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Formation of Homo- and Heteronuclear Platinum(II) and Palladium(II) Carbene Complexes in the Reactions of Coordinated Isocyanides with Aminothiazaheterocycles

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Abstract—The reaction of 5-(trifluoromethyl)-1,3,4-thiadiazol-2-amine with *cis*-dichlorobis(2,6-dimethylphenyl isocyanide)platinum(II) (*cis*-[$PtCl_2(CNXyl)_2$], Xyl = 2,6-$Me_2C_6H_3$) gave platinum(II) monocarbene complex whose deprotonation with an organic base generated a nucleophilic species capable of reacting with palladium(II) and platinum(II) bis(isocyanide) complexes to afford homo- and heteronuclear isocyanide/carbene structures.

Keywords: platinum(II) diaminocarbene complexes, palladium(II) diaminocarbene complexes, heteronuclear carbene complexes, isocyanide ligands, aminothiazaheterocycles

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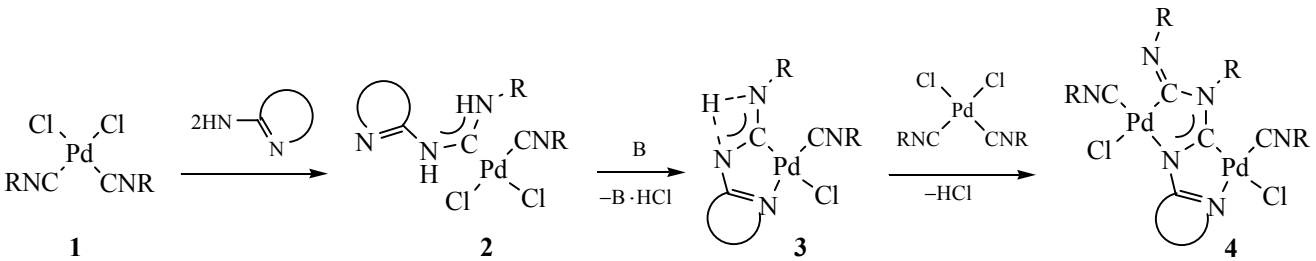
At present, reactions of nitrogen nucleophiles with isocyanide ligands in late transition metal complexes, especially gold, platinum, and palladium complexes, are extensively studied [1–3]. The reason is that the diaminocarbene complexes formed in reactions with mono-N-nucleophiles exhibit unique catalytic [4–13] and biological properties [14, 15]. Reactions of coordinated isocyanides with polyfunctional nucleophiles have been less studied, and their mechanism is more complicated. For example, bis-isocyanide platinum(II) complexes **1** react with such polynucleophiles as aminoazaheterocycles to give initially monocarbene complexes **2**, and the latter are capable of undergoing further transformations leading to deprotonated (**3**) or even dinuclear structures (**4**, Scheme 1) [16–24].

Of particular interest are reactions with aminothiazaheterocycles, which provide analogous chemical diversity [21–24]. In this case, the carbene fragment contains an additional sulfur atom, so that the resulting carbene complexes can be regarded as convenient models for studying certain weak interactions in transition metal complexes, primarily chalcogen bonds which were not studied previously in these systems but now attract keen interest 25–28]. Furthermore, weak interactions in aminocarbene complexes containing a thiazole fragment play an important role both in the solid state and in solution [22] and affect not only isomerization equilibria involving different carbene complexes but also their reactivity and regioselectivity of reactions [21].

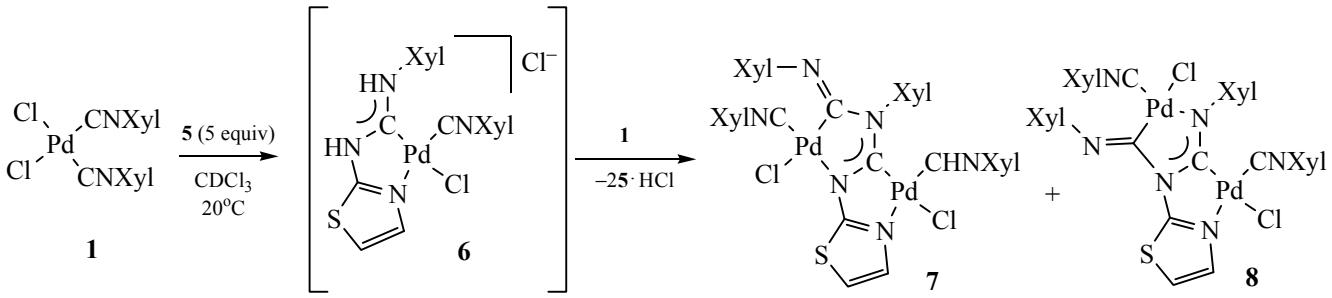
Taking into account that the formation of dinuclear carbene complexes **4** is a multistep process, it may be presumed that such complexes containing different isocyanide ligands could be synthesized by using in

Scheme 1.



1 **2** **3** **4**

Scheme 2.



the last stage a bis-isocyanide complex other than that used in the first stage. However, examples of synthesis of dinuclear carbene complexes from different isocyanide complexes have not been reported so far. Therefore, the goal of the present work was to explore the possibility of synthesizing such compounds.

Initially, we examined the reaction of *cis*-dichlorobis(2,6-dimethylphenyl isocyanide)palladium(II) (**1**) with 1,3-thiazol-2-amine (**5**). To achieve the above goal, it was necessary to find conditions hampering reaction of monocarbene intermediate with the second isocyanide complex molecule. Unfortunately, even when the reaction was carried out in chloroform at room temperature with 5 equiv of the nucleophile in the absence of a base, we obtained a mixture of isomeric dinuclear complexes **7** and **8** instead of expected monocarbene derivative **6** (Scheme 2) [21].

Obviously, in this reaction the nucleophile also acts as a base, and the resulting deprotonated form behaves as nucleophile and attacks the second molecule of complex **1**, yielding dinuclear structures **7** and **8**. Thus, excess nucleophile favors not only formation of monocarbene complex **6** but also its deprotonation.

We then tried to use less basic 5-(trifluoromethyl)-1,3,4-thiadiazol-2-amine (**9**) instead of thiazole **5**, but the reaction of **9** with complex **1** under analogous conditions also afforded only a mixture of dinuclear complexes **10** and **11** (Scheme 3). Presumably, the lower basicity of nucleophile **9** is compensated by the higher acidity of the corresponding monocarbene complex.

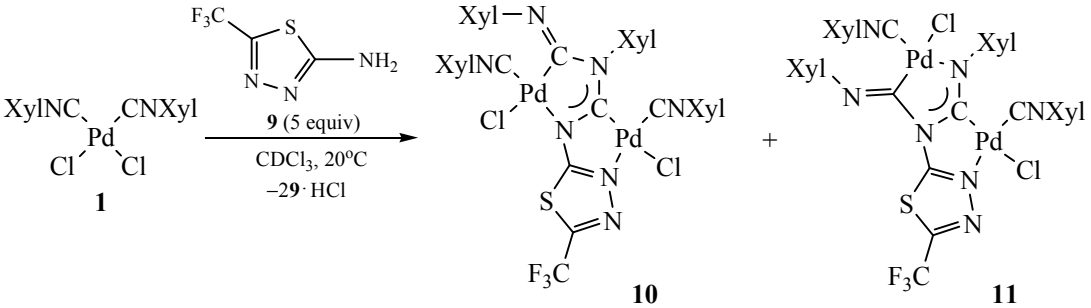
The product structure was determined by ^{1}H and ^{19}F NMR spectroscopy (including COSY and NOESY experiments), mass spectrometry in solution, and IR spectroscopy in the solid state.

The rate of the reaction under study was lowered by using analogous platinum(II) complexes instead of bis-isocyanide palladium(II) complexes. Platinum(II) complexes are more inert than their palladium analogs, and they can be used to isolate and identify assumed intermediates in reactions of coordinated isocyanides with polyfunctional nucleophiles [16].

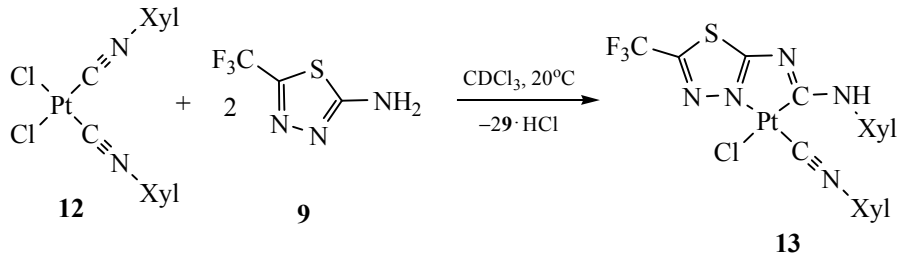
In fact, by reacting *cis*-dichlorobis(2,6-dimethylphenyl isocyanide)platinum(II) (**12**) even with 2 equiv of 5-(trifluoromethyl)-1,3,4-thiadiazol-2-amine (**9**) we obtained neutral monocarbene complex **13** (Scheme 4) whose structure was determined by ^{1}H, ^{19}F, and ^{195}Pt NMR spectroscopy, mass spectrometry in solution, and IR spectroscopy (in the solid state).

No further reaction occurred when 1 equiv of **12** or **9** was added to complex **13**. On the other hand, the addition of an equivalent amount of a base to a mixture of equimolar amounts of **13** and **12** led to the formation of a mixture of isomeric dinuclear complexes **14** and **15** (Scheme 5) whose ratio depended on the

Scheme 3.



Scheme 4.



temperature. At room temperature, the major product was complex **14** (**14**:**15** = 10:1) which was isolated in the pure state by recrystallization. When an equimolar mixture of **12**, **13**, and a base was heated under reflux, the ratio **14**:**15** was 1:1.1. These findings suggest that isomer **14** is a kinetically controlled product, and isomer **15**, thermodynamically controlled (as reported previously for their palladium analogs [21].

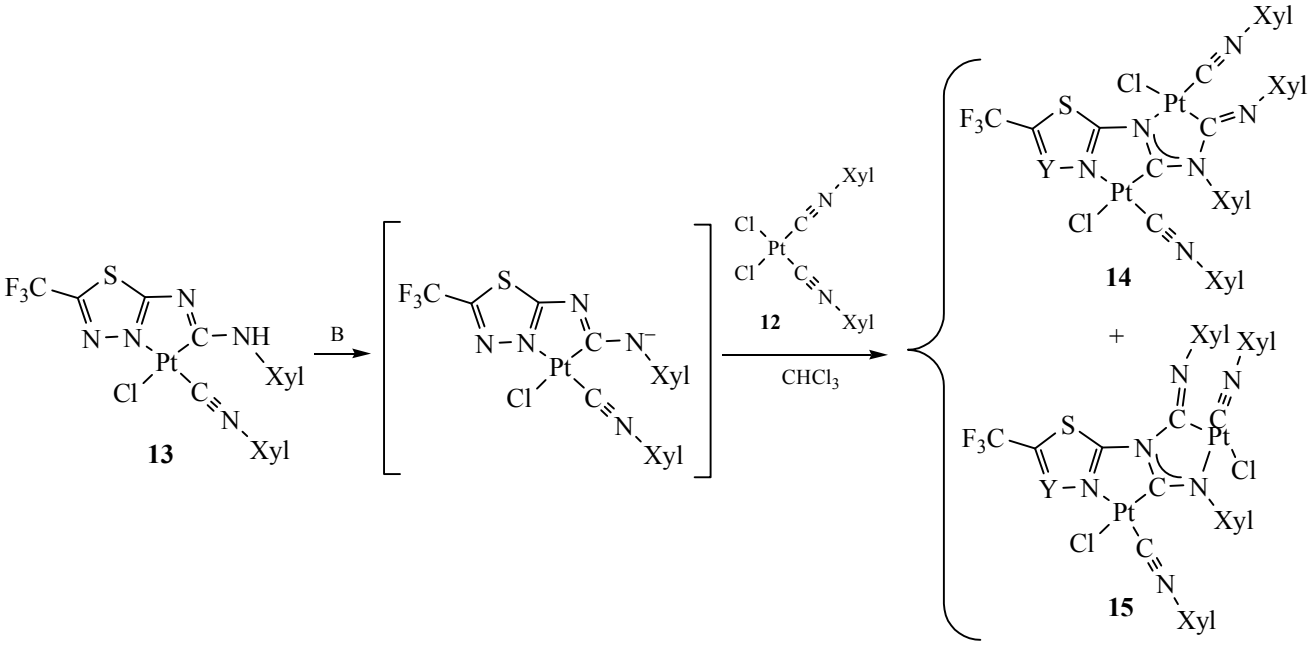
The structure of complexes **14** and **15** was confirmed by NMR, IR, and mass spectra. The ^{195}Pt NMR spectra of both complexes displayed two signals with equal intensities due to two nonequivalent platinum centers.

The isolation of monocarbene intermediate **13** opens the possibility of synthesizing new dinuclear complexes. For example, the reaction of **13** with bis-isocyanide palladium(II) complex **1** gave mixed dinuclear complexes **16** and **17** containing different metal centers, palladium and platinum (Scheme 6).

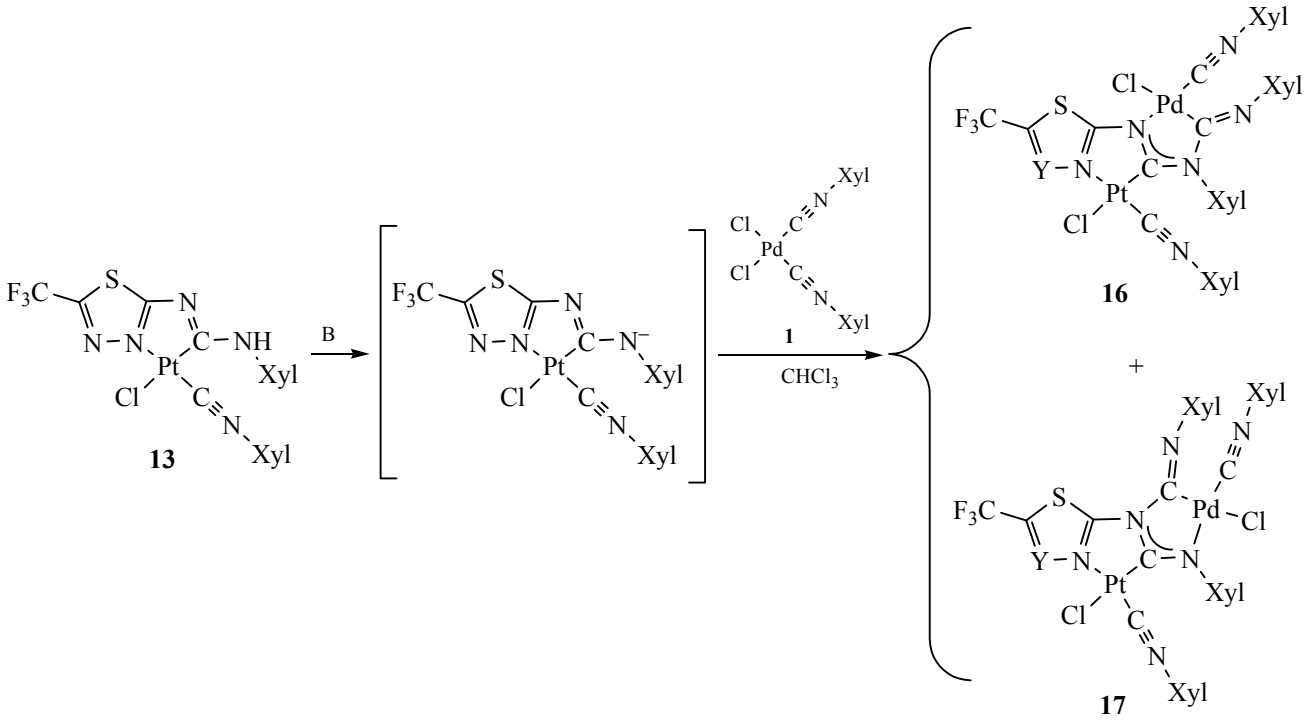
In this case, the product ratio also depended on the reaction conditions. The reaction at room temperature afforded kinetically controlled isomer **16** as the major product, the ratio **16**:**17** being 5:1. Under reflux conditions, the amounts of isomers **16** and **17** were approximately equal. In the ^{195}Pt NMR spectra of **16** and **17** we observed only one platinum signal, and their mass spectra showed isotope peaks typical of ions containing both palladium and platinum atoms ([*M* – Cl]$^+$, $C_{39}H_{36}N_7F_3SClPdPt^+$).

In summary, we have studied reactions of *cis*-bis-(2,6-dimethylphenyl isocyanide) palladium(II) and platinum(II) complexes {*cis*-[$MCl_2(CNXyl)_2$]; M = Pd, Pt; Xyl = 2,6-$Me_2C_6H_3$} with weakly nucleophilic 5-(trifluoromethyl)-1,3,4-thiadiazol-2-amine. In the reaction with the palladium-coordinated bis-isocyanide, this nucleophile behaves similarly to more nucleophilic thiazole-2-amines, giving rise to isomeric dinuclear complexes. Excess 5-(trifluoromethyl)-1,3,4-thiadiazol-

Scheme 5.



Scheme 6.



2-amine reacts with *cis*-dichlorobis(2,6-dimethylphenyl isocyanide)platinum(II) to give monocarbene complex which undergoes deprotonation in the presence of the organic base and acts as nucleophile toward bis-isocyanide palladium(II) and platinum(II) complexes; as a result homo- and heteronuclear isocyanide/carbene complexes are formed.

EXPERIMENTAL

Unless otherwise stated, organic and inorganic reagents and solvents were commercial products (Aldrich) used without additional purification.

The IR spectra were recorded on a Shimadzu IR Affinity spectrometer (4000–400 cm^{-1}) from samples prepared as KBr discs. The mass spectra were obtained on a Bruker micrOTOF spectrometer (electrospray ionization; solvent MeOH or MeOH–CH_2Cl_2; a.m.u. range 50–3000 Da); *m*/*z* values are given for most abundant isotopes. The ^1H, ^{19}F, and ^{195}Pt NMR spectra were measured on a Bruker Avance spectrometer (400 MHz for ^1H) at room temperature using $CDCl_3$ as solvent.

***cis*-[$PdCl_2(CNXyl)_2$] (1).** Solid 2,6-dimethylphenyl isocyanide, 0.5 g (3.8 mmol), was added to a suspension of 0.5 g (1.9 mmol) of $PdCl_2(NCMe)_2$ in 10 mL of 1,2-dichloroethane. The mixture was refluxed for 30 min with stirring, cooled to room temperature, and evaporated to a volume of 2 mL. The product was precipitated with hexane (10 mL), separated by centrifugation, washed with hexane (2×10 mL), and air-dried. Yield 0.89 g (88%). IR spectrum, ν, cm^{-1}: 2229, 2212 s (C≡N). ^1H NMR spectrum, δ, ppm (*J*, Hz): 2.52 s (12H, CH_3), 7.20 d (4H, *m*-H, *J* = 7.8), 7.35 t (2H, *p*-H, *J* = 7.8). The spectral parameters of **1** coincided with those reported in [21].

***cis*-[$PtCl_2(CNXyl)_2$] (12)** was synthesized in a similar way from 0.5 g (1.33 mmol) $PtCl_2(NCEt)_2$ and 0.38 g (2.66 mmol) of 2,6-dimethylphenyl isocyanide. Yield 625 mg (89%). IR spectrum, ν, cm^{-1}: 2229, 2201 s (C≡N). ^1H NMR spectrum, δ, ppm (*J*, Hz): 2.51 s (12H, CH_3), 7.19 d (4H, *m*-H, *J* = 7.6), 7.34 t (2H, *p*-H, *J* = 7.6). ^{195}Pt NMR spectrum: δ_{Pt} –3753 ppm, quint (*J* = 105.0 Hz). The spectral parameters of **12** coincided with those reported in [29].

Dinuclear complexes 10 and 11. A suspension of complex **1** (24 mg, 0.055 mmol) in 5 mL of CH_2Cl_2 was added to solid 5-(trifluoromethyl)-1,3,4-thiadiazol-2-amine (**9**) (14 mg, 0.083 mmol), and the mixture was stirred for 24 h at room temperature. The mixture was filtered from 5-(trifluoromethyl)-1,3,4-thiadiazol-2-amine hydrochloride, and the filtrate was evaporated

under reduced pressure at room temperature. Yield 25 mg (94%), isomer ratio **10**:**11** = 1:1.1. IR spectrum, ν, cm^{-1}: 2964, 2904 s (C–H), 2211, 2206 s (C≡N), 1638, 1620, 1559, 1490 s (N=C), 798, 773 br [δ(C–H)]. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.19 s (6H, CH_3, **10**), 2.23 s (6H, CH_3, **11**), 2.25 s (6H, CH_3, **10**), 2.27 s (6H, CH_3, **11**), 2.28 s (6H, CH_3, **10**), 2.30 s (6H, CH_3, **11**), 2.44 s (6H, CH_3, **10** + **11**), 6.18 t (1H, *p*-H, *J* = 7.5, **10**), 6.31 t (1H, *p*-H, *J* = 7.5, **11**), 6.39 t (1H, *p*-H, *J* = 7.5, **11**), 6.51 t (1H, *p*-H, *J* = 7.5, **10**), 6.68 d (2H, *m*-H, *J* = 7.5, **10**), 6.83 d (2H, *m*-H, *J* = 7.5, **11**), 6.88 d (2H, *m*-H, *J* = 7.5, **11**), 6.93 d (2H, *m*-H, *J* = 7.5, **10**), 6.99 d (2H, *m*-H, *J* = 7.5, **10** + **11**), 7.07 d (2H, *m*-H, *J* = 7.5, **10** + **11**), 7.16 t (1H, *p*-H, *J* = 7.5, **10** + **11**), 7.27–7.19 m (1H, *p*-H, *J* = 7.5, **10** + **11**). ^{19}F NMR spectrum, δ_F, ppm: –59.42 (**11**), –59.98 (**10**). Mass spectrum: *m*/*z* 940.0475 $[M - Cl]^+$ (calculated for $C_{39}H_{36}ClF_3N_7Pd_2S^+$: 940.0462).

Complex 13 was synthesized in a similar way from 25 mg (0.151 mmol) of 5-(trifluoromethyl)-1,3,4-thiadiazol-2-amine (**9**) and 40 mg (0.075 mmol) of $PtCl_2(CNXyl)_2$ (**12**). Yield 40 mg (80%). IR spectrum, ν, cm^{-1}: 2958 s (C–H), 2229 s (C≡N), 1638, 1635, 1500, 14510 s (N=C), 775 br [δ(C–H)]. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.25 s (6H, CH_3), 2.47 s (6H, CH_3), 6.52 t (1H, *p*-H, *J* = 7.6), 6.68 d (2H, *m*-H, *J* = 7.6), 6.83 d (2H, *m*-H, *J* = 7.6), 6.90 d (2H, *m*-H, *J* = 7.6), 6.93 d (2H, *m*-H, *J* = 7.6), 7.07 d (2H, *m*-H, *J* = 7.6), 7.24 t (1H, *p*-H, *J* = 7.6), 8.15 br.s (1H, NH). ^{19}F NMR spectrum: δ_F –59.71 ppm. ^{195}Pt NMR spectrum: δ_{Pt} –3862.59 ppm. Mass spectrum: *m*/*z* 661.0723 $[M + H]^+$ (calculated for $C_{21}H_{20}ClF_3N_5PtS^+$: 661.0718).

Dinuclear complexes 14 and 15. A solution of complex **13** (15 mg, 0.023 mmol) in 5 mL of $CHCl_3$ was added to a mixture of $PtCl_2(CNXyl)_2$ (**12**) (12 mg, 0.023 mmol) and tribenzylamine (7 mg, 0.024 mmol). The mixture was stirred for 24 h at room temperature (to obtain complex **14**) or under reflux (to obtain a mixture of **14** and **15**). It was then evaporated under reduced pressure to a volume of 2 mL, and 2 mL of diethyl ether was added. The products were isolated by crystallization upon slow evaporation of the solution at room temperature. Yield of pure complex **14** 11 mg (42%). Complex **15** was isolated in a mixture with isomer **14** (2:1); yield 19 mg (73%).

Complex **14**. IR spectrum, ν, cm^{-1}: 2954 s (C–H), 2228 s (C≡N), 1638, 1500, 1410 s (N=C), 775 br [δ(C–H)]. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.06 s (6H, CH_3), 2.24 s (6H, CH_3), 2.27 s (6H, CH_3), 2.42 s (6H, CH_3), 6.08 t (1H, *p*-H, *J* = 7.5), 6.44 t (1H, *p*-H, *J* = 7.6), 6.61 d (2H, *m*-H, *J* = 7.5), 6.90 d (2H, *m*-H, *J* = 7.6), 6.97 d (2H, *m*-H, *J* = 7.6), 7.05 d (2H, *m*-H, *J* = 7.6), 7.12 t (1H, *p*-H, *J* = 7.6), 7.18 t (1H, *p*-H, *J* = 7.6). ^{19}F NMR spectrum: δ_F –60.04 ppm. ^{195}Pt NMR spectrum, δ_{Pt}, ppm: −3844.05, −3790.60. Mass spectrum: *m*/*z* 1117.1680 $[M - Cl]^+$ (calculated for $C_{39}H_{36}N_7F_3SClPt_2^+$: 1117.1691).

Complex **15**. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.21 s (6H, CH_3), 2.26 s (6H, CH_3), 2.29 s (6H, CH_3), 2.41 s (6H, CH_3), 6.22 t (1H, *p*-H, *J* = 7.5), 6.34 t (1H, *p*-H, *J* = 7.6), 6.77 d (2H, *m*-H, *J* = 7.5), 6.87 d (2H, *m*-H, *J* = 7.6), 6.96 d (2H, *m*-H, *J* = 7.6), 7.05 d (2H, *m*-H, *J* = 7.6), 7.12 t (1H, *p*-H, *J* = 7.6), 7.19 t (1H, *p*-H, *J* = 7.6). ^{19}F NMR spectrum: δ_F −59.57 ppm. ^{195}Pt NMR spectrum, δ_{Pt}, ppm: −3801.55, −3747.25.

Heteronuclear complexes 16 and 17. A solution of complex **13** (15 mg, 0.023 mmol) in 5 mL of $CHCl_3$ was added to a mixture of $PdCl_2(CNXyl)_2$ (**1**) (12 mg, 0.023 mmol) and tribenzylamine (7 mg, 0.024 mmol). The mixture was stirred for 24 h at room temperature and evaporated under reduced pressure to a volume of 2 mL, and 2 mL of diethyl ether was added. The products were isolated by crystallization upon slow evaporation of the solution at room temperature. Complexes **16** and **17** were isolated as a 2:1 mixture; yield 18 mg (74%). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.07 s (6H, CH_3, **16**), 2.23 s (6H, CH_3, **17**), 2.26 s (6H, CH_3, **16**), 2.28 s (6H, CH_3, **17**), 2.29 s (6H, CH_3, **16**), 2.31 s (6H, CH_3, **17**), 2.44 s (6H, CH_3, **16**), 2.45 s (6H, CH_3, **17**), 6.18 t (1H, *p*-H, *J* = 7.5, **16**), 6.31 t (1H, *p*-H, *J* = 7.5, **17**), 6.36 t (1H, *p*-H, *J* = 7.5, **17**), 6.47 t (1H, *p*-H, *J* = 7.5, **16**), 6.68 d (2H, *m*-H, *J* = 7.5, **16**), 6.83 d (2H, *m*-H, *J* = 7.5, **17**), 6.86 d (2H, *m*-H, *J* = 7.5, **17**), 6.93 d (2H, *m*-H, *J* = 7.5, **16**), 6.99 d (2H, *m*-H, *J* = 7.5, **17**), 7.00 d (2H, *m*-H, *J* = 7.5, **16**), 7.06 d (2H, *m*-H, *J* = 7.5, **17**), 7.07 d (2H, *m*-H, *J* = 7.5, **16**), 7.15 t (1H, *p*-H, *J* = 7.5, **16** + **17**), 7.27–7.19 m (1H, *p*-H, *J* = 7.5, **16** + **17**). ^{19}F NMR spectrum, δ_F, ppm: –60.09 (**16**), –59.52 (**15**). ^{195}Pt NMR spectrum, δ_{Pt}, ppm: –3797.35 (**16**), –3755.40 (**17**). Mass spectrum: *m*/*z* 1027.1112 $[M - Cl]^+$ (calculated for $C_{39}H_{36}N_7F_3SClPdPt^+$: 1027.1076).

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CONFLICT OF INTERESTS

No conflict of interests was declared by the authors.

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