Mono- and Di-nuclear Platinum σ-Acetylide Complexes of Tetraethynylethene

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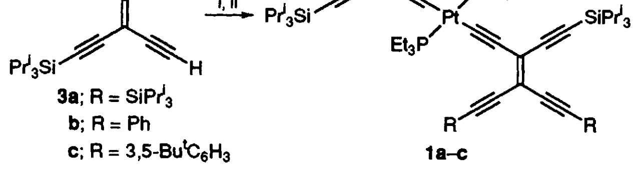
Syntheses and X-ray structural characterizations of two types of platinum σ-acetylide complexes in which the metals are bound to tetraethynylethene skeletons are reported; these complexes are closely related to the basic constituents of a metal-linked carbon network and are prepared to explore the feasibility of thermodynamically controlled metal-acetylenic self assembly.

Transition metal σ-acetylide complexes have recently emerged as promising building blocks in the design of materials with enhanced nonlinear optical behaviour.[1] This finding, in conjunction with our interest in acetylenic carbon networks,[2] has prompted us to explore the potential of tetraethynylethene[3] as an η^1-ligand of square-planar metal centres. Systems of this type are of fundamental importance in the assembly of acetylenic networks under thermodynamic control: judicious choice of metal and its ligands should allow to reversibly generate σ-bis(acetylide) substructures, and subsequent C–C bond formation *via* reductive elimination at the metal centres should generate the desired networks. We report here syntheses and structural characterizations of the platinum σ-acetylide complexes **1a–c** and **2** as the first steps towards this goal.

For the synthesis of **1a–c**, the mono-deprotected tetraethynylethenes **3a–c** were obtained as previously described (Scheme 1).[3b] They were derivatized by $\mathrm{Me_3SnNMe_2}$ to the corresponding trimethyltin acetylides which were then coupled to *trans*-$\mathrm{PtCl_2(PEt_3)_2}$ in the presence of CuI[4] to furnish **1a–c**† as yellow, crystalline solids.

Single crystals of **1b** suitable for X-ray diffraction studies‡ were grown from hexane solution (Fig. 1). A low-temperature structure analysis (85 K) confirmed the *trans*-arrangement of the two sets of ligands around the square-planar platinum core. The tetraethynylethene units in centrosymmetric **1b** are planar within ± 0.01 Å and coplanar to each other, indicating possible conjugation across the metal centre. Both, distal and proximal phenyl groups are turned out of the plane defined by the tetraethynylethene carbon-atoms by 72°, suggesting that their contribution to electronic delocalization is negligible in the solid state. The C(3)–C(2)–C(1)–Pt(1) subunit shows clear bond length alternation typical for single, triple, and again single bonds, thereby excluding cumulene-type substructures. Bond lengths and angles around the platinum core are all within the range typically found for related Pt-complexes.[5] The phosphine ligands are 1.42 Å above and below the tetraethynylethene plane. Severe disorder in the regions around the $\mathrm{SiPr^i_3}$, the $\mathrm{PEt_3}$, and the distal phenyl groups prevented further structural refinement beyond $R(F) = 0.045$.



3a; R = $\mathrm{SiPr^i_3}$
b; R = Ph
c; R = 3,5-$\mathrm{Bu^tC_6H_3}$

1a–c

Scheme 1 *Reagents and conditions*: i, $\mathrm{Me_3SnNMe_2}$, $\mathrm{Et_2O}$, 20 °C; ii, *trans*-$\mathrm{PtCl_2(PEt_3)_2}$, CuI, PhMe, 20 °C (a: 70%, b: 52%, c: 24%)

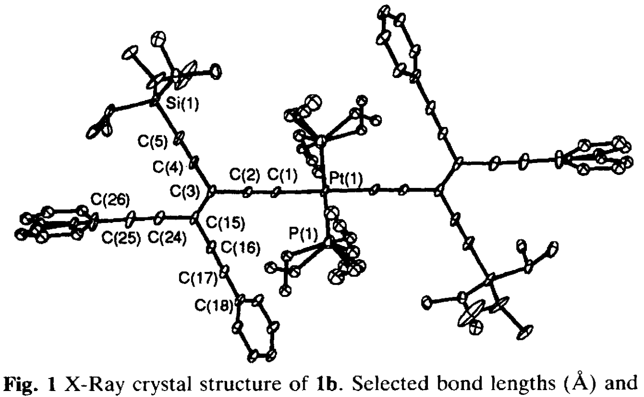
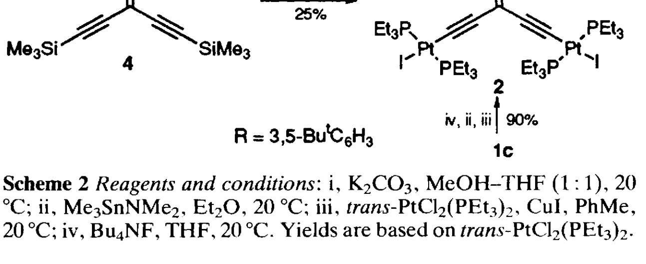


Fig. 1 X-Ray crystal structure of **1b**. Selected bond lengths (Å) and angles (°): Pt(1)–C(1) 1.998(7), C(1)–C(2) 1.170(9), C(2)–C(3) 1.457(9), C(3)–C(4) 1.438(10), C(3)–C(15) 1.363(11), P(1)–Pt(1)–C(1) 93.8(2), Pt(1)–C(1)–C(2) 177.7(7), C(1)–C(2)–C(3) 178.5(6). Owing to static disorder, the listed values are much less reliable than the esds (in parentheses) might suggest.

Initial attempts to obtain the dinuclear species **2** in which two metals are attached to one set of the geminal ethynyl groups of the tetraethynylethene skeleton started from geminally protected **4**,[6] but were hampered by the formation of untractable polymeric material leading to **2** in only fair yield (Scheme 2). Rather unexpectedly, however, **1c** turned out to be a suitable starting material for **2**. Reaction of the $\mathrm{Me_3Sn}$-derivative of **1c**, prepared *in situ* by protodesilylation and treatment with $\mathrm{Me_3SnNMe_2}$, with *trans*-$\mathrm{PtCl_2(PEt_3)_2}$ in the presence of excess CuI furnished **2**† as yellow crystals in 90% yield. While mechanistic details for this transformation still need to be elucidated, it is evident that one platinum–carbon bond of **1c** is cleaved in the course of the reaction. Further exploration of this pathway therefore may ultimately lead to a thermodynamically controlled method of $\mathrm{C_{sp}}$–$\mathrm{C_{sp}}$ bond formation by reductive elimination of ethynyl fragments from transition metal centres.[7]

Crystals of **2** suitable for X-ray diffraction studies‡ were grown by slow evaporation of a benzene solution (Fig. 2) and structural analysis at 293 K revealed that the compound crystallizes in the monoclinic space group *C*2/*m*, rather surprising for such a complex molecule. The crystallographic mirror plane contains, in addition to the tetraethynylethene skeleton and the two platinum atoms, the two phosphorus atoms at Pt(1) and the phenyl ring *trans* to it.

The phosphines at Pt(2), on the other hand, are located above and below the plane, as is the remaining aryl substituent. This alternating pattern of planar and perpendicular substructures is clearly dictated by the steric demand of the bulky *tert*-butyl groups and the phosphine ligands. Such steric crowding is also visible in comparing the bond angles around the two platinum centres: While those of Pt(1) reflect an almost ideal square-planar environment, the angles C(10)–



4

2

1c

R = 3,5-$\mathrm{Bu^tC_6H_3}$

Scheme 2 *Reagents and conditions*: i, $\mathrm{K_2CO_3}$, MeOH–THF (1 : 1), 20 °C; ii, $\mathrm{Me_3SnNMe_2}$, $\mathrm{Et_2O}$, 20 °C; iii, *trans*-$\mathrm{PtCl_2(PEt_3)_2}$, CuI, PhMe, 20 °C; iv, $\mathrm{Bu_4NF}$, THF, 20 °C. Yields are based on *trans*-$\mathrm{PtCl_2(PEt_3)_2}$.

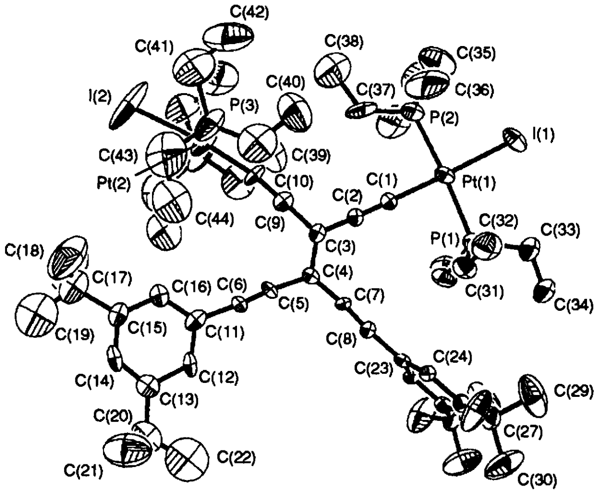


Fig. 2 X-Ray crystal structure of **2**. Selected bond lengths (Å) and angles (°): Pt(1)–C(1) 2.054(24), Pt(1)–I(1) 2.651(3), C(1)–C(2) 1.212(35), Pt(2)–C(10) 1.888(28), Pt(2)–I(2) 2.645(6), C(9)–C(10) 1.227(41), C(1)–Pt(1)–I(1) 178.5(7), C(2)–C(1)–Pt(1) 179.5(17), C(10)–Pt(2)–I(2) 173.2(8), C(9)–C(10)–Pt(2) 170.7(22).

Pt(2)–I(2) [173.9(8)°] and C(9)–C(10)–Pt(2) [170.7(22)°] deviate significantly from linearity. In addition to fulfilling such packing requirements, the conformation of **2** in the crystal is ideally suited for efficient electron delocalization across the entire molecule from Pt(1) to C(14), and also allows interactions between the π system of the perpendicular phenyl group and adjacent in-plane acetylenic orbitals. Disorder in the region around Pt(2) unfortunately led to large standard deviations in the determined bond lengths, thereby preventing a meaningful discussion of this parameter.

The extent of electronic delocalization in the novel platinum complexes can be assessed by inspection of their electronic absorption spectra. On the basis of spectral data for relevant σ-bis(acetylide) complexes,[5e,8] the low-energy absorptions of **1a–c** and **2** can be assigned as metal-to-ligand charge-transfer bands which, in case of the former set of molecules, may result in transmission of electron density across the metal centre.[9] While the mononuclear species with aryl substituents on the tetraethynylethene moiety exhibit λ_{max} values of 429 (**1b**) and 432 nm (**1c**), respectively, the hexa(triisopropylsilyl)-derivative **1a** has an end-absorption of only 388 nm. A comparison with UV–VIS data for closely related mono- and di-meric tetraethynylethene derivatives suggests that in **1b** the electronic delocalization is indeed operational throughout the entire molecule.[10] The extinction coefficient of **1b** at λ_{max} (ε 104 700) is significantly larger than the corresponding value of **1c** (ε 61 700), emphasizing the importance of coplanarity of the aryl-subunits with the tetraethynylethene backbone for high-intensity absorptions. The UV–VIS spectrum of **2** shows the lowest-energy absorption at a λ_{max} of 397 nm with a greatly reduced extinction coefficient of ε 10 700.

Support from the Swiss National Science Foundation is gratefully acknowledged.

Received, 20th April 1994; Com. 4/02356K

Footnotes

† All new compounds were fully characterized by their spectroscopic data and gave satisfactory elemental analyses.

‡ *Crystal data* for **1b** at 85 K: $C_{74}H_{92}P_2PtSi_2$, M = 1294.7, triclinic space group $P\bar{1}$ (no. 2), Z = 1, D_c = 1.25 g cm^{-3}, a = 9.108(2), b = 12.823(5), c = 15.535(4) Å, α = 95.54(3)°, β = 99.22(2)°, γ = 103.31(2)°, V = 1725.8(9) Å^3. X-Ray data were measured on an Enraf-Nonius CAD 4 diffractometer with Mo-Kα radiation using ω–θ scans. The structure was solved by the Patterson method and refined by full-matrix least-squares analysis. The structure is highly disordered. The static disorder could be resolved only for a few carbon atoms (see Fig. 1); they were refined isotropically with a population parameter of 0.5. All other heavy atoms were refined anisotropically with a population parameter of 1.0 (H-atoms omitted). Final $R(F)$ = 0.045, $wR(F)$ = 0.046 for 349 variables and 5125 observed reflections with $I_o > 3\sigma(I_o)$ and θ < 25°.

For **2** at 293 K: $C_{62}H_{102}I_2P_4Pt_2$, M = 1615.3, monoclinic space group $C2/m$, Z = 4, D_c = 1.500 g cm^{-3}, a = 28.519(9), b = 13.779(5), c = 18.331(8) Å, β = 96.80°, V = 7153(5) Å^3. X-Ray data were measured on a Syntex P21 diffractometer with Mo-Kα radiation using ω scans. The structure was solved by the Patterson method and refined anisotropically to give $R(F)$ = 0.065, $wR(F)$ = 0.062 for 364 variables and 2377 observed reflections with $F > 6.0\ \sigma(F)$ and $3.0 < 2\theta < 40°$.

Atomic coordinates, bond lengths and angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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