

A remarkably stable copper(I) ethylene complex: synthesis, spectroscopy and structure

Bernd F. Straub, Frank Eisenträger and Peter Hofmann*

Organisch-Chemisches Institut der Universität Heidelberg, Im Neuenheimer Feld 270, D-69120 Heidelberg, Germany. E-mail: ph@phindigo.oci.uni-heidelberg.de

Received (in Basel, Switzerland) 29th September 1999, Accepted 9th November 1999

The novel copper(I) ethylene complex $[\text{Bu}^t_2\text{P}(\text{NSiMe}_3)_2-\kappa^2\text{N}]\text{Cu}(\eta^2\text{-C}_2\text{H}_4)$ and its norbornene analogue have been synthesized and characterized and their solid state structures determined.

Copper(I) olefin complexes play an important role in biochemistry and modern organic chemistry. Copper-catalyzed addition of carbanions to α,β -unsaturated carbonyls and copper-catalyzed cyclopropanation of alkenes by α -carbonyl diazoalkanes involve copper olefin complexes as catalytically active species or resting states.^{1–4} Ethylene, the smallest plant hormone, binds tightly to the copper receptor site ETR 1,^{5,6} participating in a variety of stress responses and developmental processes.⁷ Thompson *et al.* synthesized and characterized the first stable copper(I) ethylene complex, $[\text{HB}(3,5\text{-Me}_2\text{-}1,2\text{-HC}_3\text{N}_2)_3\text{-}\kappa^3\text{N}]\text{Cu}(\eta^2\text{-C}_2\text{H}_4)$, in 1983.⁸ Nevertheless, the stability of the ethylene/receptor complex is much higher than that of any reported artificial copper ethylene complex.^{5,6,9}

Owing to the notorious lability of ethylene coordination in known copper(I) complexes, only one extrapolated ¹³C NMR chemical shift relative to free ethylene ($\Delta\delta = 31.1$)¹⁰ and no ¹J_{CH} coupling constant for copper(I) coordinated ethylene could be determined. Obviously, such data are highly relevant for an understanding of the copper(I)–ethylene bond.

Here, we report a remarkably stable copper(I) ethylene complex **1**, which is easily accessible by utilizing a tailor-made sterically demanding and electron-rich iminophosphanamide, first described by Scherer and Schieder more than 30 years ago,¹¹ as a co-ligand, generated by *in situ* deprotonation (Scheme 1).¹²

The stability of **1** in the solid state and in solution is unprecedented. Colorless crystals of **1** can be dried at 10^{-3} mbar at ambient temperature without decomposition. Complex **1** melts at 108 °C to a colorless liquid which only slowly decomposes at that temperature. Protonated **1** could be observed in the gas phase (CI + MS, 2-methylpropane). No free ethylene is detected by ¹H NMR spectroscopy upon dissolving **1** in C₆D₆, CDCl₃ or toluene-*d*₈ in an argon atmosphere. The presence of additional ethylene leads to separate broad signals of free and of coordinated C₂H₄, indicating associative olefin exchange.

The C–C distance of ethylene in **1** is 1.362(6) Å, which does not differ significantly from the corresponding distance in free ethylene [1.3369(16) Å].¹³ The sp²-character of the C₂H₄ carbons is in accordance with a ¹J_{CH} coupling constant of 158 Hz, which is even larger than in free ethylene (156 Hz).¹⁴

The ¹H NMR resonance of the ethylene protons at δ 3.48 (C₆D₆, 298 K; for free ethylene δ 5.24 under the same

conditions) is shifted by 0.5 ppm to higher field than the most upfield copper(I) ethylene signal (δ 4.0) reported so far.¹⁵ The ¹³C NMR signal is detected at δ 73.0 with an upfield shift of 50 ppm compared to free ethylene. Lower temperatures and aromatic solvents lead to an upfield shift of the ethylene protons (δ 3.35, toluene-*d*₈, 233 K; δ 3.63, CDCl₃, 223 K).

The norbornene complex $[\text{Bu}^t_2\text{P}(\text{NSiMe}_3)_2-\kappa^2\text{N}]\text{Cu}(\eta^2\text{-C}_7\text{H}_{10})$ **2** could be obtained in a similar way.[†] Its solid state geometry, structurally analogous to **1**, is shown in Fig. 2.

Unlike **1**, complex **2** allows determination of the rotational barrier of the olefin ligand as $\Delta G^\ddagger = 41.5 \pm 2.0$ kJ mol^{−1} (VT ¹³C {¹H}NMR) through coalescence of the signals of both the diastereotopic C(CH₃)₃ and C(CH₃)₃ carbons.

The high basicity of the anionic iminophosphanamide σ - and π -donor ligand and the small bite angle N–Cu–N of 77.80(9)° in the four-membered neutral chelate ring system seem to be responsible for the unprecedented stability and unusual spectral properties of **1**. The high HOMO and the low LUMO energy of a d¹⁰-ML₂ fragment with a small bite angle¹⁶ lead to increased π -back bonding towards the olefin and a strong olefin-to-metal dative bond, thus causing an increased ethylene ligand dissociation energy compared to other neutral and, even more so, cationic copper(I) units. Formation of stable dinuclear olefin-free copper(I) complexes with nearly linear N–Cu–N fragments and concomitant weak d¹⁰–d¹⁰ interaction as known from other systems⁸ is hampered by the sterically demanding iminophosphanamide ligand system with its SiMe₃ groups bent towards the olefin side (P–N–Si \approx 150°).

Complex **1** catalyzes cyclopropanation of styrene with α -carbonyl diazoalkanes at room temperature. The extremely high

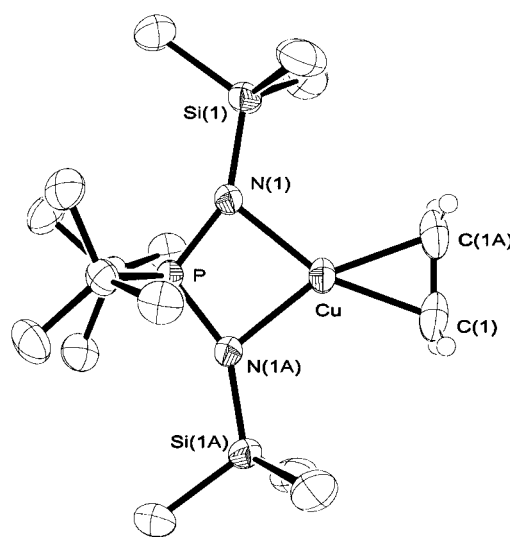
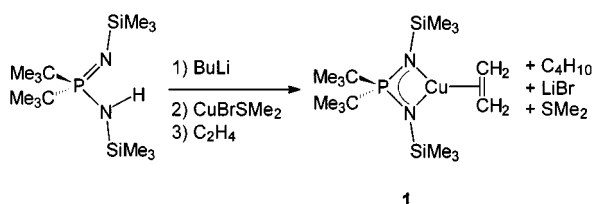


Fig. 1 ORTEP diagram of the solid state structure of **1**.[‡] Hydrogen atoms of the methyl groups are omitted for clarity. Selected bond lengths (Å) and angles (°): P–N(1) 1.6013(16), Si(1)–N(1) 1.7055(17), Cu–N(1) 2.0140(16), Cu–C(1) 1.987(3), C(1)–C(1A) 1.362(6); P–N(1)–Si(1) 151.35(11), N(1)–P–N(1A) 104.33(12), P–N(1)–Cu 88.93(8), N(1)–Cu–N(1A) 77.80(9).



Scheme 1 Synthesis of **1**[†]

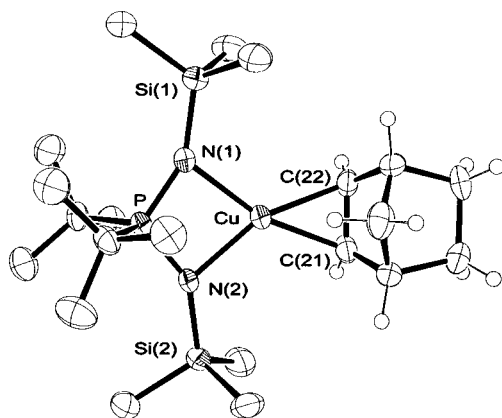


Fig. 2 ORTEP diagram of the solid state structure of **2**.[†] Hydrogen atoms of the methyl groups are omitted for clarity. Average values of the three independent molecules with assumed C_s -symmetry in the asymmetric unit (standard deviation) are quoted. Selected bond lengths (Å) and angles (°): P–N(1) 1.599(5), Si(1)–N(1) 1.704(9), Cu–N(1) 2.031(7), Cu–C(2) 2.026(23), C(21)–C(22) 1.377(20); P–N(1)–Si(1) 149.4(1.5), N(1)–P–N(2) 104.7(3), P–N(1)–Cu 89.0(4), N(1)–Cu–N(2) 77.1(1).

solubility of **1** even in alkanes and its NMR active nuclei (^1H , ^{13}C , ^{29}Si and especially ^{31}P) now offer an ideal chance to investigate mechanistic aspects of organometallic copper(I) chemistry, especially of copper(I)-catalyzed cyclopropanation.

Support of this work by a PhD stipend of the Fonds der Chemischen Industrie for B. F. S. is gratefully acknowledged.

Notes and references

[†] *Synthesis of 1*: 13 ml 1.6 M Bu^nLi in hexane (21 mmol) were added to 5.78 g (18.0 mmol) $\text{Bu}^n_2\text{P}[\text{N}(\text{SiMe}_3)]\text{NH}(\text{SiMe}_3)^{11}$ in 20 ml of hexane under an argon atmosphere, and the solution was refluxed for 1 min,¹² then added to a suspension of 4.97 g (24 mmol) CuBrSm_2 in 20 ml of hexane at -78°C and stirred while warming to ambient temperature. Ethylene (99.7%) was bubbled into the black suspension for 2 min. The suspension was filtered through Celite under an ethylene atmosphere. From the slightly yellow solution crude **1** was crystallized at -78°C . Recrystallization yielded 3.21 g (7.8 mmol, 43.4%) of **1**; crystallization from the collected organic phases yielded another batch of 2.80 g (6.6 mmol, 36.7%) (purity $>97\%$ **1**). Colorless crystals, mp 108°C (slow gas evolution and decomp. of the colorless liquid); IR (KBr/ cm^{-1}): ν 1516 (C=C); ^1H NMR (298 K, C_6D_6 , 300.13 MHz): δ 3.48 (s + sat, $^1J_{\text{CH}}$ 158 Hz, CH_2 ; 4H), 1.21 [d + sat, $^3J_{\text{PH}}$ 14 Hz, $^1J_{\text{CH}}$ 126.5 Hz, $\text{C}(\text{CH}_3)_3$; 18H], 0.21 [s + sat, $^1J_{\text{CH}}$ 117 Hz, $\text{Si}(\text{CH}_3)_3$; 18H]; ^{13}C NMR (gated decoupling) (298 K, C_6D_6 , 75.47 MHz): δ 73.0 (t, $^1J_{\text{CH}}$ 158 Hz, $^2J_{\text{CH}}$ 4 Hz, CH_2), 37.2 [dd, $^1J_{\text{CP}}$ 64 Hz, $^2J_{\text{CH}}$ 4 Hz, $\text{C}(\text{CH}_3)_3$], 28.2 [q sept d, $^1J_{\text{CH}}$ 126.5 Hz, $^3J_{\text{CH}}$ 5.1 Hz, $^2J_{\text{CP}}$ 2.6 Hz, $\text{C}(\text{CH}_3)_3$], 5.6 [q' oct' + sat, $^1J_{\text{CSi}}$ 57 Hz, $^3J_{\text{CH}} \approx 2 \text{ Hz} \approx ^3J_{\text{PC}}$, $\text{Si}(\text{CH}_3)_3$]; $^{29}\text{Si}\{^1\text{H}\}$ NMR (DEPT) (298 K, C_6D_6 , 59.63 MHz): δ -14.2 (d + sat, $^2J_{\text{PSi}}$ 14.8 Hz, $^1J_{\text{CSi}}$ 57 Hz); $^{31}\text{P}\{^1\text{H}\}$ NMR (298 K, C_6D_6 , 121.50 MHz): δ 61.2 (s + sat, $^1J_{\text{CP}}$ 64 Hz, $^2J_{\text{PSi}}$ 14.8 Hz); CI-MS (%): m/z 764.3 (L_2Cu_2^+) (77), 687.3 ($\text{L}_2\text{Cu} - \text{CH}_3 + \text{H}^+$) (57), 629.3 ($\text{L}_2\text{Cu}^+ - \text{CH}_3 - \text{C}_4\text{H}_9$) (75.1), 411.2 ($\text{M} + \text{H}^+$) (2.1), 395.2 ($\text{M}^+ - \text{CH}_3$) (16), 383.2 ($\text{LCu} + \text{H}^+$) (35), 321.2 ($\text{LH} + \text{H}^+$) (100); elemental analysis for $\text{C}_{16}\text{H}_{40}\text{N}_2\text{CuPSi}_2$; calc: C, 46.74; H, 9.80; N, 6.81; P, 7.53; found: C, 46.38; H 10.04; N, 6.89; P, 7.24%.

Spectroscopy of 2: ^1H NMR (298 K, C_6D_6 , 300.13 MHz): δ 4.16 (s + sat, $^1J_{\text{CH}}$ 164 Hz, =CH; 2H), 2.96 (br. s, CH, 2H), 1.38 (dt, $^2J_{\text{HH}}$ 9.5 Hz, $^3J_{\text{HH}}$ 1.8 Hz, *syn*-CHH; 1H), 1.24 [d, $^3J_{\text{PH}}$ 14 Hz, $\text{C}(\text{CH}_3)_3$; 18H], 1.22 (dd, J_{HH} 2 and 13 Hz, *exo*-CHH; 2H), 0.74 (dd, J_{HH} 2.3 and 7.7 Hz, *endo*-CHH; 2H), 0.68 (dt, $^2J_{\text{HH}}$ 9.5 Hz, $^3J_{\text{HH}}$ 1.4 Hz, *anti*-CHH; 1H), 0.36 [s, $\text{Si}(\text{CH}_3)_3$; 18H];

$^{13}\text{C}\{^1\text{H}\}$ NMR (298 K, C_6D_6 , 75.47 MHz): δ 93.1 (s, =CH), 43.7 (s, CH), 42.9 (s, CH_2), 37.7 [d, $^1J_{\text{CP}}$ 64 Hz, $\text{C}(\text{CH}_3)_3$], 28.2 [d, $^2J_{\text{CP}}$ 2.4 Hz, $\text{C}(\text{CH}_3)_3$], 25.5 (s, CH_2CH_2), 5.8 [d, $^3J_{\text{PC}}$ 2 Hz, $\text{Si}(\text{CH}_3)_3$]; $^{29}\text{Si}\{^1\text{H}\}$ NMR (DEPT) (298 K, C_6D_6 , 59.63 MHz): δ -14.8 (d, $^2J_{\text{PSi}}$ 15 Hz); $^{31}\text{P}\{^1\text{H}\}$ NMR (298 K, C_6D_6 , 121.50 MHz): δ 60.1 (s + sat, $^1J_{\text{CP}}$ 65 Hz, $^2J_{\text{PSi}}$ 15 Hz); VT $^{13}\text{C}\{^1\text{H}\}$ NMR (toluene- d_8 , 75.47 MHz): $\text{C}(\text{CH}_3)_3$, $T_c = 197.5 \pm 4.0 \text{ K}$, $k_c = 42 \text{ Hz}$; $\text{C}(\text{CH}_3)_3$, $T_c = 200.5 \pm 4.0 \text{ K}$, $k_c = 68 \text{ Hz}$; temperature calibration by external MeOH. Addition of norbornene has no effect on the coalescence temperatures, ruling out associative mechanisms for the observed degenerate rearrangement.

[†] Data were collected on a Bruker SMART CCD instrument and the structure solutions were performed using SHELXTL V5.10,¹⁷ respectively. Intensities were corrected for Lorentz and polarization effects, an empirical absorption correction was applied using SADABS¹⁸ based on the Laue symmetry of the reciprocal space.

Crystal data of 1: $\text{C}_{16}\text{H}_{40}\text{CuN}_2\text{PSi}_2$, $M = 411.19$, monoclinic, space group $C2/c$, $a = 11.6400(2)$, $b = 15.9236(3)$, $c = 12.6352(2)$ Å, $\beta = 95.949(1)^\circ$, $V = 2329.33(7)$ Å³, $Z = 4$, half a molecule per asymmetric unit, $\mu = 1.11 \text{ mm}^{-1}$, 8508 reflections measured at -73°C , 2002 independent reflections ($R_{\text{int}} = 0.0239$), 1679 reflections observed [$I > 2\sigma(I)$], final agreement factors for 115 parameters: $R1 = 0.027$, $wR2 = 0.064$ (observed reflections) and $R1 = 0.037$, $wR2 = 0.068$ (all data).

2: $\text{C}_{21}\text{H}_{46}\text{CuN}_2\text{PSi}_2$, $M = 477.29$, monoclinic, space group $P2_1/n$, $a = 10.2429(2)$, $b = 42.4725(1)$, $c = 18.6134(4)$ Å, $\beta = 98.442(1)^\circ$, $V = 8009.9(3)$ Å³, $Z = 12$, three independent molecules per asymmetric unit, $\mu = 0.98 \text{ mm}^{-1}$, 59684 reflections measured at -73°C , 13850 independent reflections ($R_{\text{int}} = 0.1098$), 7346 reflections observed [$I > 2\sigma(I)$], final agreement for 790 parameters: $R1 = 0.078$, $wR2 = 0.159$ (observed reflections), and $R1 = 0.167$, $wR2 = 0.195$ (all data).

CCDC 182/1478. See <http://www.rsc.org/suppdata/cc/1999/2507/> for crystallographic files in .cif format.

- G. Hallnemo, T. Olsson and C. Ullenius, *J. Organomet. Chem.*, 1985, **282**, 133.
- S. Mori and E. Nakamura, *Chem. Eur. J.*, 1999, **5**, 1534 and references therein.
- M. Mar Díaz-Requejo, M. C. Nicasio and P. J. Pérez, *Organometallics*, 1998, **17**, 3051.
- M. Mar Díaz-Requejo, T. Belderrain, M. C. Nicasio, F. Prieto and P. J. Pérez, *Organometallics*, 1999, **18**, 2601.
- G. E. Schaller and A. B. Bleecker, *Science*, 1995, **270**, 1809.
- F. I. Rodríguez, J. J. Esch, A. E. Hall, B. M. Binder, G. E. Schaller and A. B. Bleecker, *Science*, 1999, **283**, 996.
- J. R. Ecker, *Science*, 1995, **268**, 667 and references therein.
- J. S. Thompson, R. L. Harlow and J. F. Whitney, *J. Am. Chem. Soc.*, 1983, **105**, 3522.
- M. Munakata, S. Kitagawa, S. Kosome and A. Asahara, *Inorg. Chem.*, 1986, **25**, 2622.
- A. Borg, T. Lindblom and R. Vestin, *Acta. Chem. Scand., Ser. A*, 1975, **29**, 475.
- O. J. Scherer and G. Schieder, *Chem. Ber.*, 1968, **101**, 4184.
- W. Wolfsberger and W. Hager, *Z. Anorg. Allg. Chem.*, 1977, **433**, 247.
- L. S. Bartell, E. A. Roth, C. D. Hollowell, K. Kuchitsu and J. E. Young, Jr., *J. Chem. Phys.*, 1965, **42**, 2683.
- H. Friebolin, *Basic One- and Two-dimensional NMR spectroscopy*, VCH, Cambridge, 1992.
- W. Kläui, B. Lenders, B. Hessner and K. Evertz, *Organometallics*, 1988, **7**, 1357.
- P. Hofmann, H. HeiB and G. Müller, *Z. Naturforsch., Teil B*, 1987, **42**, 395.
- G. M. Sheldrick, Bruker Analytical X-Ray-Division, Madison, WI, 1997.
- G. M. Sheldrick, 1996, unpublished work, based on the method described in: R. H. Blessing, *Acta Crystallogr., Sect. A*, 1995, **51**, 33.

Communication 9/07928I