

Ethynyl[2.2]paracyclophanes and 4-isocyano[2.2]paracyclophane as ligands in organometallic chemistry

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Dedicated to Prof. Manfred Christl on the occasion of his 65th anniversary.

Abstract

An alternative synthesis of (\pm)-4-ethynyl[2.2]paracyclophane (PCP–C \equiv CH) (**5**) and 4,16-diethynyl[2.2]paracyclophane (**6**) via the Corey–Fuchs reaction has been developed. The olefinic intermediate 4-dibromovinyl[2.2]paracyclophane (**3**) has been isolated and structurally characterized. The racemic terminal alkyne **5** was employed as starting material for assembling of a luminescent extended π -conjugated system containing a thiophene unit and for a catalytic bis-silylation reaction yielding the olefinic dithioether Z-PhSCH₂Me₂SiC(H)=C(PCP)SiMe₂CH₂SPh (**9**). The dimetallatetrahedran [Co₂(CO)₆(μ - η^2 -PCP–CCH)] (**10**) has been prepared and its crystal structure determined by an X-ray diffraction analysis. Alkyne **5** has also been used for the preparation of the Pt(0) complex [Pt(PPh₃)₂(PCP–C \equiv CH)] (**11**) and the heterodinuclear dimetallacyclopentenone [(OC)₂Fe{ μ -C(=O)C(PCP)=C(H)}(μ -dppm)Pt(PPh₃)] (**12**). The synthesis and reactivity of 4-isocyano[2.2]paracyclophane (**15**) towards heterobimetallic iron–platinum and palladium–platinum complexes is also presented. Opening of the dative iron \rightarrow platinum bond of [(OC)₄Fe(μ -dppm)PtCl₂] (**16**) occurred upon addition of **15** to a CH₂Cl₂ solution of **16** leading to [(OC)₄Fe{ μ -dppm}PtCl₂(C \equiv N–PCP)] (**17**). Treatment of [CIPd(μ -dppm)₂PtCl] (**18**) with isocyanide **15** in a 1:1 ratio affords the A-frame compound [CIPd(μ -dppm)₂(μ -C=N–PCP)PtCl] (**19**), resulting from formal insertion of **15** into the Pd–Pt bond. Addition of 2 equiv. of **15–18** leads to the ionic A-frame compound [CIPd(μ -dppm)₂(μ -C=N–PCP)Pt(C \equiv N–PCP)]Cl (**20**).

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1. Introduction

Since the isolation of the parent compound by Brown and Farthing in 1949 [1a] and its first synthesis by Cram in 1951 [1b], interest in molecules containing the unique structural features of [2.2]paracyclophanes (PCP) has never decreased. PCPs are used for various applications such as chiral catalysis [2], the design of new optoelectronic

(NLO) materials [3], π -conjugated arrays, electron transfer processes and molecular electronics [4a,4b,4c]. PCP-functionalized chiral metallocenes have been used as olefin polymerization catalysts after activation with methylalumoxane [4d]. Even biomedical applications are emerging [4e]. Many of these interesting chemical, electrochemical and photophysical properties arise from the high steric compression of the neighboring rings (also called decks), the separation between the *ipso*-carbons of the stacked rings being about 2.8 Å. The orbital overlap between the two rings of [2.2]paracyclophane is therefore important and could possibly lead to an electronic connection

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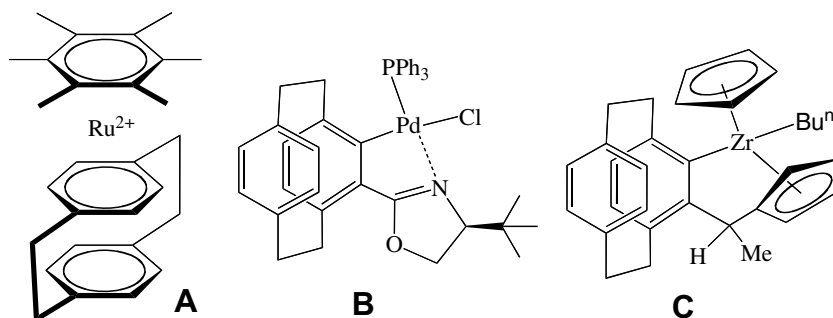


Chart 1.

between appropriate substituents on both rings [5]. For this reason, [2.2]PCP derivatives containing one or two *para*-connected carbon–carbon triple bonds have been studied for organic transformations such as cycloaddition reactions, synthesis of carbon rich compounds and in material science [6,7,8b]. However, we are not aware of any organometallic complexes bearing a PCP motif attached on a metal center via a metal–carbon bond, apart from some examples with η^6 -coordination of the PCP moiety on Ru(II) and Cr(0) of type **A** and the Pd and Zr complexes **B** and **C** having a M– σ -aryl bond (Chart 1) [4d,8,9].

As part of our research interest in the activation of alkynes by dinuclear transition metal compounds [10], we embarked on a study on the organometallic reactivity on this unsaturated compound. In extension of this project, we attempted also the synthesis of a hitherto unknown isocyanoparacyclophane. This functionalization of a PCP-building block with an isocyanide group having a reactive C \equiv N triple bond should also allow an interesting entry in organometallic chemistry.

2. Results and discussion

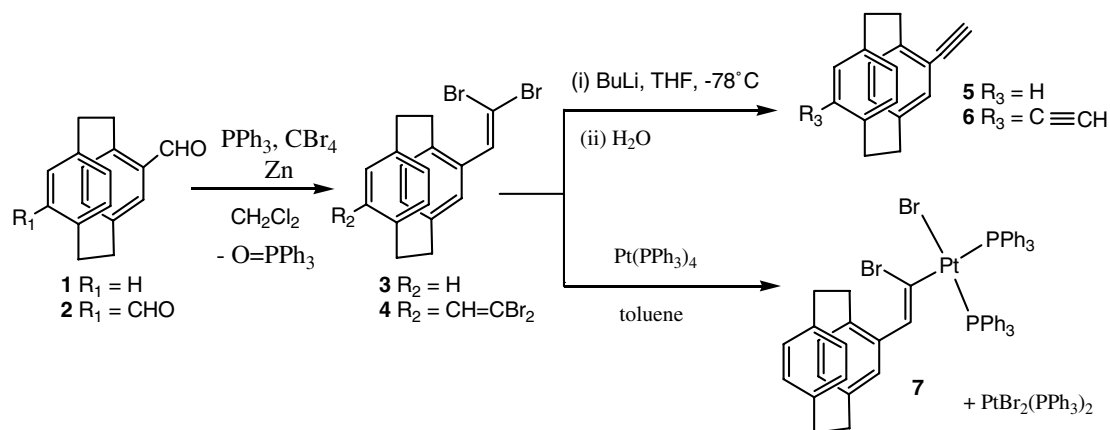
2.1. Syntheses, crystal structure and reactivity of dibromovinylparacyclophanes

Ethynyl[2.2]PCP's have been previously prepared by Hopf and co-workers from formyl derivatives [6b] or via

Pd-catalyzed Sonogashira coupling and removal of the alkyne-protecting group [11a,11b,11c]. It seemed for us desirable to develop first a more convenient and less expensive synthetic alternative leading to ethynyl[2.2]paracyclophanes. The ethynyl derivatives **5** and **6** were prepared via the Corey–Fuchs reaction in a two-step synthesis [12]. The first step of Scheme 1 implies generation of ylide species, formed in situ by the interaction of zinc dust, CBr₄ and PPh₃, which then react with the formyl derivatives **1**–**2** leading to **3**–**4** in 90–95% yield.

The molecular structure of the vinylic intermediate **3** was elucidated by an X-ray diffraction study (Fig. 1). Noteworthy is the strong tilting of the vinyl substituent. The out of plane deformation between the best plane of the aromatic cycle defined by C10–C15 and the vinyl plane defined by Br(1)–Br(2)–C(2)–C(1) amounts to 51.05°, the dihedral angle C(10)–C(1)–C(2)–Br(1) being 175.79°.

Treatment of the dibromoolefins **3** and **4** with 2 equiv. of *n*-BuLi in THF at –78°C, followed by hydrolysis, afforded after work-up the terminal alkynes **5** and **6** in 80–90% yield. Several studies have shown that the oxidative addition of vinyl halides to low-valent Pt-centers leads to Pt(II) complexes bearing an σ -alkenyl ligand [13]. For example, treatment of [Pt(PPh₃)₃] with 2,3-dibromobicyclo[2.2.1]hept-2-ene results in formation of an isomeric mixture of *cis*- and *trans*-[(3-bromobicyclo[2.2.1]hept-2-en-2-yl)-(bromo)bis(triphenylphosphine)platinum] [13d]. Unfortunately, oxidative addition of **3** across [Pt(PPh₃)₄] in toluene



Scheme 1. Synthesis and reactivity of dibromovinylparacyclophanes.

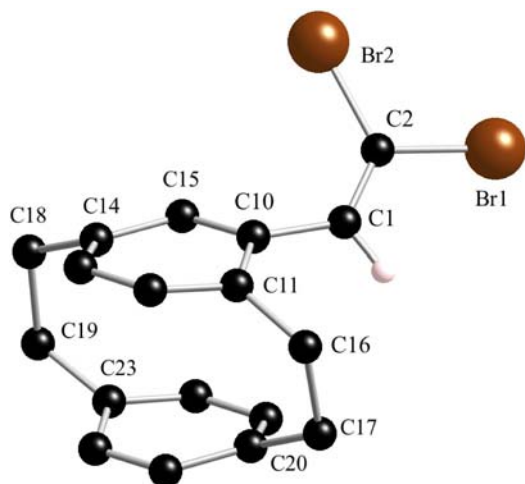


Fig. 1. View of the crystal structure of **3**. Selected bond lengths (Å) and angles (°): C(2)–Br(1) 1.885(2), C(2)–Br(2) 1.883(2), C(1)–C(2) 1.320(3), C(1)–C(10) 1.474(3); Br(1)–C(2)–Br(2) 113.63(12), Br(1)–C(2)–C(1) 120.92(19), Br(2)–C(2)–C(1) 125.44(19), C(2)–C(1)–C(10) 128.1(2), C(1)–C(10)–C(11) 120.3(2), C(1)–C(10)–C(15) 120.0(2).

at 70 °C was less straight forward. Examination of the crude reaction mixture revealed formation of a large amount of *cis*-[PtBr₂(PPh₃)₂] (ca. 45%, singlet at δ 14.8 with $^1J(\text{Pt}–\text{P}) = 3614$ Hz) [14], some O=PPh₃, and some other minor species. In addition, a doublet of doublets resonance centered at 15.3 and 13.7 with a $^2J(\text{P}–\text{P})$ coupling of 15 Hz was observed (ca. 35%). We tentatively attribute the latter AX-type signal, which is flanked by ^{195}Pt satellites with rather large $^1J(\text{Pt}–\text{P})$ couplings of 3611 and 3645 Hz, to the σ -alkenyl complex **7**, having two *cis*-arranged PPh₃ ligands. Unfortunately, we did not succeed to separate the reaction mixture; therefore, a complete and unambiguous characterization of **7** was not possible.

2.2. Functionalization of (\pm)-4-ethynyl[2.2]paracyclophane with main group elements

The choice of PCP as tunable center appears especially attractive in combination with a thiophene unit since the electron affinity of the π -electron-rich thiophene heterocy-

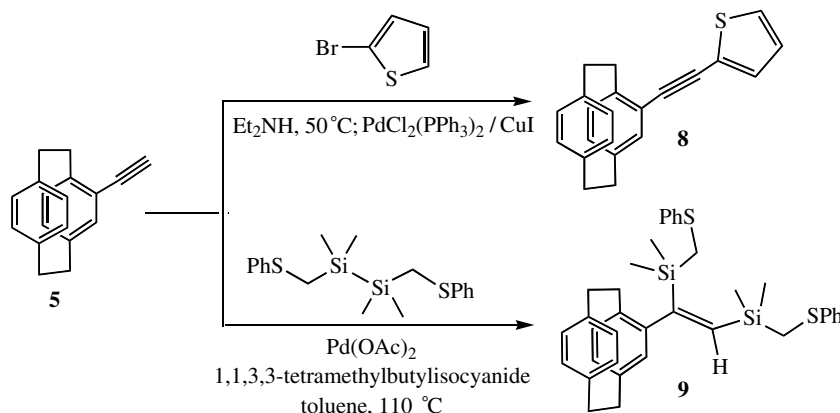
cle is similar to that of PCP. It is known that [2.2]paracyclophanes end-capped with oligothiophenes exhibit an intriguing electrochemistry (enhanced stability of both the cation radicals and dication oxidation products) [15] and fluorescence properties (high quantum yield) [16]. In order to evaluate the effect of the incorporation of an alkynyl-spacer between a PCP-moiety and a thiophene unit on the electrochemical and photophysical propensities, we have prepared the colorless internal alkyne **8**. This synthesis was achieved in 85% yield by Pd-catalyzed Sonogashira coupling of **5** with α -bromothiophene (Scheme 2).

Compound **8** exhibits a well-defined cyclic voltammogram, with formation of the radical cation as indicated by an irreversible one-electron oxidation at ca. +1.47 V vs. a silver reference electrode at 100 mV/s. Whereas **5** is not fluorescent in solution at ambient temperature, the internal alkyne **8** displays an emission at 378 nm after excitation at 319 nm (Fig. 2).

We have recently reported on the chemistry of 1,1,2,2-tetramethyl-1,2-bis(diphenylthiomethyl)disilane and exploited its potential for catalytic bis-silylation (double silylation) reactions [17]. In a similar manner, **5** was bis-silylated using Pd(OAc)₂/1,1,3,3-tetramethylbutylisocyanide as catalyst (Scheme 2), affording the olefinic dithioether **9** in 67% yield. The structural assignment of this yellow waxy solid, which displays a *cis* configuration about the olefinic double bond, is strongly supported by its spectroscopic data. In the ^1H NMR spectrum, the 4 diastereotopic Si–CH₃ groups appear at δ 0.25, 0.30, 0.54 and 0.59 as singlet resonances, the vinylic hydrogen is found at δ 6.20. Due to the non-equivalence of the SiCH₂SPh groups, the $^{29}\text{Si}\{^1\text{H}\}$ spectrum consists of two singlets at $\delta = -6.53$ and -9.94 ppm.

2.3. Coordination of (\pm)-4-ethynyl[2.2]paracyclophane on transition metals

Transition metal-mediated organic transformations serve more and more as a valuable tool for synthetic chemists [18a]. Important examples are Co₂(CO)₈-mediated reactions. The most widely known process involving



Scheme 2. Functionalization of racemic of (\pm)-4-ethynyl[2.2]paracyclophane.

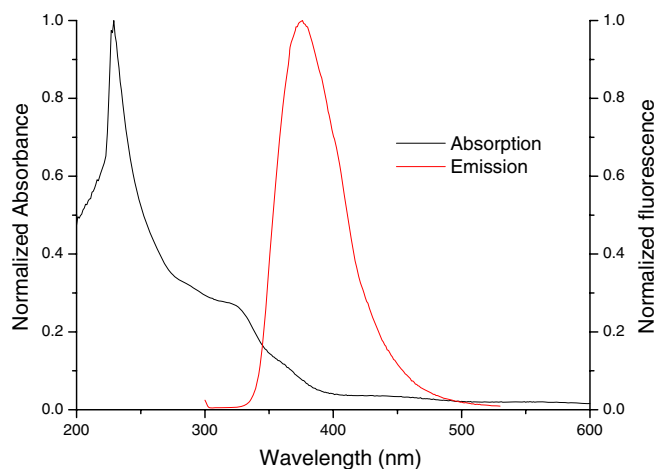


Fig. 2. Normalized absorption and emission spectra of **8** in CH_2Cl_2 at 298 K.

$\text{Co}_2(\text{CO})_8$ is the [2+2+1] cycloaddition of alkynes, alkenes and carbon monoxide (Pauson–Khand reaction) for the preparation of cyclopentenones [18b,18c]. This reagent is furthermore known to mediate alkyne trimerisation or to catalyse hydrosilylation reaction across the $\text{C}\equiv\text{C}$ bond [19,20]. **5** reacts smoothly at room temperature with $\text{Co}_2(\text{CO})_8$ in THF leading to the dinuclear complex **10** in good yield (74%). The IR spectra of **10** exhibits three strong absorptions in the carbonyl region at 2028, 2054 and 2088 cm^{-1} with spectral patterns similar to those observed for related cobalt-alkyne clusters [21]. In the ^1H NMR spectrum, the chemical shifts for the [2.2]PCP core and $\text{C}\equiv\text{CH}$ are found to be very sensitive to cobalt complexation on the adjacent alkyne bond. A significant downfield shift is observed for the resonances of the [2.2]PCP core and terminal protons in the metallatetrahedran by ca. 0.10 and 3.15 ppm with respect to the free ligand, in accordance with the reduction of the $\text{C}\equiv\text{C}$ triple-bond character [23]. The ^{13}C NMR resonances of the six carbonyls appear as a single broadened signal at δ 199.5, suggesting that they are rapidly interchanging on the NMR time scale. The molecular structure of **10** has been established by X-ray diffraction (Fig. 3) and reveals a Co–Co bond length of 2.4800(9) Å, which is shorter than in $\text{Co}_2(\text{CO})_8$ (2.52 Å) [22a]. The Co–C(alkyne) bonds distances span the range 1.964(3)–2.014(2) Å, revealing a quite symmetric dimetallatetrahedran core. The distance between the alkyne carbons C(17) and C(18) amounts to 1.339(4) Å and displays the expected elongation relative to an uncoordinated terminal $\text{C}\equiv\text{C}$ triple bond [1.20(2)–1.22(1) Å]. Moreover, the angle C(18)–C(17)–C(15) of $146.0(3)^\circ$ deviates significantly from linearity. Compared to **3**, the mean separation of the ipso carbon atoms of the PCP moiety is somewhat shorter in **10** (2.804 vs. 2.783 Å). Overall, the structural parameters of the organometallic part are similar to those described previously for other dicobalt complexes [21,22].

Reaction of **5** with $[\text{Pt}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2]$ in toluene at ambient temperature for 2 h affords $[\text{Pt}(\text{PCP}-\text{C}\equiv\text{CH})(\text{PPh}_3)_2]$ (**11**) as colorless powder, coordinated with **5** in a *side-on*

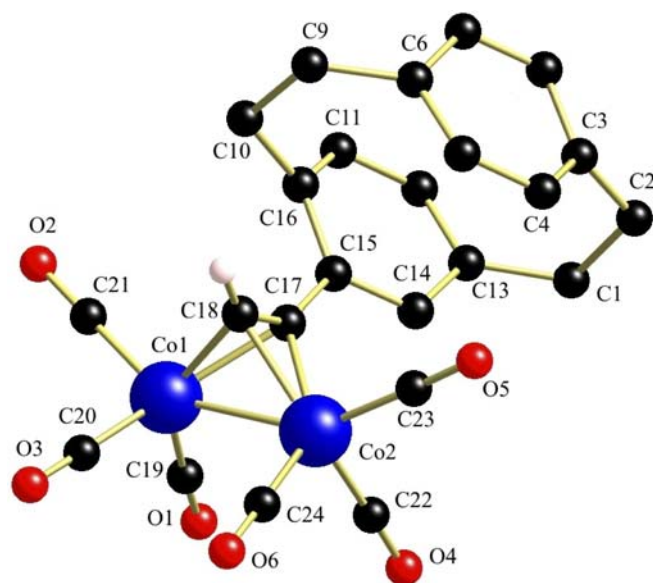
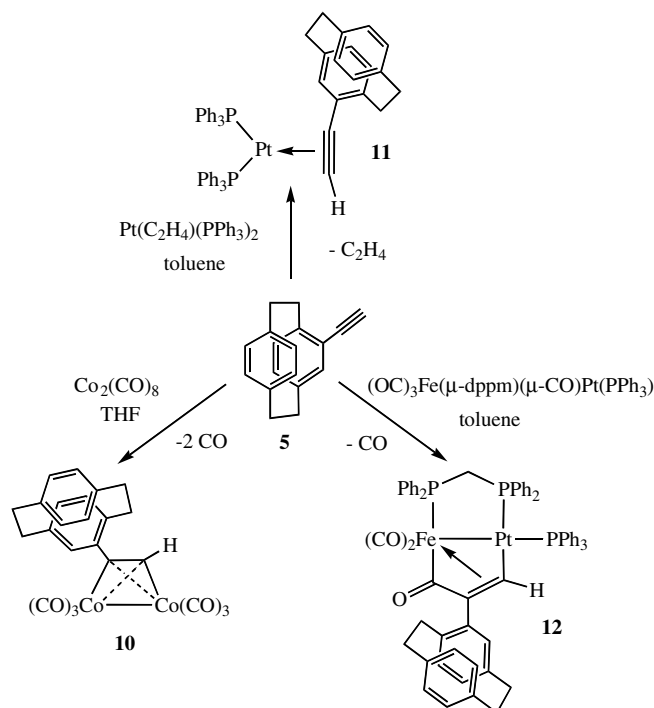


Fig. 3. View of the crystal structure of **10**. Selected bond lengths (Å) and angles ($^\circ$): Co(1)–Co(2) 2.4800(9), C(17)–Co(2) 1.979(3), C(17)–Co(1) 2.014(2), C(18)–Co(1) 1.964(3), C(18)–Co(2) 1.974(3), C(19)–Co(1) 1.814(3), C(20)–Co(1) 1.829(3), C(21)–Co(1) 1.789(3), C(22)–Co(2) 1.837(3), C(23)–Co(2) 1.802(3), C(24)–Co(2) 1.809(4), C(17)–C(18) 1.339(4), Co(2)–C(17)–Co(1) 76.79(9), C(17)–C(18)–Co(1) 72.34(16), C(17)–C(18)–Co(2) 70.42(17), Co(1)–C(18)–Co(2) 78.07(10), C(18)–C(17)–C(15) 146.0(3).

manner according Scheme 3. The ^{31}P spectrum of **11** exhibits two doublets of equal intensity at δ 27.5 and 32.1 with $^1J(\text{Pt}-\text{P})$ couplings of 3447 and 3525 Hz, respectively. In the IR spectrum, the $\text{C}\equiv\text{C}$ stretching vibration of free **5**



Scheme 3. Coordination of **5** on mono- and dinuclear complexes.

at 2098 cm^{-1} is replaced by a band occurring at 1687 cm^{-1} , the typical region expected for C=C stretching frequencies of π -coordinated acetylenes bonded on a Pt(0) center [24].

The ability of **5** for carbon–carbon coupling reactions was tested towards the heterodinuclear complex $[(\text{OC})_3\text{Fe}(\mu\text{-dppm})(\mu\text{-CO})\text{Pt}(\text{PPh}_3)]$ [25a]. After heating a toluene solution of this carbonyl-bridged compound with an slight excess of **5**, coupling of the $\mu\text{-CO}$ ligand with **5** led to $[(\text{OC})_2\text{Fe}\{\mu\text{-C(=O)C(PCP)=C(H)}\}(\mu\text{-dppm})\text{Pt}(\text{PPh}_3)]$ (**12**). The IR spectrum in the carbonyl region was indicative of the presence of two terminal carbonyl ligands and a ketonic carbonyl [$\nu(\text{C=O})$ 1686 cm^{-1}]. Furthermore, all NMR data of this orange compound were consistent with the formulation as dimetallacyclopentenone complex.

The $^{31}\text{P}\{^1\text{H}\}$ and proton NMR resonances and patterns arising from **12** are quite similar to chemical shifts and couplings reported by Shaw for related dimetallacyclopentenone complexes [25a]. Our structural proposition is furthermore supported by the $^{195}\text{Pt}\{^1\text{H}\}$ NMR spectrum. Fig. 4 shows a doublet of doublets of doublets resonance centered at $\delta -2823$, stemming from the coupling of the ^{195}Pt -nucleus of **12** with the three phosphorus nuclei.

2.4. Synthesis of (\pm)-4-isocyano[2.2]paracyclophane (**15**)

Isocyanides are versatile reactives with an interesting functional group, owing to their unusual reactivity, acting as both nucleophiles and electrophiles in the course of a reaction. Numerous applications of isocyanides in organic synthesis [26,27], grafting as SAMs on substrate surfaces [28] and in particular, coordination chemistry [29] are well

documented. In the context of our research interest on the chemistry of heterodinuclear systems towards organic RNC ligands (insertion reactions, examination of the bonding mode (bridging vs. terminal), transformation to aminocarbene ligands via electrophilic addition and photo-physic) [30], we extended our study on PCP's functionalized by triple bonds on the three-step synthesis (Scheme 4) and coordination chemistry of 4-isocyano[2,2]paracyclophane (**15**).

First racemic amine **13** was prepared by metallation of 4-bromo[2.2]PCP with *n*-BuLi and successive amination of the resulting 4-lithio derivative with MeLi/methoxyamine according to a literature procedure [31]. The formamide **14** was obtained by refluxing **13** in ethyl formate as solvent. The ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of **14** reveals the presence of two conformers (*cis* and *trans*) due to a hindered C–N rotation. In fact, the ^1H NMR spectrum shows two doublets at $\delta = 7.75$ and 8.41 assigned to C(=O)H and C(=O)H'. The observed ^{13}C NMR signals of **14** confirm its proposed structure by the appearance of two distinct methylene systems at δ 32.4, 32.8, 33.7, 33.8 (C-1, C-2, C-9, C-10) and δ 34.9, 35.0, 35.2, 35.3 (C-1', C-2', C-9', C-10'). We also observed two signals for C-17 and C-17' at δ 158.4 and 163.8. The complete spectroscopic data, all corroborating the given structural assignment of two conformations, are gathered in Section 4. Finally, **14** was transformed in 75% yield into the corresponding solid isocyanide **15**, using P(=O)Cl_3 in the presence of NEt_3 . The IR spectrum of **15** reveals a strong absorption at 2114 cm^{-1} , assigned to the $\nu(\text{C}\equiv\text{N})$ stretching vibration. In the ^{13}C spectrum, the isocyanide-type carbon C-17 appears at δ 164.5 ppm.

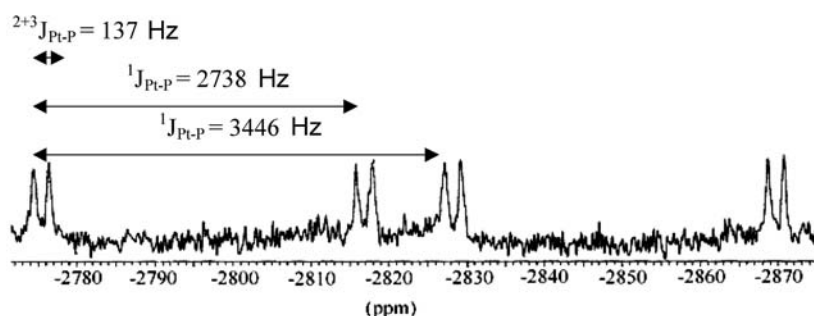
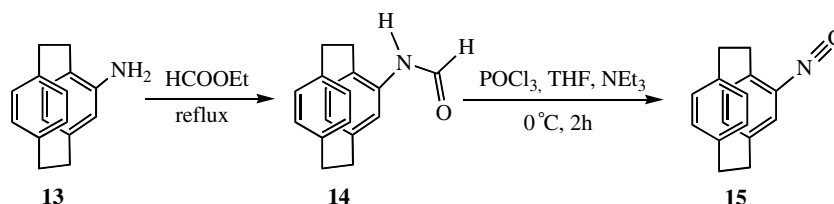


Fig. 4. $^{195}\text{Pt}\{^1\text{H}\}$ NMR spectrum of **12** (CDCl_3 at 293 K, referenced towards K_2PtCl_4 in H_2O).



Scheme 4. Synthesis of 4-isocyano[2.2]paracyclophane.

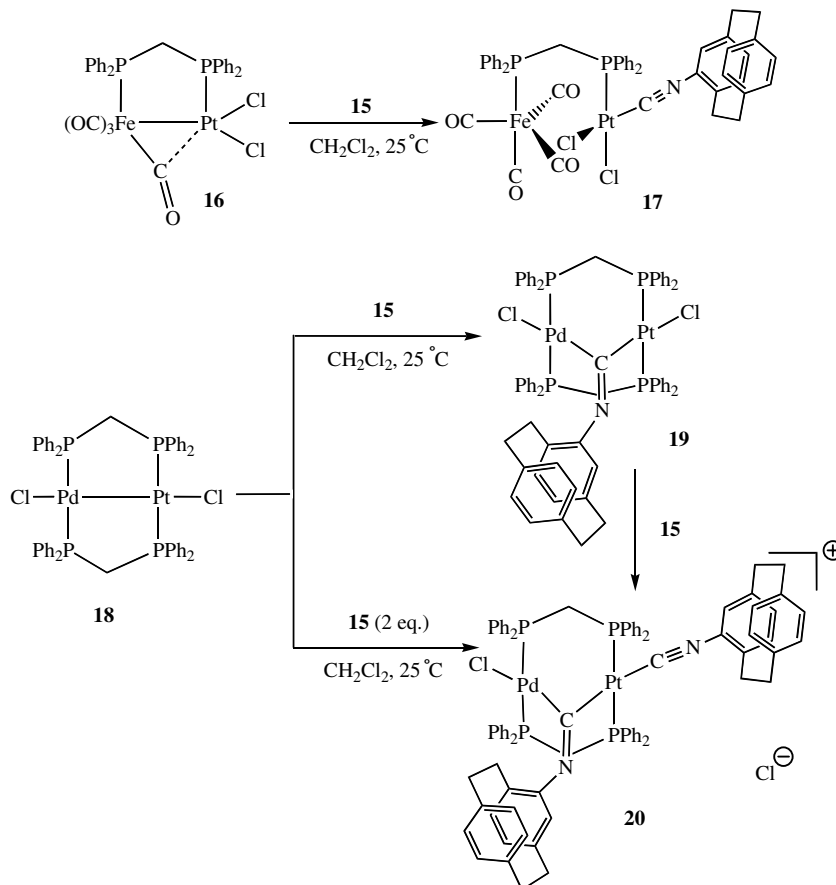
2.5. Coordination chemistry of 4-isocyano [2,2]paracyclophane

We first examined the reactivity of **15** towards the heterodimetallic complex $[(OC)_4Fe(\mu-dppm)PtCl_2]$ (**16**), possessing a semi-bridging carbonyl ligand [25b]. Instantaneous opening of the dative iron \rightarrow platinum bond occurred at ambient temperature upon addition of stoichiometric amounts of ligand **15** to a CH_2Cl_2 solution of **16**. The resulting complex $[(OC)_4Fe\{\mu-dppm\}PtCl_2(CN-PCP)]$ (**17**) was isolated in high yields as a brownish solid. It shows poor solubility in hexane or Et_2O , but is very soluble in THF or CH_2Cl_2 . Both the IR and $^{31}P\{^1H\}$ spectrum indicate the breaking of the Fe–Pt bond. The pattern and position of the four $\nu(CO)$ stretching bands at 2052, 1976, 1941 and 1931 cm^{-1} is very similar to that of $[(OC)_4Fe(\eta^1-dppm)]$. A strong $\nu(C\equiv N)$ vibration at 2204 cm^{-1} is assigned to the terminally bound isocyanide ligand on Pt. Due to the absence of a metal–metal bond, the $^2J(P-P)$ coupling of the two doublets found at δ 24.9 (P_{Fe}) and 1.7 ppm (P_{Pt}) in the $^{31}P\{^1H\}$ NMR spectrum is reduced to 20 Hz compared with the 51 Hz reported for the precursor **16**.

We have recently reported that upon addition of xilylisonocyanide to a CH_2Cl_2 solution of the d^9-d^9 system $[ClPd(\mu-dppm)_2PtCl]$ (**18**), the Pt-bound chloro-ligand is rapidly

substituted by CNR, giving exclusively the cationic complex $[ClPd(\mu-dppm)_2Pt(C\equiv Nxylyl)]Cl$ ligated by a terminal isocyanide ligand [30g]. Surprisingly, treatment of **18** with isocyanide **15** in a 1:1 ratio affords the A-frame compound $[ClPd(\mu-dppm)_2(\mu-C=N-PCP)PtCl]$ (**19**), resulting from formal insertion of **15** into the Pd–Pt bond. The bridging bonding mode of the isocyanide ligand is deduced from the IR spectrum, which exhibits a $\nu(C=N)$ vibration at 1609 cm^{-1} . This frequency lies midway between those reported for the homobimetallic A-frame compounds $[ClPd(\mu-dppm)_2(\mu-C=N-p\text{-tolyl})PdCl]$ (1627 cm^{-1}) and $[ClPt(\mu-dppm)_2(\mu-C=N-p\text{-tolyl})PtCl]$ (1531 cm^{-1}) [32]. Addition of a further equivalent of **15** to compound **19**, or addition of 2 equiv. of **15** to a CH_2Cl_2 solution of **18**, leads to the ionic A-frame compound $[ClPd(\mu-dppm)_2(\mu-C=N-PCP)Pt(C\equiv N-PCP)]Cl$ (**20**) in high yield (Scheme 5).

The coordination of **20** by both a bridging and a terminal PCP–NC ligand follows from the IR spectrum, which displays a $\nu(C=N)$ vibration of medium intensity at 1611 and a second strong $\nu(C\equiv N)$ band at 2160 cm^{-1} . The $^{31}P\{^1H\}$ NMR spectra of **19** and **20** are very broad at ambient temperature thus excluding a detailed analyses of the AA'XX' spin systems [33]. However, chemical shifts and $^1J(Pt-P)$ couplings are in the expected range (see Section 4) [30g]. Probably due to this broadness of the reso-



Scheme 5. Coordination chemistry of isocyanide ligand **15**.

nances, we failed to obtain the $^{195}\text{P}\{^1\text{H}\}$ NMR spectra despite long data acquisition periods. The preference for the *bridging* bonding mode vs. *terminal* of ligand **15** in A-frame compound **18** deserves some comments. Based on the theoretical work of Howell [34a] and our empirical observations on heterodinuclear Fe–Pt and W–Pt systems [30b,30d,30e], it seems that essentially the π -acceptor propensity of a CNR ligand is decisive for the bonding mode. Isocyanide ligands possessing a dominating σ -donor character prefer a terminal bonding mode, whereas isocyanides with sufficiently strong π -acceptor propensities may also adopt a bridging bonding mode in heterodinuclear systems. Note also that a given CNR ligand enhances markedly his π -acceptor capability by strong bending of the angle CN–R, whereas the σ -donation is not much affected by the bending [34a]. We therefore conclude that compared to xylilisocyanide, PCP-isocyanide behaves as a somewhat poorer σ -donor and more powerful π -acceptor ligand [34b]. We are aware that this hypothesis needs further experimental verification.

3. Conclusion

We have described an alternative route to synthesize in high yield alkyne-substituted [2.2]paracyclophanes. These [2.2]paracyclophanes derivatives may be modified with 2-bromothiophene to afford a thiophene functionalized alkyne or by double silylation to give an olefinic dithioether using 1,1,2,2-tetramethyl-1,2-bis(diphenylthiomethyl)disilane. Ligand $\text{PCP}-\text{C}\equiv\text{CH}$ (**5**) has also been coordinated to various mono- and dinuclear complexes and used for a carbon–carbon coupling reaction. Moreover, the isocyanide congener $\text{PCP}-\text{N}\equiv\text{C}$ (**15**) has been synthesized for the first time and coordinated on different heterobimetallic systems in a terminal and bridging bonding mode.

The emphasis of this present work was mainly an evaluation of the synthetic potential of the unsaturated ligands **5** and **15** for organometallic chemistry. We investigate actually more in detail the electrochemical and photochemical properties of all new compounds. In the light of the rich redox properties and promising propensities of mononuclear and polynuclear transition metal acetylides $\text{L}_n\text{M}-\text{C}\equiv\text{C}-\text{R}$ for photophysical applications (even with “simple” R substituents) [35], we are currently extending our project on the preparation of metal acetylides functionalized with a [2.2]paracyclophane fragment.

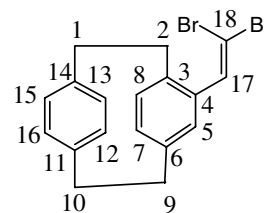
4. Experimental

General. All reactions were performed in Schlenk-tube flasks under purified nitrogen. 4-Amino[2.2]PCP (**13**), 4-formyl[2.2]PCP (**1**), 4,16-diformyl[2.2]PCP (**2**), and $[\text{Pt}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2]$ were prepared according to a literature procedure [31,36]. All solvents were predried and distilled from appropriate drying agents. IR spectra have been recorded on a Nicolet Nexus 470 spectrometer. All NMR spectra were recorded in CDCl_3 on a Bruker Avance 300

(^1H 300.13 MHz, ^{13}C 75.48 MHz and ^{31}P 121.49 MHz) using the solvent as reference, except for the ^{31}P NMR, where the chemical shifts are relative to H_3PO_4 85% in D_2O . UV–Vis spectra were recorded on a Varian Cary 50 spectrophotometer, emission spectra on a Jobin-Yvon Fluorolog-3 spectrometer.

Electrochemical set-up. Analytical experiments were performed in a three-compartment cell fitted with an AgNO_3 (0.1 M in CH_3CN) Ag reference electrode, a glassy carbon electrode (diameter 3 mm) and a platinum counter electrode. The electrochemical apparatus was an Autolab PGSTAT 20 Potentiostat Galvanostat (Ecochemie). The solvent was spectroscopic grade CH_2Cl_2 with $[\text{NBu}_4][\text{PF}_6]$ (TBAF) as supporting electrolyte. Concentration of the monomeric substrate was 2×10^{-3} M. Under these conditions, the $E_{1/2}$ of $\text{Cp}_2\text{Fe}^{+/0}$ was found to be $0.11 \text{ V} \pm 0.01 \text{ V}$ vs. an Ag reference.

4.1. General procedure for the preparation of the dibromo olefins **3** and **4**



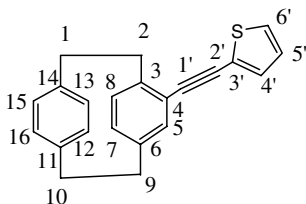
PPh_3 (2.40 g, 8.5 mmol), CBr_4 (2.80 g, 8.5 mmol) and zinc dust (0.55 g, 8.5 mmol) are placed in a Schlenk tube and CH_2Cl_2 (25 mL) is added slowly. The mixture is stirred at room temperature for 28 h. Then, **1** (1.00 g, 4.24 mmol), dissolved in CH_2Cl_2 (10 mL), is added and stirring is continued for 2 h. The reaction mixture is extracted with three 50 mL portions of pentane. CH_2Cl_2 is added when the reaction mixture became too viscous for further extractions. The extracts are filtered and evaporated under reduced pressure. Crystallization from pentane gave 1.578 g of **3** in 95% yield. m.p. 153–154 °C. Anal. Calc. for $\text{C}_{18}\text{H}_{16}\text{Br}_2$: C, 55.13; H, 4.11. Found: C, 55.35; H, 4.28%. ^1H NMR: δ 2.95 (m, 7H, CH_2), 3.24 (ddd, 1H, $J_1 = 9.4$, $J_2 = 7.0$, $J_3 = 2.4$ Hz, CH_2), 6.45 (m, 7H_{aromat}), 7.31 (s, 1H, $\text{CH}=\text{CBr}_2$). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 33.9, 34.7, 35.2, 35.5 (C-1, C-2, C-9, C-10), 90.1 (C-18), 130.2, 132.4, 133.2, 133.25, 133.3, 133.4, 135.0, 136.5 (C-5, C-7, C-8, C-12, C-13, C-15, C-16, C-17), 135.6 (C-4), 138.4, 139.3, 139.6, 139.9 (C-3, C-6, C-11, C-14). UV–Vis (CH_2Cl_2) [λ_{max} , nm (ϵ): 229 (15849 $\text{M}^{-1} \text{cm}^{-1}$), 289 (5623 $\text{M}^{-1} \text{cm}^{-1}$). Compound **4** was obtained in a similar manner from **2** with 94% yield. m.p. 183 °C. Anal. Calc. for $\text{C}_{20}\text{H}_{16}\text{Br}_4$: C, 41.71; H, 2.80. Found: C, 41.63; H, 2.71%. ^1H NMR: δ 3.00 (m, 7H, CH_2), 3.24 (m, 1H, CH_2), 6.43 (d, 2H, $J = 8.2$ Hz, H_{aromat}), 6.59 (d, 2H, $J = 2.1$ Hz, H_{aromat}),

6.65 (dd, 2H, $J = 8.2$, $J = 2.1$ Hz, H_{aromat}), 7.43 (s, 2H, $CH=CBR_2$). $^{13}C\{^1H\}$ NMR: δ 34.9, 35.4 (C-1, C-2, C-9, C-10), 90.5 (C-18, C-20), 130.5, 134.0, 135.7, 135.8 (C-5, C-7, C-8, C-12, C-13, C-15, C-16, C-17), 136.2 (C-4, C-16), 138.1, 139.3 (C-3, C-6, C-11, C-14). UV–Vis (CH_2Cl_2) [λ_{max} nm (ϵ): 229 (57600 $M^{-1} cm^{-1}$), 266 (20500 $M^{-1} cm^{-1}$).

4.2. Conversion of dibromoolefins **3** and **4** to **5** and **6**

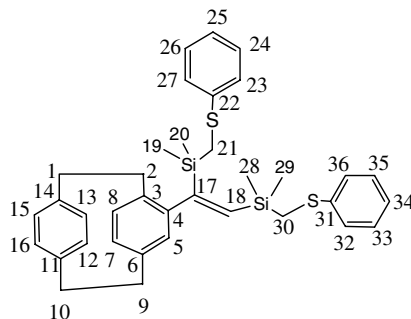
A solution of 3.5 mmol of **3** in 25 mL of dry THF is cooled to $-78^\circ C$. 7.0 mmol of *n*-BuLi (2.5 M) is added dropwise to the cold solution. After cooling 1 h at $-78^\circ C$, the mixture is allowed to warm to room temperature and stirring is continued one additional hour. The mixture is poured into water and extracted with CH_2Cl_2 . The organic layer is dried over Na_2SO_4 and evaporated under reduced pressure. The residue is then purified by column chromatography on silica gel with CH_2Cl_2 /petroleum ether ($v/v = 1:4$) as eluent to give **5** (91% yield). **6** is obtained in a similar manner from **4** in 90% yield.

4.3. Sonogashira coupling of **5** with 3-bromothiophene



Diethylamine (20 mL), **5** (232 mg, 1 mmol), CuI (5 mg, 0.026 mmol), 2-bromothiophene (163 mg, 1 mmol) and $PdCl_2(PPh_3)_2$ (15 mg, 0.021 mmol) are placed in a flask. The mixture is first degassed, then purged with Ar and heated to $50^\circ C$ for 48 h. Then the mixture is poured into water and extracted with CH_2Cl_2 . The extract is dried over Na_2SO_4 and evaporated under reduced pressure. The residue is purified by column chromatography on silica gel with petroleum ether/ CH_2Cl_2 ($v/v = 3:7$) as eluent affording 267 mg (85% yield) of **8** as a pale yellow powder. Anal. Calc. for $C_{23}H_{22}S$: C, 83.59; H, 6.70; S, 9.70. Found: C, 83.45; H, 6.62; S, 9.65%. IR (KBr): 2192(w) cm^{-1} . 1H NMR: δ 3.10 (m, 7H, CH_2), 3.60 (m, 1H, CH_2), 6.55 (m, 7H, H-6', H-5, H-7, H-12, H-13, H-15, H-16), 7.00 (d, 1H, $J = 7.6$ Hz, H-8), 7.10 (dd, 1H, $J = 4.1$, $J = 4.7$ Hz, H-5'), 7.35 (d, 1H, $J = 4.1$ Hz, H-4'). $^{13}C\{^1H\}$ NMR: δ 34.3, 34.5, 35.1, 35.4 (C-1, C-2, C-9, C-10), 85.9 (C-1'), 93.4 (C-2'), 123.8 (C-3'), 124.4 (C-4), 127.0, 127.2, 130.1, 131.4, 132.4, 132.7, 132.9, 133.3, 133.9 (C-4', C-5', C-6', C-7, C-8, C-12, C-13, C-15, C-16), 136.7 (C-5), 139.3, 139.5, 139.7 (C-6, C-11, C-14), 142.4 (C-3). UV–Vis (CH_2Cl_2) [λ_{max} nm (ϵ): 229 (46800 $M^{-1} cm^{-1}$), 319 (12900 $M^{-1} cm^{-1}$).

4.4. Preparation of *Z*-PhSCH₂Me₂SiC(H)=C(PCP)SiMe₂CH₂SPh (**9**)



To a toluene solution (10 mL) containing 1,1,2,2-tetramethyl-1,2-bis(diphenylthiomethyl)disilane (181 mg, 0.5 mmol), **5** (100 mg, 0.43 mmol) and palladium acetate (4 mg, 0.019 mmol) was added 1,1,3,3-tetramethylbutyl isocyanide (12 mg, 0.084 mmol). The yellow mixture turned quickly to red after heating to $110^\circ C$. Agitation was continued for 20 h, then all volatiles were removed under reduce pressure. The residue is purified by column chromatography on silica gel with petroleum ether/ CH_2Cl_2 ($v/v = 4:1$) as eluent and afforded 171 mg (67% yield) of **9** as a yellow waxy solid. Anal. Calc. for $C_{36}H_{42}S_2Si_2$: C, 72.67; H, 7.11; S, 10.78. Found: C, 72.86; H, 7.34; S, 10.52%. 1H NMR: δ 0.25 (s, 3H, $SiCH_3$), 0.30 (s, 3H, $SiCH_3$), 0.54 (s, 3H, $SiCH_3$), 0.59 (s, 3H, $SiCH_3$), 1.93 (d, 1H, $SiCH_2$, $J_1 = 12.1$ Hz), 2.04 (d, 1H, $SiCH_2$, $J_1 = 12.1$ Hz), 2.52 (s, 2H, $SiCH_2$), 3.10 (m, 7H, CH_2), 3.60 (m, 1H, CH_2), 6.20 (s, 1H, $C=CH$), 6.60–7.20 (m, $17H_{\text{aromat}}$). $^{13}C\{^1H\}$ NMR: δ -0.80 , -0.72 , -0.54 , -0.44 (C-19, C-20, C-28, C-29), 18.4, 18.5 (C-21, C-30), 35.35, 35.25, 35.15, 34.4 (C-1, C-2, C-9, C-10), 124.5, 124.8, 125.8, 126.0, 126.2, 126.5, 128.4, 128.6, 128.7, 129.8, 129.9, 132.1, 132.2, 132.5, 133.0, 134.2, 135.3 (C-5, C-7, C-8, C-12, C-13, C-15, C-16, C-23, C-24, C-25, C-26, C-27, C-32, C-33, C-34, C-35, C-36), 139.3, 139.4, 139.5, 139.7, 139.9, 140.1, 145.4 (C-3, C-4, C-6, C-11, C-14, C-22, C-31), 146.4 (C-18), 164.5 (C-17). $^{29}Si\{^1H\}$ NMR: -6.53 (s), -9.94 (s). UV–Vis (hexane) [λ_{max} nm (ϵ): 228 (13600 $M^{-1} cm^{-1}$), 258 (8500 $M^{-1} cm^{-1}$), 286 (4600 $M^{-1} cm^{-1}$).

4.5. Preparation of $[Co_2(CO)_6(\mu-\eta^2-PCP-CCH)]$ (**10**)

Compound **5** (116 mg, 0.5 mmol) is added in small portions to a THF solution (7 mL) of dicobalt octacarbonyl (171 mg, 0.5 mmol). The mixture is stirred for 2 h at room temperature. The solvent is removed under vacuum and the dark residue extracted with hot hexane. After several days at $5^\circ C$, **10** is isolated from the hexane extract in the form of dark crystals (192 mg, 74% yield). Anal. Calc. for $C_{24}H_{16}Co_2O_6$: C, 55.62; H, 3.11. Found: C, 55.48; H, 3.09%. IR (KBr): $\nu(C\equiv O)$ 2088(vs), 2054(vs), 2028(vs).

^1H NMR: δ 3.10 (m, 7H, CH_2), 3.30 (m, 1H, CH_2), 6.35 (d, 1H, $J = 7.6$ Hz, $\text{H}_{\text{aromatic}}$), 6.40 (d, 1H, $J = 7.6$ Hz, $\text{H}_{\text{aromatic}}$), 6.45 (s, 1H, $\text{H}_{\text{acetylenic}}$), 6.50 (s, 1H, $\text{H}_{\text{aromatic}}$), 6.55 (s, 1H, $\text{H}_{\text{aromatic}}$), 6.65 (s, 3H, $\text{H}_{\text{aromatic}}$). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 34.3, 35.1 (X2), 35.3, (C-1, C-2, C-9, C-10), 75.9 (C-18), 90.7 (C-17), 130.0, 132.4, 132.7, 132.9, 133.3, 135.1, 135.7, (C-5, C-7, C-8, C-12, C-13, C-15, C-16), 136.2 (C-4), 137.5 (C-6), 139.3, 139.6 (C-11, C-14), 140.7 (C-3), 199.6 (C-19–24). UV–Vis (CH_2Cl_2) [λ_{max} nm (log ϵ): 229 (18 700 $\text{M}^{-1} \text{cm}^{-1}$), 318 (17 000 $\text{M}^{-1} \text{cm}^{-1}$).

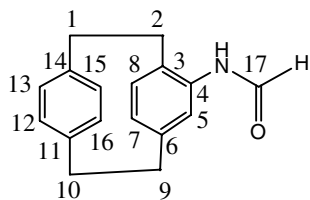
4.6. Preparation of $[\text{Pt}(\text{PPh}_3)_2(\text{PCP}-\text{CCH})]$ (**11**)

Compound **5** (116 mg, 0.3 mmol) was dissolved in toluene (3 mL) and $[\text{Pt}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2]$ (224 mg, 0.3 mmol) was added. A gas was evolved and the mixture was stirred at room temperature for 2–3 h. The resulting solution was concentrated and the product was precipitated with ether petroleum and dried under vacuum. Yield: 68%. Anal. Calc. for $\text{C}_{54}\text{H}_{46}\text{P}_2\text{Pt}$: C, 68.14; H, 4.84. Found: C, 68.18; H, 4.89%. IR (CH_2Cl_2): 1687 ($\nu\text{C}\equiv\text{C}$) cm^{-1} . ^1H NMR: δ 2.65–3.31 (m, 8H, CH_2), 5.99 (d, 1 H_{aromat} , $J_1 = 7.5$ Hz), 6.17 (d, 1 H_{aromat} , $J_2 = 7.7$ Hz), 6.32 (d, 1 H_{aromat} , $J_2 = 7.7$ Hz), 6.51 (m, 3 H_{aromat}), 6.78 (d, 1 H_{aromat} , $J_1 = 7.5$ Hz), 7.06–7.52 (m, 30H, Ph). $^{31}\text{P}\{^1\text{H}\}$ NMR: δ 27.5 (d, $^2J(\text{P}-\text{P}) = 37$, $^1J(\text{Pt}-\text{P}) = 3447$ Hz), 32.1 (d, $^2J(\text{P}-\text{P}) = 37$, $^1J(\text{Pt}-\text{P}) = 3525$ Hz).

4.7. Preparation of $[(\text{OC})_2\text{Fe}\{\mu-\text{C}(=\text{O})\text{C}(\text{PCP})\text{CH}\}]$ ($\mu\text{-dppm}$) $\text{Pt}(\text{PPh}_3)]$ (**12**)

To a solution of $[(\text{OC})_3\text{Fe}(\mu\text{-dppm})(\mu\text{-CO})\text{Pt}(\text{PPh}_3)]$ (151 mg, 0.15 mmol) in toluene, 1.5 equiv. of **5** (53 mg) were added. After stirring for 2–3 h at 60 °C, all volatiles were removed in vacuo, the orange residue washed with hexane and dried in vacuo. Yield: 142 mg (78%). Anal. Calc. for $\text{C}_{64}\text{H}_{53}\text{FeO}_3\text{P}_3\text{Pt}$: C, 63.32; H, 4.40. Found: C, 63.22; H, 4.38%. IR (KBr): 1958(vs), 1910(vs) $\nu(\text{C}\equiv\text{O})$, 1686 (s) ($\nu\text{C}=\text{O}$). $^{31}\text{P}\{^1\text{H}\}$ NMR: δ 9.5 ($\text{P}_{2\text{Pt}}$), dd, $^2J(\text{P}_2-\text{P}_3)$, $^{2+3}J(\text{P}_2-\text{P}_1) = 57$ Hz), 32.0 (P_{3PPh_3} , dd, $^2J(\text{P}_2-\text{P}_3) = 5$, $^{3+4}J(\text{P}_1-\text{P}_3) = 36$ Hz), 62.7 ($\text{P}_{1\text{Fe}}$, dd, $^2J(\text{P}_1-\text{P}_3) = 36$, $^{2+3}J(\text{P}_1-\text{P}_2) = 57$ Hz). $^{195}\text{Pt}\{^1\text{H}\}$ NMR: δ -2823 (ddd, $^{2+3}J_{\text{Pt}-\text{P}_1} = 137$, $^1J(\text{Pt}-\text{P}_2) = 2738$, $^1J(\text{Pt}-\text{P}_3) = 3446$ Hz).

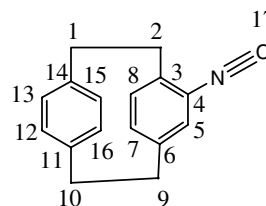
4.8. Preparation of 4-formamido [2.2]paracyclophane (**14**)



Compound **13** (348 mg, 1.5 mmol) was dissolved in ethyl formate and refluxed for 12 h, and then the excess ethyl formate was removed under reduced pressure. The resulting

mixture was chromatographed on silica gel with CH_2Cl_2 as eluent. Yield: 83%. m.p. 195–196 °C. Anal. Calc. for $\text{C}_{17}\text{H}_{16}\text{NO}$: C, 81.57; H, 6.44. Found: C, 81.45; H, 6.28%. IR (CH_2Cl_2): 3238 ($\nu\text{N}-\text{H}$), 1693 ($\nu\text{C}=\text{O}$) cm^{-1} . ^1H NMR: 2.72–2.79 (m, 1H, CH_2), 2.88–3.1 (m, 6H, CH_2), 3.2–3.26 (m, 1H, CH_2), 6.01 (s, 1H, NH), 6.35–6.53 (m, 6 $\text{H}_{\text{aromatic}} + \text{NH}'$), 6.75 (dd, $J_1 = 1.3$, $J_2 = 5.9$ Hz), 7.75 (d, 1H, $\text{C}(=\text{O})\text{H}$, $J_3 = 7.1$ Hz), 8.41 (d, 1H, $\text{C}(=\text{O})\text{H}'$, $J_4 = 8.6$ Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 32.4, 32.8, 33.7, 33.8 (C-1, C-2, C-9, C-10), 34.9, 35.0, 35.2, 35.3 (C-1', C-2', C-3', C-4'), 125.0, 126.8, 128.0, 128.2, 129.4, 129.5, 130.3, 130.8, 131.7, 132.3, 133.2, 133.3, 133.6, 135.2, 135.4, 135.7, 136.0, 138.6, 139.2, 139.3, 139.5, 141.4, 141.8 (C-5, C-5', C-7, C-7', C-8, C-8', C-12, C-12', C-13, C-13', C-15, C-15', C-16, C-16', C-3, C-3', C-4, C-4', C-6, C-6', C-11, C-11', C-14, C-14'), 158.4 (C-17), 163.8 (C-17'). UV–Vis (CH_2Cl_2) [λ_{max} nm (ϵ): 229 (2290 $\text{M}^{-1} \text{cm}^{-1}$), 273 (5300 $\text{M}^{-1} \text{cm}^{-1}$).

4.9. Preparation of 4-isocyano[2.2]paracyclophane (**15**)



To a solution of **14** (251 mg, 1 mmol) and NEt_3 (696 μL , 5 mmol) in THF (4 mL) was added at 0 °C dropwise over 10 min $\text{O}=\text{PCl}_3$ (102 μL , 1.1 mmol) in THF (1 mL). The reaction mixture was stirred for 2 h at 0 °C and then poured into water. After extracted with ethyl acetate, the organic layer was dried over anhydrous Na_2SO_4 , filtered and concentrated under reduced pressure. Chromatography on silica gel with CH_2Cl_2 /petroleum ether ($v/v = 1:1$) as eluent gave **15** in form of a brownish powder. Yield: 75%. m.p. 133–134 °C. Anal. Calc. for $\text{C}_{17}\text{H}_{15}\text{N}$: C, 87.52; H, 6.48; N, 6.00. Found: C, 87.42; H, 6.38; N, 5.92%. IR (KBr): 1436, 1501, 1594, 2114 ($\nu\text{N}\equiv\text{C}$), 2854, 2894, 2926, 3038 cm^{-1} . ^1H NMR: δ 2.85–3.28 (m, 8H, CH_2), 6.36 (s, 1 H_{aromat}), 6.51 (m, 4 H_{aromat}), 6.62 (dd, 1 H_{aromat} , $J_1 = 1.8$, $J_2 = 7.9$ Hz), 7.09 (dd, 1 H_{aromat} , $J_1 = 1.8$, $J_2 = 7.9$ Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 32.4 (C-1), 33.5 (C-2), 34.8, 35.2 (C-9, C-10), 128.5 (C-4), 131.9 (C-15), 132.4, 132.9 (C-7, C-12), 133.5 (C-13, C-16), 133.7, 134.7 (C-8), 135.0 (C-5), 136.8 (C-11), 139.2 (C-6, C-14), 141.5 (C-3), 164.5 (C-17). UV–Vis (CH_2Cl_2) [λ_{max} nm (ϵ): 229 (14 200 $\text{M}^{-1} \text{cm}^{-1}$), 272 (2400 $\text{M}^{-1} \text{cm}^{-1}$).

4.10. Preparation of $[(\text{OC})_4\text{Fe}\{\mu\text{-dppm}\}\text{PtCl}_2(\text{CN}-\text{PCP})]$ (**17**)

To a suspension of **16** (62 mg, 0.075 mmol) in CH_2Cl_2 (2 mL), the equivalent amount of **15** (17 mg, 0.075 mmol)

dissolved in 1 mL of CH_2Cl_2 was added over 5 min. The resulting clear solution was stirred for a further 10 min, then the solvent was removed affording **17** in almost quantitative yield. Anal. Calc. for $\text{C}_{46}\text{H}_{37}\text{Cl}_2\text{FeNO}_4\text{P}_2\text{Pt} \cdot \text{CH}_2\text{Cl}_2$: C, 49.60; H, 3.43; N, 1.23. Found: C, 49.52; H, 3.38; N, 1.21%. IR (CH_2Cl_2): 2204 (s), $\nu(\text{C}\equiv\text{N})$; 2052 (s), 1976 (s), 1941(vs), 1931(vs) $\nu(\text{CO}) \text{ cm}^{-1}$. $^{31}\text{P}\{^1\text{H}\}$ NMR: δ 1.70 (d, P_{Pt} , $^2J(\text{P}_{\text{Pt}}-\text{P}_{\text{Fe}}) = 20$, $^1J(\text{Pt}-\text{P}_{\text{Pt}}) = 3319$ Hz), 24.88 (d, P_{Fe} , $^2J(\text{P}_{\text{Pt}}-\text{P}_{\text{Fe}}) = 20$, $^3J(\text{Pt}-\text{P}_{\text{Fe}}) = 123$ Hz). ^1H NMR: δ 2.78–3.25 (m, 8H, CH_2), 4.21 (m, 2H, CH_2), 6.12–6.83 (m, 7 H_{aromat}), 7.43–7.96 (m, 20H, Ph).

4.11. General procedure for the preparation of the A-frame compounds **19** and **20**

One equivalent (23 mg, 0.1 mmol) or two equivalent (46 mg, 0.2 mmol) of **13**, diluted in 2 mL of CH_2Cl_2 , were added within 30 min to a stirred solution of **18** (114 mg, 0.1 mmol) in 3 mL of CH_2Cl_2 . The reddish solution was stirred for 1 d and then evaporated to dryness. The orange residue, obtained in almost quantitative yield, was washed with 5 mL of Et_2O and dried in vacuum.

Compound **19**: Anal. Calc. for $\text{C}_{67}\text{H}_{59}\text{Cl}_2\text{NP}_4\text{PdPt} \cdot \text{CH}_2\text{Cl}_2$: C, 55.89; H, 4.18; N, 0.96. Found: C, 55.87; H, 4.08; N, 0.95%. IR (KBr): 1609(m) cm^{-1} $\nu(\text{C}\equiv\text{N})$. $^{31}\text{P}\{^1\text{H}\}$ NMR: δ 15.5 (m, unresolved, P_{Pt} , $^1J(\text{Pt}-\text{P}) = 3523$ Hz), 13.1 (m, unresolved, P_{Pd}). ^1H NMR: δ 2.10–2.52 (m, 8H, CH_2), 2.79 (m, 4H, PCH_2P), 5.62 (d, 1 H_{aromat} , $J_1 = 7.9$ Hz), 5.70 (d, 1 H_{aromat} , $J_1 = 7.9$ Hz), 6.01 (d, 1 H_{aromat} , $J_1 = 7.9$ Hz), 6.09 (d, 1 H_{aromat} , $J_1 = 7.9$ Hz), 6.28 (d, 1 H_{aromat} , $J_1 = 7.9$ Hz), 6.33 (d, 1 H_{aromat} , $J_1 = 7.9$ Hz), 6.36 (s, 1H), 7.01–8.3 (m, 40H, Ph). UV–Vis (CH_2Cl_2) [λ_{max} nm (ϵ): 228 (55920 $\text{M}^{-1} \text{ cm}^{-1}$), 273 (59630 $\text{M}^{-1} \text{ cm}^{-1}$), 396 (4290 $\text{M}^{-1} \text{ cm}^{-1}$).

Compound **20**: Anal. Calc. for $\text{C}_{84}\text{H}_{74}\text{Cl}_2\text{N}_2\text{P}_4\text{PdPt}$: C, 62.75; H, 4.64; N, 1.74. Found: C, 62.87; H, 4.68; N, 1.75%. IR (CH_2Cl_2): 1611(m) cm^{-1} $\nu(\text{C}\equiv\text{N})$, 2160 (s) $\nu(\text{C}\equiv\text{N}) \text{ cm}^{-1}$; $^{31}\text{P}\{^1\text{H}\}$ NMR: δ 18.8 (m, unresolved, $^1J(\text{Pt}-\text{P}) = 3740$ Hz). ^1H NMR: δ 2.31 (m, br, 4H, PCH_2P), 2.44–2.94 (m, 16H, CH_2), 5.95 (s, 1 H_{aromat}), 6.23 (m, br, 4 H_{aromat}), 6.98–8.23 (m, 49H, Ph + H_{aromat}). UV–Vis (CH_2Cl_2) [λ_{max} nm (ϵ): 228 (62870 $\text{M}^{-1} \text{ cm}^{-1}$), 273 (31050 $\text{M}^{-1} \text{ cm}^{-1}$), 395 (6620 $\text{M}^{-1} \text{ cm}^{-1}$), 468 (4250 $\text{M}^{-1} \text{ cm}^{-1}$).

4.12. Crystal structure determinations

Relevant crystallographic details are given in Table 1. Measurements were carried out on a Stoe IPDS diffractometer (**10**) and a Bruker APEX-CCD diffractometer (**3**). The intensities of **10** were determined and corrected by the program INTEGRATE in IPDS (Stoe & Cie, 1999). An empirical absorption correction was employed using the FACET-program in IPDS (Stoe & Cie, 1999). The intensities of **3** were determined and corrected by the programs Smart version 5.622 (Bruker AXS, 2001) and SaintPlus version 6.02 (Bruker AXS, 1999). An empirical absorption correction was

Table 1
Crystallographic and refinement data for **3** and **10**

	3	10
Formula	$\text{C}_{18}\text{H}_{16}\text{Br}_2$	$\text{C}_{24}\text{H}_{16}\text{Co}_2\text{O}_6$
Formula weight (g mol^{-1})	392.13	518.23
T (K)	173(2)	193(2)
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$C2/c$
a (Å)	16.8119(16)	20.385(5)
b (Å)	8.1412(8)	7.6128(12)
c (Å)	11.1957(11)	29.280(5)
β (°)	105.340(2)	108.59(2)
V (Å ³)	1477.8(2)	4306.9(14)
Z	4	8
ρ_{calc} (mg m^{-3})	1.763	1.598
μ (mm^{-1})	5.472	1.579
$F(000)$	776	2096
θ Range (°)	1.6–26.04	2.11–26.00
Index ranges	$-20 \leq h \leq 20$, $-10 \leq k \leq 10$, $-13 \leq l \leq 13$	$-25 \leq h \leq 25$, $-9 \leq k \leq 9$, $-35 \leq l \leq 35$
Collected reflections	29779	30116
Independent reflections [R_{int}]	2902 [0.0354]	4193 [0.0658]
Data/restraints/parameters	2902/0/181	4193/0/293
Largest differences in peak and hole (e Å^{-3})	0.947 and -0.456	0.565 and -0.882
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0253$, $wR_2 = 0.0747$	$R_1 = 0.0516$, $wR_2 = 0.1432$
R indices (all data)	$R_1 = 0.0300$, $wR_2 = 0.0855$	$R_1 = 0.0593$, $wR_2 = 0.1517$
Goodness-of-fit on F^2	1.01	1.062

employed using Sadabs version 2.01 (Bruker AXS, 1999). All structures were solved applying direct and Fourier methods, using SHELXS-90 (G.M. Sheldrick, University of Göttingen 1990) and SHELXL-97 (G.M. Sheldrick, SHELXL97, University of Göttingen 1997). Refinement of the structures was carried out by full-matrix least-squares methods based on F_o^2 (SHELXL-97). The non-hydrogen atoms were refined with anisotropic thermal parameters for all non-H atoms in the final cycles. All of the H-atoms were placed in geometrically calculated positions and each was assigned a fixed isotropic displacement parameter based on a riding-model. All calculations were performed using the WinGX crystallographic software package, using the programs SHELXS-90 and SHELXL-97 [37].

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Appendix A. Supplementary material

CCDC 298766 and 298767 contain the supplementary crystallographic data for **3** and **10**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic

Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.10.039.

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