\bigcirc	H	25/≤2 ^[h]	79/4:1 ^[i]
10 ^[f]	1c	n-Bu	n-Bu	25/≤2 ^[h]	76/3:1 ^[i]

[a] Major diastereomer depicted. [b] [Nuc] = 0.32 M. [c] Reaction displayed pseudo first-order kinetics to \geq 3 half-lives. [d] Yield and dr determined by ¹H NMR versus internal standard. [e] [Nuc] = 0.22 M. [f] [Nuc] = 0.15 M. [g] [Nuc] = 0.20 M. [h] Estimated half-life. [i] Yield and dr determined by GC analysis versus internal standard.

COMMUNICATION

Treatment of (tetramethylene)sulfonium benzylide complex 1a (32 mM) with excess p-methoxystyrene (2; 10 equiv) at 75 °C led to first-order decay ($t_{1/2}$ = 51 min) to form 1-phenyl-2anisylcyclopropane (3) in 95% yield (1H NMR) as a 6:1 mixture of cis/trans diastereomers and the gold THT complex [(P1)Au(THT)]⁺ in guantitative yield (Table 2, entry 1). In a similar manner, treatment of 1a with excess DMSO at 75 °C led to firstorder decay ($t_{1/2}$ = 95 min) to form benzaldehyde in 75% yield and a mixture of gold THT and dimethylsulfide complexes (Table 2, entry 4).^[34-36] The reactivity of gold sulfonium benzylide complexes 1 toward both 2 and DMSO increased significantly in the order **1a** < **1b** < **1c** (Table 2, entries 2, 3, 5, and 6),^[37] such that the reactions of 1c with 2 and DMSO were complete within ~2 min at 25 °C (Table 2, entries 5 and 6). Owing to the high reactivity of 1c toward 2, we considered that 1c might likewise undergo benzylidene transfer to less reactive alkenes. Indeed, 1c reacted efficiently with styrene, norbornene, cyclohexene, and 1-hexene at room temperature within 5 min to form the corresponding cyclopropanes in good yield (Table 2, entries 7-10).

To probe the mechanism of benzylidene transfer from sulfonium benzylide complexes **1**, we studied the kinetics of the reaction of **1c** with styrene in [D₈]toluene at 25 °C employing ¹H NMR spectroscopy. To this end, pseudo-first-order rate constants for the reaction of **1c** (16 mM) with styrene were determined as a function of [styrene] (0 - 1.53 M) at constant [Ph₂S] (150 mM) and as a function of [Ph₂S] (0 - 610 mM) at constant [styrene] (150 mM). A plot of k_{obs} versus [styrene] at constant [Ph₂S] established the positive, non-integer dependence of the rate on [styrene], while a plot of k_{obs} versus [Ph₂S] at constant [styrene] established the negative, non-integer dependence of the rate on [Ph₂S] (Figure 3).



Figure 3. Plots of k_{obs} versus [styrene] for the reaction of **1c** (15 mM) with styrene in [D₈]toluene containing Ph₂S (150 mM) at 25 °C (O) and k_{obs} versus [Ph₂S] for the reaction of **1a** with styrene (150 mM) in toluene at 25 °C (×) (left plot). Plot of $1/k_{obs}$ versus [Ph₂S]/[styrene] for the reaction of **1c** with styrene in [D₈]toluene at 25 °C (right plot).

Strong inhibition of the rate of reaction of **1c** with styrene by Ph₂S rules out mechanisms for benzylidene transfer involving either direct attack of styrene on **1c** or irreversible loss of Ph₂S from **1c**, both of which would display zero-order rate dependence on [Ph₂S]. Rather, our kinetic data are consistent with a mechanism involving reversible generation of gold benzylidene complex I followed by irreversible carbene transfer to styrene (Scheme 2). Steady state treatment of intermediate I generates rate equation 2, which is of the same form as the experimentally determined rate law. Under conditions of excess [Ph₂S] and

[styrene], rate equation 2 can be expressed as: rate = $k_{obs}[1c]$ with k_{obs} defined by eq 3 and $1/k_{obs}$ defined by eq 4. In accord with this latter relationship, a plot of $1/k_{obs}$ versus [Ph₂S]/[styrene] was linear, which provided the values $k_1 = 1.3 \pm 0.4 \times 10^{-2} \text{ s}^{-1}$ ($\Delta G^{\ddagger} = 20.0 \pm 0.2 \text{ kcal/mol}$) and $k_{-1}/k_2 = 3.5 \pm 1.1$. The former value corresponds to the first-order rate constant for dissociation of Ph₂S from **1c** while latter value corresponds to the relative kinetic affinities of Ph₂S and styrene toward benzylidene intermediate **I**.



Scheme 2. Kinetic model for the reaction of 1c with styrene to form 1,2-diphenylcyclopropane.

rate =
$$\frac{k_1 k_2 [1c][\text{styrene}]}{k_{-1} [\text{Ph}_2 S] + k_2 [\text{styrene}]} \qquad \text{eq } 2$$

rate = $k_{\text{obs}} [1c]$, where $k_{\text{obs}} = \frac{k_1 k_2 [\text{styrene}]}{k_{-1} [\text{Ph}_2 S] + k_2 [\text{styrene}]} \qquad \text{eq } 3$
 $\frac{1}{k_{\text{obs}}} = \frac{k_{-1} [\text{Ph}_2 S]}{k_1 k_2 [\text{styrene}]} + \frac{1}{k_1} \qquad \text{eq } 4$

In summary, we have synthesized the thermally stable gold sulfonium benzylide complexes 1, which undergo benzylidene transfer to alkenes and DMSO under mild conditions without external activation. The reactivity of complexes 1 increased significantly in the order 1a < 1b < 1c such that the diphenylsulfonium benzylide complex 1c reacts with vinyl arenes, aliphatic alkenes, and DMSO within minutes at room temperature. Kinetic analysis of the reaction of 1c with styrene established a mechanism involving reversible formation of the free gold benzylidene complex I followed by irreversible benzylidene transfer to styrene. Ongoing studies in our laboratory are directed toward kinetic analysis of carbene transfer from gold sulfonium benzylide complexes as a function of supporting ligand, C1-aryl group, and alkene.

Acknowledgements

We thank the NSF (CHE-1213957) for support of this research. All X-ray crystallography measurements were made Dr. Roger Sommer in the Molecular Education, Technology, and Research Innovation Center (METRIC) at North Carolina State University.

Keywords: Carbenoids • gold • kinetics • carbenes • alkenes

a) C. Obradors, A. M. Echavarren, Acc. Chem. Res. 2014, 47, 902-912;
 b) A. Fürstner, Acc. Chem. Res. 2014, 47, 925-938; c) P. Y. Toullec, V. Michelet, Top. Curr. Chem. 2011, 302, 31-80; d) C. Obradors, A. M. Echavarren, Chem. Commun. 2014, 50, 16-28; e) Z. Zheng, Z. Wang, Y. Wang, L. Zhang, Chem. Soc. Rev. 2016, 45, 4448-4458; f) R. K.

COMMUNICATION

Shiroodi, V. Gevorgyan, *Chem. Soc. Rev.* **2013**, *42*, 4991-5001; g) F. Miege, C. Meyer, J. Cossy, *Beilstein J. Org. Chem.* **2011**, 7, 717-734;

- [2] R. J. Harris, R. A. Widenhoefer, Chem. Soc. Rev. 2016, 45, 4533-4551.
- [3] Y. Wang, M. E. Muratore, A. M. Echavarren, Chem. Eur. J. 2015, 21, 7332–7339.
- [4] D. Qian, J. Zhang, Chem. Soc. Rev. 2015, 44, 677–698.
- [5] M. Brookhart, W. B. Studabaker, Chem. Rev. 1987, 87, 411–432.
- [6] M. P. Doyle, J. H. Griffin, V. Bagheri, R. L. Dorow, Organometallics 1984, 3, 53–61.
- [7] a) M. P. Doyle, *Chem. Rev.* **1986**, *86*. 919–939; b) C. Rodriguez-Garcia,
 A. Oliva, R. M. Ortuno, V. Branchadell, *J. Am. Chem. Soc.* **2001**, 123, 6157-6163; c) J. M. Fraile, J. I. Garcia, V. Martinez-Merino, J. A. Mayoral,
 L. Salvatella, *J. Am. Chem. Soc.* **2001**, 123, 7616-7625; d) F. Bernardi,
 A. Bottoni, G. P. Miscione, *Organometallics* **2001**, 20, 2751-2758; e) B.
 F. Straub, *J. Am. Chem. Soc.* **2002**, *124*, 14195 –14201; f) I. Iwakura,
 T. Ikeno, T. Yamada, *Org. Lett.* **2004**, 6, 949-952.
- [8] a) D. S. Wulfman, R. S. McDaniel Jr, B.W. Peace, *Tetrahedron* 1976, 32,1241-1249; b) A. J. Anciaux, J. A. Hubert, A. F. Noels, N. Petiniot, P. Teyssie, *Tetrahedron Lett.* 1973, 2233-2236; c) A. Nakamura, T. Koyama, S. Otsuka, *Bull. Chem. Soc. Jpn.* 1978, *51*, 593–595; d) A. Nakamura, T. Koyama, R. Tsujitani, M. Kudo, S. Otsuka, *J. Am. Chem. Soc.* 1978, *100*, 3449–3461.
- [9] R. G. Salomon, J. K. Kochi, J. Am. Chem. Soc. 1973, 95, 3300–3310.
- [10] J. L. Maxwell, K. C. Brown, D. W. Bartley, T. Kodadek, Science 1992, 256, 1544–1547.
- a) S. G. Bratsch, J. Chem. Educ. 1988, 65, 34-41; b) J. E. Huheey, E. A. Keiter, R. L. Keiter, *Inorganic Chemistry: Principles of Structure and Reactivity*, HarperCollins, New York, USA, 4th ed., 1993.
- [12] D. Benitez, N. D. Shapiro, E. Tkatchouk, Y. Wang, W. A. Goddard III, F. D. Toste, *Nat. Chem.* 2009, *1*, 482–486.
- [13] R. E. M. Brooner, R. A. Widenhoefer, *Angew. Chem.* 2013, *125*, 11930-11941; *Angew. Chem. Int. Ed.* 2013, *52*, 11714-11724; b) A. C. Jones, *Top. Curr. Chem.* 2015, *357*, 133-165; c) H. Schmidbaur, A. Schier, *Organometallics* 2010, *29*, 2-23; d) M. A. Cinellu, in Modern Gold Catalyzed Synthesis, ed. A. S. K. Hashmi, D. F. Toste, Wiley-VCH, 2012, p. 153.
- [14] C. Nieto-Oberhuber, S. Lopez, M. P. Munoz, E. Jiménez-Núñez, E. Buñuel, D. J. Cárdenas, A. M. Echavarren, *Chem. Eur. J.* 2006, *12*, 1694–1702.
- [15] P. Pérez-Galán, E. Herrero-Gómez, D. T. Hog, N. J. A. Martin, F. Maseras, A. M. Echavarren, *Chem. Sci.* 2011, 2, 141–149.
- [16] L. Batiste, A. Fedorov, P. Chen, Chem. Commun. 2010, 46, 3899–3901.
- [17] A. Fedorov, L. Batiste, A. Bach, D. M. Birney, P. Chen, J. Am. Chem. Soc. 2011, 133, 12162–12171.
- [18] a) D. H. Ringger, P. Chen, Angew. Chem. 2013, 125, 4784-4787;
 Angew. Chem. Int. Ed. 2013, 52, 4686-4689; b) D. H. Ringger, I. J.
 Kobylianskii, D. Serra, P. Chen, Chem. Eur. J. 2014, 20, 14270-14281.
- [19] a) A. Fedorov, M. Moret, P. Chen, J. Am. Chem. Soc. 2008, 130, 8880-8881; b) A. Fedorov, P. Chen, Organometallics 2009, 28, 1278-1281; c)
 C. A. Swift, S. Gronert, Organometallics 2014, 33, 7135–7140.
- [20] a) G. Seidel, A. Fürstner, Angew. Chem. 2014, 126, 4907-4911; Angew. Chem. Int. Ed. 2014, 53, 4807-4811; b) C. Werlé, R. Goddard, A. Fürstner, Angew. Chem. 2015, 127, 15672-15676; Angew. Chem. Int. Ed. 2015, 54, 15452-15456.
- [21] N. Kim, R. A. Widenhoefer, Chem. Sci. 2019, 10, 6149-6156.
- [22] C. Garcia-Morales, X.-L. Pei, J. M. Sarria Toro, A. M. Echavarren, Angew. Chem. 2019, 131, 3997-4001; Angew. Chem. Int. Ed. 2019, 58, 3957-3961.
- [23] We employ the carbene/carbenoid terminology suggested by Echavarren,^[3] in which the former term refers to a gold atom bound to a divalent carbon atom bearing full or partial positive charge, whereas the latter refers to a gold atom bound to formally uncharged carbon atom bearing an α or a conjugated γ -leaving group.
- [24] J. M. Sarria Toro, C. García-Morales, M. Raducan, E. S. Smirnova, A. M. Echavarren, *Angew. Chem.* **2017**, *129*, 1885-1889; *Angew. Chem. Int. Ed.* **2017**, *56*, 1859-1863.

- [25] For additional examples of mononuclear gold(I) carbenoid complexes see refs 22. 23. and: a) H. Schmidbaur, R. Franke, Angew. Chem. 1973,85, 499; Angew. Chem. Int. Ed. Engl. 1973, 12, 416-417; (b) H. Schmidbaur, R. Franke, Chem. Ber. 1975, 108, 1321-1328; (c) H. Schmidbaur, R. Franke, Inorg. Chim. Acta 1975, 13, 79-83; (d) H. Schmidbaur, R. Franke, Inorg. Chim. Acta 1975, 13, 84-89; e) Y. Yamamoto, Chem. Lett. 1980, 311-312; f) A. Fürstner, M. Alcarazo, R. Goddard, C. W. Lehmann, Angew. Chem. 2008, 120, 3254-3258.; Angew. Chem. Int. Ed. 2008, 47, 3210-3214; g) H. Kneuper, K. Harms, G. Boche, J. Organomet. Chem. 1989, 364, 275-279; h) J. Vicente, M.T. Chicote, I. Saura-Llamas, J. Turpin, J. Femandez-Baeza, J. Organomet. Chem. 1987, 333, 129-137; i) Y. Yamamoto, Z. Kanda, Bull. Chem. Soc. Jpn. 1979, 52, 2560-2562; j) A. N. Nesmeyanov, E. G. Perevalova, E. I. Smyslova, V. P. Dyadchenko, K. I. Grandberg, Izv. Akad. Nauk SSSR Ser. Khim. 1977, 2610-2612; k) R. Uson, A. Laguna, M. Laguna, A. Uson, M. C. Gimeno, Inorg. Chim. Acta 1986, 114, 91-94; I) C. J. Aguirre, M. C. Gimeno, A. Laguna, M. Laguna, J. M. Lopez de Luzuriaga, F. Puente, Inorg. Chim. Acta 1993, 208, 31-36; m) D. A. Briggs, R. G. Raptis, J. P. Fackler Jr., Acta Cryst. 1988, C44, 1313-1315; n) L. C. Porter, H. Knachel, J. P. Fackler Jr., Acta Cryst. 1987, C43, 1833-1835; o) L. C. Porter, H. Knachel, J. P. Fackler Jr., Acta Cryst. 1986, C42, 1125-1128.
- [26] D. Steinborn, S. Becke, R. Herzog, M. Ggnther, R. Kircheisen, H. Stoeckli-Evans, C. Bruhn, Z. Anorg. Allg. Chem. 1998, 624, 1303–1307.
- [27] a) E. J. O'Connor, S. Brandt, P. Helquist, J. Am. Chem. Soc. 1987, 109, 3739–3747; b) K. A. M. Kremer, P. Helquist, R. C. Kerber, J. Am. Chem. Soc. 1981, 103, 1862-1864; c) S. Brandt, P. Helquist, J. Am. Chem. Soc. 1979, 101, 6473-6475; d) P. McCarten, E. K. Barefield, Organometallics 1998, 17, 4645–4648; e) E. J. O'Connor, P. Helquist, J. Am. Chem. Soc. 1982, 104, 1869-1874.
- a) M. Gandelman, B. Rybtchinski, N. Ashkenazi, R. M. Gauvin, D. Milstein, J. Am. Chem. Soc. 2001, 123, 5372–5373. b) M, Gandelman, K, M. Naing, B. Rybtchinski, E. Poverenov, Y. Ben-David, N. Ashkenazi, R. M. Gauvin, D. Milstein, J. Am. Chem. Soc. 2005, 127, 15265-15272.
- [29] Examples of gold(I) sulfonium ylide complexes are limited to a pair of thermally unstable sulfonium allenylide and allylide complexes synthesized in our laboratory.^[21,30] For an example of a stable gold(III) sulfonium methylide complex see reference 31.
- [30] N. Kim, R. A. Widenhoefer, Angew. Chem. 2018, 130, 4812-4816; Angew. Chem. Int. Ed. 2018, 57, 4722-4726.

[31] J. P. Fackler, Jr., C. Paparizos, J. Am. Chem. Soc. 1977, 99, 2363-2364.

- [32] For additional examples of transition metal complexes containing unstabilized sulfonium ylides as ligands see: a) L. Weber, Angew. Chem. 1983, 95, 539-551; Angew. Chem. Int. Ed. Engl. 1983, 22, 516-528; b)
 F. B. McCormick, W. B. Gleason, X. Zhao, P. C. Heah, J. A. Gladysz, Organometallics 1986, 5, 1778-1785; c) H. Fischer, J. Schmid S. Zeuner Chem. Ber. 1987, 120, 583-587; d) P. Leoni, F. Marchetti, M. Paoletti, Organometallics 1997, 16, 2146-2151; e) P. Bravo, G. Fronza, C. Ticozzi, G. Gaudiano, J. Organomet. Chem. 1974, 74, 143-154; f) T. Collins, W. Roper, J. C. S. Chem. Comm. 1977, 901-910; g) J. G. Davidson, E. K. Barefleld, D. G. Van Derveer, Organometallics 1985, 4, 1178-1184.
- [33] a) D. Darwish, S. H. Hui, R. Tomilson, J. Am. Chem. Soc. 1968, 90, 5631-5632; b) D. Darwish, C. E. Scott, Can. J. Chem. 1973, 51, 3647-3648; c) K. R. Brower, T.-l. Wu, J. Am. Chem. Soc. 1970, 92, 5303-5305; d) R. Scartazeini, K. Mislow, Tetrahedron Lett. 1967, 2719-2722; e) K. K. Andersen, M. Cinquini, N. E. Papanikolaou J. Org. Chem. 1970, 85, 706-710; f) A. Garbesi, N. Corsia, A. Fava, Helv. Chim. Acta 1970, 53, 1499-1502; g) M. Oki, Y. Yamada, S. Murata, Bull. Chem. Soc. Jpn. 1988, 61, 707-714; h) T. K. Green, J. R. Whetstine, E.-J.-R. Son, Tetrahedron: Asymmetry 1997, 8, 3175-3181.
- [34] Analogous oxygen atom transfer to gold carbene moieties have been observed under catalytic conditions^[35] and from well-defined gold carbene complexes^[36] including B^[21] and C. ^[22]
- [35] a) C. A. Witham, P. Mauleón, N. D. Shapiro, B. D. Sherry, F. D. Toste, J. Am. Chem. Soc. 2007, 129, 5838–5839; b) J. T. Bauer, M. S. Hadfield,

COMMUNICATION

A.-L. Lee, *Chem. Commun.* 2008, 6405–6407; c) M. S. Hadfield, J. T. Bauer, P. E. Glen, A.-L. Lee, *Org. Biomol. Chem.* 2010, *8*, 4090–4095.
[36] R. J. Harris, R. A. Widenhoefer, *Angew. Chem.* 2014, *126*, 9523-9525; *Angew. Chem. Int. Ed.* 2014, *53*, 9369-9371.

[37] This trend mirrors the relative reactivities of the corresponding iron sulfonium methylide complexes: E. K. Barefield, P. McCarten, M. C. Hillhouse, *Organometallics* **1985**, *4*, 1682-1684.

Accepted Manuscript

COMMUNICATION

Entry for the Table of Contents (Please choose one layout)

COMMUNICATION

Ar Ph

Gold sulfonium benzylide complexes undergo facile and efficient benzylidene transfer to alkenes via the intermediacy of a cationic gold benzylidene complex.

Robert G. Carden and Ross A. Widenhoefer*



Gold Sulfonium Benzylide Complexes Undergo Efficient Benzylidene Transfer to Alkenes