# **ORGANOMETALLICS**

# Diboration of Dialkynes with [2]Boraferrocenophanes

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Supporting Information

**ABSTRACT:** A series of new [4]diboradicarbametalloarenophanes was synthesized via transition-metal-mediated diboration of selected dialkynes by  $[Fe{\eta^5-C_5H_4B(NMe_2)}_2]$  (3) and  $[Fe{\eta^5-C_5H_4B(NMe_2)}_2Pt(PEt_3)_2]$  (18), respectively. Hereby, we have found three different structural motifs: (i) single diboration of the dialkynes to afford  $[Fe{\eta^5-C_5H_4B(NMe_2)}_{2^-}$  ${R}C=C-X-C\equiv C-R]$  (R = Me, no X; R = Ph, no X; R = SiMe\_3, X = C\_2H\_2; R = SiMe\_3, X = 1,4-C\_6H\_4), (ii) single diboration with additional coordination of the pendent C $\equiv$ C triple bond to a



 $[Pt(PEt_3)_2] \text{ fragment affording the dinuclear complexes } [(3,4-\eta^2-Fe{\eta^5-C_5H_4B(NMe_2)}_2{R}C=C-C\equiv C-R)Pt(PEt_3)_2] (R = Me; R = Ph), and (iii) double diboration of one dialkyne yielding <math>[1,4-(Fe{\eta^5-C_5H_4B(NMe_2)}_2{Me_3Si}C=C)_2C_6H_4]$ . Additionally, a series of mononuclear and dinuclear platinum alkyne complexes,  $[(Et_3P)_2Pt(1,2-\eta^2-R-C\equiv C-X-C\equiv C-R)]$  and  $[{(Et_3P)_2Pt}_2(\mu-1,2-\eta^2-3,4-\eta^2-R-C\equiv C-X-C\equiv C-R)]$  (R = Me, no X; R = Ph, no X; R = SiMe\_3, X = 1,4-C\_6H\_4), and the platinum alkene complexe  $[(Et_3P)_2Pt(3,4-\eta^2-E-R-C\equiv C-C{H}=C{H}=C{H}-C\equiv C-R)]$  (R = SiMe\_3) were derived from the reaction of  $[Pt(PEt_3)_3]$  (11) with the corresponding dialkynes. All compounds thus obtained were fully characterized by high-resolution NMR spectroscopy and, in selected cases (that is 14, 24, 26a, 27b, and 29), additionally by X-ray diffraction analysis.

### INTRODUCTION

After Akira Suzuki, Richard F. Heck, and Ei-ichi Negishi were awarded the Nobel Prize in chemistry 2010,<sup>1</sup> boron reagents have moved into the spotlight once again. The Suzuki–Miyaura cross-coupling reaction was discovered in 1979<sup>2,3</sup> and since then has been studied intensively. Today it is one of the most widely used C-C cross-coupling reactions,<sup>4,5</sup> not least due to its versatility. While the first examples generally featured activated aryl and vinyl reagents, the scope of this reaction has since greatly increased.<sup>6</sup> In addition to the number of possible substrates being expanded, the reaction no longer relies on the use of palladium as a catalyst. Thus Miyaura used different nickel-based catalytic systems to synthesize a number of biaryls.<sup>7,8</sup> By expanding this method, Fu et al. found that nickel complexes are highly efficient for alkyl–alkyl cross-coupling reactions,<sup>9</sup> even with nonactivated secondary alkyl halides as electrophiles.<sup>10,11</sup>

In the course of exploring this coupling reaction the demand for boron-containing precursors increased and various catalytic protocols have been developed to obtain these compounds. The wellestablished hydroboration reaction<sup>12–14</sup> was joined by transitionmetal-catalyzed diboration, first described in 1993 by Suzuki, Miyaura, and co-workers,<sup>15</sup> employing bis(pinacolato)diborane(4) to transform alkynes into the corresponding bis(boryl)alkenes via platinum-mediated catalysis.

In only two decades catalytic diboration has developed into an exceptionally useful pathway toward boron-functionalized compounds.<sup>13,16–26</sup> Although most reactions feature alkenes<sup>27–44</sup> or alkynes<sup>45,46</sup> as substrates, the reaction is not limited to their use. Diazo<sup>47</sup> and carbonyl compounds<sup>48–56</sup> and even arynes,<sup>57</sup>



Figure 1. Different compounds derived from the diboration of alkynes.

allenes,<sup>58,59</sup> isocyanides,<sup>60</sup> and carbenoids<sup>61–63</sup> can be used analogously, making the transition-metal-catalyzed diboration a very versatile method for the functionalization of unsaturated compounds. The diborane(4) most commonly employed is bis-(pinacolato)diborane(4) (pinB–Bpin); however other compounds such as bis(catecholato)diborane(4) (catB–Bcat) or bis(neopentylglycolato)diborane(4) (neopB–Bneop) were also applied in this reaction.<sup>64,65</sup>

Much effort has focused on the elucidation of the reaction mechanism,<sup>66-69</sup> and it was postulated that the diborane(4) initially undergoes oxidative addition to a zerovalent platinum fragment to form a bis(boryl)platinum(II) complex. Meanwhile several corresponding representatives have been isolated and characterized.<sup>66,70,71</sup> This proposed mechanism easily explains the fact that the substrates are usually diborated in 1,2-position. However, 1,1-diboration also has precedence, although only found in uncatalyzed reactions. Thus, in 1994 Berndt et al.

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**Figure 2.** Selected strained [*n*]borametalloarenophanes and important geometrical parameters,  $\alpha$  = tilt angle,  $\delta$  = deformation angle,  $\gamma$  = torsion angle, indicating conformation of the rings.



Figure 3. The two diastereomers 12 (left) and 13 (right).

reported the synthesis of 1,1-bis(boryl)alkenes by insertion of (trimethylsilyl)alkynes into the B–B bond of 1,2-di-*tert*-butyl-1,2-dichlorodiborane(4) (1) and subsequent rearrangement at room temperature (Figure 1, left). They also reported analogous products using 1,2-dichloro-1,2-bis(dimethylamino)diborane-(4) (2), however requiring harsher conditions. Interestingly, the regioselectivity of the noncatalyzed diboration of alkynes strongly depends on the substitution pattern of the unsaturated substrate. Thus, products of 1,2-diboration were often obtained from alkynes without trimethylsilyl substituents under similar reaction conditions.<sup>72</sup> Some years later Herberich et al. used BF<sub>3</sub>·OEt<sub>2</sub> for diboration reactions.<sup>73,74</sup> In this context it should be noted that metal-free 1,2-diboration of alkynes has long been known for tetrahalodiboranes(4).<sup>75</sup>

More recently 1,2-bis(boryl)alkenes derived from 2 were reported by the groups of Lesley and Norman. The reactions of the diboranes(4) with different terminal and internal alkynes using catalytic amounts of  $[Pt(PPh_3)_2(\eta^2-H_2C=CH_2)]$  led to boron-containing heterocycles (Figure 1, right). Although the exact mechanism could not be clarified, the authors assume a 1,2-diboration of the alkyne followed by rearrangement of the boron-bound substituents.<sup>76</sup>

[2]Borametallocenophanes such as  $3^{77}$  or  $4^{78}$  (Figure 2) are usually considered strained complexes. However, their reactive B–B bond, which bridges the two carbocyclic ligands of the sandwich complex, adds to the interest in these somewhat unusual diborane(4) derivatives. The first example was published in 1997, when Herberhold and Wrackmeyer reported that the reaction between 1,1'-dilithiated ferrocene and 2 afforded the [2]boraferrocenophane 3.<sup>77</sup> Some years later, we disclosed an alternative approach to 3 by applying the "flytrap method". Here, the ligand precursor **5** (and accompanying isomers)<sup>79</sup> is dimetalated and subsequently reacted with FeCl<sub>2</sub>. Additionally we were able to prove the molecular structure of **3** by X-ray diffraction.<sup>80</sup> In recent years, a great range of different [2]borametalloarenophanes derived from various sandwich complexes has been reported.<sup>78,81–86</sup>

Ansa-complexes often represent highly strained and thus very reactive species. The tilt angle  $\alpha$  as measured between the ring planes of the cyclic ligands (Figure 2) is generally considered a good indicator for geometric distortion and molecular strain in *ansa*-species. The largest tilt angle reported so far can be found in the [1]boraferrocenophane **6** (Figure 2,  $\alpha = 32.4^{\circ}$ ),<sup>87,88</sup> whereas [2]borametalloarenophanes are usually less strained, thus displaying tilt angles around \_10-12°.<sup>78,80</sup>

The highly strained [1]metalloarenophanes have proven to be versatile precursors for ring-opening polymerizations (ROP),<sup>89,90</sup> while the chemistry of somewhat lesser strained [2]metalloarenophanes is commonly dominated by cleavage and insertion reactions of the diatomic ansa-bridge. Beginning in 2006, we disclosed the Pt-mediated diboration of various unsaturated substrates employing [2]borametalloarenophanes as diborane(4) equivalents. The key step of this reaction is the oxidative addition of the boron–boron bond to a suitable Pt<sup>0</sup> complex followed by insertion of the substrate. This protocol has been successfully applied to diboration of alkynes<sup>91</sup> and, for the first time, also the diboration of diazocompounds (Figure 4).<sup>47</sup> Interestingly, the metal-mediated insertion of alkynes into the B-B bond of [2]borametalloarenophanes with formation of [4] diboradicarbametalloarenophanes 7–10 can be achieved stoichiometrically as well as under conditions of homogeneous and, most notably, heterogeneous catalysis.<sup>91</sup>

Recently, we employed catalytic or stoichiometric amounts of  $[Pt(PEt_3)_3]$  (11) to successfully expand this diboration strategy toward dialkynes, thus generating, for example, the diastereomers p*S*,p*R*-12 and p*S*,p*S*-13 (Figure 3), respectively, which can be interconverted upon heating in solution.<sup>92</sup>

It should be stated that in 1996 Marder and Norman had earlier reported the double diboration of a dialkyne using pinB-Bpin or catB-Bcat.<sup>66</sup>

In contrast to the above systems, the reaction of isocyanides with [2]borametallarenophanes does not require metal activation, nor does it proceed via 1,2-diboration but instead favors 1, 1-diboration, thus giving access to bis(boryl)imine complexes (Figure 4).<sup>60</sup> Likewise, insertion of elemental sulfur and selenium into the B–B bond occurs readily in the absence of platinum catalysts (Figure 4).<sup>93</sup>

In this paper we present full details on our studies on the transition-metal-catalyzed diboration of dialkynes with [2]bora-metallocenophanes.

#### RESULTS AND DISCUSSION

The [4] ferrocenophanes 14–17 are prepared by transitionmetal-mediated diboration of the corresponding dialkyne. It should be noted that two dialkynes with a spacer group X (*E*-vinylene  $-C_2H_2-$  and 1,4-phenylene  $-C_6H_4-$ , respectively), between the triple bonds, were chosen. In a noncatalyzed approach (Scheme 1, top), [3] ferrocenophane 18 was reacted with an excess of dialkyne (1.5 equiv for 19, 20, and 22; 2 equiv in the case of 21) in benzene at elevated temperature to cleanly



**Figure 4.** Different [*n*]metalloarenophanes derived from insertion reactions of [2]borametalloarenophanes.

afford 14-17 within 1 h. An excess of the organic substrates was required in order to avoid formation of unwanted side products (vide infra). After workup, the products were isolated in yields between 58% and 78%. For the catalytic reactions (Scheme 1, bottom) a benzene solution of **3** and the corresponding dialkyne, together with 10 mol % (or 20 mol % in the case of 16) of  $[Pt(PEt_3)_3]$  (11), was heated for several days, affording the same products, which were isolated in yields between 24% and 78% after workup. Complexes 14 and 15 were alternatively obtained in comparable yields in the presence of a heterogeneous catalyst, i.e., 10 mol % Pd/C, and heating at 100 °C for 17 to 20 d. While the [4] ferrocenophanes 14, 15, and 17 were obtained analytically pure after crystallization from pentane or hexanes at -30 °C, attempts to fully purify 16 failed due to its high solubility in all common organic solvents. While multinuclear NMR data (vide infra) clearly confirm the constitution of 16 in solution, this species was always contaminated with varying amounts of  $[Pt(PEt_3)_3]$  even after repeated crystallization.

The multinuclear NMR data meet expectations and are in good agreement with previous results for [4] diboradicarbaferrocenophanes.<sup>91,92</sup> Thus, the <sup>1</sup>H NMR spectrum of each compound shows four singlets between 2.48 and 2.94 ppm representing the NMe<sub>2</sub> groups, indicating hindered rotation around the B=N double bond. Additionally, a series of multiplets (4.12-4.63 ppm) is resolved for the protons of the Cp rings. The hydrogen atoms of the spacer unit X are detected as two doublets  $(^{1}J_{H-H} = 16 \text{ Hz})$  at 5.85 and 7.60 ppm in the case of the vinylene unit (16) and as two multiplets at 7.57 and 7.59 ppm for the phenylene-bridged complex (17), respectively. The terminal substituents R are represented either by two singlets (14, R = Me:1.91, 2.39 ppm; 16, R = SiMe<sub>3</sub>: 0.20, 0.33; 17, R = SiMe<sub>3</sub>: 0.15, 0.27 ppm) or by a series of multiplets (15, R = Ph: 6.94 - 8.18 ppm)in the expected regions. Consistent with these data, <sup>13</sup>C{<sup>1</sup>H} NMR spectra show four resonances in the range of 40 and 43 ppm for the dimethylamino groups and eight well-resolved singlets for the CH groups of the two chemically inequivalent Cp rings of 16 and 17. However, in the case of 14 and 15 these resonances between 69 and 80 ppm are significantly broadened and only poorly resolved; the ipso-carbon atoms cannot be detected for any compound due to the quadrupolar momentum of the directly bound boron nuclei.<sup>94</sup> This finding is consistent with our previous studies.<sup>91,92</sup> The alkyne



Scheme 1. Formation of the Diboration Products 14-17 by Stoichiometric and Catalytic Reaction

carbon atoms give rise to two resonances for each compound in the range between 80 and 107 ppm. As expected, for the carbon atoms of the spacer groups X two (16, X = E-C<sub>2</sub>H<sub>2</sub>: 110.89, 147.28 ppm) and four (17, X = 1,4-C<sub>6</sub>H<sub>4</sub>: 121.33, 128.74, 131.87, 148.63 ppm) singlets, respectively, can be observed. The carbon atoms of the bis(boryl)alkene moiety were detected as very broad peaks at very low field (Table 1) using long-range  ${}^{13}C^{-1}H$  correlation

Table 1.  $^{13}\text{C}\{^1\text{H}\}$  NMR Resonances of the Bis(boryl)alkene Moieties of 14–17



Figure 5. Molecular structure of pR-14. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 50% probability level. Selected bond lengths (Å) and angles (deg): C1–C2: 1.514(2); C2–C3: 1.353(2); C3–C4: 1.447(2); C4–C5: 1.199(2); C5–C6: 1.470(2); B1–N1: 1.401(2); B2–N2: 1.396(2); C1–C2–C3: 122.32(14); C2–C3–C4: 123.00(14); C3–C4–C5: 173.75(16); C4–C5–C6: 177.98(17); α: 1.0; δ: 179.4; γ: 1.7.

experiments. While for the inequivalent boron atoms two signals are to be expected for each compound,  ${}^{11}B{}^{1}H{}$  NMR spectra show only one very broad resonance between 39.9 and 41.1 ppm, as reported earlier for related systems.<sup>91,92</sup>

As a representative example, the molecular structure of 14 (Figure 5) in the solid state was elucidated by X-ray diffraction. In doing so, it was found that 14 is a chiral compound, which crystallizes as a racemate in the triclinic space group  $P\overline{1}$ , thus agreeing with previous findings.<sup>91,92</sup> The ferrocene unit and dimethylamino moieties lie opposite each other with regard to the chiral plane C1–C2{B1}=C3{B2}–C4, consisting of the bis(boryl)alkene moiety and the directly bound methyl and alkynyl substituents (Figure 6). Thus, the stereodescriptors pS and pR were assigned according to the CIP rules.<sup>95</sup>

As found for related compounds, the overall geometry of the ferrocenophane fragment is virtually unstrained. This is indicated by a decrease of the tilt angle  $\alpha$  to  $1.0^\circ$  from  $12.8^\circ$  in 3 and, analogously, by an increase of the deformation angle  $\delta$  to 179.4° (3: 170.1°). Furthermore, the decrease of the torsion angle  $\gamma$  to  $1.7^{\circ}$  (3: 16.0°) indicates the eclipsed conformation of the ferrocene moiety. The remaining structural parameters of the ferrocene subunit are unobtrusive. The former triple bond C2-C3 is lengthened to 1.353(2) Å upon diboration, clearly indicating the presence of a 1,2-diborylethylene unit, while the remaining alkyne bond distance C4–C5 (d = 1.199(2) Å) resembles that of the starting compound 19 (d = 1.203 Å).<sup>96</sup> Angular sums of 359.95° and 359.91°, respectively, indicate trigonal-planar coordination for both boron atoms, and the B=N separations of 1.401(2) and 1.396(2) Å corroborate the existence of corresponding double bonds (vide supra). In summary, the structural parameters of 14 closely resemble those of related [4]diboradicarbametallocenophanes.<sup>91,92</sup>

In the course of our experimental studies we found that the ratio between the [3]ferrocenophane 18 and the chosen diyne substrate has a decisive influence on the course of the reaction depicted in Scheme 1 (top). Interestingly, different products are obtained by performing this reaction with a slight excess of the [3]ferrocenophane under otherwise identical conditions. Thus, reaction of only 0.95 equiv of  $R-C \equiv C-C \equiv C-R$  (19: R = Me; 20: R = Ph) with 18 in benzene at elevated temperature leads selectively to the diborated products 23 and 24 within 1 h. In contrast to the aforementioned syntheses for which an excess dialkyne was employed, the liberated platinum phosphine fragment now coordinates to the remaining  $C \equiv C$  triple bond with formation of a platinum alkyne complex. Monitoring the reaction



Figure 6. Representation of the chiral plane in pS-14 (left) and pR-14 (right).







Figure 7. Extreme cases of the bonding situation in platinum alkyne complexes: side-on complex (left) and platinacyclopropene (right).

by multinuclear NMR spectroscopy revealed a clean conversion into the new species 23 and 24 without formation of soluble byproducts (Scheme 2).

Analytically pure 24 can be isolated as yellow crystals in 55% yield from a concentrated solution in hexanes. Attempts to purify 23 analogously resulted in a yellow-orange crystalline material (42%), which gave satisfactory microanalytical results. However, multinuclear NMR spectroscopy always revealed a small contamination (<5%) with the platinum-free species 14. These findings made in the case of 23 already indicate a somewhat weak coordination of the alkyne moiety to the platinum center. Subsequent studies (*vide infra*) provided further evidence for this assumption.

The spectral data of 23 and 24 are comparable to those obtained for the mononuclear species 14-17 (vide supra). As anticipated, the <sup>1</sup>H NMR spectra of both [4] ferrocenophanes show four singlets representing the CH<sub>3</sub> groups bound to nitrogen and the signals for the Cp ring protons in the expected region. The ethyl groups of the phosphine ligands form a series of multiplets in the range 0.91-1.61 (24) and 0.99-1.85 ppm (23), respectively. The terminal methyl groups of 23 are detected at 2.39 and 2.88 ppm as complex multiplets due to coupling to both P and Pt nuclei. The protons of the terminal phenyl substituents in the case of 24 are displayed by a series of multiplets in the range 7.02–7.86 ppm. In the  ${}^{13}C{}^{1}H$  NMR spectra, the signals of the carbon atoms of the terminal substituents, the NMe2 and Cp groups, are found in the expected regions. By employing long-range  ${}^{13}C-{}^{1}H$  coupling experiments the carbon atoms of the boron-substituted double bonds are again detected at lower field as very broad peaks (23: 142.67, 144.78 ppm; 24: 143.34, 148.65 ppm). The carbon atoms directly bound to the platinum center of 23 can be detected as doublets of doublets at 121.57  $({}^{2}J_{C-P}{}^{cis} = 68 \text{ Hz},$  ${}^{2}J_{C-P}^{trans} = 10 \text{ Hz}, {}^{1}J_{C-Pt} = 286 \text{ Hz}) \text{ and } 123.35 \text{ ppm } ({}^{2}J_{C-P}^{cis} = 65 \text{ Hz}, {}^{2}J_{C-P}^{trans} = 7 \text{ Hz}, {}^{1}J_{C-Pt} = 268 \text{ Hz}), \text{ as they show }$ coupling to both phosphorus nuclei. In case of 24, the signals are detected further downfield at 130.88 ( ${}^{2}J_{C-P}^{cis} = 73$  Hz,  ${}^{2}J_{C-P}^{trans} = 9 \text{ Hz}, {}^{1}J_{C-Pt} = 289 \text{ Hz}$ ) and 134.26 ppm ( ${}^{2}J_{C-P}^{cis} = 68 \text{ Hz}, {}^{2}J_{C-P}^{trans} = 7 \text{ Hz}, {}^{1}J_{C-Pt} = 263 \text{ Hz}$ ), respectively. The  $^{11}B{}^{1}H{}$  NMR shifts of 39.1 (24) and 40.3 ppm (23) lie in the expected region for [4]diboradicarbametalloarenophanes.<sup>91,92</sup>

The <sup>31</sup>P{<sup>1</sup>H} NMR spectra show the characteristics expected for an unsymmetrical square-planar *cis*-bis(phosphine)platinum complex, i.e., two doublets (**23**:  $\delta$  = 10.93, 12.79, <sup>2</sup> $J_{P-P}$  = 42 Hz; **24**:  $\delta$  = 8.60, 10.94, <sup>2</sup> $J_{P-P}$  = 33 Hz) that are flanked by <sup>195</sup>Pt satellites (**23**: <sup>1</sup> $J_{P-Pt}$ : 3262, 3243 Hz; **24**: <sup>1</sup> $J_{P-Pt}$ : 3252, 3410 Hz).

Platinum alkyne complexes resemble a well-established class of organometallic compounds, and their bonding situation is commonly described to lie between the two forms depicted in Figure 7. They can be seen either as zerovalent platinum complexes with a side-on coordinated alkyne (Figure 7, left) or as platinacyclopropenes (Figure 7, right), which comprise a platinum center in the formal oxidation state +II.<sup>97</sup>

Vibrational spectroscopy constitutes a convenient method to assess this bonding situation. Usually, the side-on coordination of a C=C triple bond to a transition metal induces a decrease of  $\nu$ (C=C) by 130–500 cm<sup>-1</sup> with respect to the free alkyne ( $\nu_{\rm C=C} = 2300-2100 \text{ cm}^{-1}$ ), while significantly lower stretching frequencies indicate the presence of the metallocyclopropene motif.<sup>98,99</sup>

In the characteristic region, the IR spectrum of **23** (neat) shows only one broad band at 1744 cm<sup>-1</sup>. This large deviation of  $\nu(C \equiv C)$  compared to those of the free alkyne **23** ( $\nu_{C \equiv C}$ <sup>in-phase</sup> = 2149,  $\nu_{C \equiv C}$ <sup>out-of-phase</sup> = 2212 cm<sup>-1</sup>)<sup>100</sup> indicates a pronounced  $\pi$  back-donation from the platinum center to the  $C \equiv C$  triple bond.<sup>97</sup> Hence, **23** can be described as a platinacyclopropene (Figure 7, right) rather than a side-on complex. Furthermore, it should be noted that an absorption at 1557 cm<sup>-1</sup> was assigned to the C=C stretching mode of the bis(boryl)alkene moiety by comparison with comparable borylalkenes.<sup>101,102</sup> The IR spectrum of **24** shows analogous results, also favoring the description as a platinacyclopropene. Here, the C=C stretching frequencies were found at 1736 cm<sup>-1</sup> (24:  $\nu_{C \equiv C}$  = 2155 (op), 2222 (ip) cm<sup>-1</sup>).<sup>103</sup> A band at 1586 cm<sup>-1</sup> is assigned to the C=C stretching mode of the bis(boryl)alkene unit (*vide supra*).

We were able to confirm the proposed constitution of 24 by carrying out a single-crystal X-ray diffraction study (Figure 8). It was found that 24, similar to the above-mentioned 14, exhibits a chiral plane C1–C2{B1}=C3{B2}–C4. Therefore two enantiomers, pS-24 and pR-24, are found in the crystal, and the asymmetric unit contains one molecule of each. As the structural parameters are very similar, only one enantiomer, i.e., pS-24, will be discussed. As expected, the molecular strain is marginal ( $\alpha = 1.8^\circ$ ;  $\delta = 178.7^\circ$ ). The C2–C3 separation amounts to 1.364(4) Å, confirming the presence of a double bond. However, the distance between C4 and C5 (d = 1.297(4) Å) lies between typical values for a corresponding double and triple bond. The platinum center is coordinated in a distorted square-planar manner (angular sum: 359.7°) with an acute C4–Pt–C5 angle of only 36.6° and a much wider P1–Pt–P2 angle of 104.6°.

coordination with angular sums of  $359.9^{\circ}$  and  $360.0^{\circ}$ , respectively. Further structural parameters meet the expectations and resemble those found for **15**.

It was already mentioned that purification of 23 was hampered by the presence of the corresponding platinum-free species 14, which indicates a certain lability of the alkyne—platinum interaction. While 24 contrastingly proved to be stable in common



Figure 8. Molecular structure of *p*S-24. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 50% probability level. The asymmetric unit contains two very similar molecules. Selected bond lengths (Å) and angles (deg): C1–C2: 1.486(4); C2–C3: 1.364(4); C3–C4: 1.456(4); C4–C5: 1.297(4); C5–C6: 1.464(4); C4–Pt: 2.093(3); C5–Pt: 2.033(3); Pt1–P1 2.2764(8); Pt–P2 2.2576(8); B1–N1: 1.402(5); B2–N2: 1.396(5); C4–Pt–P1: 114.25(9); P1– Pt–P2: 104.62(3); P2–Pt–C5: 104.22(8); C5–Pt–C4: 36.60(12); C1–C2–C3: 125.2(3); C2–C3–C4: 127.8(3); C3–C4–C5: 143.6(3); C4–C5–C6: 148.1(3);  $\alpha$ : 1.8;  $\delta$ : 178.7;  $\gamma$ : 3.1.

Scheme 3. Pt-Transfer Reaction between 23/24 and 14/15

aromatic and aliphatic solvents as well as in thf, it also readily liberates the  $[(Et_3P)_2Pt]$  fragment upon dissolution in CH<sub>2</sub>Cl<sub>2</sub> at room temperature with formation of *trans-*[(Et<sub>3</sub>P)<sub>2</sub>Pt-(Cl)CH<sub>2</sub>Cl], as identified by <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy.<sup>104</sup> Apparently, the latter is formed by oxidative addition of one C-Cl bond to the platinum center with dissociation of the alkyne. It should be noted that the remainder of the molecule remains unaffected upon contact with chlorinated solvents and can be detected as 15. Another indicator for the lability of the platinum fragment is provided by carrying out the diboration reaction employing between 0.95 and 1.5 equiv of the dialkyne, which leads to a mixture of the two possible products 14/23 and 15/24, respectively, in varying ratios, as indicated by multinuclear NMR spectroscopy. Furthermore, the reaction of isolated 23 or 24 with  $R-C \equiv C-C \equiv C-R$  (R = Me, Ph) leads to transfer of the platinum fragment to the dialkyne and formation of the mononuclear species 14 and 15, respectively (Scheme 3). In order to achieve complete transfer of the  $[(Et_3P)_2Pt]$  fragment, an approximately 1.5-fold excess of the diyne was required in each case. These findings explain the aforementioned observation (Scheme 1, top) that the [4]diboradicarbaferrocenophanes 14-17 with a pendent alkynyl group were obtained free from platinum-containing side products only when an excess of  $\geq 1.5$ equiv of the corresponding dialkyne was employed.

In order to complete these studies on the reactivity of  $[Pt(PEt_3)_3]$  (11) toward the organic substrates employed here, the former was directly reacted with the diynes 19, 20, 21, and 22 (Scheme 4). All stoichiometric reactions of 11 with 1 equiv of the respective dialkyne led to a mixture of the mononuclear platinum complexes 25a-27a and small amounts of the dinuclear complexes 25b-27b. By increasing the amount of 11 to 2 equiv the dinuclear complexes 25-27b could be obtained free from side products. It should be noted that all these reactions initially afford [Pt(PEt\_3)\_4], which is formed by 11 and liberated PEt\_3.<sup>105</sup> However, all conversions can be driven to completeness by repeatedly evaporating the reaction mixtures and redissolving the residue in pentane, thus exploiting the volatility of PEt\_3. All







	$^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ NMR data			<sup>13</sup> C{ <sup>1</sup> H} NMR data		
compound	$\delta$ (PtPEt <sub>3</sub> )	$^{2}J_{\mathrm{P-P}}$ [Hz]	${}^{1}J_{\mathrm{P-Pt}}$ [Hz]	$\delta (\{Pt\}C \equiv C)$	${}^{2}J_{\mathrm{C-P}}{}^{a}$ [Hz]	${}^{1}J_{\rm C-Pt}$ [Hz]
25a	11.82		3160	105.13	72; 6	251
	16.23	32	3471	130.76	73; 9	310
26a	9.05		3191	112.93	74; 5	241
	14.52	23	3468	139.79	80; 9	358
27a	13.02		3345	124.95	53; 9	Ь
	14.54	38	3443	151.66	59; 10	337
25b	12.89		3242	114.38	b	Ь
	15.40	с	3414	120.00	b	Ь
26b	9.10		3250	d		
	13.21	с	3412	d		
27b	13.53		3573	121.79	52; 9	b
	14.77	с	3398	137.60	Ь	Ь

Table 2. Selected  ${}^{31}P{}^{1}H$  and  ${}^{13}C{}^{1}H$  NMR Data of the Platinum Alkyne Complexes 25–27a and 25–27b

<sup>a 2</sup> J<sub>cis</sub>; <sup>2</sup> J<sub>trans</sub>. <sup>b</sup> Signal too broad to quantify the coupling constant. <sup>c</sup> Complex multiplet. <sup>d</sup> The appropriate peaks could not be identified unambiguously.



products can be isolated either by crystallization from a concentrated pentane solution at -30 °C (**27a**: 23%, **26b**: 46%) or by slow evaporation of the solvent at room temperature under an inert atmosphere (**25a**, **26a**, **25b**: 60%, **27b**: 83%, **28**: 85%).

The <sup>1</sup>H NMR spectra of 25a-27a are in good agreement with the proposed structures. As expected, the protons of the terminal substituents R in the case of 25a and 27a give rise to two different resonances (R = Me: 2.02, 2.79 ppm; R = SiMe<sub>3</sub>: 0.27, 0.39 ppm). In the case of 26a (R = Ph), the six multiplets can similarly be separated into two groups. For the protons of the phenylene spacer in 27a two multiplets at 7.29 and 7.49 ppm can be detected. The signals for the protons of the phosphine ligands are unobtrusive and lie in the expected region. The  ${}^{31}P{}^{1}H$ NMR spectra of 25-27a show the characteristic pattern that has been described for 23 and 24 (vide supra). The signals can be detected in the same region (Table 2). It should be noted that in all three cases one <sup>195</sup>Pt-<sup>31</sup>P coupling constant is significantly larger ( $\Delta J = 100-310$  Hz) than the other one. The overall  $^{13}{
m C}\{^1{
m H}\}$  NMR data correspond to the results described for the <sup>1</sup>H NMR spectra. The carbon atoms of the  $\{Pt\}C \equiv C$  moieties can be detected as doublets of doublets due to the coupling to both phosphorus nuclei. Additionally, <sup>195</sup>Pt satellites are visible in some cases (Table 2). While 25a-27a gave first-order

<sup>31</sup>P{<sup>1</sup>H} NMR spectra, the four phosphorus centers of each dinuclear complex **25–27b** constitute an AA'BB' spin system, thus resulting in more complex signal groups. However, the basic pattern of two major <sup>31</sup>P{<sup>1</sup>H} NMR resonances flanked by platinum satellites can still be recognized (see Figure 9). As expected for more symmetrical compounds, the number of signals observed in the <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra is reduced compared to **25–27a**; only one signal is found for the terminal substituents R = Me (**25b**) and R = SiMe<sub>3</sub> (**27b**). Analogously, the phenylene spacer gives rise to only one resonance in the <sup>1</sup>H NMR and two in the <sup>13</sup>C{<sup>1</sup>H} NMR spectra, respectively. In the case of **27b**, the <sup>13</sup>C{<sup>1</sup>H} NMR signals of the coordinated alkyne could not be unambiguously assigned due to overlap with the resonances of the terminal phenyl substituents.

The IR spectrum (neat) of **25a** shows two bands at 2195 and 1743 cm<sup>-1</sup> in the relevant region (*vide supra*). The former represents the stretching vibration of the uncoordinated triple bond, thus resembling that of the starting dialkyne (**19**:  $\nu_{C \equiv C}$ <sup>in-phase</sup> = 2212 cm<sup>-1</sup>;  $\nu_{C \equiv C}$ <sup>out-of-phase</sup> = 2149 cm<sup>-1</sup>).<sup>100</sup> The latter band at 1743 cm<sup>-1</sup> can be assigned to the triple bond coordinated to the platinum center. As already discussed for the platinum complexes **23** and **24**, this resonance is significantly shifted to lower frequency, indicating a strong metal-to-ligand back-donation.<sup>97</sup> The band found

in the solid-state IR spectrum of **25b**  $(1699 \text{ cm}^{-1})$  is shifted to even lower frequency than in the case of **25a**. It should also be noted that these data are confirmed by solution (hexanes) infrared spectra. Therefore, **25a** and **25b** both should be described as platinacyclopropenes rather than side-on Pt<sup>0</sup> alkyne complexes (Figure 7).

The IR data for **26a** and for the platinum complexes derived from **22**<sup>107</sup> can be interpreted analogously (Table 3), also supporting the description as platinacyclopropenes (Figure 7, right). However, the IR spectrum of **26b** (solid-state) is more complicated. This is probably due to the  $\pi$  electrons being delocalized to a considerable extent, as it was already shown for the free dialkyne.<sup>103,106</sup> In the expected region two absorptions were found at 1757 and 1661 cm<sup>-1</sup>, presumably representing the *in-phase* (ip) and *out-of-phase* (op) stretching modes of the coordinated dialkyne. Another band at 1587 cm<sup>-1</sup> was assigned to the C=C valence modes of the phenyl substituents by comparison with unsubstituted diphenylbutadiyne (**20**).<sup>106</sup>

The molecular structures of **27a** and **26b** were determined by single-crystal X-ray diffraction (Figure 10), and the data closely resemble those determined for analogous complexes with one or two metal fragments coordinated to one dialkyne.<sup>108–111</sup> In **27a** C1–C2 displays a bond length of 1.304(6) Å, which ranges between a double and a triple bond. The same situation arises for

Table 3. C=C Stretching Frequencies of the Platinum Complexes 25-27a/b and the Corresponding Free Dialkynes

compound	$\nu(C \equiv C) [cm^{-1}]$		
19	2212, 2149 <sup>[100]</sup>		
25a	2195, 1743		
25b	1699		
20	2222, 2155 <sup>[103;106]</sup>		
26a	2153, 1695 (broad)		
26b	1757, 1661 <sup><i>a</i></sup>		
22	2154 [107]		
27a	2148, 1716		
27b	1716 (broad)		
The resonance could not be iden	tified unambiguously (see text)		

C2–C3/C4–C5 in **26b** with a bond length of 1.310(4) Å. The platinum centers in **27a** and **26b** all show a distorted squareplanar coordination environment with angular sums of 360°. The P–Pt–P planes are only slightly twisted (**27a**:  $5.8^\circ$ ; **26b**:  $4.1^\circ$ ) with respect to the C–Pt–C planes. In **26b**, the metallacycle moieties are twisted against each other by  $63.5^\circ$ .

Interestingly, no platinum alkyne complex is obtained from corresponding reactions employing the bis(alkynyl)alkene **21** (Scheme 5). Instead, only the double bond is coordinated to the platinum center, irrespective of the amount of  $[Pt(PEt_3)_3]$  used.

A possible explanation for the preference of C=C double- versus C=C triple-bond ligation can be provided by comparing the corresponding group electronegativities. While the C=C double bond is surrounded by two highly electron-withdrawing alkynyl groups (EN<sub>C=CH</sub> = 3.10),<sup>112</sup> each triple bond is substituted by one trimethylsilyl group (EN = 2.06),<sup>113</sup> increasing the electron density on the alkynyl moiety. As reported earlier, electron-poor alkenes or alkynes increase the metal-to-ligand  $\pi$  back-donation, thus leading to more stable complexes.<sup>97,114–116</sup> It should be stated that a compound similar to **28** has been isolated from the reaction of Z-Me<sub>3</sub>Si-C=C-C{H}=C{H}-C{H}-C=C-SiMe<sub>3</sub> with an electronrich osmium complex,<sup>117</sup> whereas more commonly enediynes act as four-electron donors in cluster complexes, thus bridging two metal centers via one C=C triple bond.<sup>118,119</sup>

Consistent with formation of the symmetrical complex **28**, the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum shows only one signal at 14.81 ppm - ( ${}^{1}J_{P-Pt} = 3539$  Hz). Analogously, only one singlet (0.21 ppm) is detected for the protons of the SiMe<sub>3</sub> units. The <sup>1</sup>H NMR spectrum also shows three multiplets ( $CH_2$ : 0.93 ppm,  $CH_3$ : 1.59, 1.68 ppm) for the PEt<sub>3</sub> groups. The signal for the protons of the vinylene group exhibits a significant upfield shift to 3.12 from 6.13 ppm in **21**, <sup>120</sup> underlining the aliphatic character of the coordinated  $C_2H_2$  moiety. The corresponding <sup>13</sup>C{<sup>1</sup>H} NMR resonance can be found at 31.22 ppm, while the carbon atoms of the triple bond are detected at 80.48 and 114.33 ppm. The NMR data are thus fully consistent with the formation of the platina-cyclopropane species **28**. Vibrational data confirm the identity of **28**. While the unsubstituted dialkyne **21** shows two bands at 2158 and 2110 cm<sup>-1</sup> for the symmetrical and asymmetrical  $C \equiv C$ 



**Figure 10.** Molecular structures of **27a** and **26b**. Hydrogen atoms and the disorder in one ethyl group of **26b** are omitted for clarity. Thermal ellipsoids are shown at the 50% probability level. Selected bond lengths (Å) and angles (deg): (**27a**) Si1–C1: 1.831(5); C1–C2: 1.304(6); C2–C3: 1.475(6); C4–C5: 1.451(7); C5–C6: 1.200(7); C6–Si2: 1.841(6); C1–Pt: 2.082(4); C2–Pt: 2.031(4); Si1–C1–C2: 145.4(2); C1–C2–C3: 142.1(4); C4–C5–C6: 178.3(6); C5–C6–Si2: 177.6(6); C1–Pt–P1: 112.61(13); P1–Pt–P2: 100.66(4); P2–Pt–C2: 109.89(13); C2–Pt–C1: 36.94(17); (**26b**) C1–C2: 1.450(5) C2–C3: 1.310(4); C3–C4: 1.413(6); C4–C5: 1.310(4); C5–C6: 1.450(5); C2–Pt1: 2.047(3); C3–Pt1: 2.064(3); C4–Pt2: 2.064(3); C5–Pt2: 2.047(3); C1–C2–C3: 135.5(3); C2–C3–C4: 145.6(4); C3–C4–C5: 145.6(4); C4–C5–C6: 135.5(3); C2–Pt1–P1: 112.31(9); P1–Pt1–P2: 102.17(3); P2–Pt1–C3: 108.43(9); C3–Pt1–C2: 37.17(12); C5–Pt2–P4: 112.31(9); P4–Pt2–P3: 102.17(3); P3–Pt2–C4: 108.43(9); C4–Pt2–C5: 37.17(12).

# Scheme 5. Reaction of 21 with $[Pt(PEt_3)_3]$



#### Scheme 6. Attempted Double Diboration of 19



#### Scheme 7. Formation of 29 and 30 by Double Diboration of 22



stretching along with an absorption at 1748 cm<sup>-1</sup> for the C=C stretching,<sup>120</sup> the solid-state IR spectrum of **28** shows only one broad band at 2114 cm<sup>-1</sup>, representing the C=C stretching vibrations. A signal that could be assigned to the C=C stretching mode, however, can no longer be detected.

After compiling the full spectroscopic details of the mono- and dinuclear platinum complexes described here, it was possible to answer questions that arose with the synthesis of the diboration products, particularly concerning the ratio between the [3]diboraplatinaferocenophane (18) and the alkyne substrates 19, 20, 21, and 22 (Scheme 1, top). Thus, the platinum-containing side-products that were formed during the reaction could be unambiguously identified by multinuclear NMR spectroscopy as the alkyne complexes 25-27a/b. Apparently, the platinum fragment [Pt(PEt<sub>3</sub>)<sub>2</sub>] prefers the sterically less congested binding site of the free dialkynes over the pendent C=C triple bond of the [4]diboradicarbaferrocenphanes 14 and 15. Thus, a small excess of diyne is always needed to obtain these compounds cleanly, while the dinuclear species 23 and 24 are obtained according to Scheme 2 only in the absence of surplus diyne.

As depicted in Figure 3, we recently communicated the first example of a double diboration employing the *E*-ene(diyne) substrate **21**. In an attempt to broaden the scope of this reaction, we treated the dialkynes **19** and **20** with 2 equiv or even an excess of the [3] diboraplatinaferrocenophane **18**. However, instead of the desired

tetrakis(boryl)dialkene, a mixture of the aforementioned dinuclear complexes 23 and 24 together with unidentified decomposition products is obtained upon heating. Likewise, the attempt to synthesize the desired products alternatively by reaction of the diplatinum complex 26b with 2 equiv of the [2]diboraferrocenophane 3 also failed. This reaction leads to a 1:1 mixture of the dinuclear complex 24 and [3]diboraplatinaferrocenopane (18) even at room temperature (Scheme 6). Further heating leads to partial degradation of the platinum-containing products.

These findings indicate that double diboration of adjacent  $C \equiv C$  triple bonds in diyne substrates fails due to the steric demand of the bis(boryl)ferrocene moieties. However, by employing the dialkyne **22**, in which the  $C \equiv C$  triple bonds are separated by a *para*-phenylene spacer, the corresponding product of a double diboration is obtained as a mixture of two diastereomers **(29, 30)** in a ratio of 1.3 to 1 according to Scheme 7. It should be noted that **29/30** can be obtained by both methods already elaborated on earlier systems (Scheme 1), i.e., the stoichiometric reaction of 2 equiv of the [3]diboraplatinaferrocenophane **18** with the substrate (see (b) in Scheme 7) and the corresponding platinum-mediated reaction of the [2]diboraferrocenophane **3** (see (a) in Scheme 7), both of which resulted in the same diastereomeric ratio.

As already shown for the corresponding complexes 12 and 13, which comprise a vinylene spacer (Figure 3),<sup>92</sup> the diastereomers 29/30 can be interconverted. A diluted solution of pure 29 in



The pure diastereomer 29 can be isolated in crystalline form in 25% yield after repeated crystallizations from a diluted solution in hexanes. However, a full separation of both diastereomers, as reported for 12 and 13, is hampered by the fast equilibration even at lower temperature. Thus, the second diastereomer 30 can only be slightly enriched in solution after repeated precipitation of 29. Consequently, NMR data of 30 could be obtained only from corresponding mixtures of both diastereomers. A freshly dissolved sample of isolated 29 gives a clean <sup>1</sup>H NMR spectrum, in which all resonances can be unambiguously assigned, e.g., one singlet for the trimethylsilyl group (29: 0.33 ppm) and four singlets for the protons of the dimethylamino groups (29:  $\delta$  = 2.55, 2.51, 2.79, 2.80; it should be added that VT NMR experiments showed no sign of coalescence in the range between room temperature and 100 °C). However, both diastereomers give rise to a broad resonance at 41.3 ppm in the  ${}^{11}B{}^{1}H{}$  NMR spectrum, which cannot be resolved further. Due to extended acquisition time required for <sup>13</sup>C{<sup>1</sup>H} NMR spectroscopy, only corresponding spectra of both diastereomers were obtained.

The constitution of pR,pR-**29** could be proven unequivocally by single-crystal X-ray diffraction studies (Figure 12). In accordance with **12** (*vide supra*) the former also crystallizes as a racemate in the triclinic space group  $P\overline{I}$ . The major structural difference in comparison to the vinylene-bridged species **12** and **13** concerns the dihedral angle C1–C2–C5–C6. In pR,pR-**29** it adopts a value of 31.9°, which is significantly larger than in pS,pR-**12** (8.8°) and pS,pS-**13** (0°), respectively. This divergence is presumably due to steric repulsion between the phenylene spacer and the adjacent SiMe<sub>3</sub> and NMe<sub>2</sub> groups.

# CONCLUSION

We have reported the synthesis of a series of new chiral [4]diboradicarbaferrocenophanes that were obtained by diboration of different dialkynes by [2]borametalloarenophanes. All

Figure 12. Molecular structure of pR,pR-29. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 50% probability level. Selected bond lengths (Å) and angles (deg): C1-C2: 1.355(4); C2-C3: 1.492(3); C4-C5: 1.506(3); C5-C6: 1.350(4); B1-N1: 1.401(4); B12-N2: 1.396(4); B3-N3: 1.394(4); B4-N4: 1.393(3); Si1-C1-C2: 127.3(2); C1-C2-C3: 123.8(2); C4-C5-C6: 122.7(2); C5-C6-Si2: 124.7(2); C1-C2-C5-C6: 31.9;  $\alpha$ : 1.1/2.2;  $\delta$ : 179.2/ 178.3;  $\gamma$ : 0.2/2.2.

substances were characterized by high-resolution NMR spectroscopy and, in selected cases, by X-ray diffraction. This comprehensive study revealed that, depending on the reaction conditions, three different types of products can be formed: (i) mononuclear [4] diboradicarbaferrocenophanes with a pendent alkyne moiety, which are formed by selective diboration of one  $C \equiv C$  triple bond of the diyne substrate, (ii) related dinuclear complexes in which a  $[Pt(PEt_3)_2]$  fragment coordinates to the pendent alkyne fragment with formation of a platinacylopropene subunit, and (iii) dinuclear bis-[4] diboradicarbaferrocenophanes, which were obtained by diboration of both  $C \equiv C$  triple bonds by the [2]borametalloarenophane **3**.



The latter turned out to be a facile diborane(4)-type reagent for such Pt-mediated 1,2-diboration reactions under both stoichiometric and homogeneous as well as heterogeneous catalytic conditions. Model reactions between the employed diynes and  $[Pt(PEt_3)_3]$  confirmed the assumption that the formation of 14/ 15 versus 23/24 is determined by the stoichiometry of the reaction alone. Thus, as the  $[Pt(PEt_3)_2]$  fragment coordinates preferably to the diyne substrate, complexes 23/24 are formed only when the diboration reagent 18 is used in small excess. Moreover, it was found that the formation of bis-[4]diboradicarbaferrocenophanes 29/30 with diboration of both triple bonds is successful only for sterically less congested substrates in

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Figure 11.  $\ln[29]$  vs *t* diagram:  $[29]_0 = 2 \ \mu \text{mol} \cdot \text{L}^{-1}$ ,  $T = 23 \ ^\circ\text{C}$ .

benzene fully equilibrates already after standing at room tempera-

ture overnight, and the equilibration time decreases to 2 h at 80 °C.

To quantify these observations, the equilibration was monitored by

<sup>1</sup>H NMR spectroscopy at 23 °C, recording a spectrum every 15 min.

A solution of pure 29 in benzene equilibrates to a 1.3:1 mixture of

29/30 within 16 h, after which the ratio remains constant. A plot of

tion (11 h at 80 °C).92



which the two alkyne moieties are separated by a spacer such as 1,4-phenylene. Products thus obtained (e.g., **29** and **30**) are usually formed as diastereomers, which easily equilibrate under mild thermal conditions.

#### EXPERIMENTAL SECTION

General Considerations. All manipulations were performed in an atmosphere of dry argon using standard Schlenk and glovebox techniques. Benzene, hexanes, and pentane were distilled from molten alkali metal; benzene-D<sub>6</sub> was degassed by three freeze-pump-thaw cycles. All solvents were stored over activated molecular sieves (4 Å) under argon. The starting materials  $[Fe{\eta^5-C_5H_4B(NMe_2)}_2]$  (3),<sup>77</sup>  $[Fe{\eta^5-C_5H_4B(NMe_2)}_2]$  $C_{5}H_{4}B(NMe_{2})_{2}Pt(PEt_{3})_{2}]$  (18),<sup>91</sup> 1,6-bis(trimethylsilyl)hexa-3-ene-1,5-divne (21),<sup>120</sup> and  $[Pt(PEt_3)_4]^{105}$  were prepared according to published procedures. 2,4-Hexadiyne (19), 1,4-butadiyne (20), 1, 4-bis[(trimethylsilyl)ethynyl]benzene (21), and Pt/C were purchased and used without further purification. NMR spectra were acquired on a Bruker Avance 500 (<sup>1</sup>H 500.130 MHz; <sup>11</sup>B 160.462 MHz; <sup>13</sup>C 125.758 MHz; <sup>31</sup>P 202.456 MHz) or a Bruker Avance DMX 600 (<sup>1</sup>H: 600.130 MHz, <sup>13</sup>C: 150.902 MHz), and a Bruker Avance 400 (<sup>1</sup>H: 400.130 MHz) was used for kinetic experiments. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were calibrated to Si(CH<sub>3</sub>)<sub>4</sub>; in the case of <sup>11</sup>B and <sup>31</sup>P NMR experiments BF3 · OEt2 and H3PO4 (85%) were used as external standard, respectively. All spectra were recorded at room temperature unless otherwise stated. Elemental analyses were performed on a Vario Micro Cube elemental analyzer. Infrared spectra were acquired on a Bruker Alpha FT-IR spectrometer with a Platinum ATR QuickSnap sampling module (solid state) or on a JASCO FT/IR-6200 (solution).

Synthesis of  $[Fe{\eta^5-C_5H_4B(NMe_2)}_2{Me}C=C-C=C-Me]$  (14). (a) A portion of 4.5 mg (0.0068 mmol, 10 mol %) of  $[Pt(PEt_3)_4]$  was filled into a Young NMR tube and heated to 60 °C for 20 min under vacuum to remove one PEt<sub>3</sub> ligand and thus produce  $[Pt(PEt_3)_3]$  (11). The red oil was mixed with 20 mg (0.068 mmol) of  $[Fe{\eta^5-C_5H_4B-(NMe_2)}_2]$  (3), 8.0 mg (0.10 mmol, 1.5 equiv) of 2,4-hexadiyne (19), and 0.5 mL of benzene-D<sub>6</sub>. The resulting orange solution was heated to 85 °C, and the reaction progress was monitored by NMR spectroscopy. After 15 d no 3 could be detected, and the volatiles were removed under vacuum. After extracting the orange-brown residue with hexanes (2 × 5 mL), the suspension was filtered and concentrated to approximately 25% of its original volume. The solution was cooled to -30 °C, and the product was isolated as orange-yellow crystals (6.0 mg, 0.016 mmol, 24%) after 4 d. Single crystals suitable for X-ray diffraction were obtained by crystallization from a diluted hexanes solution at -30 °C.

(b) The heterogeneously catalyzed reaction was carried out analogously to (a) with 3.6 mg of Pd/C (10 wt % Pd, 0.0068 mmol, 10 mol %) instead of [Pt(PEt<sub>3</sub>)<sub>4</sub>]. After heating the reaction mixture to 100 °C for 20 d, the product was obtained in comparable yield.

(c) In an NMR tube 20 mg (0.028 mmol) of  $[Fe{\eta^5-C_5H_4B-(NMe_2)}_2Pt(PEt_3)_2]$  (18) and 3.2 mg (0.041 mmol, 1.5 equiv) of 19 were dissolved in 0.5 mL of benzene-D<sub>6</sub>. The reaction was monitored by <sup>1</sup>H NMR spectroscopy, while the solution was heated to 70 °C. After 1 h

no 18 could be detected, and the volatiles were removed *in vacuo*. The orange residue was extracted with hexanes  $(2 \times 3 \text{ mL})$ , and the suspension was filtered. The resulting yellow solution was cooled to -30 °C, yielding the product as orange crystals (6.0 mg, 0.016 mmol, 58%) after 4 d.

<sup>1</sup>H NMR (500.130 MHz,  $C_6D_6$ ):  $\delta$  1.91 (s, 3H, C=CCH<sub>3</sub>), 2.39 (s, 3H, C=CCH<sub>3</sub>), 2.61 (s, 3H, NCH<sub>3</sub>), 2.64 (s, 3H, NCH<sub>3</sub>), 2.65 (s, 3H, NCH<sub>3</sub>), 2.89 (s, 3H, NCH<sub>3</sub>), 4.21 (m, 3H,  $C_5H_4$ ), 4.27 (m, 4H,  $C_5H_4$ ), 4.56 ppm (m, 1H,  $C_5H_4$ ). <sup>11</sup>B{<sup>1</sup>H} NMR (160.462 Hz,  $C_6D_6$ ):  $\delta$  40.0 ppm (br). <sup>13</sup>C{<sup>1</sup>H} NMR (125.758 MHz,  $C_6D_6$ ):  $\delta$  4.89 (s, C=CCH<sub>3</sub>), 21.51 (s, C=CCH<sub>3</sub>), 40.48 (s, NCH<sub>3</sub>), 40.58 (s, NCH<sub>3</sub>), 41.00 (s, NCH<sub>3</sub>), 42.34 (s, NCH<sub>3</sub>), 69.6-80.1 (m, vbr,  $C_5H_4$ ), 81.18 (s, C=C), 91.75 (s, C=C), 131.31 (vbr, BC=CB), 158.31 ppm (vbr, BC=CB). Anal. Calcd (%) for  $C_{20}H_{26}B_2FeN_2$  (371.90): C 64.59, H 7.05, N 7.53. Found: C 64.55, H 7.21, N 7.51.

Synthesis of  $[Fe{\eta^{5-}C_{5}H_{4}B(NMe_{2})]_{2}{Ph}C=C-C\equiv C-Ph]$  (**15**). (a) In a Young NMR tube, 6.8 mg (0.010 mmol, 10 mol %) of  $[Pt(PEt_{3})_{4}]$ was heated to 60 °C under vacuum for 20 min. The resulting  $[Pt(PEt_{3})_{3}]$ was treated with 30.0 mg (0.102 mmol) of  $[Fe{\eta^{5-}C_{5}H_{4}B(NMe_{2})]_{2}]$ (3), 41.3 mg (0.153 mmol, 1.5 equiv) of 1,4-diphenylbutadiyne (**20**), and 0.5 mL of benzene-D<sub>6</sub>. The orange solution was heated to 100 °C, and after 14 d no 3 could be detected by NMR spectroscopy. The solvent was pumped off at room temperature before an excess of dialkyne was removed by sublimation at 70 °C. The residue was then extracted with hexanes (3 × 5 mL) and filtered. The red solution was concentrated and cooled to -30 °C for crystallization. After 4 d the product was isolated as red crystals (40 mg, 0.081 mmol, 78%).

(b) The heterogeneously catalyzed reaction was carried out analogously to (a) with 3.6 mg of Pd/C (10 wt % Pd, 0.0068 mmol, 10 mol %) instead of [Pt(PEt<sub>3</sub>)<sub>3</sub>]. After heating the reaction mixture to 100 °C for 17 d, the product was obtained in comparable yield.

(c) A 20 mg (0.028 mmol) amount of  $[Fe{\eta^5-C_5H_4B(NMe_2)}_2Pt-(PEt_3)_2]$  (18) and 8.2 mg (0.041 mmol, 1.5 equiv) of 20 were filled into an NMR tube and dissolved in 0.5 mL of benzene-D<sub>6</sub>. The resulting orange solution was heated to 80 °C, and after 1 h no 18 was detected. The volatiles were removed at room temperature and 70 °C, respectively (see above). The red residue was extracted with hexanes (2 × 3 mL), and the resulting suspension was filtered and concentrated before cooling to -30 °C. The product was isolated as red crystals in a yield of 8.0 mg (0.016 mmol, 58%).

<sup>1</sup>H NMR (500.130 MHz,  $C_6D_6$ ):  $\delta$  2.61 (s, 3H, NCH<sub>3</sub>), 2.69 (s, 3H, NCH<sub>3</sub>), 2.70 (s, 3H, NCH<sub>3</sub>), 2.94 (s, 3H, NCH<sub>3</sub>), 4.12–4.42 (m, vbr, 7H,  $C_5H_4$ ), 4.63 (m, vbr, 1H,  $C_5H_4$ ), 6.94 (m, 1H,  $C_6H_5$ ), 6.99 (m, 2H,  $C_6H_5$ ), 7.18 (m, 1H,  $C_6H_5$ ), 7.36 (m, 2H,  $C_6H_5$ ), 7.49 (m, 2H,  $C_6H_5$ ), 8.18 ppm (m, 2H,  $C_6H_5$ ). <sup>11</sup>B{<sup>1</sup>H} NMR (160.462 MHz,  $C_6D_6$ ):  $\delta$  39.4 ppm (br). <sup>13</sup>C{<sup>1</sup>H} NMR (125.758 MHz,  $C_6D_6$ ):  $\delta$  40.77 (s, NCH<sub>3</sub>), 40.77 (s, NCH<sub>3</sub>), 41.57 (s, NCH<sub>3</sub>), 41.91 (s, NCH<sub>3</sub>), 70.6–73.1 (m, vbr,  $C_5H_4$ ), 77.9–78.9 (m, vbr,  $C_5H_4$ ), 29.95 (s,  $C \equiv CC_6H_5$ ), 97.06 (s,  $C \equiv CC_6H_5$ ), 125.80 (s,  $C_6H_5$ <sup>quarternary</sup>), 127.18 (s,  $C_6H_5$ ), 128.40 (s,  $C_6H_5$ ), 128.55 (s,  $C_6H_5$ ), 129.23 (s,  $C_6H_5$ ), 131.85 (s,  $C_6H_5$ ), 135.15 (vbr, BC=CB), 143.47 (s,  $C_6H_5$ <sup>quarternary</sup>), 161.07 ppm (vbr, BC=CB). Anal. Calcd (%) for  $C_{30}H_{30}B_2FeN_2$  (496.03): C 72.64, H 6.10, N 5.65. Found: C 72.51, H 6.12, N 5.49.

Synthesis of  $[Fe\{\eta^{5}-C_{5}H_{4}B(NMe_{2})\}_{2}\{Me_{3}Si\}C=C-C_{2}H_{2}-C\equivC-SiMe_{3}J_{1}$ (**16**). (a) A 22.7 mg (0.0340 mmol) portion of  $[Pt(PEt_{3})_{4}]$  was filled into a Young NMR tube and heated to 60 °C for 20 min to produce  $[Pt(PEt_{3})_{3}]$ . Subsequently, 50 mg (0.17 mmol) of  $[Fe\{\eta^{5}-C_{5}H_{4}B(NMe_{2})\}_{2}]$  (3) and 56.3 mg (0.255 mmol, 1.5 equiv) of 1,6-bis(trimethylsilyl)hex-3-ene-1,5diyne (21) were added, and the mixture was dissolved in 0.5 mL of benzene- $D_{6}$ . The solution was heated to 90 °C for 14 d until no signals for 3 were detected by <sup>1</sup>H NMR spectroscopy. The solvent was pumped off at reduced pressure before removing excess dialkyne at 70 °C by sublimation. The yellow residue was extracted with hexanes (2 × 3 mL). After filtration of the suspension and removal of the solvent *in vacuo*, **16** was afforded as a yellow solid (76 mg), slightly ( $\leq$ 5% by NMR spectroscopy) contaminated with [Pt(PEt\_{3})\_{3}]. (b) A portion of 30 mg (0.041 mmol) of  $[Fe{\eta^5-C_5H_4B(NMe_2)}_2Pt-(PEt_3)_2]$  (18) and 18.2 mg (0.0827 mmol, 2 equiv) of 21 were added to an NMR tube and dissolved in 0.5 mL of benzene-D<sub>6</sub>. The solution was heated to 80 °C while the progress of the reaction was monitored by <sup>1</sup>H NMR spectroscopy. After 1 h, the signals of 21 could no longer be detected. Analogous workup (see above) afforded the product again contaminated with  $\leq 5\%$  of  $[Pt(PEt_3)_3]$ .

<sup>1</sup>H NMR (500.130 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  0.20 (s, 9H, C=CSiCH<sub>3</sub>), 0.33 (s, 9H, C=CSiCH<sub>3</sub>), 2.55 (s, 3H, NCH<sub>3</sub>), 2.56 (s, 3H, NCH<sub>3</sub>), 2.62 (s, 3H, NCH<sub>3</sub>), 2.67 (s, 3H, NCH<sub>3</sub>), 4.11 (m, 2H, C<sub>5</sub>H<sub>4</sub>), 4.17 (m, 1H, C<sub>5</sub>H<sub>4</sub>), 4.21 (m, 1H, C<sub>5</sub>H<sub>4</sub>), 78.19 (s, C<sub>5</sub>H<sub>4</sub>), 78.18 (s, C=CSi), 106.63 (s, C=CSi), 110.89 (s, C<sub>2</sub>H<sub>2</sub>), 147.28 (s, C<sub>2</sub>H<sub>2</sub>), 164.78 (vbr, BC=C{B}Si), 165.63 ppm (vbr, BC=C{B}Si).

Synthesis of [Fe{ $\eta^5$ -C<sub>5</sub>H<sub>4</sub>B(NMe<sub>2</sub>)}<sub>2</sub>{Me<sub>3</sub>Si}C=C-C<sub>6</sub>H<sub>4</sub>-C≡C-SiMe<sub>3</sub>] (**17**). (a) A Young NMR tube was loaded with 11.4 mg (0.0170 mmol) of [Pt(PEt<sub>3</sub>)<sub>4</sub>] and heated to 60 °C for 20 min under vacuum. To the resulting red oil were added 50 mg (0.17 mmol) of [Fe{ $\eta^5$ -C<sub>3</sub>H<sub>4</sub>B(NMe<sub>2</sub>)}<sub>2</sub>] (3), 69.1 mg (0.255 mmol, 1.5 equiv) of 1,4-bis[2-(trimethylsilyl)ethynyl]benzene (21), and 0.5 mL of benzene-D<sub>6</sub>, and the orange-yellow solution was heated to 80 °C. Within 2 d the starting diborane(4) precursor was consumed completely, as monitored by NMR spectroscopy. After that the solvent was pumped off under reduced pressure, and the remaining dialkyne was removed by sublimation at 100 °C under high vacuum. The orange residue was extracted with hexanes (2 × 3 mL), before the suspension was filtered, concentrated, and cooled to -30 °C. The yellow solid thus produced was washed with pentane (2 × 1 mL, -100 °C) and dried *in vacuo*, yielding the product as a yellow solid (65.0 mg, 0.115 mmol, 68%).

(b) A 20 mg (0.028 mmol) sample of  $[Fe{\eta^5-C_5H_4B(NMe_2)}_2Pt-(PEt_3)_2]$  (18) and 11.2 mg (0.0410 mmol, 1.5 equiv) of 21 were filled into an NMR tube and dissolved in 0.5 mL of benzene-D<sub>6</sub>. The yellow solution was heated to 80 °C, and after 1 h no signal for 18 could be detected by <sup>1</sup>H NMR spectroscopy. The reaction was worked up analogously (see above), providing the target product in comparable yield.

<sup>1</sup>H NMR (500.130 MHz,  $C_6D_6$ ):  $\delta$  0.15 (s, 9H, C=CSiCH<sub>3</sub>), 0.27 (s, 9H, C=CSiCH<sub>3</sub>), 2.48 (s, 3H, NCH<sub>3</sub>), 2.54 (s, 3H, NCH<sub>3</sub>), 2.70 (s, 3H, NCH<sub>3</sub>), 2.74 (s, 3H, NCH<sub>3</sub>), 4.16 (m, 1H,  $C_5H_4$ ), 4.20 (m, 1H,  $C_5H_4$ ), 4.26 (m, 1H,  $C_5H_4$ ), 4.27–4.30 (m, 4H,  $C_5H_4$ ), 4.42 (m, 1H,  $C_5H_4$ ), 7.35 (m, 2H,  $C_6H_4$ ), 7.58 ppm (m, 2H,  $C_6H_4$ ). <sup>11</sup>B{<sup>1</sup>H} NMR (160.462 MHz,  $C_6D_6$ ):  $\delta$  39.9 ppm (vbr). <sup>13</sup>C{<sup>1</sup>H} NMR (125.758 MHz,  $C_6D_6$ ):  $\delta$  0.16 (s, SiCH<sub>3</sub>), 2.69 (s, SiCH<sub>3</sub>), 40.87 (s, NCH<sub>3</sub>), 41.06 (s, NCH<sub>3</sub>), 41.82 (s, NCH<sub>3</sub>), 42.00 (s, NCH<sub>3</sub>), 70.64 (s,  $C_5H_4$ ), 71.13 (s,  $C_5H_4$ ), 72.01 (s,  $C_3H_4$ ), 72.71 (s,  $C_3H_4$ ), 72.18 (s,  $C_5H_4$ ), 72.33 (s,  $C_6H_4$ ), 77.58 (s,  $C_5H_4$ ), 72.77 (s,  $C_3H_4$ ), 94.21 (s, C=CSiCH<sub>3</sub>), 106.57 (s, C=CSiCH<sub>3</sub>), 121.33 (s,  $C_6H_4$ ), 128.74 (s,  $C_6H_4$ ), 131.87 (s,  $C_6H_4$ ), 148.63 (s,  $C_6H_4$ ), 159.92 (vbr, BC=C{B}Si), 170.35 ppm (vbr, BC=C{B}Si). Anal. Calcd (%) for  $C_{30}H_{42}B_2FeN_2Si_2$  (564.31): C 63.85, H 7.50, N 4.97. Found: C 63.32, H 7.85, N 4.85.

Synthesis of  $[(3,4-\eta^2-Fe\{\eta^5-C_5H_4B(NMe_2)\}_2\{Me\}C=C-C\equiv C-Me)$ Pt(PEt\_3)\_2] (**23**). A 30 mg (0.041 mmol) portion of  $[Fe\{\eta^5-C_5H_4B-(NMe_2)\}_2Pt(PEt_3)_2]$  (**18**) and 3.1 mg (0.039 mmol, 0.95 equiv) of 2, 4-hexadiyne (**19**) were filled into an NMR tube and dissolved in 0.5 mL of benzene-D<sub>6</sub>. The orange solution was heated to 60 °C, and the reaction progress was monitored by NMR spectroscopy. After 1 h no further decrease of the signals of **18** could be detected. The volatiles were removed *in vacuo*, and the orange residue was extracted with pentane  $(2 \times 2 \text{ mL})$ . The resulting suspension was filtered, concentrated to a third of its original volume, and cooled to -30 °C for crystallization. After 5 d the product was isolated as orange-yellow crystals (16 mg, 0.017 mmol, 42%), after washing with pentane (1 mL, -100 °C) and drying under vacuum. The product thus obtained contains a small amount of **14** (<5% by NMR spectroscopy).

<sup>1</sup>H NMR (500.130 MHz,  $C_6D_6$ ):  $\delta$  0.99 (m, 9H, PCH<sub>2</sub>CH<sub>3</sub>), 1.09 (m, 9H, PCH<sub>2</sub>CH<sub>3</sub>), 1.62 (m, 6H, PCH<sub>2</sub>CH<sub>3</sub>), 1.85 (m, 6H, PCH<sub>2</sub>CH<sub>3</sub>), 2.37 (m, 3H, {B}C=C{B}CH<sub>3</sub>), 2.76 (s, 3H, NCH<sub>3</sub>), 2.79 (s, 3H, NCH<sub>3</sub>), 2.83 (dd,  ${}^{4}J_{H-P}{}^{cis} = 8 \text{ Hz}, {}^{4}J_{H-P}{}^{trans} = 2 \text{ Hz}, {}^{3}J_{H-Pt} = 38 \text{ Hz}, 3H$ , {Pt}C = CCH<sub>3</sub>), 2.90 (s, 3H, NCH<sub>3</sub>), 3.01 (s, 3H, NCH<sub>3</sub>), 4.13-4.99 ppm (m, 8H, C<sub>5</sub>H<sub>4</sub>). <sup>11</sup>B{<sup>1</sup>H} NMR (160.462 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  40.9 ppm (br).  ${}^{13}C{}^{1}H$  NMR (125.758 MHz,  $C_6D_6$ ):  $\delta$  8.76 (m, PCH<sub>2</sub>CH<sub>3</sub>), 8.90 (m, PCH<sub>2</sub>CH<sub>3</sub>), 15.67 (dd,  ${}^{3}J_{C-P}{}^{cis} = 14$  Hz,  ${}^{3}J_{C-P}{}^{trans} = 9$  Hz, {Pt}C=CCH<sub>3</sub>), 19.75 (s, BC=C{B}CH<sub>3</sub>), 20.99 (dd,  ${}^{1}J_{C-P} = 22$  Hz,  ${}^{3}J_{C-P} = 4$  Hz, PCH<sub>2</sub>CH<sub>3</sub>), 21.30 (dd,  ${}^{1}J_{C-P} = 21$  Hz,  ${}^{3}J_{C-P} = 4$  Hz, PCH<sub>2</sub>CH<sub>3</sub>), 40.73 (s, NCH<sub>3</sub>), 40.89 (s, NCH<sub>3</sub>), 41.13 (s, NCH<sub>3</sub>), 42.83 (m, NCH<sub>3</sub>), 69.3–80.1 (m, vbr,  $C_5H_4$ ), 121.57 (dd,  ${}^2J_{C-P}{}^{cis}$  = 68  $\begin{array}{l} \text{Hz}_{r}^{2}J_{C-P}^{\text{trans}} = 10 \text{ Hz}_{r}^{1}J_{C-Pt} = 286 \text{ Hz}_{r} \{\text{Pt}\}C \equiv \text{CCH}_{3}, 123.35 \\ (\text{dd}, {}^{2}J_{C-P}^{\text{cis}} = 65 \text{ Hz}_{r}^{2}J_{C-P}^{\text{trans}} = 7 \text{ Hz}_{r}^{1}J_{C-Pt} = 268 \text{ Hz}_{r}, \end{array}$ {Pt}C=CCH<sub>3</sub>), 142.67 (m, vbr, BC=CB), 144.78 ppm (m, vbr, BC=CB). <sup>31</sup>P{<sup>1</sup>H} NMR (202.456 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  10.93 (d, <sup>1</sup>J<sub>P-Pt</sub> = 3261 Hz,  ${}^{2}J_{P-P}$  = 41 Hz, PtPCH<sub>2</sub>CH<sub>3</sub>), 12.79 ppm (d,  ${}^{1}J_{P-Pt}$  = 3243 Hz,  ${}^{2}J_{P-P} = 41 \text{ Hz}, \text{PtPCH}_{2}\text{CH}_{3}$ ). IR (neat, cm<sup>-1</sup>): 1557 (w,  $\nu_{BC=CB}$ ), 1744 (w, br,  $\nu_{\rm {Pt}C=C}$ ). Anal. Calcd (%) for C<sub>32</sub>H<sub>56</sub>B<sub>2</sub>FeP<sub>2</sub>Pt (803.29): C 47.84, H 7.02, N 3.49. Found: C 48.35, H 6.90, N 3.56.

Synthesis of  $[(3,4-\eta^2-Fe\{\eta^5-C_5H_4B(NMe_2)\}_2\{Ph\}C=C-C\equiv C-Ph)$ Pt(PEt\_3)\_2] (**24**). An NMR tube was filled with 30 mg (0.041 mmol) of  $[Fe\{\eta^5-C_5H_4B(NMe_2)\}_2Pt(PEt_3)_2]$  (**18**), 7.9 mg (0.039 mmol, 0.95 equiv) of 1,4-diphenylbutadiyne (**20**), and 0.5 mL of benzene-D<sub>6</sub>. The orange-red solution was heated to 80 °C while monitored by NMR spectroscopy. After 1 h no further decrease of the signals of **20** could be observed. Thereafter the solvent was evaporated *in vacuo* at room temperature before removing the excess dialkyne at 70 °C. The resulting orange-red residue was extracted with hexanes (2 × 5 mL) and filtered. The orangecolored solution was concentrated to one-third of the original volume and cooled to -30 °C. The product was isolated as orange-yellow crystals (21 mg, 0.023 mmol, 55%) after two days and recrystallized from hexanes at -30 °C to obtain crystals suitable for X-ray diffraction.

<sup>1</sup>H NMR (600.130 MHz, C<sub>6</sub>D<sub>6</sub>): δ 0.89 (m, 9H, PCH<sub>2</sub>CH<sub>3</sub>), 0.93 (m, 9H, PCH<sub>2</sub>CH<sub>3</sub>), 1.33 (m, 3H, PCH<sub>2</sub>CH<sub>3</sub>), 1.43 (m, 6H, PCH<sub>2</sub>CH<sub>3</sub>), 1.61 (m, 3H, PCH<sub>2</sub>CH<sub>3</sub>), 2.60 (s, 3H, NCH<sub>3</sub>), 2.61 (s, 3H, NCH<sub>3</sub>), 2.77 (s, 3H, NCH<sub>3</sub>), 2.78 (s, 3H, NCH<sub>3</sub>), 4.32 (m, 1H, C<sub>5</sub>H<sub>4</sub>), 4.34 (m, 1H,  $C_{5}H_{4}$ , 4.35 (m, 2H,  $C_{5}H_{4}$ ), 4.37 (m, 1H,  $C_{5}H_{4}$ ), 4.43 (m, 1H,  $C_{5}H_{4}$ ), 4.60  $(m, 1H, C_5H_4), 4.87 (m, 1H, C_5H_4), 7.02 (m, 1H, {Pt}C = CC_6H_5), 7.07$ (m, 1H, BC=C{B}C<sub>6</sub>H<sub>5</sub>), 7.21 (m, 2H, {Pt}C=CC<sub>6</sub>H<sub>5</sub>), 7.27 (m, 2H, BC=C{B}C<sub>6</sub>H<sub>5</sub>), 7.32 (m, 2H, {Pt}C=CC<sub>6</sub>H<sub>5</sub>), 7.86 ppm (m, 1H, BC=C{B}C<sub>6</sub>H<sub>5</sub>). <sup>11</sup>B{<sup>1</sup>H} NMR (160.462 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  39.1 ppm (br). <sup>13</sup>C{<sup>1</sup>H} NMR (150.902 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  8.67 (m, PCH<sub>2</sub>CH<sub>3</sub>), 8.83 (m, PCH<sub>2</sub>CH<sub>3</sub>), 20.20 (dd,  ${}^{1}J_{C-P} = 9$  Hz,  ${}^{3}J_{C-P} = 3$  Hz, PCH<sub>2</sub>CH<sub>3</sub>), 21.38  $(dd, {}^{1}J_{C-P} = 9 Hz, {}^{3}J_{C-P} = 3 Hz, PCH_2CH_3), 40.63 (s, NCH_3), 40.88$ (s, NCH<sub>3</sub>), 42.05 (s, NCH<sub>3</sub>), 42.17 (s, NCH<sub>3</sub>), 70.27 (s, C<sub>5</sub>H<sub>4</sub>), 70.53 (s, C5H4), 71.42 (s, C5H4), 71.95 (s, C5H4), 71.96 (s, C5H4), 72.18 (s, C<sub>5</sub>H<sub>4</sub>), 72.41 (br, C<sub>5</sub>H<sub>4</sub><sup>quarternary</sup>), 76.65 (br, C<sub>5</sub>H<sub>4</sub><sup>quarternary</sup>), 78.78  $(s, C_5H_4), 79.92 (s, C_5H_4), 124.01 (m, {Pt}C = CC_6H_5), 124.75 (s, BC = C-6H_5), 124.75 ($  $\{B\}C_6H_5$ , 126.92 (m,  $\{Pt\}C\equiv CC_6H_5$ ), 127.39 (m,  $\{Pt\}C\equiv CC_6H_5$ ), 127.56 (s, BC=C{B}C<sub>6</sub>H<sub>5</sub>), 130.50 (m, BC=C{B}C<sub>6</sub>H<sub>5</sub>), 130.88 (dd,  ${}^{2}J_{C-P}{}^{cs} = 72 \text{ Hz}, {}^{2}J_{C-P}{}^{trans} = 9 \text{ Hz}, {}^{1}J_{C-Pt} = 289 \text{ Hz}, {}^{Pt}S \subset C), 134.26 \text{ (dd,} 232 \text{ C}), 134.26 \text{ (dd,} 342 \text{ C})$ (s, vbr, BC= $C{B}C_{6}H_{5}$ ), 144.15 (m, {Pt}C= $CC_{6}H_{5}$ <sup>quartemary</sup>), 144.88 (m, BC=C{B} $C_6H_5^{\text{quarternary}}$ ), 148.65 ppm (s, vbr, BC=C{B} $C_6H_5$ ). <sup>31</sup>P{<sup>1</sup>H} NMR (202.456 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  8.60 (d, <sup>2</sup>J<sub>P-P</sub> = 33 Hz, <sup>1</sup>J<sub>P-Pt</sub> = 3252 Hz, PtPCH<sub>2</sub>CH<sub>3</sub>), 10.94 ppm (d,  ${}^{2}J_{P-P}$  = 33 Hz,  ${}^{1}J_{P-Pt}$  = 3410 Hz, PtPCH<sub>2</sub>CH<sub>3</sub>). IR (neat, cm<sup>-1</sup>): 1586 (w,  $\nu_{BC=CB}$ ), 1736 (w,  $\nu_{\{Pt\}C=C}$ ). Anal. Calcd (%) for C42H60B2FeN2P2Pt (927.43): C 54.39, H 6.52, N 3.02. Found: C 54.04, H 6.66, N 3.08.

General Synthetic Procedure for  $[(Et_3P)_2Pt(1,2-\eta^2-R-C = C-X-C = C-R)]$ (**25a**: R = Me, no X; **26a**: R = Ph, no X; **27a**:  $R = SiMe_3$ ,  $X = 1,4-C_6H_4$ ),  $[\{(Et_3P)_2Pt\}_2(\mu-1,2-\eta^2-3,4-\eta^2-R-C = C-X-C = C-R)]$  (**25b**: R = Me, no X; **26b**: R = Ph, no X; **27b**:  $R = SiMe_3$ ,  $X = 1,4-C_6H_4$ ), and  $[(Et_3P)_2Pt(3,4-\eta^2-E-R-C = C-C\{H\} = C\{H\} - C = C-R)]$  (**28**:  $R = SiMe_3$ ). [Pt(PEt\_3)\_4] was heated to 60 °C *in vacuo* for 20 min to remove one PEt\_3 ligand. The resulting red oil was then dissolved in 0.5 mL of benzene-D<sub>6</sub>, before adding the dialkyne (**25–27a**: 1 equiv; **25–27b**: 0.5 equiv). In doing so, a change in color from orange-red to yellow or pale yellow was observed. After removing the volatiles *in vacuo*, the residue was taken up in pentane (2 mL). This procedure was repeated twice, and the resulting solution was filtered before the products were obtained either by crystallization at -30 °C (**27a**: 23%, **26b**: 46%) or by slow evaporation of the solvent at room temperature in an atmosphere of an inert gas (**25a**, **26a**, **25b**: 60%, **27b**: 83%, **28**: 85%).

Analytical Data. 25a: <sup>1</sup>H NMR (500.130 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  0.94 (m, 9H, PCH<sub>2</sub>CH<sub>3</sub>), 1.05 (m, 9H, PCH<sub>2</sub>CH<sub>3</sub>), 1.55 (m, 6H, PCH<sub>2</sub>CH<sub>3</sub>), 1.74 (m, 6H, PCH<sub>2</sub>CH<sub>3</sub>), 2.02 (m, 3H, C≡CCH<sub>3</sub>), 2.79 ppm (m, 3H, {Pt}C≡CCH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (125.758 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  5.70 (m, C≡CCH<sub>3</sub>), 8.89 (m, PCH<sub>2</sub>CH<sub>3</sub>), 8.91 (m, PCH<sub>2</sub>CH<sub>3</sub>), 16.08 (m, {Pt}C≡CCH<sub>3</sub>), 21.07 (dd, <sup>1</sup>J<sub>C-P</sub> = 24 Hz, <sup>3</sup>J<sub>C-P</sub> = 3 Hz, <sup>2</sup>J<sub>C-Pt</sub> = 30 Hz, PCH<sub>2</sub>CH<sub>3</sub>), 21.97 (dd, <sup>1</sup>J<sub>C-P</sub> = 24 Hz, <sup>3</sup>J<sub>C-P</sub> = 4 Hz, <sup>2</sup>J<sub>C-Pt</sub> = 36 Hz, PCH<sub>2</sub>CH<sub>3</sub>), 52.46 (m, C≡C), 93.42 (m, C≡C), 105.13 (dd, <sup>2</sup>J<sub>C-P</sub><sup>cis</sup> = 72 Hz, <sup>2</sup>J<sub>C-P</sub><sup>trans</sup> = 6 Hz, <sup>1</sup>J<sub>C-Pt</sub> = 251 Hz, {Pt}C≡CCH<sub>3</sub>), 130.76 ppm (dd, <sup>2</sup>J<sub>C-P</sub><sup>cis</sup> = 73 Hz, <sup>2</sup>J<sub>C-P</sub><sup>trans</sup> = 9 Hz, <sup>1</sup>J<sub>C-Pt</sub> = 310 Hz, {Pt}C≡CCH<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (202.456 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  11.82 (d, <sup>2</sup>J<sub>P-P</sub> = 32 Hz, <sup>1</sup>J<sub>Pt-P</sub> = 3160 Hz, PtPCH<sub>2</sub>CH<sub>3</sub>), 16.23 ppm (d, <sup>2</sup>J<sub>P-P</sub> = 32 Hz, <sup>1</sup>J<sub>Pt-P</sub> = 3471 Hz, PtPCH<sub>2</sub>CH<sub>3</sub>). IR (neat, cm<sup>-1</sup>): 1743 (w,  $\nu_{{Pt}}_{{C=C}}$ ), 2195 (w,  $\nu_{{C=C}}$ ). Anal. Calcd (%) for C<sub>18</sub>H<sub>36</sub>P<sub>2</sub>Pt (506.49): C 42.43, H 7.16. Found: C 41.97, H 7.15.

**26a**: <sup>1</sup>H NMR (500.130 MHz,  $C_6D_6$ ):  $\delta$  0.92 (m, 9H, PCH<sub>2</sub>CH<sub>3</sub>), 1.03 (m, 9H, PCH<sub>2</sub>CH<sub>3</sub>), 1.64 (m, 6H, PCH<sub>2</sub>CH<sub>3</sub>), 1.78 (m, 6H, PCH<sub>2</sub>CH<sub>3</sub>), 6.98 (m, 1H, C=CC<sub>6</sub>H<sub>5</sub>), 7.07 (m, 3H, C=CC<sub>6</sub>H<sub>5</sub> + {Pt}C=CC<sub>6</sub>H<sub>5</sub>), 7.27 (m, 2H, C=CC<sub>6</sub> $H_5$ ), 7.55 (m, 2H, {Pt}C=CC<sub>6</sub> $H_5$ ), 7.96 ppm (m, 2H, {Pt}C=CC<sub>6</sub>H<sub>5</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (125.758 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  8.86 (m, PCH<sub>2</sub>CH<sub>3</sub>), 9.13 (m, PCH<sub>2</sub>CH<sub>3</sub>), 20.42 (dd,  ${}^{1}J_{C-P} = 25$  Hz,  ${}^{3}J_{C-P} =$ 2 Hz,  ${}^{2}J_{C-Pt} = 31$  Hz, PCH<sub>2</sub>CH<sub>3</sub>), 22.06 (dd,  ${}^{1}J_{C-P} = 26$  Hz,  ${}^{3}J_{C-P} = 4$  Hz,  ${}^{2}J_{C-Pt} = 36 \text{ Hz}, PCH_{2}CH_{3}), 86.52 \text{ (m, } C \equiv C), 102.90 \text{ (m, } C \equiv C), 111.93 \text{$  $(dd, {}^{2}J_{C-P}{}^{cis} = 74 Hz, {}^{2}J_{C-P}{}^{trans} = 5 Hz, {}^{1}J_{C-Pt} = 241 Hz, {Pt}C \equiv CC_{6}H_{5}),$ 126.39 (s, C<sub>6</sub>H<sub>5</sub>), 126.67 (m, C<sub>6</sub>H<sub>5</sub>), 127.08 (s, C<sub>6</sub>H<sub>5</sub>), 128.55 (s, C<sub>6</sub>H<sub>5</sub>), 128.61 (s, C<sub>6</sub>H<sub>5</sub>), 129.83 (m, C<sub>6</sub>H<sub>5</sub>), 131.19 (m), 136.96 (m, C<sub>6</sub>H<sub>5</sub>), 139.79 ppm (dd,  ${}^{2}J_{C-P}^{cis}$  = 80 Hz,  ${}^{2}J_{C-P}^{trans}$  = 9 Hz,  ${}^{1}J_{C-Pt}$  = 358 Hz, {Pt}C=CC<sub>6</sub>H<sub>5</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (202.456 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  9.05 (d, <sup>2</sup>J<sub>P-P</sub> = 23 Hz,  ${}^{1}\!J_{\rm P-Pt}$  = 3191 Hz, PtPCH2CH3), 14.52 ppm (d,  ${}^{2}\!J_{\rm P-P}$  = 23 Hz,  ${}^{1}J_{P-Pt} = 3468 \text{ Hz}, \text{ PtPCH}_{2}\text{CH}_{3}$ ). IR (neat, cm<sup>-1</sup>): 1695 (w, br,  $\nu_{\{Pt\}C=C}$ ), 2153 (w,  $\nu_{C=C}$ ). Anal. Calcd (%) for (633.64): C 53.07, H 6.36. Found: C 52.29, H 6.21.

**27a**: <sup>1</sup>H NMR (500.130 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  0.27 (s, 9H, C=CSiCH<sub>3</sub>), 0.39 (s, 9H, C=CSiCH<sub>3</sub>), 0.82 (m, 9H, PCH<sub>2</sub>CH<sub>3</sub>), 0.99 (m, 9H, PCH<sub>2</sub>CH<sub>3</sub>), 1.45 (m, 6H, PCH<sub>2</sub>CH<sub>3</sub>), 1.71 (m, 6H, PCH<sub>2</sub>CH<sub>3</sub>), 7.29 (m, 2H, C<sub>6</sub>H<sub>4</sub>), 7.49 ppm (m, 2H,  $C_6H_4$ ). <sup>13</sup>C{<sup>1</sup>H} NMR (125.758 MHz,  $C_6D_6$ ):  $\delta$  0.23  $(C \equiv CSiCH_3)$ , 1.39 (d,  ${}^{4}J_{C-P} = 2 Hz$ ,  ${}^{3}J_{C-Pt} = 10 Hz$ , {Pt}C  $\equiv CSiCH_3$ ), 8.78 (m, PCH<sub>2</sub>CH<sub>3</sub>), 9.03 (m, PCH<sub>2</sub>CH<sub>3</sub>), 21.56 (dd,  ${}^{1}J_{C-P}$  = 24 Hz,  ${}^{3}J_{C-P} = 3 \text{ Hz}, {}^{2}J_{C-Pt} = 34 \text{ Hz}, \text{ PCH}_{2}\text{CH}_{3}), 22.50 \text{ (dd, } {}^{1}J_{C-P} = 23 \text{ Hz}, {}^{3}$  $J_{C-P} = 4 \text{ Hz}, {}^{2}J_{C-Pt} = 36 \text{ Hz}, PCH_{2}CH_{3}), 93.42 \text{ (s, } C \equiv CSiCH_{3}), 107.23$ (s, C=CSiCH<sub>3</sub>), 119.80 (m,  $C_6H_4$ ), 124.95 (dd,  ${}^2J_{C-P}^{cis}$  = 53 Hz,  ${}^{2}J_{C-P}^{trans} = 9 \text{ Hz}, \{Pt\}C \equiv CSiCH_{3}\} 127.10 (m, C_{6}H_{4}), 131.66$ (m,  $C_6H_4$ ), 142.91 (m,  $C_6H_4$ ), 151.66 ppm (dd,  ${}^2J_{C-P}{}^{cis}$  = 59 Hz,  ${}^{2}J_{C-P}$ <sup>trans</sup> = 10 Hz,  ${}^{1}J_{C-Pt}$  = 337 Hz, {Pt}C=CSiCH<sub>3</sub>).  ${}^{31}P{}^{1}H$  NMR (202.456 MHz,  $C_6D_6$ ):  $\delta$  13.02 (d,  ${}^2J_{P-P}$  = 38 Hz,  ${}^1J_{P-Pt}$  = 3345 Hz, PtPCH<sub>2</sub>CH<sub>3</sub>), 14.54 ppm (d,  ${}^{2}J_{P-P}$  = 38 Hz,  ${}^{1}J_{P-Pt}$  = 3443 Hz, PtPCH<sub>2</sub>CH<sub>3</sub>). IR (neat, cm<sup>-1</sup>): 1716 (w,  $v_{\{Pt\}C=C}$ ), 2148 (w,  $v_{C=C}$ ). Anal. Calcd (%) for C<sub>28</sub>H<sub>52</sub>P<sub>2</sub>PtSi<sub>2</sub> (701.91): C 47.91, H 7.47. Found: C 48.53, H 7.48.

**25b**: <sup>1</sup>H NMR (500.130 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  1.06 (m, 18H, PCH<sub>2</sub>CH<sub>3</sub>), 1.09 (m, 18H, PCH<sub>2</sub>CH<sub>3</sub>), 1.65 (m, 12H, PCH<sub>2</sub>CH<sub>3</sub>), 1.75 (m, 12H, PCH<sub>2</sub>CH<sub>3</sub>), 2.92 ppm (m, 6H, {Pt}C=CCH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (125.758 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  9.09 (m, PCH<sub>2</sub>CH<sub>3</sub>), 16.04 (m br, C=CCH<sub>3</sub>), 20.89 (m, PCH<sub>2</sub>CH<sub>3</sub>), 22.38 (m, PCH<sub>2</sub>CH<sub>3</sub>), 114.38 (m, {Pt}C=CCH<sub>3</sub>), 120.00 ppm (m, {Pt}C=CCH<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (202.456 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  12.89 (m, PtPCH<sub>2</sub>CH<sub>3</sub>), 15.40 ppm (m, PtPCH<sub>2</sub>CH<sub>3</sub>). IR (neat, cm<sup>-1</sup>): 1699 (w,  $\nu_{\text{Pt}C=C}$ ). Anal. Calcd (%) for C<sub>30</sub>H<sub>66</sub>P<sub>4</sub>Pt<sub>2</sub> (940.86): C 38.29, H 7.07. Found: C 38.47, H 7.03.

**26b**: <sup>1</sup>H NMR (500.130 MHz,  $C_6D_6$ ):  $\delta$  0.94 (m, 18H, PCH<sub>2</sub>CH<sub>3</sub>), 1.03 (m, 18H, PCH<sub>2</sub>CH<sub>3</sub>), 1.64 (m, 12H, PCH<sub>2</sub>CH<sub>3</sub>), 1.75 (m, 12H, PCH<sub>2</sub>CH<sub>3</sub>), 7.02 (m, 2H,  $C_6H_5$ ), 7.26 (m, 4H,  $C_6H_5$ ), 7.83 ppm (m, 4H,  $C_6H_5$ ). <sup>13</sup>C{<sup>1</sup>H} NMR (125.758 MHz,  $C_6D_6$ ):  $\delta$  8.97 (m, PCH<sub>2</sub>CH<sub>3</sub>), 9.31 (m, PCH<sub>2</sub>CH<sub>3</sub>), 20.03 (m, PCH<sub>2</sub>CH<sub>3</sub>), 22.44 (m, PCH<sub>2</sub>CH<sub>3</sub>), 124.27 (m,  $C_6H_5^{CH}$ ), 126.48 (br m), 126.84 (br m), 128.15 (m,  $C_6H_5^{CH}$ ), 128.58 (br m), 129.93 (m,  $C_6H_5^{CH}$ ), 138.72 ppm (m,  $C_6H_5^{quarternary}$ ). <sup>31</sup>P{<sup>1</sup>H} NMR (202.456 MHz,  $C_6D_6$ ):  $\delta$  9.10 (m, PtPCH<sub>2</sub>CH<sub>3</sub>), 13.21 ppm (m, PtPCH<sub>2</sub>CH<sub>3</sub>). IR (neat, cm<sup>-1</sup>): 1757 (w,  $\nu_{\{Pt\}C=C}$ ). Anal. Calcd (%) for C<sub>40</sub>H<sub>70</sub>P<sub>4</sub>Pt<sub>2</sub> (1064.99): C 45.11, H 6.62. Found: C 45.44, H 6.61.

**27b**: <sup>1</sup>H NMR (500.130 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  0.46 (s, 18H, {Pt}C≡ CSiCH<sub>3</sub>), 0.93 (m, 18H, PCH<sub>2</sub>CH<sub>3</sub>), 1.04 (m, 18H, PCH<sub>2</sub>CH<sub>3</sub>), 1.60 (m, 12H, PCH<sub>2</sub>CH<sub>3</sub>), 1.77 (m, 12H, PCH<sub>2</sub>CH<sub>3</sub>), 7.47 ppm (br s, 4H, C<sub>6</sub>H<sub>4</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (125.758 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  1.52 (m, {Pt}C≡CSiCH<sub>3</sub>), 8.96 (m, PCH<sub>2</sub>CH<sub>3</sub>), 9.10 (m, PCH<sub>2</sub>CH<sub>3</sub>), 21.41 (m, PCH<sub>2</sub>CH<sub>3</sub>), 22.65 (m, PCH<sub>2</sub>CH<sub>3</sub>), 121.79 (dd, <sup>2</sup>J<sub>C-P</sub><sup>cis</sup> = 52 Hz, <sup>2</sup>J<sub>C-P</sub><sup>trans</sup> = 9 Hz, {Pt}C≡CSiCH<sub>3</sub>), 126.84 (m, C<sub>6</sub>H<sub>4</sub>), 137.60 (m br, C<sub>6</sub>H<sub>4</sub>), 152.44 ppm (m, {Pt}C≡CSiCH<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (202.456 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  13.53 (m, PtPCH<sub>2</sub>CH<sub>3</sub>), 14.77 ppm (m, PtPCH<sub>2</sub>CH<sub>3</sub>). IR (neat, cm<sup>-1</sup>): 1716 (w, br,  $\nu_{\{Pt\}C≡C}$ ). Anal. Calcd (%) for C<sub>40</sub>H<sub>82</sub>P<sub>4</sub>Pt<sub>2</sub>Si<sub>2</sub> (1133.27): C 42.39, H 7.29. Found: C 42.21, H 7.10.

**28**: <sup>1</sup>H NMR (500.130 MHz,  $C_6D_6$ ):  $\delta$  0.21 (s, 18H, C=CSiCH<sub>3</sub>), 0.93 (m, 18H, PCH<sub>2</sub>CH<sub>3</sub>), 1.59 (m, 6H, PCH<sub>2</sub>CH<sub>3</sub>), 1.68 (m, 6H, PCH<sub>2</sub>CH<sub>3</sub>), 3.12 ppm (m, 2H,  $C_2H_2$ ). <sup>13</sup>C{<sup>1</sup>H} NMR (125.758 MHz,  $C_6D_6$ ):  $\delta$  0.89 (s, C=CSiCH<sub>3</sub>), 8.68 (m, PCH<sub>2</sub>CH<sub>3</sub>), 20.14 (m, PCH<sub>2</sub>CH<sub>3</sub>), 22.35 (m, PCH<sub>2</sub>CH<sub>3</sub>), 31.22 (m,  $C_2H_2$ ), 80.48 (m, C=CSiCH<sub>3</sub>), 114.33 ppm (m, C=CSiCH<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (202.456 MHz,  $C_6D_6$ ):  $\delta$  14.81 ppm (s, <sup>1</sup>J<sub>P-Pt</sub> = 3538 Hz, PtPCH<sub>2</sub>CH<sub>3</sub>). IR (neat, cm<sup>-1</sup>): 2114 (w, br,  $\nu_{C=C}$ ). Anal. Calcd (%) for C<sub>24</sub>H<sub>50</sub>P<sub>2</sub>PtSi<sub>2</sub> (651.85): C 44.22, H 7.73. Found: C 43.39, H 7.68.

Synthesis of  $[1,4-(Fe\{\eta^5-C_5H_4B(NMe_2)\}_2\{Me_3Si\}C=C)_2C_6H_4]$  pR, *pR-/pS,pS-* (**29**) and *pS,pR-* (**30**). (a) A 5.7 mg (0.0085 mmol) portion of [Pt(PEt<sub>3</sub>)<sub>4</sub>] was heated to 60 °C for 20 min in a Young NMR tube, and to the resulting red oil (11) were added 50 mg (0.17 mmol) of  $[Fe{\eta^{5}-C_{5}H_{4}B(NMe_{2})}_{2}]$ , 23 mg (0.085 mmol) of 1,4-bis[2-(trimethylsilyl)ethynyl]benzene (22), and 0.5 mL of benzene- $D_6$ . The solution was heated to 80 °C, and after 1 d no starting material was visible in the proton NMR spectrum. An orange-yellow solid containing the two diastereomers pR,pR-/pS,pS-29 and pS,pR-30 in a 1.3 to 1 ratio was obtained after removal of the volatiles in vacuo. The crude product was washed with pentane (1 mL, -100 °C) to remove 11, dried under high vacuum, taken up in hexanes  $(2 \times 2 \text{ mL})$ , filtered, and cooled to -30 °C. By doing so, **29** was isolated as orange crystals (18 mg, 0.021 mmol, 25%) suitable for X-ray diffraction. The other isomer can be enriched in the solid state by concentrating the mother liquor, cooling to -30 °C, and filtering off precipitated **29**, before drying the solution *in* vacuo. The solution should not be kept at room temperature for more than a few minutes, to avoid re-equilibration.

(b) In an NMR tube were added 60 mg (0.082 mmol) of  $[Fe{\eta^5}-C_5H_4B(NMe_2)]_2Pt(PEt_3)_2$ ] (18) and 11.1 mg (0.0411 mmol) of 22, and these were dissolved in 0.5 mL of benzene-D<sub>6</sub>. The orange solution was heated to 80 °C for 1 h before proton NMR indicated the end of the reaction, as no further decrease of the signals of 18 could be detected. The volatiles were removed *in vacuo*, and after extraction of the residue

ARTICLE

with hexanes  $(2 \times 5 \text{ mL})$ , the suspension was filtered and the solvent was removed *in vacuo* again. By doing so, the two isomers were obtained contaminated with 11 in the same ratio as described above.

(c) The synthesis of **29** and **30** starting from  $[Fe{\eta^5-C_5H_4B(NMe_2)}_2 (Me_3Si)C=C-C_6H_4-C=C-SiMe_3]$  (17) proceeds analogously. Hereby, 25.7 mg (0.0354 mmol) of  $[Fe{\eta^5-C_5H_4B(NMe_2)}_2Pt(PEt_3)_2]$  (18) and 20 mg (0.035 mmol) of 17 were mixed together in an NMR tube and treated as described above, leading to the same mixture of diastereomers.

**29**: <sup>1</sup>H NMR (500.130 MHz,  $C_6D_6$ ):  $\delta$  0.34 (s, 18H, SiCH<sub>3</sub>), 2.55 (s, 6H, NCH<sub>3</sub>), 2.62 (s, 6H, NCH<sub>3</sub>), 2.79 (m, 6H, NCH<sub>3</sub>), 2.80 (s, 6H, NCH<sub>3</sub>), 4.21 (m, 2H,  $C_5H_4$ ), 4.24 (m, 2H,  $C_5H_4$ ), 4.32 (m, 8H,  $C_5H_4$ ), 4.39 (m, 2H,  $C_5H_4$ ), 4.65 (m, 2H,  $C_5H_4$ ), 7.55 ppm (s, 4H,  $C_6H_4$ ).

**30**: <sup>1</sup>H NMR (500.130 MHz,  $C_6D_6$ ):  $\delta$  0.33 (s, 18H, SiCH<sub>3</sub>), 2.57 (s, 6H, NCH<sub>3</sub>), 2.67 (s, 6H, NCH<sub>3</sub>), 2.79 (s, 6H, NCH<sub>3</sub>), 2.82 (s, 6H, NCH<sub>3</sub>), 4.20 (m, 2H,  $C_5H_4$ ), 4.24 (m, 2H,  $C_5H_4$ ), 4.34 (m, 8H,  $C_5H_4$ ), 4.38 (m, 2H,  $C_5H_4$ ), 4.63 (m, 2H,  $C_5H_4$ ), 7.56 ppm (s, 4H,  $C_6H_4$ ).

<sup>11</sup>B{<sup>1</sup>H} NMR (160.462 MHz,  $C_6D_6$ ):  $\delta$  41.3 ppm (29+30, vbr). <sup>13</sup>C{<sup>1</sup>H} NMR (125.758 MHz,  $C_6D_6$ ):  $\delta$  2.99 (29, s, SiCH<sub>3</sub>), 3.00 (30, s, SiCH<sub>3</sub>), 40.87 (s, NCH<sub>3</sub>), 41.05 (s, NCH<sub>3</sub>), 41.98 (s, NCH<sub>3</sub>), 42.02 (s, NCH<sub>3</sub>), 42.04 (s, NCH<sub>3</sub>), 70.58 (s,  $C_5H_4$ ), 70.59 (s,  $C_5H_4$ ), 71.09 (s,  $C_5H_4$ ), 71.99 (s,  $C_5H_4$ ), 72.01 (s,  $C_5H_4$ ), 72.04 (s,  $C_5H_4$ ), 72.23 (s,  $C_5H_4$ ), 72.26 (s,  $C_5H_4$ ), 77.79 (s,  $C_5H_4$ ), 77.86 (s,  $C_5H_4$ ), 78.10 (s,  $C_5H_4$ ), 128.19 (s,  $C_6H_4$ ), 128.20 (s,  $C_6H_4$ ), 145.52 (29, s,  $C_6H_4^{ispo}$ ), 145.53 (30, s,  $C_6H_4^{ipso}$ ), 158.00 (29+30, m, br, BC=C{B}Si), 171.16 (29/30, m, br, BC=C{B}Si), 171.30 ppm (29/30, m, br, BC=C{B}Si). Anal. Calcd (%) for  $C_{44}H_{62}B_4Fe_2N_4Si_2$  (858.10): C 61.58, H 7.28, N 6.53. Found: C 61.26, H 7.36, N 6.43.

**Crystal Structure Determination.** The crystal data of 14 and 24 were collected on a Bruker X8Apex diffractometer with CCD area detector and multilayer mirror monochromated Mo K $\alpha$  radiation; those of **26b**, **27a**, and **29** were collected on a Bruker Apex diffractometer with CCD area detector and graphite-monochromated Mo K $\alpha$  radiation. The structures were solved using direct methods, refined with the Shelx software package, <sup>121</sup> and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were assigned idealized positions and were included in structure factor calculations.

Crystal data for 14:  $C_{20}H_{26}B_2FeN_2$ ,  $M_r = 371.90$ , clear block,  $0.17 \times 0.08 \times 0.05 \text{ mm}^3$ , triclinic space group  $P\overline{1}$ , a = 8.7429(2) Å, b = 8.8365(2) Å, c = 13.2645(4) Å,  $\alpha = 108.0790(10)^\circ$ ,  $\beta = 105.6600(10)^\circ$ ,  $\gamma = 92.5300(10)^\circ$ , V = 928.81(4) Å<sup>3</sup>, Z = 2,  $\rho_{calcd} = 1.330 \text{ g} \cdot \text{cm}^{-3}$ ,  $\mu = 0.816 \text{ mm}^{-1}$ , F(000) = 392, T = 101(2) K,  $R_1 = 0.0280$ ,  $wR_2 = 0.0701$ , 3644 independent reflections  $[2\theta \le 52.06^\circ]$  and 232 parameters.

Crystal data for 24:  $C_{42}H_{60}B_2FeN_2P_2Pt$ ,  $M_r = 927.42$ , orange plate,  $0.20 \times 0.10 \times 0.02 \text{ mm}^3$ , monoclinic space group  $P2_1/n$ , a = 20.9288(7)Å, b = 16.8368(5) Å, c = 25.5324(8) Å,  $\beta = 113.8790(10)^\circ$ , V = 8226.8(4) Å<sup>3</sup>, Z = 8,  $\rho_{calcd} = 1.498 \text{ g} \cdot \text{cm}^{-3}$ ,  $\mu = 3.859 \text{ mm}^{-1}$ , F(000) = 3760, T = 100(2) K,  $R_1 = 0.0457$ ,  $wR_2 = 0.0546$ , 16 124 independent reflections  $[2\theta \le 52.08^\circ]$  and 921 parameters.

Crystal data for 27a:  $C_{28}H_{52}P_2PtSi_2$ ,  $M_r = 701.91$ , yellow plate,  $0.32 \times 0.175 \times 0.015$ , monoclinic space group  $P2_1/n$ , a = 14.181(3) Å, b = 11.478(2) Å, c = 21.343(6) Å,  $\beta = 101.311(5)^\circ$ , V = 3406.4(14) Å<sup>3</sup>, Z = 4,  $\rho_{calcd} = 1.369$  g·cm<sup>-3</sup>,  $\mu = 4.297$  mm<sup>-1</sup>, F(000) = 1424, T = 173(2) K,  $R_1 = 0.0418$ ,  $wR_2 = 0.0859$ , 6675 independent reflections  $[2\theta \le 52.12^\circ]$  and 298 parameters.

Crystal data for **26b**:  $C_{40}H_{70}P_4Pt_2$ ,  $M_r = 1065.02$ , yellow block,  $0.57 \times 0.38 \times 0.145$ , monoclinic space group C2/c, a = 16.623(4) Å, b = 13.633(3) Å, c = 19.673(4) Å,  $\beta = 90.927(7)^\circ$ , V = 4457.6(17) Å<sup>3</sup>, Z = 4,  $\rho_{calcd} = 1.587$  g·cm<sup>-3</sup>,  $\mu = 6.438$  mm<sup>-1</sup>, F(000) = 2104, T = 174(2) K,  $R_1 = 0.0331$ ,  $wR_2 = 0.0833$ , 5520 independent reflections  $[2\theta \le 56.62^\circ]$  and 235 parameters.

Crystal data for **29**:  $C_{44}H_{62}B_4Fe_2N_4Si_2$ ,  $M_r = 858.10$ , yellow plate, 0.07 × 0.155 × 0.38, triclinic space group  $P\overline{1}$ , a = 12.970(2) Å, b = 14.376(2) Å, c = 14.832(2) Å,  $\alpha = 98.219(2)^\circ$ ,  $\beta = 112.305(2)^\circ$ ,  $\gamma = 12.305(2)^\circ$ ,  $\gamma = 12.3$  110.796(2)°, V = 2265.4(6) Å<sup>3</sup>, Z = 2,  $\rho_{calcd} = 1.258$  g·cm<sup>-3</sup>,  $\mu = 0.728$  mm<sup>-1</sup>, F(000) = 908, T = 167(2) K,  $R_1 = 0.0815$ ,  $wR_2 = 0.1511$ , 11 249 independent reflections  $[2\theta \le 56.72^{\circ}]$  and 519 parameters.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Center as supplementary publication nos. CCDC-815908 (14), 815909 (24), 815910 (27a), 815911 (26b), and 815912 (29). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif.

# ASSOCIATED CONTENT

**Supporting Information.** CIF files giving crystallographic data for compounds **14**, **24**, **27a**, **26b**, and **29**. This material is available free of charge via the Internet at http://pubs.acs.org.

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