Linear and Cyclic Platinum σ-Acetylide Complexes of Tetraethynylethene

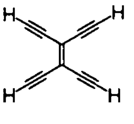
Rüdiger Faust, François Diederich,* Volker Gramlich, and Paul Seiler

Abstract: The syntheses of the first organometallic mono- and dinuclear platinum complexes bearing the tetraethynylethene unit as an η^1-ligand are reported. Structural characterization of two of the *trans* σ-bis(acetylide) derivatives by X-ray crystallography reveals coplanarity of the acetylenic π-ligands and indicates possible electronic delocalization across the metal center. This notion is further supported by comparing the electronic absorption spectra of the platinum-containing compounds with those of related tetraethynylethene derivatives without metals. The solid-state structure of a dinuclear complex with two iodoplatinum fragments attached to one set of geminal acetylenes of tetraethynylethene was also investigated by X-ray diffraction. Hay coupling of a mononuclear species leads to the incorporation of the σ-bis(acetylide) moiety into a diplatinated metallacycle. This macrocyclic compound represents a novel structural motif in the design of a transition metal linked carbon network based on tetraethynylethene.

Keywords
alkyne complexes · carbon networks · macrocycles · platinum compounds · tetraethynylethene

Introduction

The chemistry of transition metal σ-acetylide complexes[1] is dominated by a combination of two factors: On the one hand, there is electronic interaction between metal fragment and alkynyl ligand that gives rise to such diverse phenomena as, for example, stabilized vinylidene intermediates[2] and electronic delocalization across the metal center.[3] While the former characteristic is relevant for specific C–C bond forming processes,[4] the latter may dramatically influence the electrooptical properties of metal acetylenic systems, as was recently suggested by the finding that organometallic rigid-rod polymers with bridging polyyne units exhibit enhanced nonlinear optical behavior.[5] On the other hand, the metal fragment simply serves as a spacer[6] that effectively prevents proximal groups from interfering with one another in both the solid state and in solution.



1

We were intrigued by the possibility of imparting some of the above properties on tetraethynylethene (1),[7] a cross-conjugated building block that has been suggested as the repeat unit of a variety of planar carbon networks.[8] An exciting aspect and a long-term goal of this research is the development of a transition metal linked carbon network (Fig. 1), a design that offers several incentives: The metal-template approach to an all-carbon network is principally superior to conventional acetylene polymerizations through oxidative coupling, where errors occurring in the course of irreversible $C_{sp}-C_{sp}$ bond formation lead to greatly reduced crystallinity. In contrast, judicious choice of transition metal and ligands should allow the reversible formation of σ-bis(acetylide) substructures leading to the assembly of a metal-acetylenic network under thermodynamic control with error checking. In a second step, the all-carbon network could then be generated by reductive elimination[9] at the metal centers. Furthermore, while the ligands serve as spacers between potentially reactive carbon layers, the metal-centered d orbitals may guarantee some electronic delocalization within the plane.

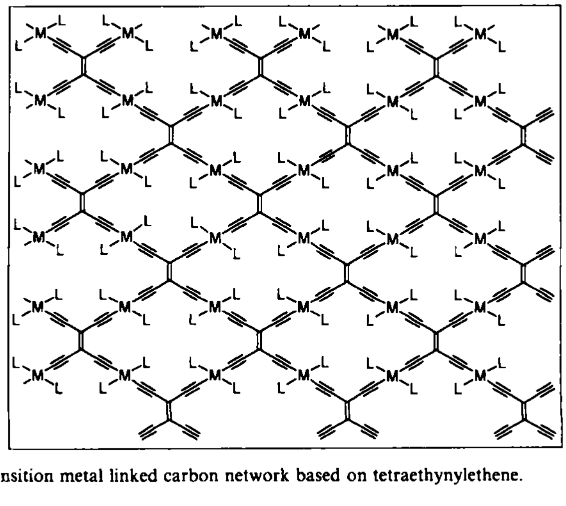


Fig. 1. Transition metal linked carbon network based on tetraethynylethene.

---

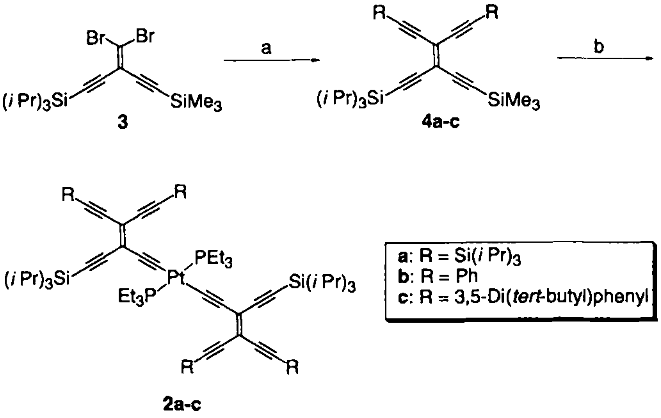
[*] Prof. Dr. F. Diederich, Dr. R. Faust,[+] P. Seiler
Laboratorium für Organische Chemie, ETH Zentrum
Universitätstr. 16, CH-8092 Zürich (Switzerland)
Telefax: Int. code + (1)632-1109

[+] New address: Pharmazeutisch-Chemisches Institut der Universität
Im Neuenheimer Feld 364, D-69120 Heidelberg (Germany)
Dr. V. Gramlich
Institut für Kristallographie und Petrographie
Sonneggstr. 5, CH-8092 Zürich (Switzerland)

In an effort to explore the synthetic and structural feasibility of our approach, linear and cyclic architectures involving tetraethynylethene and *trans*-bis(triethylphosphine)platinum fragments have been explored and full details of their preparation, structural characterization, and their optical properties are delineated below.[10]

Results and Discussion

The syntheses of the mononuclear platinum complexes **2a**–**c** (Scheme 1) is based on methodology developed previously[7b,g] for the construction of oligomeric derivatives of tetraethynylethene. Thus, palladium-mediated alkynylation of dibromoolefin **3** led to the differentially bis(silyl)-protected tetraethynylethenes **4a**–**c**. Regiospecific protodesilylation with K_2CO_3 in MeOH/THF permitted the removal of the trimethylsilyl groups and furnished the corresponding monodeprotected alkynes that were used as dilute solutions without isolation. While it is possible to convert these sensitive compounds to their trimethyltin derivatives by deprotonation with lithium diisopropylamine (THF, −78 °C) followed by quenching with Me_3SnCl, the method developed by Lappert and Jones[11] for the deprotrimethylstannylation of terminal acetylenes does not require tedious workup and was found to be superior in effecting this transformation. Hence, treatment of the monodeprotected tetraethynylethenes with Me_3SnNMe_2 in diethyl ether at room temperature and subsequent copper(I)-mediated coupling to *trans*-$[PtCl_2(PEt_3)_2]$ in toluene[12] furnished **2a**–**c** as yellow, crystalline solids that are stable to the atmosphere over periods of months and have surprisingly high melting points of between 169 (**2b**) and 276 °C (**2a**).



Scheme 1. a: R-C≡C-H, $[PdCl_2(PPh_3)_2]$, $n\mathrm{BuNH_2}$, CuI, benzene, 20 °C (**4a**: 27%, **4b**: 50%, **4c**: 32%). b: 1) K_2CO_3, MeOH/THF (1:1), 20 °C (**a**–**c**: 98%); 2) Me_3SnNMe_2, Et_2O, 20 °C; 3) *trans*-$[PtCl_2(PEt_3)_2]$, CuI, PhMe, 20 °C (**2a**: 70%, **2b**: 51%, **2c**: 56%).

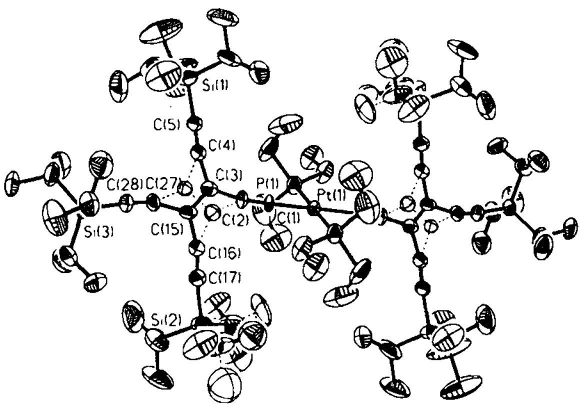


Fig. 2. X-ray crystal structure of **2a**. Selected bond lengths (Å) and angles (°): Pt(1)–C(1) 2.000(7), C(1)–C(2) 1.161(10), C(2)–C(3) 1.490(12), C(3)–C(15) 1.298(13), P(1)-Pt(1)-C(1) 88.0(2), Pt(1)-C(1)-C(2) 177.9(6), C(3)-C(4)-C(5) 167.5, C(15)-C(27)-C(28) 164.5(9).

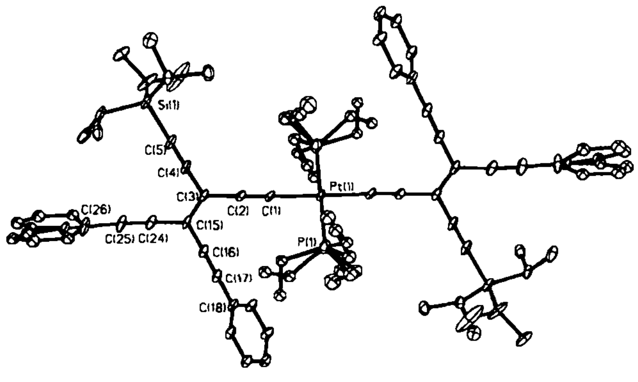
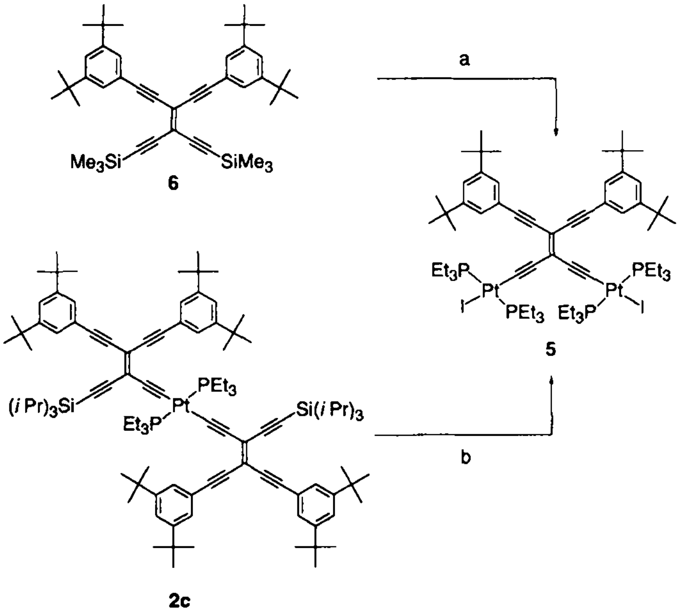


Fig. 3. X-ray crystal structure of **2b**. Selected bond lengths (Å) and angles (°): Pt(1)–C(1) 1.998(7), C(1)–C(2) 1.170(9), C(2)–C(3) 1.457(9), C(3)–C(4) 1.438(10), C(3)–C(15) 1.363(11), P(1)-Pt(1)-C(1) 93.8(2), Pt(1)-C(1)-C(2) 177.7(7). Owing to static disorder, the listed values are much less reliable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

The solid state structures of **2a** and **2b**[10] were investigated by crystallographic methods (Figs. 2 and 3). Both compounds crystallize in the centrosymmetric space group $P\bar{1}$ with platinum in the center of inversion and show the expected *trans*-arrangement of the ligands in an almost square-planar coordination sphere around the metal. Interestingly, one quarter of the molecules present in the crystal of **2a** adopts a conformation that is rotated by 180° about the Pt(1)–C(1) axis (Fig. 2, dashed structure) with an almost perfect superposition of the triple bonds. The discussion of the structural properties of **2a**, however, will focus on the dominant conformer. The great steric congestion in hexakis(triisopropylsilyl)-substituted **2a** forces the phosphine ligands to be located 2.02 Å above and below the plane defined by the two tetraethynylethene backbones, whereas the corresponding value for less encumbered **2b** is only 1.42 Å. Bond lengths and angles around the respective platinum cores are all within the range typically found for related *trans*-bis(acetylide)–Pt complexes.[13] The more spacious platinum environment in **2b** leads to greater rotational freedom of the phosphine ethyl chains and results in severe disorder in this region of the molecule; disorder is also observed in the distal phenyl and the triisopropylsilyl groups (Fig. 3). The tetraethynylethene substructures in both species are perfectly planar to within ±0.03 Å in **2a** and ±0.01 Å in **2b** and, owing to their centrosymmetric nature, are coplanar to each other; this indicates possible electronic delocalization across the metal center. This notion is further supported by inspection of their corresponding UV/Vis spectra (vide infra). Despite the fact that distal and proximal phenyl groups in **2b** are twisted out of the tetraethynylethene plane by 72°, the electronic delocalization between the phenyl ring and the adjacent cross-conjugated π-system is noticeable in the relatively long ethene bond [C(3)–C(15) = 1.363(11) Å] compared to that in **2a** [1.298(13) Å], where the lack of such interactions imparts more double-bond character onto C(3)–C(15). The steric bulk of six triisopropylsilyl groups in **2a** provokes severe bending of the triple bonds thereby enforcing C≡C–C angles as low as 164.5(9)° [C(15)-C(27)-C(28)]. Such distorted bond angles have been observed previously along the cyclic perimeter of a highly strained [12]annulene structure derived from tetraethynylethene,[7c] but the values found in acyclic **2a** seem to be remarkable.[14]

Having demonstrated the potential of the tetraethynylethene moiety to serve as an η^1-ligand in organometallic complexes, an obvious step towards the construction of the transition metal linked carbon network depicted in Figure 1 was the attachment of more than one metal fragment to the cross-conjugated carbon backbone. A promising candidate in these exploratory studies was the dinuclear species **5** (Scheme 2) with platinum centers connected to one set of geminal ethynyl groups. Initial attempts to synthesize **5** started from the geminally silyl-protected tetraethynylethene derivative **6**. Protodesilylation, conversion of the free acetylene to the corresponding Me$_3$Sn derivative, and subsequent coupling to *trans*-[PtCl$_2$(PEt$_3$)$_2$] in the presence of excess CuI indeed furnished **5**, but the yields were moderate due to the concurrent formation of an untractable, polymeric material, most likely arising from multiple couplings between the divalent species. Rather unexpextedly, however, **2c** turned out to be a suitable starting material for **5** (Scheme 2). Fluoride-mediated removal of the triisopropylsilyl groups and the standard deprotostannylation/coupling sequence with Me$_3$SnNMe$_2$, *trans*-[PtCl$_2$(PEt$_3$)$_2$], and excess CuI led to the formation of **5** in excellent yield (90%). While mechanistic details of this transformation are not clear, it is evident that one Pt–C bond in **2c** is cleaved in the course of the reaction, a pathway that might find future application as a method for metal-mediated *thermodynamically controlled* C$_{sp}$–C$_{sp}$ bond formation. The dinuclear species **5** is a yellow, crystalline solid that melts with decomposition at 196–198 °C. Crystals suitable for the investigation of its solid state structure by X-ray diffraction[10] were obtained from benzene solutions (Fig. 4).



Scheme 2. a: 1) K$_2$CO$_3$, MeOH/THF (1/1), 20 °C; 2) Me$_3$SnNMe$_2$, Et$_2$O, 20 °C; 3) *trans*-[PtCl$_2$(PEt$_3$)$_2$], CuI, PhMe, 50 °C, 25%. b: 1) Bu$_4$NF, THF, 20 °C; 2) Me$_3$SnNMe$_2$, Et$_2$O, 20 °C; 3) *trans*-[PtCl$_2$(PEt$_3$)$_2$], CuI, PhMe, 50 °C, 90%.

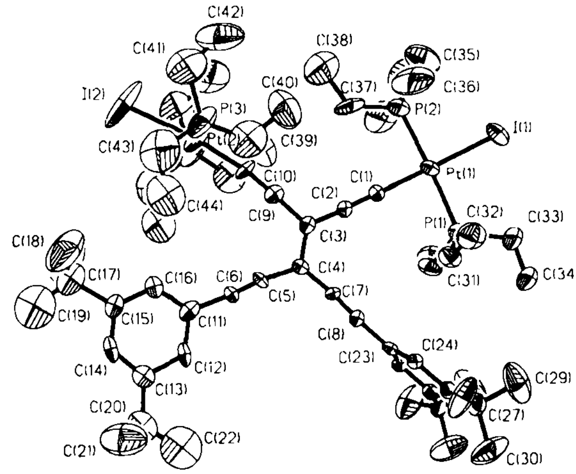
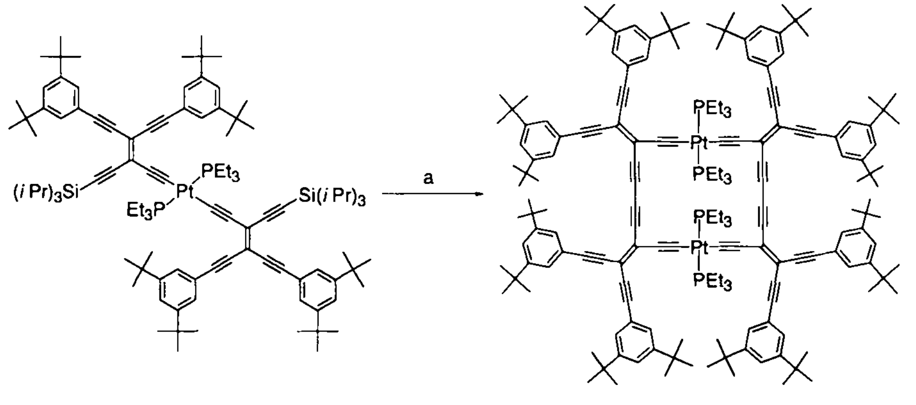


Fig. 4. X-ray crystal structure of **5**. Selected bond lengths (Å) and angles (°): Pt(1)-C(1) 2.054(24), Pt(1)-I(1) 2.651(3), C(1)-C(2) 1.212(35), Pt(2)-C(10) 1.888(28), Pt(2)-I(2) 2.645(6), C(9)-C(10) 1.227(41), C(1)-Pt(1)-I(1) 178.5(7), C(2)-C(1)-Pt(1) 179.5(17), C(10)-Pt(2)-I(2) 173.2(8), C(9)-C(10)-Pt(2) 170.7(22).

Complex **5** crystallized in the monoclinic space group *C*2/*m*, which is rather surprising for a molecule with such a complex substitution pattern. The crystallographic mirror plane contains, in addition to the tetraethynylethene skeleton and the two platinum atoms, the two phosphorous 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 detectable when comparing the bond angles around the two platinum centers: While those of Pt(1) reflect an almost ideal square-planar environment, the angles C(10)-Pt(2)-I(2) [173.9(8)°] and C(9)-C(10)-Pt(2) [170.7(22)°] deviate significantly from linearity. The conformation adopted by **5** in the solid state 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 leads to large standard deviations in the determined bond lengths and thereby prevents a meaningful discussion of this parameter.

Considerable effort has been devoted lately to the construction of cyclic arrays of oligoalkyne units.[7d, 8b, 14] Despite many reports about macrocyclic polyyne–metal complexes of higher hapticity[15] and the recently developed transition metal based "molecular boxes",[16] the incorporation of linear transition metal σ-bis(acetylide) moieties into cyclooligoalkynes has not yet been reported to the best of our knowledge.[6c, 17] This structural motif, however, is of fundamental importance for the assembly of a transition metal linked carbon network (Fig. 1), and hence synthetic entries to metal-containing macrocycles were sought. Previous experience[18] with successful oxidative acetylene coupling reactions in the presence of redox-active methanofullerenes fueled our hopes that platinum-containing molecules such as **2c** could also undergo this transformation without disruption of the metal carbon bonds. A similar synthetic strategy led to the preparation of expanded, perethynylated radialenes,[7d] in that case, however, in the absence of a metal fragment. Gratifyingly, protodesilylation of **2c** with Bu$_4$NF and submission of the resulting terminally bisdeprotected alkyne as dilute solution in chlorobenzene to the Hay coupling conditions [CuCl, *N,N,N',N'*-tetramethylethylenediamine (TMEDA), O$_2$] furnished the "dimeric" metallacycle **7** in 92% yield as an orange-red, amorphous solid (Scheme 3). Conclusive evidence for

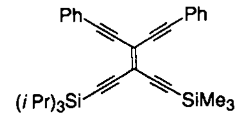


2c **7**

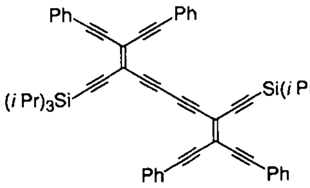
Scheme 3. a: 1) Bu_4NF in THF, chlorobenzene, 20 °C; 2) CuCl, TMEDA, molecular sieves (4 Å), O_2, chlorobenzene, 20 °C, 92%.

the integrity of the cyclic diplatinooligoalkyne structure was derived from matrix-assisted laser-desorption time-of-flight mass spectrometry (MALDI-TOF-MS) in the positive ion mode with sinapic acid as the matrix. The molecular ion is characterized by a peak at m/z = 2856.9, which corresponds to the base peak (m/z 2856) of the molecular ion cluster calculated for $C_{176}H_{228}P_4Pt_2$. It is noteworthy that the molecular ion of **7** could not be detected with fast atom bombardment (FAB) MS techniques, since this method led to complete fragmentation of the molecule. In contrast, no significant fragmentation was detected in the MALDI-TOF-MS spectrum, and only weaker peaks at m/z = 3064.9 and 3081.8 arising from adduct formation of **7** with the sinapic acid matrix were observed. These findings once more underline the growing importance of MALDI-TOF-MS in the characterization of carbon-rich materials.[7d, 19] Further proof of the structure of **7** was provided by the absence of signals corresponding to terminal acetylene protons in the ^1H NMR spectrum and by the two sets of signals for the di(*tert*-butyl)phenyl groups along with the expected ten resonances for the tetrakis(tetraethynylethene) substructure in its ^{13}C NMR spectrum.

To gain further insight into the electronic properties of these novel platinum derivatives, their UV/Vis absorption spectra were investigated and compared to those of nonmetalated and "dimeric" tetraethynylethene species. The mononuclear platinum complexes **2a–c** have their lowest energy absorption maxima at λ_{max} = 388 (ε = 58900), 429 (104700), and 432 nm (61600), respectively. This indicates that, firstly, the phenyl π-systems in **2b,c** are an integral part of the chromophores and, secondly, that the inability of **2c** to achieve a coplanar conformation of the aryl subunits significantly lowers the extinction coefficient. On the basis of spectral data for relevant σ-bis(acetylide) complexes[13c, 20] the above transitions can be assigned as metal-to-ligand charge-transfer (MLCT) bands, which may result in transmission of electron density across the metal center.[3] A rough guideline for the extent of electron delocalization in **2b** can be obtained by comparing its UV/Vis spectrum to those of the tetraethynylethene derivatives **4b**[7g] and **8**[21] (Fig. 5). The highest end absorption is shown by the all-carbon chromophore of **8** (λ_{max} = 466 nm, ε = 25500), followed by **2b** (λ_{max} = 429 nm, ε = 104700), and finally **4b** (λ_{max} = 384 nm, ε = 17900). The fact that λ_{max} of **2b** is bathochromically shifted with respect to the simple tetraethynylethene derivative **4b** and is only slightly smaller than the end absorption of **8** suggests that electronic delocalization in the platinum complex is indeed operational throughout the entire molecule, albeit to a smaller extent than in **8**. In addition to its intense electronic absorption spectrum, **2b** also shows broad, structureless fluorescence (λ_{em} = 473 nm) when irradiated at 430 nm, a behavior that is different from the more flexibly substituted and hence nonemitting derivatives **2a,c**. Clearly, the UV/Vis spectroscopic features warrant further exploration of the nonlinear optical properties of this class of compounds, and such studies are now underway.



4b



8

An informative comparison can also be made between the di(*tert*-butyl)phenyl-substituted derivatives **2c**, **4c**, **5**, and **7** (Fig. 6). The UV/Vis spectra of the platinum-containing molec-

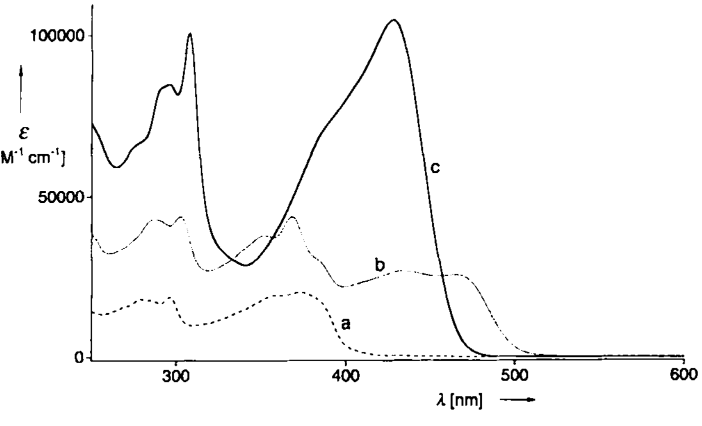


Fig. 5. Electronic absorption spectra of **2b** (trace c, CH_2Cl_2), **4b** (trace a, *n*-hexane), and **8** (trace b, *n*-hexane) at T = 293 K.

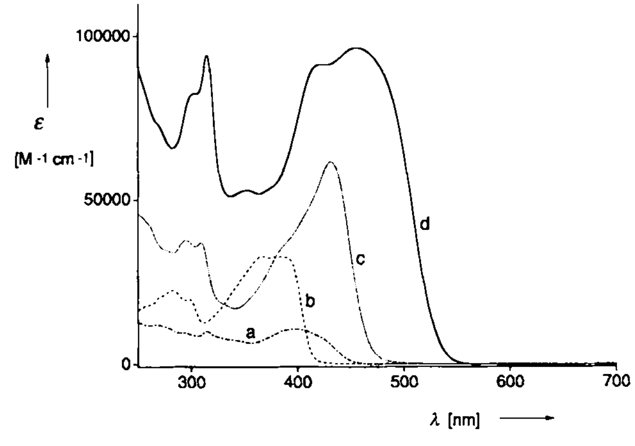


Fig. 6. Electronic absorption spectra of **2c** (trace c, CH_2Cl_2), **4c** (trace b, *n*-hexane), **5** (trace a, CH_2Cl_2), and **7** (trace d, CH_2Cl_2) at T = 293 K.

ules are dominated by MLCT bands, the wavelengths of which become increasingly red-shifted with the growing number of tetraethynylethene units. This trend culminates in the end absorption of **7** that extends well beyond 500 nm and thereby provides additional support for significant electronic communication along the rectangular perimeter of **7**. While the bulky, flexible substituents in dinuclear **5** (vide supra) lead only to weak, unstructured absorptions relative to nonmetalated **4c**, the increase in intensity from **4c** through **2c** to **7** proceeds in substantial increments and reaches the maximum value with the extinction coefficient of the latter. In addition, the skeleton of **7** appears to be sufficiently rigid to induce a broad, featureless fluorescence band (λ_{em} = 543 nm) upon irradiation at 450 nm.

Conclusion

The present work has demonstrated the versatility of the tetraethynylethene unit to function as an η^1-ligand in transition metal complexes and has laid the synthetic foundation for the stepwise construction of larger fragmentary building blocks of a transition metal linked carbon network. The interesting structural and electronic properties of the novel organometallic derivatives make this goal an exciting prospect.

Table 1. Crystal and data collection parameters for compounds **2a**, **2b**, and **5**.

Compound	**2a**	**2b**	**5**
Formula	$C_{86}H_{156}PtP_2Si_6$	$C_{74}H_{92}PtP_2Si_2$	$C_{62}H_{102}I_2P_4Pt_2$
Molecular weight	1615.7	1294.7	1615.3
Cryst. color, habit	yellow needles	yellow platelets	yellow needles
Cryst. size [mm]	0.7 × 0.2 × 0.1	≈0.2 × 0.2 × 0.2	0.4 × 0.3 × 0.06
Space group	$P\bar{1}$ (No. 2) triclinic	$P\bar{1}$ (No. 2) triclinic	$C2/m$ monoclinic
a [Å]	9.094(5)	9.108(2)	28.519(9)
b [Å]	15.374(12)	12.823(5)	13.779(5)
c [Å]	19.418(9)	15.535(4)	18.331(8)
α [°]	105.20(5)	95.54(3)	
β [°]	99.88(4)	99.22(2)	96.80(3)
γ [°]	102.50(5)	103.31(2)	
V [Å^3]	2482(3)	1725.8(9)	7153(5)
ρ_{calcd} [gcm^{-3}]	1.081	1.25	1.500
Z	1	1	4
T [K]	293	85	293
Reflections indep.	4648	6060	3550
Reflections obs.	4476 [$F > 4.0\sigma F$]	5125 [$I > 3.0\sigma I$]	2377 [$F > 6.0\sigma F$]
Structure solution	direct methods	Patterson	Patterson
$R(F)$ [%]	4.90	4.50	6.46
w$R(F)$ [%]	6.44	4.60	6.17
μ [mm^{-1}]	1.550	2.15	4.892
2θ range [°]	3.0–40	≤50	3.0–40
Residual electron density [eÅ^{-3}]	1.09	0.9	2.02
Parameters refined	468	349	369

Experimental Procedure

Materials: All chemicals were purchased reagent grade from commercial suppliers and used as received. Solvents were purified according to standard procedures [22]. The preparations of compounds **3** [7g], **4a,b** [7g], 3-dibromomethylene-1,5-bis(trimethylsilyl)-1,4-pentadiyne [7g], and 3,5-di(*tert*-butyl)phenylacetylene [23] used in the syntheses of **4c** and **6** have been reported previously. All operations were performed in standard glassware in an argon atmosphere unless otherwise stated. Evaporations and concentrations in vacuo were done at water aspirator pressure. Column chromatography was performed on silica gel 60 (230–400 mesh) from E. Merck.

Equipment: Melting points were determined on a Büchi 510 apparatus and are uncorrected. UV/Vis spectra were recorded on a Varian-Cary 5 spectrophotometer, IR spectra on a Perkin-Elmer 1600 FT-IR instrument, and fluorescence measurements were conducted in deoxygenated CH_2Cl_2 solutions at room temperature on a SPEX 212 Fluorolog spectrometer. ^{1}H and ^{13}C NMR data were collected on either Varian Gemini-200 or -300 spectrometers or on a Bruker-AM 500 at 296 K. Me_4Si served as internal reference in ^{1}H NMR spectra, while ^{13}C chemical shifts were recorded relative to the solvent signal as reference; the values given are calculated against Me_4Si. Mass spectra (m/z, %) were recorded on either a VG-Tribrid [electron impact (EI)], a VG-ZAB-2SEQ (FAB, 3-nitrobenzyl alcohol matrix), or a Bruker-Reflex-TOF instrument (MALDI-TOF). Elemental analyses were performed by the Mikrolabor at the Laboratorium für Organische Chemie, ETH Zürich. The Chemical Abstracts Registry Service assisted in naming some of the compounds.

Crystal Structure Determinations: Crystals suitable for X-ray diffraction were grown by slow concentration of dilute solutions (ethyl acetate for **2a**, hexane for **2b**, and benzene for **5**). X-ray data (Table 1) were recorded either on a Syntex P21 diffractometer using ω scans (**2a**, **5**), or on an Enraf-Nonius CAD4 diffractometer using ω/θ scans (**2b**). In all cases, $Mo_{K\alpha}$ radiation was employed and the structural parameters were refined anisotropically by full-matrix least-squares analysis. All structures suffer from disorder to variable extents. The structure of **2a** could only be satisfactorily solved by assuming the presence of a second conformer with the two tetraethynylethenes rotated around Pt(1)–C(1) by 180°. Parameters pertaining to this minor rotamer were refined with a population parameter of ca. 25%. The structure of **2b** is highly disordered. The static disorder could only be resolved for a few C atoms (see Fig. 3); they were refined with a population parameter of 0.5. All other heavy atoms were refined anisotropically with a population parameter of 1.0 (H atoms omitted). Further details of the crystal structure investigations are available on request from the Director of the Cambridge Crystallographic Data Centre, 12 Union Road, GB-Cambridge CB2 1EZ (UK), on quoting the full journal citation [10].

6-(3,5-Di(*tert*-butyl)phenyl)-4-(3,5-di(*tert*-butyl)phenylethynyl)-1-triisopropylsilyl-3-trimethylsilylethynylhex-3-ene-1,5-diyne (4c): A solution of **3** [7g] (3.00 g, 6.49 mmol) and 3,5-di(*tert*-butyl)phenylacetylene [23] (8.35 g, 38.94 mmol) in benzene (60 mL) was deareated by passing argon through it for 20 min. $[PdCl_2(PPh_3)_2]$ (0.23 g, 0.33 mmol), nBuNH$_2$ (2.5 mL), and CuI (ca. 0.04 g, 0.21 mmol) were then added sequentially, and the reaction mixture was stirred at room temperature for 2 d. The dark solution was diluted with hexane (200 mL), filtered through a pad of silica gel, and the solvents were removed in vacuo. The residual dark, viscous oil was chromatographed (SiO_2, hexane) to furnish a yellow, viscous oil from which **4c** could be crystallized as a yellow solid by trituration with MeOH (1.52 g, 32%). M. p.: 161–162 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.50–7.39 (m, 6H), 1.37 (s, 36H), 1.17 (s, 21H), 0.31 (s, 9H); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 150.82, 150.71, 126.21, 126.13, 123.52, 123.41, 121.76, 119.07, 116.03, 104.20, 103.81, 102.18, 101.86, 100.06, 100.01, 86.28, 85.92, 34.83, 31.33, 18.67, 11.38, −0.08; IR (KBr): ν = 2956 (s), 2856 (m), 2189 (m), 2133 (m), 1583 (m), 1244 (m), 844 (m) cm^{-1}; UV/Vis (n-hexane): λ_{max} (ε) = 380 (42600), 364 (40600), 297 (23600), 282 (26000), 272 (sh, 25000), 256 (24700), 245 nm (sh, 23500); EI-MS (70 eV): 728 (100, M^+). $C_{50}H_{72}Si_2$ (729.29): calcd C 82.35, H 9.95; found C 82.27, H 10.18.

***trans*-Bis[6-triisopropylsilyl-3,4-bis(triisopropylsilylethynyl)hex-3-ene-1,5-diyn-1-yl]-bis(triethylphosphine)platinum(II) (2a)**: To a solution of **4a** [7g] (191.2 mg, 0.30 mmol) in THF (10 mL) and MeOH (10 mL) was added K_2CO_3 (47.8 mg, 0.34 mmol), and the suspension was stirred for 30 min at room temperature. The reaction mixture was partitioned between Et_2O (20 mL) and H_2O (50 mL), the organic layer washed sequentially with H_2O (3 × 20 mL) and saturated aqueous NH_4Cl solution (20 mL) and then dried over $MgSO_4$. After filtration, the solution was stirred with Me_3SnNMe_2 (62.4 mg, 0.05 mL, 0.30 mmol) for 2 h at room temperature. Removal of volatiles in vacuo (nitrogen trap) left a dark brown oil that was redissolved in toluene (30 mL). The solution was deareated by passing argon through it for 20 min and *trans*-$[PtCl_2(PEt_3)_2]$ (52.8 mg, 0.105 mmol) and CuI (ca. 10 mg, 0.05 mmol) were added. Stirring at room temperature was continued for 12 h during which time the mixture developed a yellow fluorescent color and precipitation of what was presumably Me_3SnCl occurred. Evaporation of volatiles and chromatography (SiO_2, hexane/CH_2Cl_2 4/1) afforded a bright yellow powder that was recrystallized from ethyl acetate to give **2a** as fine yellow needles (120.0 mg, 70%). M. p.: 276 °C (decomp.); ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.10–1.90 (m, 12H); 1.09 (s, 42H), 1.08 (s, 42H), 1.07 (s, 42H), 1.20–1.00 (m, 18H); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 128.58 (t, $^2J_{PC}$ = 15.0 Hz), 121.97, 110.59, 109.63, 106.39, 105.95, 105.57, 98.00, 97.72, 97.60, 18.64, 16.19 (m), 11.29, 8.11 (m); IR (KBr): ν = 2945 (s), 2867 (s), 2133 (m), 2056 (s) 1456 (m), 672 (s) cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 388 (58900), 299 (sh, 29500), 283 (35500); FAB-MS: 1614.6 $(M + H)^+$. $C_{86}H_{156}Si_6P_2Pt$ (1615.72): calcd C 63.93, H 9.73; found C 63.40, H 9.25.

***trans*-Bis[6-phenyl-4-phenylethynyl-3-triisopropylsilylethynylhex-3-ene-1,5-diyn-1-yl]bis(triethylphosphine)platinum(II) (2b)**: Starting from **4b** [7g] (151.5 mg, 0.30 mmol), **2b** was obtained in an analogous fashion as described for the preparation of **2a**. Chromatography (SiO_2, hexane/CH_2Cl_2 2/1) gave a brown-yellow oil that was crystallized from hexane to furnish **2b** as yellow plates with a gold luster (65.6 mg, 51%). M. p.: 169–170 °C (decomp.); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.51–7.48 (m, 8H), 7.33–7.28 (m, 12H), 2.10–1.95 (m, 12H), 1.09 (s, 42H), 1.09–0.95 (m, 18H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 131.62, 131.57, 128.19, 128.10, 127.99, 126.57 (t, $^{2}J_{PC}$ = 14.6 Hz), 123.61, 123.51, 121.83, 111.20, 109.87, 105.98, 97.50, 96.03, 95.69, 88.92, 88.41, 18.65, 16.33 (m), 11.35, 8.28 (m), phenyl C atom resonances are partly overlapping; IR (KBr): ν = 2933 (m), 2856 (m), 2067 (s), 750 (s), 689 (s) cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 429 (104700), 393 (sh, 74100), 308 (100000), 296 (85100), 280 (sh, 67600); FAB-MS: 1294.4 (8, M^+), 995.3 (100, $[M-2\,Si(iPr)_3]^+$). $C_{74}H_{92}Si_2P_2Pt$ (1294.74): calcd C 68.65, H 7.16; found C 68.63, H 7.03.

***trans*-Bis[6-(3,5-di(*tert*-butyl)phenyl)-4-(3,5-di(*tert*-butyl)phenylethynyl)-3-triisopropylsilylethynylhex-3-ene-1,5-diyn-1-yl]bis(triethylphosphine)platinum(II) (2c)**: Starting from **4c** (145.0 mg, 0.20 mmol), **2c** was obtained in an analogous fashion as described for the preparation of **2a**. Chromatography (SiO_2, hexane/CH_2Cl_2 3/1) gave an amorphous yellow solid (111.1 mg, 56%). M. p.: 249–250 °C (decomp.); ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.40–7.30 (m, 12H), 2.12–1.96 (m, 12H), 1.33 (s, 72H), 1.07 (s, 42H), 1.07–0.93 (m, 18H); ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 150.50, 150.37, 125.28 (t, $^{2}J_{PC}$ = 14.5 Hz), 125.23, 122.64, 122.58, 122.51, 120.91, 112.01, 109.35, 106.12, 97.33, 96.86, 96.81, 87.64, 87.29, 34.73, 34.72, 31.31, 31.29, 18.64, 16.19 (m), 11.35, 8.27; IR (KBr): ν = 2956 (s), 2856 (m), 2356 (w), 2067 (s), 1583 (w), 872 (w) cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 432 (61600), 385 (sh, 35300), 310 (36900), 295 (37600), 251 (sh, 45300), 239 nm (48000); FAB-MS: 1742.9 $(M + H)^+$. $C_{106}H_{156}Si_2P_2Pt$ (1743.60): calcd C 73.02, H 9.02; found C 73.31, 9.01.

6-(3,5-Di(*tert*-butyl)phenyl)-4-(3,5-di(*tert*-butyl)phenylethynyl)-1-trimethylsilyl-3-trimethylsilylethynylhex-3-ene-1,5-diyne (6): A solution of 3-dibromomethylene-1,5-bis(trimethylsilyl)-1,4-pentadiyne [7g] (513.9 mg, 1.36 mmol) and 3,5-di(*tert*-butyl)phenylacetylene [23] (1.304 g, 6.08 mmol) in benzene (20 mL) was deareated by passing argon through it for 20 min. $[PdCl_2(PPh_3)_2]$ (61.9 mg, 0.082 mmol), nBuNH$_2$ (1.0 mL), and CuI (ca. 0.04 g, 0.21 mmol) were then added sequentially, and the reaction mixture was stirred at room temperature for 2 d. The dark solution was diluted with hexane (200 mL), filtered through a pad of silica gel, and the solvents were removed in vacuo. The residual dark, viscous oil was chromatographed (SiO_2, hexane/CH_2Cl_2 10/1) to furnish **6** as an orange solid (287.5 mg, 33%). M. p.: 187–188 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.47–7.37 (m, 6H), 1.33 (s, 36H), 0.26 (s, 18H); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 150.96, 126.30, 123.67, 121.68, 120.24, 115.68, 104.69, 101.69, 100.33, 86.08, 34.79, 31.26, −0.17; IR (KBr): ν = 2956 (s), 2178 (m), 2144 (m), 1583 (m), 1244 (s), 844 (s) cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 390 (sh, 32400), 381 (32800), 367 (32900), 298 (19800), 282 (22500), 273 (sh, 20900), 258 nm (sh, 17700); EI-MS (70 eV): 644.4 (22, M^+), 73.1 (100, $SiMe_3^+$). HR-MS: m/z 644.4191 (calcd for $C_{44}H_{60}Si_2$: m/z 644.4233).

μ-[3-[3-(3,5-Di(*tert*-butyl)phenyl)-1-[(3,5-di(*tert*-butyl)phenyl)ethynyl]-2-propynylidene]-1,4-pentadiyne-1,5-diyl]]diiodotetrakis(triethylphosphine)diplatinum (5) (via 6): A solution of **6** (354.8 mg, 0.55 mmol) and K_2CO_3 (0.20 g, 1.4 mmol) in THF (10 mL) and MeOH (10 mL) was stirred at room temperature for 30 min, and then separated between layers of Et_2O (20 mL) and H_2O (20 mL). The organic phase was washed sequentially with H_2O (3 × 20 mL) and saturated aqueous NH_4Cl solution (20 mL), and dried over $MgSO_4$. After filtration, Me_3SnNMe_2 (249.4 mg, 0.20 mL, 1.2 mmol) was added via syringe and the resulting mixture stirred at room temperature for 2 h. Removal of volatiles in vacuo (nitrogen trap) left a yellow solid that was redissolved in toluene (50 mL). The solution was treated with *trans*-$[PtCl_2(PEt_3)_2]$ (201.9 mg, 0.40 mmol) and CuI (ca. 0.12 g, 0.66 mmol), and stirred at 50 °C for 3 h, after which time a precipitate of what was presumably Me_3SnCl had formed. Removal of solvents in vacuo and chromatography (SiO_2, hexanes/CH_2Cl_2 2/1) furnished **5** as a yellow solid (79.5 mg, 25%).

5 via 2c: To a solution of **2c** (44.7 mg, 0.026 mmol) in THF (20 mL) was added Bu_4NF (1 mL of a 1 M solution in THF) and a drop of water. The reaction mixture was stirred at room temperature for 30 min, then partitioned between layers of Et_2O (20 mL) and H_2O (20 mL). The organic phase was washed with H_2O (3 × 20 mL), saturated aqueous NH_4Cl solution (20 mL), and dried over $MgSO_4$. After filtration, Me_3SnNMe_2 (126.8 mg, 0.1 mL, 0.61 mmol) was added via syringe, and the resulting mixture stirred at room temperature for 2 h. Evaporation of volatiles in vacuo (nitrogen trap) left a yellow solid that was redissolved in toluene (30 mL). The solution was treated with *trans*-$[PtCl_2(PEt_3)_2]$ (36.3 mg, 0.072 mmol) and CuI (ca. 0.12 g, 0.66 mmol), and stirred at 50 °C for 3 h, after which time a precipitate of what was presumably Me_3SnCl had formed. Evaporation of solvents in vacuo left a green-yellow solid that was chromatographed (SiO_2, hexane/CH_2Cl_2 1/1) to furnish **5** (70.0 mg, 90%) as a yellow solid that could be recrystallized from hexane. M. p.: 196–198 °C (decomp.); ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.32–7.28 (m, 6H), 2.28–2.15 (m, 24H), 1.29 (s, 36H), 1.15–0.97 (m, 36H); ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 150.44, 125.72, 123.12, 122.18, 105.83, 102.42 (t, $^{2}J_{PC}$ = 14.7 Hz), 101.25, 95.08, 94.80, 88.45, 34.74, 31.33, 16.55 (m), 8.27; IR (KBr): ν = 2962 (s), 2863 (m), 2346 (w), 2071 (m), 1029 (m), 765 (m) cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 397 (10700), 342 (sh, 7300), 315 (10000), 293 (9500), 268 nm (12100); FAB-MS: 1615.0 $(M + H)^+$. $C_{62}H_{102}P_4Pt_2I_2$ (1615.36): calcd C 46.10, H 6.36; found C 46.34, H 6.24.

Bis[μ-[3,8-bis[3-[3,5-di(*tert*-butyl)phenyl]-1-[[3,5-di(*tert*-butyl)phenyl]ethynyl]-2-propynylidene]-1,4,6,9-decatetrayne-1,10-diyl]]tetrakis(triethylphosphine)diplatinum(II) (7): A solution of **2c** (56.6 mg, 0.032 mmol) in chlorobenzene (20 mL) was treated with Bu_4NF (0.75 mL of a 1 M solution in THF, 0.75 mmol) and stirred at room temperature for 30 min. The reaction mixture was partitioned between layers of chlorobenzene (100 mL) and H_2O (100 mL). The organic layer was washed with H_2O (3 × 50 mL) and dried over $MgSO_4$. After filtration, activated molecular sieves (4 Å, 5 g), CuCl (1.27 g, 12.8 mmol), and TMEDA (1.49 g, 1.92 mL, 12.8 mmol) were added and the suspension was vigorously stirred at room temperature under an atmosphere of dry oxygen for 15 h. The reaction mixture was diluted with CH_2Cl_2 (100 mL) and filtered through a pad of SiO_2. Evaporation of solvents in vacuo left an orange solid that was chromatographed (SiO_2, hexane/CH_2Cl_2 2/1) to furnish **7** (19.6 mg, 92%) as an amorphous, red-orange solid. M. p.: 239–240 °C (decomp.); ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.36–7.24 (m, 24H), 2.18–1.98 (m, 24H), 1.30 (s, 72H), 1.14 (s, 72H), 1.27–1.05 (m, 36H); ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 150.62, 150.58, 128.70 (t, $^{2}J_{PC}$ = 15.1 Hz), 125.89, 125.87, 123.09, 122.79, 122.41, 122.10, 120.57, 110.38, 110.18, 98.56, 98.25, 87.28, 86.94, 81.38, 34.78, 34.56, 31.33, 31.24, 16.62 (m), 8.44; IR (KBr): ν = 2963 (s), 2068 (s), 1742 (w), 1588 (m), 1363 (m), 1247 (m), 1035 (m), 876 (m), 704 (m) cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 458 (96400), 422 (91200), 353 (5300), 315 (94100), 303 (82400), 270 nm (sh, 72600); MALDI-TOF-MS (sinapic acid matrix): 2856.9 (100, M^+, calcd molecular ion cluster for $C_{176}H_{228}P_4Pt_2$: 2854/2855/2856/2857/2858 (70/97/100/83/59)). $C_{176}H_{228}P_4Pt_2 \cdot CH_2Cl_2$: calcd C 72.24, H 7.88; found C 72.11, H 7.97.

Acknowledgment: Support by the Schweizerischer Nationalfonds zur Förderung der wissenschaftlichen Forschung is gratefully acknowledged.

Received: December 5, 1994 [F30]

---

[1] a) W. Beck, B. Niemer, M. Wieser, *Angew. Chem.* **1993**, *105*, 969–1160; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 923–949; b) M. H. Chisholm, *ibid.* **1991**, *103*, 690–691 and **1991**, *30*, 673–674; c) R. R. Tykwinski, P. J. Stang, *Organometallics* **1994**, *13*, 3203–3208 and references therein.

[2] a) M. I. Bruce, *Chem. Rev.* **1991**, *91*, 197–257; b) T. Rappert, O. Nürnberg, N. Mahr, J. Wolf, H. Werner, *Organometallics* **1992**, *11*, 4156–4164; c) D. Touchard, C. Morice, V. Cadierno, P. Haquette, L. Toupet, P. H. Dixneuf, *J. Chem. Soc. Chem. Commun.* **1994**, 859–860; d) Y. Wakatsuki, N. Koga, H. Yamazaki, K. Morokuma, *J. Am. Chem. Soc.* **1994**, *116*, 8105–8111.

[3] For spectroscopic evidence of π-interactions across organometallic fragments see: a) D. L. Lichtenberger, S. K. Renshaw, R. M. Bullock, *J. Am. Chem. Soc.* **1993**, *115*, 3276–3285; b) D. L. Lichtenberger, S. K. Renshaw, A. Wong, C. D. Tagge, *Organometallics* **1993**, *12*, 3522–3526; c) D. L. Lichtenberger, S. K. Renshaw, A. Wong, C. D. Tagge, *Inorg. Chem.* **1993**, *12*, 3522–3526; d) J. Lewis, M. S. Khan, A. K. Kakkar, B. F. G. Johnson, T. B. Marder, H. B. Fyfe, F. Wittmann, R. H. Friend, A. E. Dray, *J. Organomet. Chem.* **1992**, *425*, 165–176.

[4] See, for example a) M. Schäfer, N. Mahr, J. Wolf, H. Werner, *Angew. Chem.* **1993**, *105*, 1377–1379; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1315–1318; b) H.-F. Klein, M. Zwiener, A. Petermann, T. Jung, G. Cordier, B. Hammerschmitt, U. Flörke, H.- J. Haupt, Y. Dartiguenave, *Chem. Ber.* **1994**, *127*, 1569–1578; c) H.-F. Klein, B. Zettel, U. Flörke, H.- J. Haupt, *ibid.* **1992**, *125*, 9–14; d) K. Onitsuka, K. Yanai, F. Takei, T. Joh, S. Takahashi, *Organometallics* **1994**, *13*, 3862–3867; e) P. J. Stang, M. H. Kowalski, *J. Am. Chem. Soc.* **1989**, *111*, 3356–3362.

[5] a) H. S. Nalwa, *Adv. Mater.* **1993**, *5*, 341–358; b) D. R. Kanis, M. A. Ratner, T. J. Marks, *Chem. Rev.* **1994**, *94*, 195–242; c) S. R. Marder, J. W. Perry, *Adv. Mater.* **1993**, *5*, 804–815; d) L. K. Meyers, C. Langhoff, M. E. Thompson, *J. Am. Chem. Soc.* **1992**, *114*, 7560–7561; e) C. C. Frazier, S. Guha, W. P. Chen, M. P. Cockerham, P. L. Porter, E. A. Chauchard, C. H. Lee, *Polymer* **1987**, *28*, 553–555; f) S. Guha, C. C. Frazier, P. L. Porter, K. Kang, S. E. Finberg, *Opt. Lett.* **1989**, *14*, 952–954; g) W. J. Blau, H. J. Byrne, D. J. Cardin, A. P. Davey, *J. Mater. Chem.* **1991**, *1*, 245–249. See also: h) D. R. Kanis, P. G. Lacroix, M. A. Ratner, T. J. Marks, *J. Am. Chem. Soc.* **1994**, *116*, 10089–10102.

[6] a) H. Lang, *Angew. Chem* **1994**, *106*, 569–572; *Angew. Chem Int. Ed. Engl.* **1994**, *33*, 547–550 and references therein; b) W. Weng, T. Bartik, J. A. Gladysz, *ibid.* **1994**, *106*, 2269–2272 and **1994**, *33*, 2199–2202; c) L. G. Mackay, H. L. Anderson, J. K. M. Sanders, *J. Chem. Soc. Chem. Commun.* **1992**, 43–44.

[7] a) Y. Rubin, C. B. Knobler, F. Diederich, *Angew. Chem.* **1991**, *103*, 708–710; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 698–700; b) A. M. Boldi, J. Anthony, C. B. Knobler, F. Diederich, *ibid.* **1992**, *104*, 1270–1273 and **1992**, *31*, 1240–1242; c) J. Anthony, C. B. Knobler, F. Diederich, *ibid.* **1993**, 105, 437–440 and **1993**, *32*, 406–409; d) A. M. Boldi, F. Diederich, *ibid.* **1994**, *106*, 482–485 and **1994**, *33*, 468–471; e) J. Anthony, C. Boudon, F. Diederich, J.-P. Gisselbrecht, V. Gramlich, M. Gross, M. Hobi, P. Seiler, *ibid.* **1994**, *106*, 794–798 and **1994**, *33*, 763–766; f) M. Schreiber, J. Anthony, F. Diederich, M. E. Spahr, R. Nesper, M. Hubrich, F. Bommeli, L. Degiorgi, P. Wachter, P. Kaatz, C. Bosshard, P. Günter, M. Colussi, U. W. Suter, C. Boudon, J.-P. Gisselbrecht, M. Gross, *Adv. Mater.* **1994**, *6*, 786–790; g) J. Anthony, A. M. Boldi, Y. Rubin, M. Hobi, V. Gramlich, C. B. Knobler, P. Seiler, F. Diederich, *Helv. Chim. Acta* **1995**, *78*, 13–45.

[8] a) F. Diederich, Y. Rubin, *Angew. Chem.* **1992**, *104*, 1123–1146; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1101–1123; b) F. Diederich, *Nature* **1994**, *369*, 199–207.

[9] a) I. Collamati, A. Furlani, *J. Organomet. Chem.* **1969**, *17*, 457–461; b) P. S. Braterman, R. J. Cross, G. B. Young, *J. Chem. Soc. Dalton Trans.* **1977**, 1892–1897; c) J. J. Low, W. A. Goddard III, *J. Am. Chem. Soc.* **1986**, *108*, 6115–6118 and references therein.

[10] A preliminary communication has appeared: F. Diederich, R. Faust, V. Gramlich, P. Seiler, *J. Chem. Soc. Chem. Commun.* **1994**, 2045–2046.

[11] a) K. Jones, M. F. Lappert, *J. Chem. Soc.* **1965**, 1944–1951; b) K. Jones, M. F. Lappert, *J. Organomet. Chem.* **1965**, *3*, 295–307.

[12] M. S. Khan, S. J. Davies, A. K. Kakkar, D. Schwartz, B. Lin, B. F. G. Johnson, J. Lewis, *J. Organomet. Chem.* **1992**, *424*, 87–97.

[13] a) A. C. Villa, A. G. Manfredotti, C. Guastini, *Cryst. Struct. Comm.* **1976**, *5*, 139–142; b) M. Ciriano, J. A. K. Howard, J. L. Spencer, F. G. A. Stone, H. Wadepohl, *J. Chem. Soc. Dalton Trans.* **1979**, 1749–1756; c) A. Sebald, B. Wrackmeyer, C. R. Theocharis, W. Jones, *ibid.* **1984**, 747–756; d) V. W.-W. Yam, L.-P. Chan, T.-F. Lai, *ibid.* **1993**, 2075–2077; (e) H. Ogawa, K. Onitsuka, T. Joh, S. Takahashi, Y. Yamamoto, H. Yamazaki, *Organometallics* **1988**, *7*, 2257–2260.

[14] a) A. de Meijere, S. Kozhushkov, T. Haumann, R. Boese, C. Puls, M. J. Cooney, L. T. Scott, *Chemistry* **1995**, *1*, 124–131; b) L. T. Scott, M. J. Cooney, C. Otte, C. Puls, T. Haumann, R. Boese, P. J. Carroll, A. B. Smith III, A. de Meijere, *J. Am. Chem. Soc.* **1994**, *116*, 10275–10283; c) Y. Rubin, C. B. Knobler, F. Diederich, *ibid.* **1990**, *112*, 4966–4968; d) F. Diederich, Y. Rubin, O. L. Chapman, N. S. Goroff, *Helv. Chim. Acta* **1994**, *77*, 1441–1457.

[15] a) D. Solooki, J. D. Bradshaw, C. A. Tessier, W. J. Youngs, R. F. See, M. Churchill, J. D. Ferrara, *J. Organomet. Chem.* **1994**, *470*, 231–236; b) U. H. F. Bunz, V. Enkelmann, *Organometallics* **1994**, *13*, 3823–3833 and references therein; c) J. D. Ferrara, C. Tessier-Youngs, W. J. Youngs, *ibid.* **1987**, *6*, 676–678; d) R. Gleiter, M. Karcher, D. Kratz, S. Rittinger, V. Schehlmann in *Organometallics in Organic Synthesis 2*, (Eds.: H. Werner, G. Erker), Springer, Berlin, **1989**; pp 109–125; e) J. D. Ferrara, C. Tessier-Youngs, W. J. Youngs, *Inorg. Chem.* **1988**, *27*, 2201–2202; f) A. Djebli, J. D. Ferrara, C. Tessier-Youngs, W. J. Youngs, *J. Chem. Soc. Chem. Commun.* **1988**, 548–549; g) J. D. Ferrara, A. Djebli, C. Tessier-Youngs, W. J. Youngs, *J. Am. Chem. Soc.* **1988**, *110*, 647–649; h) J. D. Ferrara, C. Tessier-Youngs, W. J. Youngs, *ibid.* **1985**, *107*, 6719–6721.

[16] a) P. J. Stang, J. A. Whiteford, *Organometallics* **1994**, *13*, 3776–3777; b) C. M. Drain, J.-M. Lehn, *J. Chem. Soc. Chem. Commun.* **1994**, 2313–2315; c) P. J. Stang, D. H. Cao, *J. Am. Chem. Soc.* **1994**, *116*, 4981–4982; d) M. Fujita, Y. J. Kwon, S. Washizu, K. Ogura, *ibid.* **1994**, *116*, 1151–1152; e) M. Fujita, S. Nagao, M. Iida, K. Ogata, K. Ogura, *ibid.* **1993**, *115*, 1574–1576; f) M. Fujita, J. Yazak, K. Ogura, *ibid.* **1990**, *112*, 5645–5648; g) M. Fujita, F. Ibukuro, H. Hagihara, K. Ogura, *Nature* **1994**, *367*, 720–723.

[17] For a branched organometallic network based on platinum σ-bis(acetylide) complexes of 1,3,5-triethynylbenzene, see M. S. Khan, D. J. Schwartz, N. A. Dasha, A. K. Kakkar, B. Lin, P. R. Raithby, J. Lewis, *Z. Anorg. Allg. Chem.* **1992**, *616*, 121–124.

[18] H. L. Anderson, R. Faust, Y. Rubin, F. Diederich, *Angew. Chem.* **1994**, *106*, 1427–1429; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1366–1368.

[19] T. Lange, V. Gramlich, W. Amrein, F. Diederich, M. Gross, C. Boudon, J.-P. Gisselbrecht, *Angew. Chem.* **1995**, *107*, 898–901; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 805–809.

[20] a) L. A. Sacksteder, E. Baralt, B. A. DeGraff, C. M. Lukehart, J. N. Demas, *Inorg. Chem.* **1991**, *30*, 2468–2476; b) E. Baralt, E. A. Boudreaux, J. N. Demas, P. G. Leuhart, C. M. Lukehart, A. T. McPhail, D. R. McPhail, J. B. Myers, Jr., L. Sacksteder, W. R. True, *Organometallics* **1989**, *8*, 2417–2430; c) H. Masai, K. Sonogashira, N. Hagihara, *Bull. Chem. Soc. Jpn.* **1971**, *44*, 2226–2230.

[21] A. M. Boldi, Ph.D. Thesis, University of California, Los Angeles, 1994.

[22] D. D. Perrin, W. L. F. Armarego, *Purification of Laboratory Chemicals*, 3rd ed., Pergamon, New York, 1988.

[23] D. Philp, V. Gramlich, P. Seiler, F. Diederich, *J. Chem. Soc. Perkin Trans. 2*, in press.