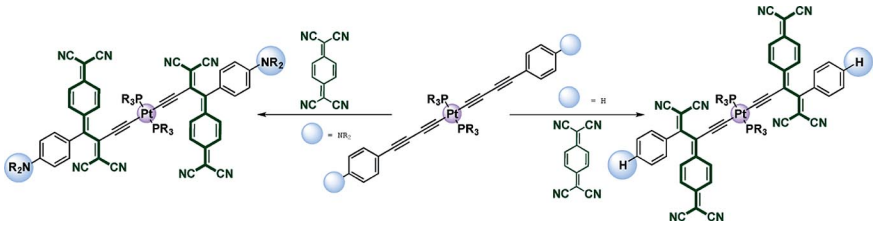
EurJOC European Journal of Organic Chemistry

Platinum Acetylides



Donor-activated triple bonds act as substrates for cycloaddition-retroelectrocyclization reactions with TCNE or TCNQ to give cyanobutadienes. Herein we showcase the activation ability of two classes of donors: organic amines and platinum(II) centers directly bound to the acetylenic moieties and compare them directly for the first time.

Keywords: Cycloaddition / Platinum / Charge transfer / Donor–acceptor systems / Regioselectivity / Alkynes

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Platinum(II) Acetylides in the Formal [2+2] Cycloaddition-Retroelectrocyclization Reaction: Organodonor Versus Metal Activation

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Keywords: Cycloaddition / Platinum / Charge transfer / Donor–acceptor systems / Regioselectivity / Alkynes

Formal cycloaddition-retroelectrocyclization (CA-RE) reactions between electron-donor-activated alkynes and electron-poor alkenes yielding cyanobuta-1,3-dienes have recently attracted increasing interest. The transformation has been subjected to a fundamental investigation of the relative degrees of alkyne activation by organic and metallorganic donor substituents by using platinum(II) σ-acetylides as model substrates and studying their behavior towards the cyano carbons TCNE and TCNQ. Various cyanobutadienes were obtained in good to excellent yields and four trends in reactivity were discerned: 1) The presence of an anilino substituent clearly dominates the regioselectivity of the TCNQ addition. 2) In the absence of an organodonor, the regioselectivity is inverted. 3) When platinum(II) complexes of buta-1,3-diynes are used, the addition always takes place at the triple bond distal to the metal center. 4) In general, *trans*-bis-acetylides are more reactive than the corresponding *cis* complexes. The structural parameters of the CA-RE adducts were investigated by X-ray crystallography and their optical properties by UV/Vis spectroscopy, giving further insights into the structural trends and degree of intramolecular charge transfer. These fundamental investigations may enable the synthesis of new Pt-based molecular dyads in which the effect of regioselectivity on photoinduced charge separation can be studied.

Introduction

The formal [2+2] cycloaddition reaction between electron-poor alkenes and organodonor-activated alkynes followed by a retroelectrocyclization of the transient cyclobutene intermediate (CA-RE cascade, Scheme 1) is a versatile transformation that has been the subject of a growing number of studies and been used in various applications.[1–4] It is a "click"-type transformation[5] that is atom-economic, does not require catalysis, proceeds under mild conditions in high yields, and exhibits high chemo- and regioselectivity. Among the best studied olefinic substrates are tetracyanoethene (TCNE)[6] and 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ).[7] The transformation yields organodonor-substituted cyanobuta-1,3-dienes as the products (Scheme 1) that are nonplanar along the butadiene backbone exhibit a significant degree of push–pull conjugation,[8] as evidenced by their intense, bathochromically shifted intramolecular CT bands. The CA-RE reaction has been used for the synthesis of novel molecular architectures[9] and materials featuring remarkable optoelectronic properties.[10,11]

Initial reports by Bruce[12] and others[13] on this reaction focused on platinum or ruthenium σ-acetylides as donors with TCNQ[12a,12b] or TCNE,[12c] and the transformation was proposed to proceed by a similar mechanism to the all-organic systems illustrated in Scheme 1, formally an enyne metathesis.

We became interested in a direct comparison between the alkyne-activating effects of organodonors and transition-metal centers such as the σ-bound Pt^{II}. If the alkynes are functionalized with both types of substituents, which one has a dominating activating effect and thereby determines the regioselectivity of the CA-RE reaction? A first step towards answering this question was made in our recent study on ferrocenyl- and *N*,*N*-dimethylanilino (DMA)-substituted alkynes and 1,3-diynes, in which we found that the neutral DMA group was superior to the ferrocene as an alkyne-activating element for the CA-RE reaction.[14] Upon protonation of the DMA group, however, the reactivity was switched and the ferrocene moiety exerted the activating effect.

Herein we report the synthesis of a series of platinum(II) σ-acetylide complexes bearing weak (phenyl) and strong (anilines) organodonors on the alkyne moieties, and their CA-RE reactions with TCNE and TCNQ. The acetylide complexes are reasonably air-stable and readily synthesized; they have therefore found widespread application as robust structural building blocks in molecular and polymeric materials.[15] Furthermore, their well-defined square-planar co-

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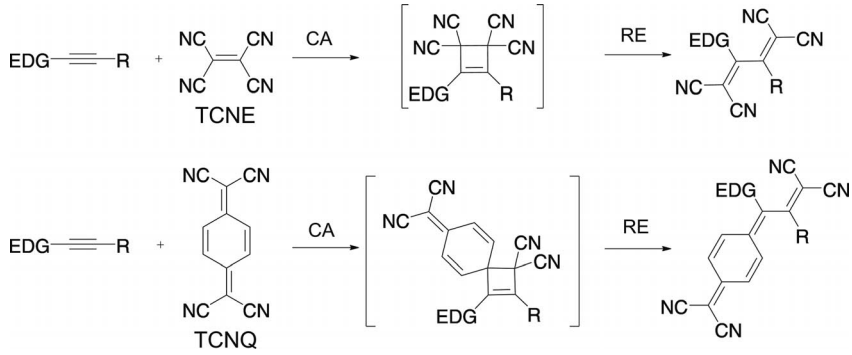


Scheme 1. General representation of the CA-RE reactions with tetracyanoethene (TCNE) and 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ). EDG = electron-donating group.

ordination geometry makes them particularly useful in the construction of shape-persistent molecular scaffolds.[16] This study has shown that the regioselectivity of CA-RE reactions of organodonor-substituted platinum(II) σ-acetylides can be controllably varied depending on the ligands on the platinum and the configuration of the complexes.

Results and Discussion

Synthesis of *trans*-Platinum(II) Bis-acetylides and Their CA-RE Reactions

We prepared a series of differently substituted *trans*-platinum(II) bis-acetylides by treating the corresponding *trans*-bis(phosphane)platinum(II) dichloride with 2 equiv. of alkyne and Cu^{I} iodide as the catalyst in diisopropylamine (Table 1).[17]

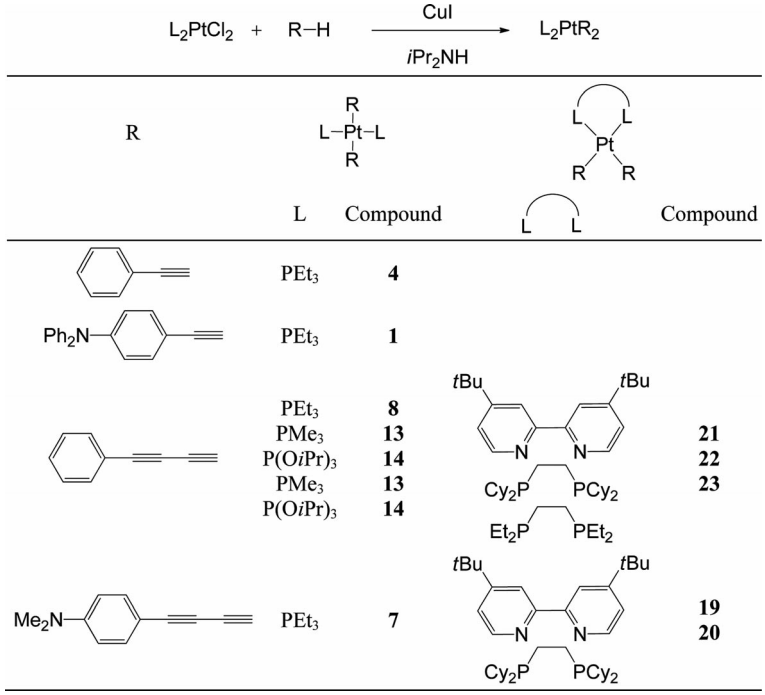
The symmetric *trans*-bis-acetylide **1** was treated with TCNE at ambient temperature for 24 h to afford bis-adduct **2** as the sole product (Scheme 2). In contrast, when the reaction was conducted with TCNQ as the acceptor, the second addition to the triple bond did not occur at all and only monoadduct **3** was formed. In the product, the dicyanoquinodimethane (DCNQ) moiety is adjacent to the *N*,*N*-diphenylanilino group (confirmed by X-ray crystallographic analysis, see Figure 2). This regioselectivity contrasts that previously observed in the case of *trans*-bis(trimethylphosphane)bis(1-propynyl)platinum(II), which lacks the aniline donor substituent.[12b] This finding gave rise to the hypothesis that the electronic nature of the substituents on the alkynes as well as the steric bulk of the phosphane ligands determine the regioselectivity of the reactions.

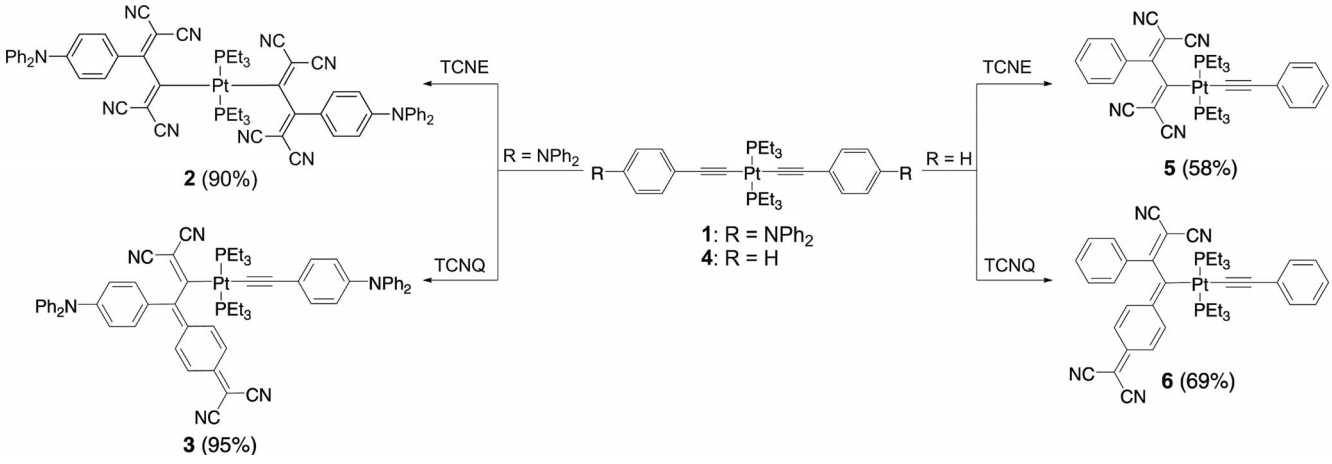
The relative reactivities of the anilino-substituted complex **1** and phenyl-substituted bis-acetylide **4** were examined to deduce the influence of the electron-donating *N*,*N*-diphenylanilino groups on the alkyne properties. In the absence of an anilino donor, compound **4** was much less reactive and full conversion was observed only at elevated reaction temperatures. Only single additions leading to adducts **5** and **6** were observed. Most importantly, the regioselectivity of the TCNQ addition to the triple bond was inverted: the DCNQ moiety in adduct **6** is on the carbon atom directly attached to the platinum (confirmed by X-ray crystallographic analysis, see Figure 2). From previous studies it is known that the C-atom of the acetylene at the β-position relative to the strongest donor substituent attacks the exocyclic dicyanovinyl center, followed by ring closure at the endocyclic quaternary sp^2 C-atom to yield the cyclobutene intermediate, which subsequently opens.[7,14,18] In the reaction of **1** with TCNQ, the nucleophilic sp C-atom is in the β-position with respect to the anilino donor, whereas in the reaction of **4**, it is the other sp C-atom in the β-position relative to the Pt^{II} center and, accordingly, a product of inverted regioselectivity is obtained.

This comparison showcases several key reactivity aspects of platinum acetylides: 1) The bis(phosphane)platinum center can act as a competent donor, promoting the CA-RE reaction of the triple bond attached to it, consistent with the findings by Bruce and co-workers,[2] 2) in the case of direct competition between platinum and the anilino donor on the same acetylene unit, the regioselectivity of TCNQ addition is determined by the anilino moiety, 3) platinum is generally a weaker donor, as deduced from the attenuated reactivity of complex **4** and the exclusive formation of mono adducts, and 4) the second CA-RE reaction is generally slower than the first reaction.

Aiming to validate these principles, we expanded our substrate studies by varying the number of alkyne units in the platinum complexes. The change from acetylide to 1,3-diacetylide ligands on the platinum added another dimension to the regioselectivity of the CA-RE reactions, namely the question of which triple bond in the buta-1,3-diynyl fragments would take part in the transformation. We prepared the *trans*-bis(buta-1,3-diynyl) complex **7** bearing two *N*,*N*-dimethylanilino (DMA) substituents and complex **8** in which the diyne moieties are capped only by phenyl rings (Scheme 3).[17] The adducts of DMA-activated complex **7** with TCNE (**9**) and TCNQ (**10**) were readily formed in CH_2Cl_2 at ambient temperature in quantitative yields. The additions occurred readily at the triple bonds next to the aniline moieties. These findings were unambiguously confirmed by X-ray crystallographic analysis and are in agreement with the expectation that the CA-RE reaction occurs at the triple bond next to the strongest donor that is also the least sterically hindered activating group. No further addition products were observed even in the presence of excess

Table 1. Overview of the *trans*- and *cis*-platinum(II) bis-acetylides used in this study.

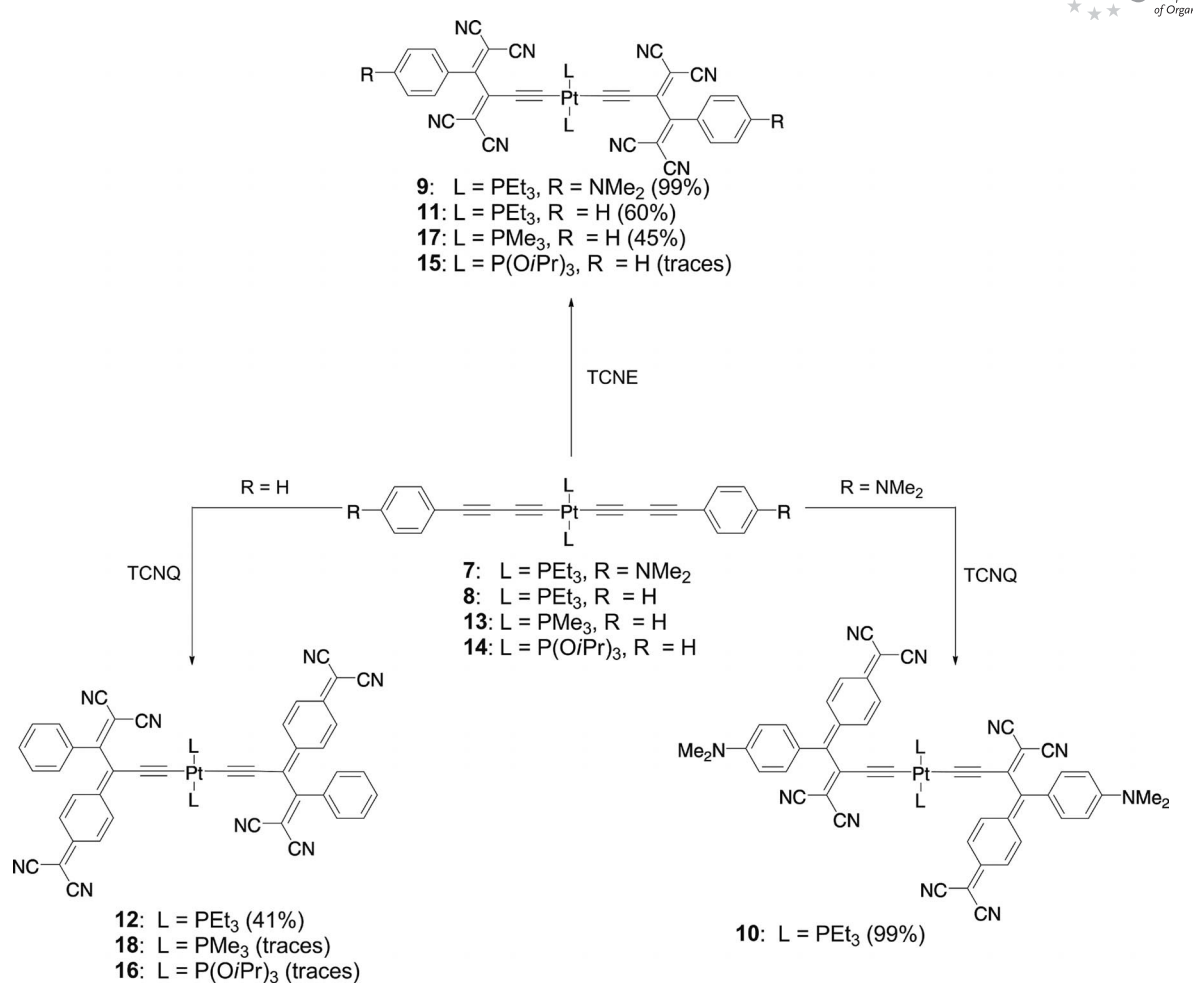




Scheme 2. Reactions of Pt complexes **1** and **4** with TCNE and TCNQ. Conditions for the synthesis of **2**: **1**, TCNE (2 equiv.), $C_2H_2Cl_4$, 25 °C, 24 h. For **3**: **1**, TCNQ (2 equiv.), $C_2H_2Cl_4$, 25 °C, 18 h. For **5**: **4**, TCNE (2 equiv.), $C_2H_2Cl_4$, 70 °C, 20 h. For **6**: **4**, TCNQ (2 equiv.), $C_2H_2Cl_4$, 80 °C, 23 h.

of the alkene reagents, which reflects the deactivation of the remaining triple bonds by the newly introduced, strongly electron-accepting tetracyanobutadiene and cyclohexadienyl-expanded tetracyanobutadiene moieties, respectively, in the adducts.[19]

Due to the absence of strong amine donors, the reactions of the bis(4-phenylbuta-1,3-diynyl) complex **8** with TCNE and TCNQ needed to be carried out at elevated temperatures (110 °C) and required longer reaction times to form bis-adducts **11** and **12**, respectively, in only moderate yields. Interestingly, X-ray crystallographic analysis of these products revealed that the acceptor compounds reacted with the triple bonds adjacent to the phenyl rings, although the platinum center was expected to be the stronger directing donor center in **8** (Scheme 3). The regioselectivity of the TCNQ addition leading to complex **12** is inverted compared with **10**. This indicates that the platinum center sufficiently activates the terminal C-atom of the bound buta-1,3-diynyl moiety, which reacts in the first step at the exocyclic C-atom of the dicyanovinyl moiety of TCNQ with the formation of a zwitterionic intermediate, which subsequently closes to the cyclobutene.[18] Furthermore, attack of the distal acetylene avoids the steric hindrance that would occur if the proximal acetylene next to the Pt-center reacts. Nevertheless, the fact that the distal triple bond, and not the one next to the bis(phosphane)platinum(II) center, is involved in the reac-



Scheme 3. Reactions of *trans*-bis(buta-1,3-diynyl)platinum(II) complexes **7**, **8**, **13**, and **14** with TCNE and TCNQ. Conditions for the synthesis of **9**: **7**, TCNE (4 equiv.), CH_2Cl_2, 25 °C, 45 min. For **10**: **7**, TCNQ (2.5 equiv.), CH_2Cl_2, 25 °C, 3 h. For **11**: **8**, TCNE (4 equiv.), $C_2H_2Cl_4$, 110 °C, 21 h. For **12**: **7**, TCNQ (5 equiv.), $C_2H_2Cl_4$, 110 °C, 15 h. For **15**: **14**, TCNE (5 equiv.), $C_2H_2Cl_4$, 140 °C, 48 h. For **16**: **14**, TCNQ (5 equiv.), $C_2H_2Cl_4$, 140 °C, 48 h. For **17**: **13**, TCNE (5 equiv.), $C_2H_2Cl_4$, 110 °C, 24 h. For **18**: **13**, TCNQ (5 equiv.), $C_2H_2Cl_4$, 110 °C, 28 h.

tions was surprising and required further investigation. We therefore investigated 1) why the reactions in *trans*-bis(buta-1,3-diynyl)platinum(II) complexes occur at the triple bond more distant from the platinum center and 2) whether other aspects of the Pt^{II} complex structure, namely the configuration (*cis* vs. *trans*), affect the reactivity pattern of this class of compounds.

To test the influence of the electronic and steric nature of the P-ligands on platinum, we focused our attention on two additional *trans*-bis(buta-1,3-diynyl) complexes, **13** and **14**, which lack DMA activation. Trimethylphosphane, the ancillary ligand in complex **13**, has approximately the same electron-donating properties as triethylphosphane in **8**, but has a significantly smaller steric demand (phosphane cone angle of 118° for PMe_3 vs. 132° for PEt_3).[20] On the other hand, triisopropyl phosphite (complex **14**) has essentially the same cone angle (130°) as PEt_3. It is, however, much less electron-donating. We treated the two complexes with TCNE and TCNQ. The phosphite complex **14** was substantially deactivated and reacted only at high temperature (140 °C) with the cyano-olefins to produce traces of the bis-adducts **15** and **16** (HR-MALDI-MS), but the majority of the starting material decomposed under the reaction conditions. The most interesting question, however, concerned the reactions of complex **13** with the two cyano-olefins. We were able to isolate and structurally characterize TCNE bis-adduct **17**, which has a structure similar to that of the corresponding DMA-substituted adduct **9**. The reaction of **13** with TCNQ, however, led to the formation of an inseparable mixture of products and the formation of bis-adduct **18** could only be observed by HR-MALDI-MS. This is a substantial difference in comparison with acetylide derivatives **1** and **4**, for which the CA-RE reaction with TCNQ stopped after the addition of 1 equiv. of the olefin. On the other hand, there is a common trend in the bis(buta-1,3-diynyl) complexes: The triple bond that takes part in the reaction is the one more distant from the platinum center.

These experiments demonstrate that the electron-donating properties of the phosphane ligand influence the outcome of the CA-RE reaction: Sufficiently electron-donating ancillary ligands are necessary for obtaining CA-RE products. The addition of buta-1,3-diynyl moieties occurs at the

distal triple bond, presumably due to shielding of the proximal triple bonds by the alkyl groups on the P ligands. This is consistent with the previous findings of Bruce and coworkers in related ruthenium diyne complexes.[2a,2b,2e,2f]

Synthesis of *cis*-Platinum(II) Bis-acetylides and Their CA-RE Reactions

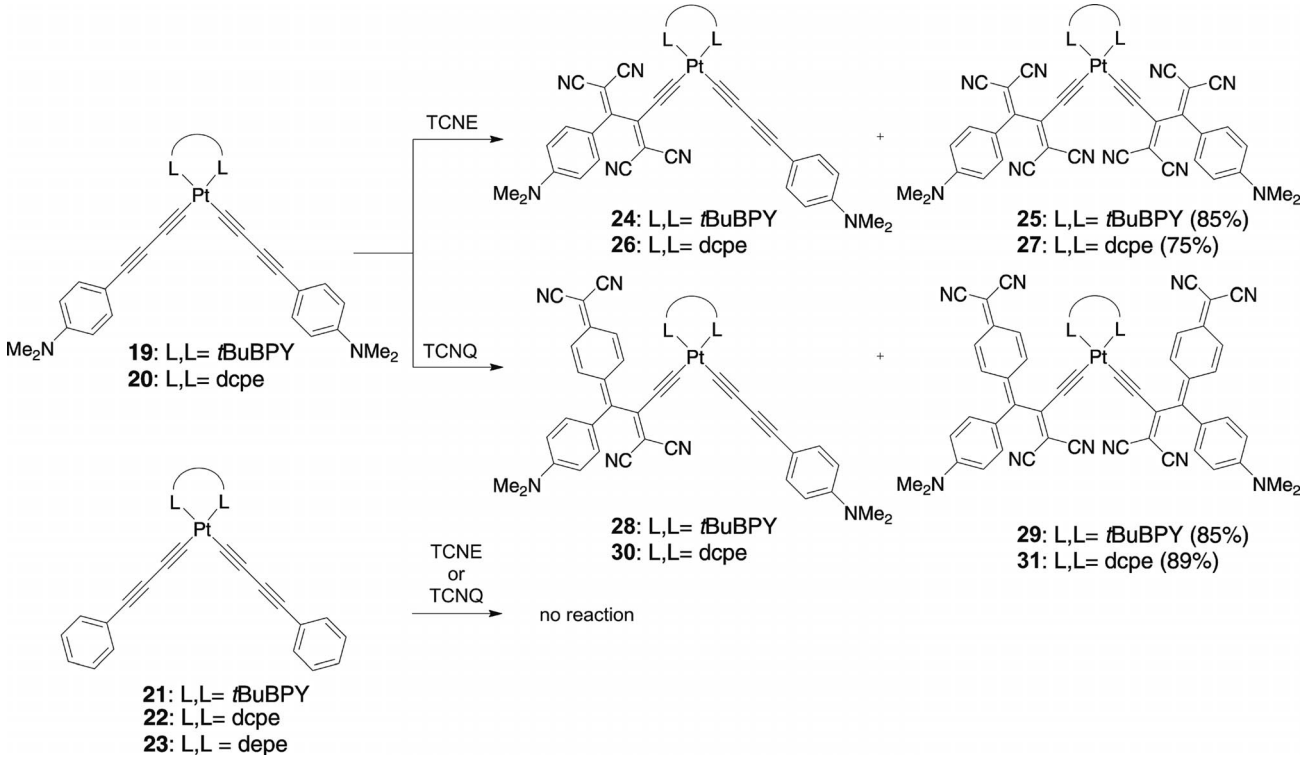
Lastly, we investigated the behavior of *cis*-platinum(II) acetylides in TCNE and TCNQ cycloaddition reactions. We prepared a series of *cis*-complexes with different bidentate ligands (**19**–**23**, Scheme 4) by treating the corresponding *cis*-dichloridoplatinum(II) complexes with 2 equiv. of the alkyne in diisopropylamine in the presence of copper(I) iodide as the catalyst (Table 1).[17]

They were subsequently subjected to CA-RE reactions with TCNE and TCNQ under conditions similar to those employed in the study of the *trans*-complexes. The starting complexes were selected to make a direct comparison between 1) a strongly donating, bulky bidentate ligand, 1,2-bis(dicyclohexylphosphanyl)ethane (dcpe), as in **20** and **22**, and a less donating, less sterically demanding ligand, 4,4′-di-*tert*-butyl-2,2′-bipyridine (*t*BuBPY), as in complexes **19** and **21**, 2) ethynyl and buta-1,3-diynyl ligands, 3) the reactivity in the presence or absence of DMA donors, and 4) the reactivity of the *cis*-complex **23** bearing a ligand, 1,2-bis(diethylphosphanyl)ethane (depe), with electronic and steric features similar to those of PEt_3 and *trans*-complex **8**.

Reaction with TCNE or TCNQ took place only in the cases of bis(buta-1,3-diynyl) complexes **19** and **20**, which bear activating DMA moieties. In sharp contrast, the bis-ethynyl derivatives **21**–**23** are completely inert and did not undergo the CA-RE reaction, even at 140 °C. Contrary to the *trans*-complexes, the second CA-RE reaction is faster than the first; when the *cis*-complexes were treated with only 1 equiv. of alkene, mixtures of mono- and bis-adducts (compounds **24**/**25**, **26**/**27**, **28**/**29**, **30**/**31**, Scheme 4) were obtained. These observations indicate that in the absence of strong organic donor moieties, the triple bonds in the *cis* starting materials are not sufficiently activated to react with either TCNE or TCNQ, as opposed to the *trans*-acetylides. This finding will be discussed further in the comparison of the crystal structures of starting complexes **23** and **13** below.

X-ray Crystal Structures

Almost all CA-RE products furnished single crystals suitable for X-ray crystallographic analysis, in most cases by slow diffusion of *n*-hexane into a CH_2Cl_2 solution of the compound. In some cases, low temperatures or slow evaporation of the solvent was necessary to obtain specimens of crystallographic quality. The crystal structures of starting Pt acetylides **13** and **23** are compared in Figure 1,



Scheme 4. CA-RE reactions of *cis*-bis(buta-1,3-diynyl)platinum(II) complexes **19** and **20** with TCNE and TCNQ. The mono-adducts **24**, **26**, **28**, and **30** were isolated in low yields when the reactions were carried out with 1 equiv. of the alkene. When 2 equiv. were used, almost full conversion to the bis-adducts was observed. Conditions for the synthesis of **25**: **19**, TCNE (2 equiv.), CH_2Cl_2, 25 °C, 48 h. For **27**: **20**, TCNE (2 equiv.), CH_2Cl_2, 25 °C, 28 h. For **29**: **19**, TCNQ (2 equiv.), CH_2Cl_2, 25 °C, 24 h. For **31**: **20**, TCNQ (2 equiv.), CH_2Cl_2, 25 °C, 24 h.

and Figure 2 shows the crystal structures of the CA-RE adducts **2**, **5**, **6**, **9**, **10**, **12**, and **17**. Further crystallographic data are summarized in Table 2 and in the Supporting Information. The crystal structures demonstrate interesting structural trends in the CA-RE products and unambiguously confirm the regioselectivity of the transformation.

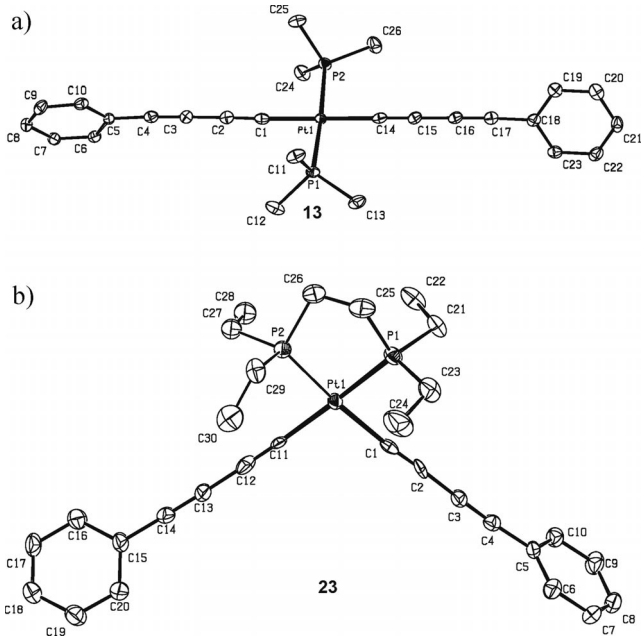


Figure 1. ORTEP representation of the molecular structures of complexes a) **13** and b) **23** in the crystal. Hydrogen atoms and solvent molecules have been removed for clarity. The positions of P2 and its ethyl substituents in **23** are disordered; only one of the positions is shown (see the Supporting Information for details). Thermal elipsoids are shown at the 50% probability level. Selected bond lengths [Å]: a) Pt1–C1 1.992(2), C1–C2 1.204(3), C2–C3 1.380(4), C3–C4 1.202(2); b) Pt1–C1 2.057(7), C1–C2 1.113(9), C11–C12 1.121(9), C2–C3 1.427(9), C12–C13 1.407(10), C3–C4 1.194(9), C13–C14 1.197(9).

The crystal structures of starting bis(buta-1,3-diynyl) complexes *trans*-**13** and *cis*-**23** suggest that the steric bulk of the ancillary phosphane ligands on Pt in both complexes prevents the reaction at the proximal acetylene activated by the metal center (Figure 1). An interesting difference in bond lengths is observed between the two structures, presumably due to a *trans*-influence of the ligands on the platinum atom. In *trans*-**13**, the Pt–C bonds are substantially shortened [1.992(2) Å for Pt1–C1 and 1.996(2) Å for Pt1–C14, compared to 2.057(7) Å and 2.077(7) Å in **23**], and the bond-length alternation is less pronounced, with C≡C bond lengths of 1.202(4) Å and a single bond length of 1.380(4) Å (C2–C3). This observation suggests that there is a higher degree of conjugation and delocalization across the platinum center in *trans*-complex **13** than in the *cis*-complex **23**. In the latter, the Pt–C bonds are longer, and more pronounced bond-length alternation is observed. The C2–C3 single bond length is 1.428(4) Å [1.408(4) Å for C12-C13] and the two acetylene groups differ strongly, with 1.113(9) Å [1.121(9) Å] for the proximal and 1.194(9) Å [1.197(9) Å] for the distal C≡C bond. The Pt–C bond elongation in **23** is consistent with the well-known *trans*-influence due to electron donation from the strong phosphane ligand in the case of the *cis*-complexes.[21] However, the C1–C2 triple bond length in **23** is short, even for a *cis*-platinum acetylide (with a typical bond length of 1.20 Å).[21] Thus, conjugation across the platinum center seems to be less effective in the *cis*-complex. A possible explanation for the observed differences in reactivity is the fact that more extended conjugation in *trans*-**13** could reduce the HOMO-LUMO gap in the π-system (unlike **23**, where the two acetylene ligands are in an orthogonal arrangement to each other), leading to easier electron transfer and thereby facilitating the formation of a charge-transfer (CT) complex, which is generally accepted as the initial step of the reaction.[2c,2d]

Comparison of the crystal structures of the CA-RE adducts yields interesting trends concerning the nature of the charge transfer in these compounds (Figure 2). All the products are donor–acceptor chromophores, and the presence of intramolecular, ground-state CT is verified by a set of structural parameters derived from X-ray crystallographic data (Table 2). A good starting point for this analysis is the quinoid character of the aromatic rings δr (defined in caption of Table 2).[6b,22] Within the subset of anilino-substituted platinum complexes (**9**, **10**, **2**), the highest value [δr = 0.056(5)] is observed for DMA derivative **9**. The analogous compound **2**, however, which lacks the extra acetylene spacer group between the Pt-center and the tetracyanobutadiene unit, exhibits a lower degree of intramolecular charge transfer [δr = 0.017(6), 0.021(6)] due to competition with the CT interactions of the tetracyanobutadiene with the bis(phosphane)platinum(II) center. The TCNQ adduct **10** shows an intermediate value [δr = 0.029(9)], which can be explained by the increased steric hindrance of the DCNQ moiety, leading to higher distortion [θ_1 = 34.4(16)°], thus reducing the degree of conjugation between the DMA donor and the DCNQ acceptor moiety. Further confirmation for the strong intramolecular CT in **9** is the diminished bond length alternation in the alkyne spacer, which is characterized by a significant shortening of the Pt–C8 bond [1.971(6) Å, numbering according to Table 2] compared with 1.992 Å for a typical Pt^{II}–C(sp) bond[23] and C5–C7 [1.409(7) Å vs. 1.456 Å],[23] as well as by a lengthening of the C7–C8 bond [1.223(8) Å vs. 1.188 Å] compared with related platinum alkynyl complexes.[23] This reduced bond length alternation indicates that there is a CT interaction between the metal center and the adjacent dicyanovinyl acceptor. Taking these findings together, the system exhibits two independent donor–acceptor fragments that do not communicate because of the nonplanarity around the C3–C5 single bond, which furthermore is substantially lengthened [1.505(6) Å].

In the absence of the strong DMA donor, the TCNQ additions in complex **12** show different regioselectivity compared with **10** because the Pt center has become the strongest donor in the system. As a result of the lack of a donor substituent on the phenyl rings, the CA-RE products **11**, **12**, and **17** exhibit essentially no quinoid character in these

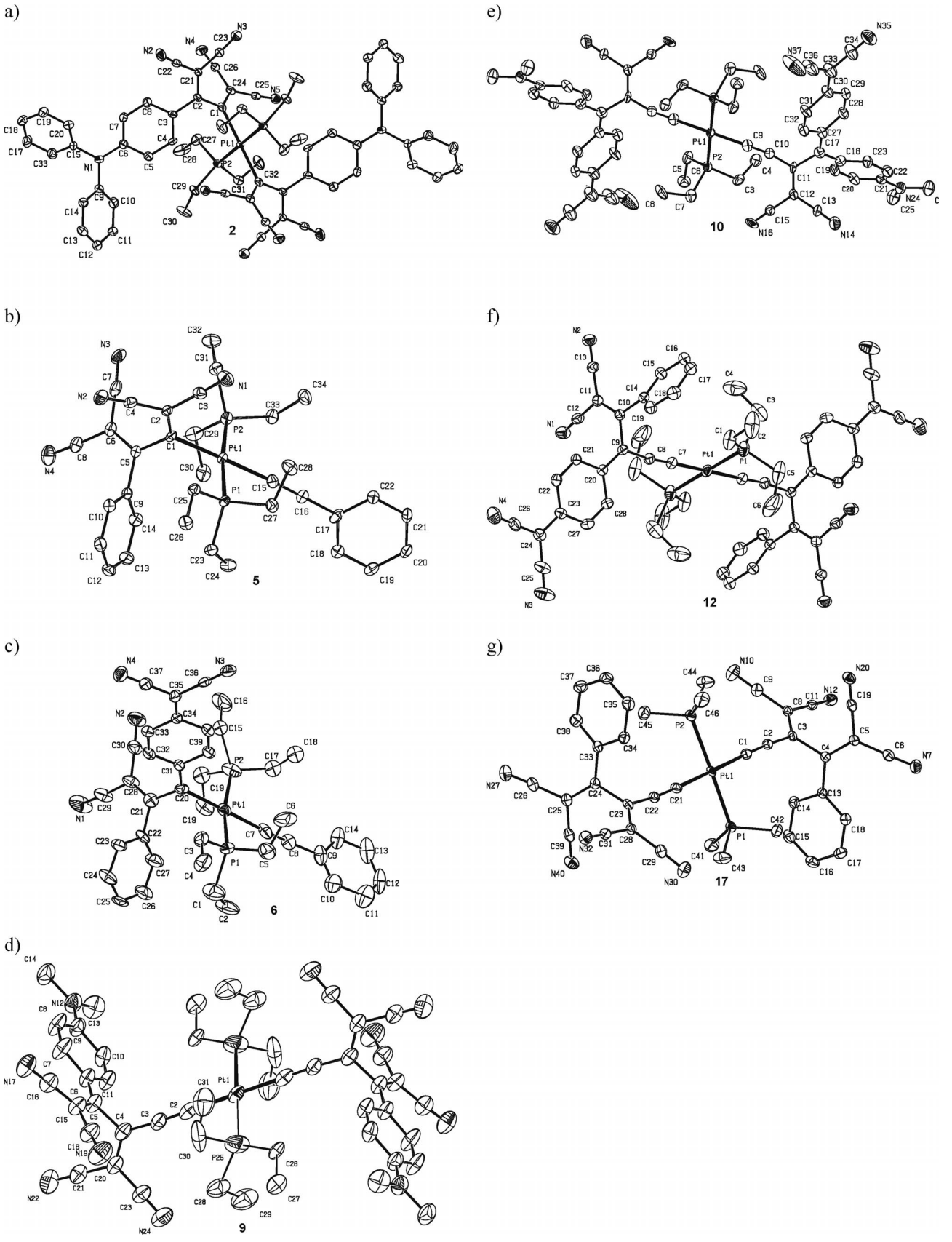
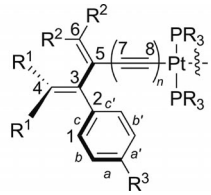


Figure 2. ORTEP representation of the molecular structures of the CA-RE adducts a) **2**, b) **5**, c) **6**, d) **9**, e) **10**, f) **12**, and g) **17** in the crystal. Hydrogen atoms and solvent molecules have been removed for clarity and only the atoms within one asymmetric unit are numbered. Thermal ellipsoids are shown at the 50% probability level.

Table 2. Selected structural parameters from the X-ray crystal structures of CA-RE adducts.



Compd.	R^1	R^2	R^3	n	θ_1 [°][a]	θ_2 [°][b]	δr [Å][c]	d(C5–C7) [Å]	d(C7–C8) [Å]	d(C8–Pt) [Å]
9	CN	CN	NMe_2	1	3.04(6)	88.0(6)	0.056(5)	1.409(7)	1.223(8)	1.971(6)
10	DCNQ	CN	NMe_2	1	34.4(16)	54.5(12)	0.029(9)	1.403(11)	1.206(12)	2.000(9)
11	CN	CN	H	1	38.6(6)	66.1(5)	0.007(5)	1.406(5)	1.210(5)	1.989(4)
					34.6(5)	70.0(5)	0.012(5)	1.395(5)	1.212(5)	1.983(4)
12	CN	DCNQ	H	1	47.26(7)	76.4(6)	0.007(6)	1.413(7)	1.207(7)	1.978(5)
17	CN	CN	H	1	22.2(4)	75.1(3)	0.010(3)	1.405(4)	1.219(4)	1.975(3)
					24.7(4)	74.9(3)	0.005(3)	1.399(4)	1.215(4)	1.983(3)
2	CN	CN	NPh_2	0	59.8(7)	56.6(7)	0.017(6)			
					51.7(7)	56.0(7)	0.021(6)			
5	CN	CN	H	0	82.2(4)	65.5(4)	0.008(4)			
6	CN	DCNQ	H	0	90.816)	65.2(15)	0.00(2)			
					97.0(16)	65.9(16)	0.06(2)			

[a] θ_1 is the absolute value of the torsion angle defined by the atoms C1–C2–C3–C4. [b] θ_2 is the absolute value of the torsion angle defined by the atoms C4–C3–C5–C6 (two values are shown in the cases in which the two angles are not symmetry-equivalent). [c] δr = {[(a+a')/2 – (b+b')/2]+[(c+c')/2 – (b + b')/2]}/2; for benzene, δr = 0.00 Å; for fully quinoid rings, δr = 0.08–0.12 Å.

rings and are twisted substantially out of the plane of the adjacent vinyl unit (defined by atoms C2–C3–C4) and thus do not participate in π conjugation. In the cases of the TCNE adducts **11** and **17**, more pronounced cumulenic character of the acetylene bridge is observed compared with the TCNQ adduct **12**. In all cases, the buta-1,3-diene unit is substantially twisted around the central single bond [θ_2 from 54.5(12) to 88.0(6)°]. Aiming to gain further insights into the CT chromophore properties of the products, and to confirm the trends observed in the X-ray structures, we analyzed their optical spectra.

UV/Vis Spectroscopy

The CA-RE adducts of the Pt^{II} acetylide complexes formed with TCNQ are usually deeply colored solids, whereas the TCNE adducts of the phenyl-substituted derivatives are bright yellow or orange. The electronic absorption spectra of almost all the TCNE and TCNQ adducts show intense low-energy CT absorption bands in acetonitrile at room temperature (Figure 3). Owing to the presence of strong DMA donors, the CT interactions in the nonplanar D–A chromophores in **9** and **10** are efficient and hence the CT bands are distinctly bathochromically shifted relative to the bands of the corresponding phenyl derivatives **11** and **12**. Interestingly, the molar extinction coefficient of the D–A transition of **12** (561 nm) is nearly as large as that of the corresponding band in **10** (679 nm), although only the platinum center acts as a donor in the former chromophore (Figure 3). This reveals that, despite being a less pronounced electron donor and having weaker alkyne activation ability for the CA-RE reaction compared with

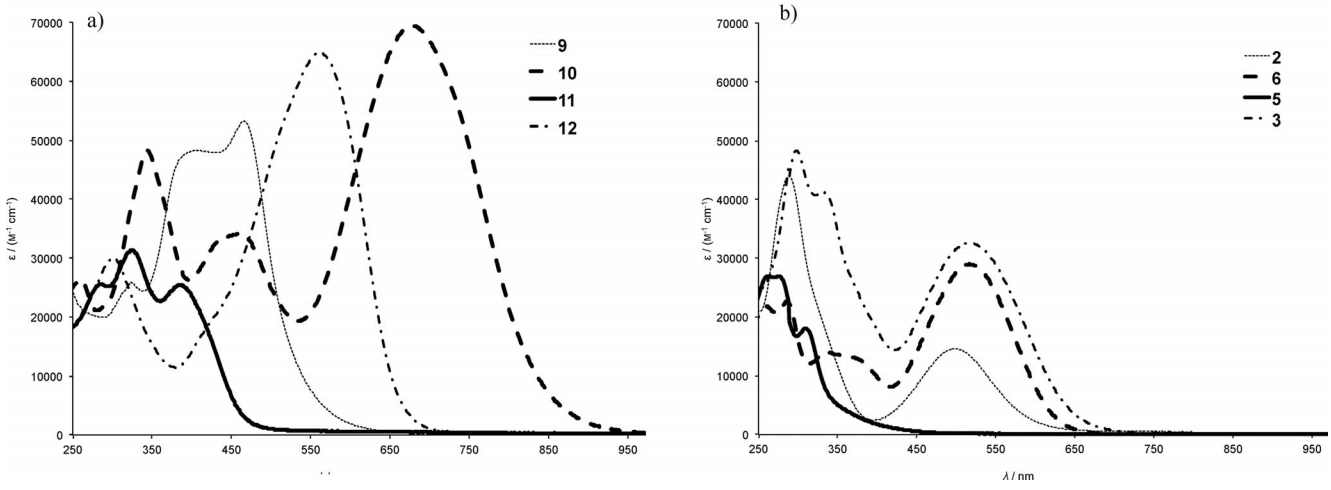


Figure 3. UV/Vis spectra of compounds **9**–**12** (a) and compounds **2**, **3**, **5**, and **6** (b) in acetonitrile at 25 °C.

DMA, the bis(phosphane)platinum(II) center can participate in efficient CT from the platinum to the DCNQ moiety. This is consistent with the observation of donor activation of the triple bonds by platinum only in the aniline-free acetylide complexes and illustrates the donating ability of the platinum center.

In contrast to this series of buta-1,3-diyne-derived adducts, the products lacking triple bond spacers **2**, **3**, **5**, **6** exhibit smaller extinction coefficients. The reduced donating ability of the diphenylanilino group, indicated by the reduced quinoid character of the aniline 1,4-phenylene ring of **2**, is further supported by its UV/Vis spectrum, in which the ε value of the CT band at around 500 nm is significantly lower than in the related DMA complex **9** (Figure 3). The unsymmetric TCNQ mono-adducts **3** and **6** exhibit very similar CT bands even though the diphenylamino donor groups are missing in **6** and the regioselectivity of the TCNQ addition is inverted compared to **3**. Thus, the strong absorptions with a λ_{max} above 500 nm have tentatively been assigned to Pt^{II}-to-DCNQ charge transfer.

To corroborate this hypothesis we performed acidification and neutralization experiments to clarify the origin of the CT bands in the UV/Vis spectra. The low-energy CT absorption bands of two representative CA-RE adducts, **9** and **10**, bearing DMA substituents were reversibly quenched and recovered by protonation with trifluoroacetic acid (TFA) and deprotonation with triethylamine (TEA), respectively (see Figure S1 in the Supporting Information). In contrast, no substantial changes in the UV/Vis spectra of complexes **11** and **12** were observed upon analogous treatment (Figure S2), which suggests that the lowest-energy absorption bands in **9** and **10** can be attributed to the charge-transfer interaction between the dimethylamino groups and the acceptor-substituted buta-1,3-diene unit.

In summary, the compounds exhibit two main sets of intense absorption bands: 1) those caused by direct CT from the platinum to the acceptor moiety, which are particularly pronounced in the case of the TCNQ adducts and 2) bands corresponding to aniline-to-dicyanovinyl or -DCNQ charge transfer, which are always bathochromically shifted relative to the metal–acceptor CT band.

Conclusions and Outlook

In this work the CA-RE reactivity patterns of the triple bonds of platinum acetylides were studied. We have shown that the presence of organodonor moieties in direct conjugation with the triple bonds facilitates the CA-RE process. The first example of direct competition between two donor moieties, an organic amine on the one hand and a bis(trialkylphosphane)platinum center on the other, has been demonstrated and indicates that the aniline substituents are more efficient activators, which is evident from the regioselectivity of the TCNQ addition reactions as well as the ease of product formation. The steric demand of the phosphane ligands is crucial for determining the preferred triple bond addition in the case of 1,3-diacetylide complexes, as even in the case of complexes bearing trimethylphosphane as an ancillary ligand, the triple bond next to the platinum did not react with TCNE or TCNQ. Reducing the electron-donating ability of the substituents on the alkyne or phosphane moiety generally leads to attenuated reactivity, as does the switching from *trans*- to *cis*-configured complexes.

These studies provide fundamental insights into the electronic preferences and regioselectivity of CA-RE reactions by using Pt^{II} acetylide complexes as the alkyne reactants. This knowledge may provide the means to access new donor–acceptor chromophores that are interesting and useful in the context of light-harvesting and energy-conversion systems derived from platinum acetylides.[24]

Experimental Section

Materials and General Methods: Chemicals were purchased from Acros, Aldrich, Fluka, and TCI, and used as received. 1-[4-(Dimethylamino)phenyl]-4-trimethylsilylbuta-1,3-diyne,[6b] 1-phenyl-4-trimethylsilylbuta-1,3-diyne,[6b] 4-ethynyl-*N*,*N*-diphenylaniline,[25] 1-phenyl-4-triisopropylsilylbuta-1,3-diyne,[6b] $[\{P(OiPr)_3\}_2PtCl_2]$,[26] $[(PMe_3)_2PtCl_2]$,[27] $[(depe)PtCl_2]$,[28] $[(dcpe)PtCl_2]$,[29] $[(t\text{BuBPY})PtCl_2]$,[30] as well as acetylides **4**,[31] **8**,[32] **19**,[15b] **20**,[33] **21**,[15b] and **22**[33] were prepared according to or similarly to literature procedures. All reactions were performed under N_2. Column chromatography (CC) and plug filtrations were carried out with Silicycle SiliaFlash F60 (particle size 40–63 μm, 230–400 mesh) or MP neutral Al_2O_3 and distilled technical solvents. TLC was conducted on aluminium sheets coated with SiO_2 60 F_{254} obtained from Merck and visualized with a UV lamp (254 or 365 nm). Melting points were measured in open capillaries with a Büchi Melting Point B540 apparatus. "Dec." refers to decomposition. ^1H and ^{13}C NMR spectra were recorded with a Varian Gemini 300 MHz, a Varian Mercury 300 MHz, a Bruker DRX 400 MHz, or a Bruker AV 400 MHz spectrometer at 25 °C. The chemical shifts are reported in ppm downfield from $SiMe_4$ with the solvent's residual signal as internal reference (^1H, ^{13}C) or phosphoric acid (85% in water) as external reference (^{31}P). Coupling constants (*J*) are given in Hz. IR spectra were recorded with a Perkin–Elmer FT1600 spectrometer. UV/Vis spectra were recorded with a Varian CARY-5 spectrophotometer. The spectra were recorded in a quartz cuvette with a pathlength of 1.00 cm at 25 °C. EI-MS spectra were recorded with a Micromass AutoSpec-Ultima spectrometer. FT-ICR-MALDI spectra were recorded with an IonSpec Ultima Fourier transform spectrometer with [(2*E*)-3-(4-*tert*-butylphenyl)-2-methylprop-2-enylidene]malononitrile (DCTB) or 3-hydroxypyridine-2-carboxylic acid (3-HPA) as matrix. MALDI-TOF mass spectra were recorded with a Bruker Daltonics UltraFlex II spectrometer with DCTB as matrix. ESI mass spectra were recorded with a Bruker Daltonics maXis spectrometer. Elemental analyses were performed by the Mikrolabor at the Laboratorium für Organische Chemie, ETH Zürich, with a LECO CHN/900 instrument.

CCDC-924638 (for **2**), -924641 (for **5**), -924639 (for **6**), -924640 (for **9**), -924642 (for **10**), -924643 (for **11**), -924644 (for **12**), -924645 (for **13**), -924646 (for **17**), and -924647 (for **23**) contain the crystallographic supplementary data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Syntheses: Only selected exemplary protocols for the synthesis of compounds **7**, **9**, **10**, **12**, **25**, **27**, **29**, and **31** are presented here.

All other synthetic protocols and compound characterizations are included in the Supporting Information.

Bis{4-[4-(dimethylamino)phenyl]buta-1,3-diynyl}bis(triethylphosphane)platinum(II) (7): 1-[4-(Dimethylamino)phenyl]-4-trimethylsilylbuta-1,3-diyne (84.6 mg, 0.35 mmol) was deprotected in situ with K_2CO_3 (110 mg, 0.80 mmol) by stirring in methanol/THF (1:1, 6 mL) for 2 h at 25 °C. Afterwards, the solution was passed through a plug of SiO_2 (CH_2Cl_2). *N*,*N*-Diisopropylamine (25 mL) was added to the filtrate and the other solvents were carefully evaporated. The mixture was then degassed by sparging with nitrogen for 30 min, and then [$Pt(PEt_3)_2Cl_2$] (80 mg, 0.16 mmol) and CuI (6 mg, 0.03 mmol) were added. After stirring the solution for 65 h at 25 °C, the solvent was evaporated and the residue subjected to CC (SiO_2; CH_2Cl_2) to afford **7** (122 mg, 100%) as a yellow solid. R_f = 0.52 (SiO_2; CH_2Cl_2), m.p. 260–261 °C (dec.). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.13–1.24 (m, 18 H), 2.07–2.19 (m, 12 H), 2.95 (s, 12 H), 6.59 (d, J = 8.5 Hz, 4 H), 7.33 (d, J = 8.9 Hz, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 8.42, 16.37 [t, J(P-C) = 17.7 Hz], 40.38, 71.40, 76.27, 91.96, 111.07, 111.97, 133.48, 149.71 (10 signals out of 11 expected) ppm. ^{31}P NMR (162 MHz, $CDCl_3$): δ = 12.42 (s), 12.42 ($^1J_{P,Pt}$ = 2324 Hz) ppm. IR (ATR): $\tilde{\nu}$ = 2960 (w), 2931 (w), 2877 (w), 2179 (w), 2048 (w), 1602 (s), 1543 (w), 1514 (s), 1478 (w), 1441 (m), 1417 (m), 1352 (s), 1260 (w), 1224 (m), 1188 (s), 1163 (s), 1053 (w), 1034 (s), 1005 (m), 942 (m), 824 (s), 795 (m), 762 (s), 731 (s), 715 (s), 674 (w), 634 (w), 619 (w) cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 270 nm (34400 M^{-1} cm^{-1}). HR-MALDI-MS (3-HPA): *m*/*z* (%) = 768.3168 (100) [M + H]$^+$ (calcd. for $C_{36}H_{51}N_2P_2{}^{195}Pt^+$: 768.3173), 599.2288 (33) [M – $C_{12}H_{10}N$ + H]$^+$ (calcd. for $C_{24}H_{51}N_2P_2{}^{195}Pt^+$: 599.2284), 569.1674 (48), 430.1399 (42), 286.1721 (47).

Bis{5,5-dicyano-3-(dicyanomethylene)-4-[4-(dimethylamino)phenyl]-pent-4-en-1-ynyl}bis(triethylphosphane)platinum(II) (9): Pt complex **7** (20 mg, 0.03 mmol) and TCNE (16.7 mg, 0.13 mmol) were dissolved in CH_2Cl_2 (5 mL) and stirred at 25 °C for 45 min. The solvent was evaporated and the residue subjected to CC (SiO_2; CH_2Cl_2 + 3% EtOAc) to afford **9** (26.4 mg, 99%) as a red solid. Red crystals of **9** suitable for X-ray crystallographic analysis, were grown by layering a CH_2Cl_2 solution of **9** with *n*-hexane. R_f = 0.42 (SiO_2; 3% EtOAc in CH_2Cl_2), m.p. 272–273 °C (dec.). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.98–1.14 (m, 18 H), 1.88–2.04 (m, 12 H), 3.16 (s, 12 H), 6.70 (d, J = 9.3 Hz, 4 H), 7.78 (d, J = 9.3 Hz, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 8.33, 16.54 [t, J(P-C) = 17.8 Hz], 40.27, 72.98, 88.76, 111.82, 111.93, 112.32, 113.07, 113.62, 114.56, 117.19, 132.34, 153.17, 154.41, 157.21, 163.16 ppm. ^{31}P NMR (162 MHz, $CDCl_3$): δ = 13.47 (s), 13.47 [d, ^1J(P-Pt) = 2188 Hz] ppm. IR (ATR): $\tilde{\nu}$ = 2967 (w), 2930 (w), 2210 (m), 2043 (s), 1603 (s), 1517 (m), 1481 (s), 1437 (s), 1382 (s), 1344 (s), 1305 (m), 1262 (m), 1231 (m), 1210 (s), 1188 (m), 1163 (s), 1063 (m), 1033 (m), 992 (m), 941 (m), 898 (w), 826 (m), 796 (m), 765 (m), 746 (m), 732 (m), 713 (m), 675 (m), 629 (m) cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 461 (48100), 419 (46400), 337 nm (28300 M^{-1} cm^{-1}). HR-ESI-MS (CH_2Cl_2/CH_3OH): *m*/*z* (%) = 1028.3463 (11), 1027.3434 (28), 1026.3428 (47), 1025.3403 (100) [M + H]$^+$ (calcd. for $C_{36}H_{51}N_{10}P_2{}^{195}Pt^+$: 1025.3421), 1024.3393 (95) [M + H]$^+$ (calcd. for $C_{48}H_{51}N_{10}P_2{}^{194}Pt^+$: 1024.3419), 1023.3367 (59). $C_{48}H_{50}N_{10}P_2Pt$ (1024.02): calcd. C 56.30, H 4.92, N 13.68; found C 55.95, H 5.26, N 13.02.

Bis(4,4-dicyano-3-{[4-(dicyanomethylene)cyclohexa-2,5-dien-1-ylidene][4-(dimethylamino)phenyl]methyl}but-3-en-1-ynyl)bis(triethylphosphane)platinum(II) (10): Pt complex **7** (20.5 mg, 0.03 mmol) and TCNQ (14.7 mg, 0.07 mmol) were dissolved in CH_2Cl_2 (5 mL) and stirred at 25 °C for 3 h. The solvent was evaporated and the crude product subjected to CC (SiO_2; 3% EtOAc in CH_2Cl_2) to afford **10** (31.2 mg, 99%) as a dark-green metallic solid. Black crystals of **10** suitable for X-ray crystallographic analysis were grown by layering a CH_2Cl_2 solution of **10** with *n*-hexane at –15 °C. R_f = 0.24 (SiO_2; 3% EtOAc in CH_2Cl_2), m.p. 151–153 °C (dec.). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.87–1.02 (m, 18 H), 1.74–1.92 (m, 12 H), 3.16 (s, 12 H), 6.74 (d, J = 9.1 Hz, 4 H), 7.18 (br. s, 5 H), 7.22 (br. s, 1 H), 7.32 (d, J = 9.0 Hz, 4 H), 7.36 (br. s, 1 H), 7.39 (br. s, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 8.35, 16.36 [t, ^1J(P-C) = 17.8 Hz], 40.56, 70.83, 112.53, 112.72, 113.98, 114.91, 115.05, 123.39, 124.21, 125.00, 129.38, 134.55, 134.74, 135.97, 152.44, 152.98, 154.57, 157.56 ppm. ^{31}P NMR (162 MHz, $CDCl_3$): δ = 13.59 (s), 13.59 [^1J(Pt-P) = 2196 Hz] ppm. IR (ATR): $\tilde{\nu}$ = 2919 (w), 2850 (w), 2224 (w), 2198 (m), 2036 (s), 1609 (w), 1578 (m), 1527 (w), 1478 (m), 1404 (w), 1366 (m), 1346 (m), 1286 (m), 1257 (m), 1203 (w), 1165 (s), 1032 (m), 941 (m), 906 (m), 843 (m), 829 (m), 800 (m), 769 (m), 729 (s), 673 (m), 641 (m) cm^{-1}. UV/Vis (CH_3CN): λ_{max} (ε) = 679 (65900), 461 (34900), 344 (45400), 259 nm (23000 M^{-1} cm^{-1}). HR-MALDI-MS (3-HPA; neg.): *m*/*z* (%) = 1178.4053 (35), 1177.4026 (61), 1176.4007 (100) [M]$^-$ (calcd. for $C_{60}H_{58}N_{10}P_2{}^{195}Pt^-$: 1176.3993), 1175.3988 (92) [M]$^-$ (calcd. for $C_{60}H_{58}N_{10}P_2{}^{194}Pt^-$: 1175.3978), 1174.3961 (49), 1078.2204 (26), 1077.2177 (27), 746.2603 (22), 745.2543 (45), 744.2492 (53), 719.2490 (28), 718.2436 (41), 717.2377 (29).

Bis{5,5-dicyano-3-[4-(dicyanomethylene)cyclohexa-2,5-dien-1-ylidene]-4-phenylpent-4-en-1-ynyl}bis(triethylphosphane)platinum(II) (12): Pt complex **8** (28 mg, 0.04 mmol) and TCNQ (42 mg, 0.21 mmol) were dissolved in 1,1,2,2-tetrachloroethane (10 mL) and stirred at 100 °C for 24 h. The solvent was evaporated and the residue subjected to CC (SiO_2; CH_2Cl_2→2% EtOAc in CH_2Cl_2) to afford **12** (10 mg, 23%) as a black solid. Black crystals of **12** suitable for X-ray crystallographic analysis were grown by layering a CH_2Cl_2 solution of **12** with *n*-hexane at –15 °C. R_f = 0.43 (SiO_2; 2% EtOAc in CH_2Cl_2), m.p. >300 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.94–1.05 (m, 18 H), 1.74–1.86 (m, 12 H), 7.04 (dd, J = 9.6, 1.9 Hz, 2 H), 7.14 (dd, J = 9.6, 1.9 Hz, 2 H), 7.31 (dd, J = 9.6, 1.9 Hz, 2 H), 7.50–7.57 (m, 4 H), 7.60–7.67 (m, 2 H), 7.68–7.75 (m, 6 H) ppm. ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 8.55, 17.18 [t, ^1J(P-C) = 17.8 Hz], 75.00, 85.26, 112.87, 113.25, 114.92, 115.08, 117.11, 125.38, 126.43, 129.94, 130.03, 132.70, 133.78, 134.31, 134.49, 135.19, 137.08, 154.73, 170.32 (21 signals out of 22 expected) ppm. ^{31}P NMR (162 MHz, CD_2Cl_2): δ = 14.09 (s), 14.09 [^1J(Pt-P) = 2236 Hz] ppm. IR (ATR): $\tilde{\nu}$ = 2967 (w), 2928 (w), 2231 (w), 2207 (m), 2026 (s), 1596 (m), 1562 (m), 1427 (s), 1345 (m), 1318 (m), 1272 (w), 1189 (s), 1033 (m), 972 (w), 846 (m), 826 (w), 757 (s), 733 (s), 710 (s), 696 (s), 656 (m), 611 (m) cm^{-1}. UV/Vis (CH_3CN): λ_{max} (ε) = 561 (64900), 300 nm (30000 M^{-1} cm^{-1}). HR-MALDI-MS (3-HPA; neg.): *m*/*z* (%) = 1093.3288 (36), 1092.3229 (57), 1091.3198 (78), 1090.3141 (100), 1089.3108 (76) [M]$^-$ (calcd. for $C_{56}H_{48}N_8P_2{}^{195}Pt^-$: 1089.3130), 1088.3076 (40).

***cis*-Bis{5,5-dicyano-3-(dicyanomethylene)-4-[4-(dimethylamino)phenyl]pent-4-en-1-ynyl}(4,4′-di-*tert*-butyl-2,2′-bipyridine)platinum(II) (25):** Pt complex **19** (16.0 mg, 0.020 mmol) and TCNE (5.0 mg, 0.040 mmol) were dissolved in CH_2Cl_2 (0.5 mL) and the mixture was stirred at 25 °C for 12 h. The solvent was evaporated and the crude product subjected to CC [SiO_2; pentane/EtOAc, 20:80 (v/v)] to afford **25** (17.9 mg, 85%) as a dark-green metallic solid. R_f = 0.25 [SiO_2; pentane/EtOAc, 20:80 (v/v)], m.p. 150 °C (dec.). ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 1.50 (s, 18 H), 3.19 (s, 12 H), 6.78 (d, J = 9.3 Hz, 4 H), 7.68 (d, J = 6.0 Hz, 2 H), 7.84 (d, J = 9.4 Hz, 4 H), 8.12 (s, 2 H), 9.35 (d, J = 6.0 Hz, 2 H) ppm. ^{13}C NMR (101 MHz, CD_2Cl_2): δ = 29.94, 40.01, 72.89, 90.74, 101.88, 111.81, 113.38, 114.08, 114.82, 117.34, 119.81, 125.45, 130.88, 132.28,

134.96, 151.87, 153.83, 154.43, 155.87, 163.66, 166.11 (21 signals observed out of 22 expected) ppm. HR-MALDI-MS (3-HPA; pos.): *m/z* (%) = 1056.3540 (100) $[M]^+$ (calcd. for $C_{54}H_{45}N_{12}{}^{195}Pt^+$: 11056.3536).

***cis*-Bis{5,5-dicyano-3-(dicyanomethylene)-4-[4-(dimethylamino)phenyl]pent-4-en-1-ynyl}[1,2-bis(dicyclohexylphosphanyl)ethane]platinum(II) (27):** Pt complex **20** (20.0 mg, 0.021 mmol) and TCNE (5.4 mg, 0.042 mmol) were dissolved in CH_2Cl_2 (0.5 mL) and the mixture was stirred at 25 °C for 12 h. The solvent was evaporated and the crude product subjected to CC (SiO_2; 1% EtOAc in CH_2Cl_2) to afford **27** (17.9 mg, 85%) as a dark-green metallic solid. R_f = 0.45 (SiO_2; 3% EtOAc in CH_2Cl_2); m.p. 145–150 °C (dec.). ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 0.97–1.55 (m, 18 H), 1.57–2.48 (m, 30 H), 3.19 (s, 12 H), 6.79 (d, J = 9.4 Hz, 4 H), 7.91 (d, J = 9.3 Hz, 4 H) ppm. ^{13}C NMR (101 MHz, CD_2Cl_2): δ = 25.75, 26.5 (m), 28.49, 29.21, 34.74 [d, ^1J(P-C) = 31.7 Hz], 40.00, 71.99, 88.64, 111.26, 111.94, 112.05, 112.74, 114.08, 114.83, 117.02, 129.02, 132.43, 153.20, 154.48, 163.19 ppm. ^{31}P NMR (121 MHz, CD_2Cl_2): δ = 64.55 (s), 64.55 [d, ^1J(P-Pt) = 2242.3 Hz] ppm. HR-MALDI-MS (3-HPA; pos.): *m/z* (%) = 1211.499 (100) $[M]^+$ (calcd. for $C_{62}H_{68}N_{10}P_2{}^{195}Pt^+$: 1211.479).

***cis*-Bis(4,4-dicyano-3-{[4-(dicyanomethylene)cyclohexa-2,5-dien-1-ylidene][4-(dimethylamino)phenyl]methyl}but-3-en-1-ynyl)(4,4′-di-*tert*-butyl-2,2′-bipyridine)platinum(II) (29):** Pt complex **19** (50.0 mg, 0.072.5 mmol) and TCNQ (30.0 mg, 0.145 mmol) were dissolved in CH_2Cl_2 (2.5 mL) and stirred at 25 °C for 12 h. The solvent was evaporated and the crude product subjected to CC (SiO_2; CH_2Cl_2/EtOAc, 100:0 to 85:15) to afford **29** (55 mg, 75%) as a dark-green metallic solid. R_f = 0.15 (SiO_2; 3% EtOAc in CH_2Cl_2), m.p. 145–150 °C (dec.). ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 1.49 (s, 18 H), 3.23 (s, 12 H), 6.83 (d, J = 9.2 Hz, 4 H), 7.15 (d, J = 9.9 Hz, 4 H), 7.34–7.51 (m, 8 H), 7.55 (dd, J = 6.0, 2.0 Hz, 2 H), 8.09 (d, J = 2.0 Hz, 2 H), 9.21 (d, J = 6.0 Hz, 2 H) ppm. ^{13}C NMR (101 MHz, CD_2Cl_2): δ = 29.69, 29.92, 36.01, 40.16, 60.22, 68.66, 91.45, 104.78, 112.22, 112.50, 114.47, 115.37, 119.76, 123.45, 125.14, 128.94, 131.82, 134.83, 151.65, 153.25, 153.50, 154.42, 155.94, 158.05, 166.06 (25 signals observed out of 28 expected) ppm. HR-MALDI-MS (3-HPA; pos.): *m/z* (%) = 1208.4163 (100) $[M + H]^+$ (calcd. for $C_{66}H_{53}N_{12}{}^{195}Pt^+$: 1208.4158).

***cis*-Bis(4,4-dicyano-3-{[4-(dicyanomethylene)cyclohexa-2,5-dien-1-ylidene][4-(dimethylamino)phenyl]methyl}but-3-en-1-ynyl)[1,2-bis-(dicyclohexylphosphanyl)ethane]platinum (31):** Pt complex **20** (20.0 mg, 0.021 mmol) and TCNQ (8.6 mg, 0.042 mmol) were dissolved in CH_2Cl_2 (0.5 mL) and the mixture was stirred at 25 °C for 12 h. The solvent was evaporated and the crude product subjected to CC (SiO_2; 2% EtOAc in CH_2Cl_2) to afford **31** (17.9 mg, 85%) as a dark-green metallic solid. R_f = 0.36 (SiO_2; 3% EtOAc in CH_2Cl_2). ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 0.92–1.43 (m, 18 H), 1.58–2.11 (m, 32 H), 3.21 (s, 12 H), 6.85 (d, J = 9.2 Hz, 4 H), 7.11–7.31 (m, 4 H), 7.31–7.43 (m, 4 H), 7.51 ppm (d, J = 9.0 Hz, 4 H). ^{13}C NMR (101 MHz, CD_2Cl_2): δ = 22.81 [dd, ^1J(P-C) = 31.8, ^2J(P-C) = 8.9 Hz], 25.66, 26.29–26.53 (m), 26.58, 28.40, 29.03, 34.67 [d, ^1J(P–C) = 31.5 Hz], 40.08, 68.31, 90.16, 112.41, 112.71, 113.31, 113.51, 113.60, 115.38, 122.68, 123.61, 124.25, 128.74, 134.95, 135.19, 136.22, 153.25, 153.37, 154.53, 157.38 ppm. ^{31}P NMR (121 MHz, CD_2Cl_2): δ = 63.88 (s), 63.88 [d, ^1J(Pt-P) = 2248.7 Hz] ppm. HR-MALDI-MS (3-HPA; pos.): *m/z* (%) = 136.5539 (100) $[M]^+$ (calcd. for $C_{74}H_{78}N_{10}P_2{}^{195}Pt^+$: 1363.5539).

Supporting Information (see footnote on the first page of this article): Further synthetic details, UV/Vis spectra, X-ray data and NMR spectra.

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