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# Acyclic Diaminocarbene Platinum(IV) Complexes Synthesized by the Oxidative Addition of MeI and $I_2$

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**Abstract**—The oxidative addition of methyl iodide or molecular iodine to the bis(C,N-chelate) deprotonated diaminocarbene platinum(II) complexes [Pt{C(N(H)Ar)(NC(N(H)Ph)N(Ph)}$_2$] (Ar = $C_6H_3$-2,6-$Me_2$ (Xyl), $C_6H_2$-2,4,6-$Me_3$ (Mes), and $C_6H_4$-4-Me (*p*Tol)) affords the corresponding platinum(IV) derivatives in a yield of 89–99%. The addition of $CF_3CO_2H$ is accompanied by the protonation of the nitrogen atoms of the diaminocarbene fragment to form the cationic complexes [PtI(X)-{C(N(H)Ar)(NC-(N(H)Ph)N(Ph)}$_2$]$CF_3CO_2H$ (X = Me, I). The structures of the compounds are determined by elemental analysis; high resolution mass spectrometry with electrospray ionization (ESI HRMS); IR spectroscopy; $^1$H, $^{13}$C{$^1$H}, $^{19}$F{$^1$H}, and $^{195}$Pt{$^1$H} NMR spectroscopy; 2D NMR spectroscopy ($^1$H,$^1$H COSY, $^1$H,$^1$H NOESY, $^1$H,$^{13}$C HSQC, $^1$H,$^{13}$C HMBC, $^1$H,$^{15}$N HSQC, $^1$H,$^{15}$N HMBC), and X-ray diffraction (XRD) and thermogravimetric analyses. The synthesized platinum(IV) complexes are thermally stable to 200–260°C and are electroneutral molecules with the octahedral coordination sphere formed by two deprotonated diaminocarbene C,N-chelate substituents and iodine and methyl or two iodine atoms localized in the apical positions.

**Keywords:** platinum complexes, acyclic diaminocarbene ligands, oxidative addition, protonation

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## INTRODUCTION

The oxidative addition of facile polar molecules, such as alkyl halides, aryl halides, halogens, and hydrogen halides, to the metallocenter are the main reactions in the design of the transition metal complexes [1, 2]. The oxidative addition of methyl iodide and molecular iodine to the complexes of the Platinum Group metals is a particular case and has a number of specific features associated with the reaction mechanism [2, 3]. The reaction is known to proceed mainly via the $S_N2$ mechanism involving the nucleophilic attack by the metallocenter to the electropositive carbon atom of alkyl halide or one of the molecular iodine atoms [1, 3]. In several cases, the *trans* product of oxidative addition can transform into the *cis* isomer immediately [4] or with time [5, 6] due to thermodynamic and/or steric factors favoring isomerization.

The oxidative addition of methyl iodide to the platinum(II) compounds most frequently occurs for the chelates with the general formula [Pt(N^X)LL'] (X = N, C; L, L' = Me, $PR_3$; R = Me, Cy, Ph) [2, 5, 7] in which the nucleophilic character of the metallocenter is tuned by the σ-donor character of the chelate [8–10] and auxiliary ligands [5]. For instance, phosphine ligands have strong σ-donor and π-acceptor properties [11] and during coordination are capable of enhancing a possibility of the oxidative addition of methyl iodide to the metallocenter [5, 7]. The influence of the substituents in the phosphine ligands (P^P [12], P^C [13, 14], and $PR_3$ [11]) was described in detail. Bulky substituents in the phosphine ligand decrease the accessibility of the metallocenter and, as a consequence, decrease the reactivity of the complexes [3].

N-Heterocyclic carbenes (NHC) and acyclic diaminocarbenes (ADC) are characterized by stronger σ-donor properties than phosphines and form nonsteric hindrances when coordinating to the metal. In addition, strong metal–carbon bonds make the diaminocarbene complexes stable in air [15]. There are known examples of the oxidative addition of methyl iodide [13, 16–18] and molecular iodine [16] to the C^N-chelate and C^N^C-pincer NHC platinum(II) complexes in which the diaminocarbene fragment is a part of the chelate ligand. At the same time, the addition of methyl iodide and molecular iodine to the acyclic diaminocarbene platinum(II) complexes has not been studied.

The oxidative addition of methyl iodide and molecular iodine to the bis(C,N-chelate) deprotonated ADC platinum(II) complexes affording platinum(IV) complexes **IIa**–**c** and **IIIa**–**c** was studied in this work.

## EXPERIMENTAL

Commercial reagents and solvents (Merck, VEKTON) were used as received, except for $CH_2Cl_2$ and $Et_2O$. Dichloromethane ($CH_2Cl_2$) was distilled over $P_2O_5$, and $Et_2O$ was distilled over metallic sodium in the presence of benzophenone. The complexes [Pt{C(N(H)Ar)(NC(N(H)Ph)N(Ph)}$_2$] (Ar = (a) Xyl, (b) Mes, and (c) *p*Tol; **Ia–c** and **Ia**·$CF_3CO_2H$) were synthesized using known procedures [19, 20].

Elemental analysis (C, H, N) was carried out on a Euro EA3028-HT elemental analyzer. Mass spectrometry was conducted on a Bruker micrOTOF (Bruker Daltonics) spectrometer with electrospray ionization (ESI HRMS) using methanol as the solvent. The values of *m/z* are presented for signals of isotopologues with the highest content. IR spectra were recorded on a Shimadzu IRAffinity-1 FT-IR spectrometer (4000–400 $cm^{-1}$, samples pelleted with KBr). $^1H$, $^{13}C\{^1H\}$, $^{19}F\{^1H\}$, and $^{195}Pt\{^1H\}$ NMR spectra were detected on a Bruker Avance II+ spectrometer (working frequency (MHz): 400.13 ($^1H$), 100.61 ($^{13}C$), 376.50 ($^{19}F$), 85.80 ($^{195}Pt$)) at room temperature using $CDCl_3$ as the solvent. $^1H$ NMR chemical shifts are presented relatively to the residual signal of $CHCl_3$ ($\delta_H$ 7.26 ppm) for solutions in $CDCl_3$. $^{13}C$ NMR chemical shifts are presented relatively to the central signal of the solvent ($\delta_C$ 77.26 ppm) for solutions in $CDCl_3$. Thermogravimetric analysis was conducted on a NETZSCH TG 209F1 Libra instrument in an aluminum crucible. Heating was conducted with a rate of 10°C/min from 30 to 500°C in air.

**Synthesis of IIa–c and IIa·$CF_3CO_2H$.** Methyl iodide (50 mg, 0.35 mmol) was added to a suspension of **Ia–c** or **Ia**·$CF_3CO_2H$ (0.020 mmol) in acetone (3 mL), and the mixture was stirred at room temperature for 1 h. The initial suspension was dissolved within this time. The reaction mixture was evaporated to dryness under reduced pressure, and the formed powder was washed with $Et_2O$ (2 × 1 mL) and dried in air at room temperature.

**Synthesis of IIa.** The yield was 20 mg (99%). $T_{decomp}$ = 233°C. MS, *m/z*: calculated for $C_{45}H_{46}N_8IPt^+$ 1020.2532, found 1020.2544 $[M+H]^+$. IR, ν, $cm^{-1}$: 3399, 3369 ν(N–H), 3061, 2911 ν(C–H), 1629, 1613, 1586, 1518 ν(C=C) and ν(C=N). $^1H$ NMR ($CDCl_3$; $\delta_H$, ppm): 1.66 (s, with satellites, $J_{H,Pt}$ = 69.4 Hz, 3H, Pt–Me), 2.17 (s, 3H, Me), 2.34 (s, 3H, Me), 2.35 (s, 3H, Me), 2.52 (s, 3H, Me), 5.71 (br.s, 1H, NH), 5.87 (br.s, 1H, NH), 6.63 (d, $J_{H,H}$ = 8.4 Hz, 2H, Ar's), 6.74–7.17 (m, 23H, Ar's, NH), 7.34 (d, $J_{H,H}$ = 7.6 Hz, 2H, Ar's), 12.48 (s, with satellites, $J_{H,Pt}$ = 35.2 Hz, 1H, NH). $^{13}C\{^1H\}$ NMR ($CDCl_3$; $\delta_C$, ppm): 2.97 (with satellites, $J_{C,Pt}$ = 554.6 Hz, Pt–Me), 18.19 (Me), 18.85 (Me), 19.11 (Me), 19.55 (Me), 119.10, 121.90, 123.77, 123.89, 125.14, 125.61, 126.32, 126.36, 126.60, 127.13, 127.32, 127.85, 127.93, 128.03, 128.16, 128.53, 128.61, 129.18, 129.50, 129.68, 129.87, 130.05, 130.67, 134.66, 135.80, 136.54, 138.33 (with satellites, $J_{C,Pt}$ = 42.9 Hz), 139.81, 140.61, 143.46 (with satellites, $J_{C,Pt}$ = 15.7 Hz), 144.25 (with satellites, $J_{C,Pt}$ = 1045.2 Hz, $C_{carbene}$), 144.26 (with satellites, $J_{C,Pt}$ = 59.6 Hz), 152.86 (with satellites, $J_{C,Pt}$ = 23.4 Hz), 167.05 (with satellites, $J_{C,Pt}$ = 78.7 Hz), 167.40 (with satellites, $J_{C,Pt}$ = 925.1 Hz, $C_{carbene}$). $^{195}Pt\{^1H\}$ NMR ($CDCl_3$; $\delta_{Pt}$, ppm): –2536.

For $C_{45}H_{45}N_8IPt$

| | | | |
|---|---|---|---|
| Anal. calcd., % | C, 52.99 | H, 4.35 | N, 10.99 |
| Found, % | C, 52.80 | H, 4.45 | N, 10.93 |

**Synthesis of IIb.** The yield was 20 mg (95%). $T_{decomp}$ = 199°C. MS, *m/z*: calculated for $C_{47}H_{50}N_8IPt^+$ 1048.2859, found 1048.2851 $[M + H]^+$. IR (ν, $cm^{-1}$): 3370 ν(N–H), 2916, 2855 ν(C–H), 1629, 1597, 1569, 1517 ν(C=C) and ν(C=N). $^1H$ NMR ($CDCl_3$; $\delta_H$, ppm): 1.65 (s, with satellites, $J_{H,Pt}$ = 68.6 Hz, 3H, Pt–Me), 2.12 (s, 3H, Me), 2.17 (s, 3H, Me), 2.29 (s, 3H, Me), 2.30 (s, 3H, Me), 2.32 (s, 3H, Me), 2.48 (s, 3H, Me), 5.69 (br.s, 1H, NH), 5.87 (br.s, 1H, NH), 6.63 (d, $J_{H,H}$ = 8.1 Hz, 2H, Ar's), 6.73–7.17 (m, 21H, Ar's, NH), 7.34 (d, $J_{H,H}$ = 8.1 Hz, 2H, Ar's), 12.46 (s, with satellites, $J_{H,Pt}$ = 36.3 Hz, 1H, NH). $^{13}C\{^1H\}$ NMR ($CDCl_3$; $\delta_C$, ppm): 2.88 (with satellites, $J_{C,Pt}$ = 556.4 Hz, Pt–Me), 18.03 (Me), 18.70 (Me), 18.96 (Me), 19.42 (Me), 20.61 (Me), 20.95 (Me), 119.11, 121.81, 123.93, 125.13, 125.52, 126.28, 126.34, 126.61, 126.94, 127.95, 128.13, 128.21, 128.45, 128.64, 129.10, 129.21, 129.45, 129.63, 129.81, 130.01, 130.35, 132.87, 134.21, 135.66, 135.69, 135.93, 136.12, 139.92, 140.70, 141.62 (with satellites, $J_{C,Pt}$ = 60.1 Hz), 143.57 (with satellites, $J_{C,Pt}$ = 16.2 Hz), 144.25 (with satellites, $J_{C,Pt}$ = 1045.8 Hz, $C_{carbene}$), 152.81 (with satellites, $J_{C,Pt}$ = 23.9 Hz), 167.01 (with satellites, $J_{C,Pt}$ = 79.1 Hz), 167.34 (with satellites, $J_{C,Pt}$ = 924.8 Hz, $C_{carbene}$). $^{195}Pt\{^1H\}$ NMR ($CDCl_3$; $\delta_{Pt}$, ppm): –2532.

For $C_{47}H_{49}N_8IPt$

| | | | |
|---|---|---|---|
| Anal. calcd., % | C, 50.52 | H, 4.34 | N, 9.68 |
| Found, % | C, 50.87 | H, 4.71 | N, 9.69 |

**Synthesis of IIc.** The yield was 19 mg (93%). $T_{decomp}$ = 223°C. MS, *m/z*: calculated for $C_{43}H_{42}N_8IPt^+$ 992.2242, found 992.2239 $[M+H]^+$. IR, ν, $cm^{-1}$: 3378 ν(N–H), 2909 ν(C–H), 1626, 1594, 1519, 1594 ν(C=C) and ν(C=N). $^1H$ NMR ($CDCl_3$; $\delta_H$, ppm): 1.52 (s, with satellites, $J_{H,Pt}$ = 69.0 Hz, 3H, Pt–Me), 2.29 (s, 6H, Me), 5.70 (br.s, 1H, NH), 5.90 (br.s, 1H, NH), 6.61 (d, $J_{H,H}$ = 6.7 Hz, 1H, Ar's), 6.66 (d, $J_{H,H}$ = 7.8 Hz, 1H, Ar's) 6.87–7.37 (m, 23H, Ar's), 7.48 (s,

with satellites, $J_{H,Pt}$ = 46.7 Hz, 1H, NH) 13.00 (s, with satellites, $J_{H,Pt}$ = 40.6 Hz, 1H, NH). $^{13}C\{^1H\}$ NMR ($CDCl_3$; $\delta_C$, ppm): 4.30 (with satellites, $J_{C,Pt}$ = 554.5 Hz, Pt–Me), 20.81, 20.93, 120.82, 121.70, 122.01, 123.44, 124.39, 125.22, 125.74, 126.19, 126.37, 126.65, 127.17, 127.84, 128.25, 128.84, 129.26, 129.54, 129.75, 129.88, 129.99, 130.09, 132.94, 133.48, 135.85, 137.73 (with satellites, $J_{C,Pt}$ = 52.0 Hz), 139.57, 140.64, 143.63 (with satellites, $J_{C,Pt}$ = 17.0 Hz), 144.11 (with satellites, $J_{C,Pt}$ = 62.8 Hz), 145.52 (with satellites, $J_{C,Pt}$ = 1048.8 Hz, $C_{carbene}$), 152.96 (with satellites, $J_{C,Pt}$ = 25.0 Hz), 164.45 (with satellites, $J_{C,Pt}$ = 931.3 Hz, $C_{carbene}$), 168.09 (with satellites, $J_{C,Pt}$ = 81.3 Hz). $^{195}Pt\{^1H\}$ NMR ($CDCl_3$; $\delta_{Pt}$, ppm): –2512.

For $C_{43}H_{41}N_8IPt$

| | | | |
|---|---|---|---|
| Anal. calcd., % | C, 51.63 | H, 4.01 | N, 11.04 |
| Found, % | C, 51.78 | H, 4.17 | N, 11.30 |

**Synthesis of IIa·$CF_3CO_2H$.** The yield was 22 mg (97%). $T_{decomp}$ = 184°C. MS, *m/z*: calculated for $C_{45}H_{46}N_8IPt^+$ 1020.2532, found 1020.2505 $[M-CF_3CO_2]^+$. IR (ν, $cm^{-1}$) 3352, 3330, 3203 ν(N–H), 3060, 2918 ν(C–H), 1787 ν(C=O), 1626, 1589, 1516, 1495, 1486 ν(C=C) and ν(C=N), 1200, 1142 ν(C–F). $^1H$ NMR ($CDCl_3$; $\delta_H$, ppm): 1.78 (s, with satellites, $J_{H,Pt}$ = 63.3 Hz, 3H, Pt–Me), 2.24 (s, 6H, Me), 2.41 (s, 6H, Me), 5.44 (br.s, 2H, NH), 6.48 (d, $J_{H,H}$ = 7.5 Hz, 2H, Ar's), 6.66–6.71 (m, 4H, Ar's), 6.75 (d, $J_{H,H}$ = 7.0 Hz, 4H, Ar's), 6.85 (t, $J_{H,H}$ = 7.5 Hz, 2H, Ar's), 6.93–7.06 (m, 12H, Ar's), 7.10 (d, $J_{H,H}$ = 8.5 Hz, 2H, Ar's), 7.84 (br.s, 2H, NH), 14.25 (s, with satellites, $J_{H,Pt}$ = 51.7 Hz, 1H, NH). $^{13}C\{^1H\}$ NMR ($CDCl_3$; $\delta_C$, ppm): 5.32 (with satellites, $J_{C,Pt}$ = 506.9 Hz, Pt–Me), 18.29, 19.03, 116.26 (q, $J_{C,F}$ = 293.7 Hz, $\underline{C}F_3$), 124.35, 125.42, 126.31, 126.80, 126.89, 128.45, 129.04, 129.06, 129.16, 129.37, 129.41, 131.42, 133.23, 135.76, 138.13, 140.52, 152.00 ($C_{carbene}$), 156.05, 162.17 (q, $J_{C,F}$ = 34.9 Hz, $CF_3\underline{C}O_2$). $^{19}F\{^1H\}$ NMR ($CDCl_3$; $\delta_F$, ppm): –75.13. $^{195}Pt\{^1H\}$ NMR ($CDCl_3$; $\delta_{Pt}$, ppm): –2585.

**Synthesis of IIIa–c and IIIa·$CF_3CO_2H$.** A solution of iodine (7 mg, 0.025 mmol) in acetone (1 mL) was added to a suspension of **Ia–c** or **Ia**·$CF_3CO_2H$ (0.020 mmol) in acetone (2 mL), and the mixture was stirred at room temperature for 1 h. Then the reaction mixture was evaporated to dryness under reduced pressure, and the formed oily precipitate was washed with hexane (2 × 5 mL) to the formation of a reddish powder that was dried in air at room temperature.

**Synthesis of IIIa.** The yield was 21 mg (93%). $T_{decomp}$ = 255°C. MS, *m/z*: calculated for $C_{44}H_{43}N_8I_2Pt^+$ 1132.1345, found 1132.1354 $[M+H]^+$. IR (ν, $cm^{-1}$): 3395, 3355 ν(N–H), 3059, 3033 ν(C–H), 1630, 1570, 1518, 1420 ν(C=C) and ν(C=N). $^1H$ NMR ($CDCl_3$; $\delta_H$, ppm): 2.33 (s, 6H, Me), 2.51 (s, 6H, Me), 5.71 (br.s, 1H, NH), 5.88 (br.s, 1H, NH), 6.74–7.18 (m, 27H, Ar's, NH), 12.43 (s, with satellites, $J_{H,Pt}$ = 28.1 Hz, 1H, NH). $^{13}C\{^1H\}$ NMR ($CDCl_3$; $\delta_C$, ppm): 19.11 (Me), 19.56 (Me), 96.14, 119.39, 122.15, 124.01, 124.14, 125.85, 126.49, 126.55, 127.02, 127.29, 127.71, 128.11, 128.28, 129.28, 129.66, 129.88, 130.42, 133.28, 135.65, 136.02, 138.50, 139.49, 140.07, 142.77 ($C_{carbene}$), 144.23, 152.84, 158.07 ($C_{carbene}$), 167.28. $^{195}Pt\{^1H\}$ NMR ($CDCl_3$; $\delta_{Pt}$, ppm): –3327.

For $C_{43}H_{41}IN_8Pt$

| | | | |
|---|---|---|---|
| Anal. calcd., % | C, 46.70 | H, 3.74 | N, 9.90 |
| Found, % | C, 47.02 | H, 3.79 | N, 9.76 |

**Synthesis of IIIb.** The yield was 21 mg (91%). $T_{decomp}$ = 260°C. MS, *m/z*: calculated for $C_{46}H_{47}N_8I_2Pt^+$ 1160.1658, found 1160.1679 $[M+H]^+$. IR (ν, $cm^{-1}$): 3399, 3364 ν(N–H), 3056, 2915, 2854 ν(C–H), 1613, 1584, 1560, 1513, 1490 ν(C=C) and ν(C=N). $^1H$ NMR ($CDCl_3$; $\delta_H$, ppm): 2.17 (s, 3H, Me), 2.28 (s, 6H, Me), 2.31 (s, 3H, Me), 2.46 (s, 6H, Me), 5.71 (br.s, 1H, NH), 5.88 (br.s, 1H, NH), 6.72–6.82 (m, 5H, Ar's), 6.91–7.18 (m, 20H, Ar's, NH), 12.41 (s, with satellites, $J_{H,Pt}$ = 27.8 Hz, 1H, NH). $^{13}C\{^1H\}$ NMR ($CDCl_3$; $\delta_C$, ppm): 19.00, 19.46, 20.60, 20.95, 119.34, 122.05, 124.10, 125.80, 125.85, 126.44, 127.01, 127.10, 128.12, 128.34, 128.87, 129.27, 129.64, 129.85, 130.08, 133.18, 133.24, 135.58, 135.75, 135.91, 139.59, 140.11, 141.61, 142.79 ($C_{carbene}$), 152.74, 158.08 ($C_{carbene}$), 167.19. $^{195}Pt\{^1H\}$ NMR ($CDCl_3$; $\delta_{Pt}$, ppm): –3323.

For $C_{46}H_{462}N_8IPt$

| | | | |
|---|---|---|---|
| Anal. calcd., % | C, 47.64 | H, 4.00 | N, 9.66 |
| Found, % | C, 47.43 | H, 3.86 | N, 9.81 |

**Synthesis of IIIc.** The yield was 20 mg (89%). $T_{decomp}$ = 245°C. MS, *m/z*: calculated for $C_{42}H_{39}N_8I_2Pt^+$ 1104.1030, found 1104.1009 $[M+H]^+$. IR (ν, $cm^{-1}$): 3394, 3374 ν(N–H), 3022, 2969, 2919, 2854 ν(C–H), 1634, 1592, 1569, 1413 ν(C=C) and ν(C=N). $^1H$ NMR ($CDCl_3$; $\delta_H$, ppm): 2.31 (s, 6H, Me), 5.74 (br.s, 1H, NH), 5.94 (br.s, 1H, NH), 6.93–7.34 (m, 28H, Ar's), 7.71 (br.s, 1H, NH) 12.99 (br.s, 1H, NH). $^{13}C\{^1H\}$ NMR ($CDCl_3$; $\delta_C$, ppm): 20.92 (Me), 120.92, 121.88, 122.30, 123.73, 124.56, 125.94, 126.59, 126.81, 127.36, 128.29, 128.38, 128.90, 129.72, 129.94, 133.42, 133.87, 135.03, 135.63, 137.56, 139.21, 140.00, 142.85, 143.69 ($C_{carbene}$), 152.91,

154.38 ($C_{carbene}$), 168.33. $^{195}Pt\{^1H\}$ NMR ($CDCl_3$; $\delta_{Pt}$, ppm): −3326.

| For $C_{42}H_{382}IN_8Pt$ | | | |
|---|---|---|---|
| Anal. calcd., % | C, 45.71 | H, 3.47 | N, 10.15 |
| Found, % | C, 45.89 | H, 3.69 | N, 9.98 |

**Synthesis of IIIa·$CF_3CO_2H$.** The yield was 22 mg (95%). MS, *m/z*: calculated for $C_{44}H_{43}N_8I_2Pt^+$ 1132.1345, found 1132.1335 $[M-CF_3CO_2]^+$. IR (ν, $cm^{-1}$) 3342, 3300, 3222 ν(N−H), 3059, 2920, 2854 ν(C−H), 1784 ν(C=O), 1628, 1588, 1566, 1496 ν(C=C) and ν(C=N), 1203, 1146 ν(C−F). $^1H$ NMR ($CDCl_3$; $\delta_H$, ppm): 2.38 (s, 12H, Me), 6.72 (t, $J_{H,H}$ = 7.8 Hz, 4H, Ar's), 6.76 (d, $J_{H,H}$ = 6.6 Hz, 4H, Ar's), 6.87 (t, $J_{H,H}$ = 7.5 Hz, 2H, Ar's), 6.93 (t, $J_{H,H}$ = 8.1 Hz, 4H, Ar's), 6.98–7.06 (m, 12H, Ar's), 7.65 (br.s, 2H, NH), 14.47 (s, with satellites, 1H, NH). The remained 2H of the NH group are distributed over 7.1–7.5 ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$; $\delta_C$, ppm): 18.94 (Me), 115.66 (q, $J_{C,F}$ = 289.7 Hz, $\underline{C}F_3$), 125.24, 126.01, 126.84, 127.26, 127.53, 129.06, 129.24, 129.28, 132.92, 134.95, 137.28 (with satellites, $J_{C,Pt}$ = 37.2 Hz), 139.37, 142.72 (with satellites, $J_{C,Pt}$ = 886.1 Hz, $C_{carbene}$), 154.95 (with satellites, $J_{C,Pt}$ = 33.4 Hz), 160.54 (q, $J_{C,F}$ = 36.7 Hz, $CF_3\underline{C}O_2$). $^{195}Pt\{^1H\}$ NMR ($CDCl_3$; $\delta_{Pt}$, ppm): −3455. $^{19}F\{^1H\}$ NMR ($CDCl_3$; $\delta_F$, ppm): −75.50.

**NMR experiment with different $CF_3CO_2H$ ratios.** A solution of complex **IIa** (0.020 mmol) in $CDCl_3$ (0.5 mL) was added with $CF_3CO_2H$ (0.020, 0.040, or 0.060 mmol) at room temperature in air. The reaction mixture was stirred for 10 min, and the NMR spectra were recorded.

Complex **IIa** + 2 equiv $CF_3CO_2H$. $^1H$ NMR ($CDCl_3$; $\delta_H$, ppm): 1.82 (s, with satellites, $J_{H,Pt}$ = 62.3 Hz, 3H, Pt–Me) 2.20 (s, 6H, Me), 2.39 (s, 6H, Me), 6.54 (d, $J_{H,H}$ = 8.1 Hz, 2H, Ar's), 6.73–6.79 (m, 8H, Ar's), 6.91 (t, $J_{H,H}$ = 7.4 Hz, 2H, Ar's), 7.03–7.07 (m, 12H, Ar's), 7.13 (d, $J_{H,H}$ = 8.2 Hz, 2H, Ar's), 8.06 (br.s, 2H, NH), 14.64 (br.s, 1H, NH). $^{13}C\{^1H\}$ NMR ($CDCl_3$; $\delta_C$, ppm): 6.17 (with satellites, $J_{C,Pt}$ = 490.1 Hz, Pt–Me), 18.04, 18.87, 125.03, 125.36, 126.59, 126.79, 127.23, 127.37, 128.73, 129.27, 129.35, 129.44, 129.53, 131.41, 133.09, 135.09, 136.99, 139.59, 139.71, 151.44 (with satellites, $J_{C,Pt}$ = 1013.4 Hz, $C_{carbene}$), 154.69 (with satellites, $J_{C,Pt}$ = 37.4 Hz). $^{195}Pt\{^1H\}$ NMR ($CDCl_3$; $\delta_{Pt}$, ppm): −2609.

Complex **IIa** + 3 equiv $CF_3CO_2H$. $^1H$ NMR ($CDCl_3$; $\delta_H$, ppm): 1.84 (s, with satellites, $J_{H,Pt}$ = 62.1 Hz, 3H, Pt–Me) 2.17 (s, 6H, Me), 2.36 (s, 6H, Me), 6.67 (d, $J_{H,H}$ = 7.0 Hz, 2H, Ar's), 6.79 (br.s, 2H, NH), 6.86 (d, $J_{H,H}$ = 6.7 Hz, 4H, Ar's), 6.90–6.93 (m, 4H, Ar's), 7.02–7.04 (m, 8H, Ar's), 7.11–7.17 (m, 6H, Ar's), 7.23 (d, $J_{H,H}$ = 6.2 Hz, 2H, Ar's), 7.76 (br.s, 2H, NH), 9.35 (br.s, 1H, NH). $^{13}C\{^1H\}$ NMR ($CDCl_3$; $\delta_C$, ppm): 6.72 (with satellites, $J_{C,Pt}$ = 484.0 Hz, Pt–Me), 17.92 (Me), 18.80 (Me), 115.24 (q, $J_{C,F}$ = 287.5 Hz, $\underline{C}F_3$), 124.95, 125.40, 126.28, 127.55, 127.59, 128.13, 128.89, 129.35, 129.94, 130.07, 130.13, 131.41, 132.91, 134.79, 136.48 (with satellites, $J_{C,Pt}$ = 47.2 Hz), 138.96, 151.87 (with satellites, $J_{C,Pt}$ = 1014.2 Hz, $C_{carbene}$), 154.31 (with satellites, $J_{C,Pt}$ = 35.8 Hz), 159.56 (q, $J_{C,F}$ = 38.9 Hz, $CF_3\underline{C}O_2$). $^{19}F\{^1H\}$ NMR ($CDCl_3$; $\delta_F$, ppm): −75.79 (s). $^{195}Pt\{^1H\}$ NMR ($CDCl_3$; $\delta_{Pt}$, ppm): −2632.

**XRD of complexes IIa, IIb, IIc, IIIa, IIIb, and IIIc** was carried out on an Xcalibur Eos diffractometer using monochromatic Mo$K_\alpha$ (λ = 0.71073 Å) and Cu$K_\alpha$ (λ = 1.54184 Å) radiations at 100 K. The structures were solved by direct methods and refined using the SHELX program [21] implemented into the OLEX2 complex [22]. An absorption correction was applied empirically in the CrysAlisPro software using spherical harmonics accomplished in the SCALE3 ABSPACK scaling algorithm [23]. The key parameters of bond and angles are listed in Table 1.

The full crystallographic information for the complexes was deposited with the Cambridge Crystallographic Data Centre (CIF files (CCDC nos. 2305931 (**IIa**), 2305932 (**IIb**), 2305933 (**IIc**), 2505934 (**IIIa**), 2505935 (**IIIb**), and 2505936 (**IIIc**); http://www.ccdc.cam.ac.uk/data_request/cif).

### *Crystallographic Data*

**Complex IIa.** $C_{48}H_{51}N_8IOpt$, *FW* = 1077.95, monoclinic crystal system, space group *Pbca*, *a* = 14.59280(10), *b* = 23.44540(10), *c* = 25.93150(10) Å, α = 90°, β = 90°, γ = 90°, *V* = 8872.05(8) Å$^3$, *Z* = 8, $\rho_{calc}$ = 1.614 g/cm$^3$, μ = 11.735 mm$^{-1}$, crystal size 0.38 × 0.25 × 0.23 mm$^3$, 2θ range for data collection 6.818–134.994, index range $-17 \le h \le 17$, $-28 \le k \le 28$, $-31 \le l \le 31$, total number of reflections 213377, independent reflections 7990 ($R_{int}$ = 0.0655, $R_{sigma}$ = 0.0152), data/restraints/parameters 7990/0/555, final *R* ($I \ge 2\sigma(I)$) $R_1$ = 0.0262, $wR_2$ = 0.0646, final *R* (all data) $R_1$ = 0.0274, $wR_2$ = 0.0654, $\rho_{min}/\rho_{max}$ = 1.68/−1.04 e/Å$^3$.

**Complex IIb.** $C_{47}H_{49}N_8IPt$, *FW* = 1047.93, orthorhombic crystal system, space group *Pbca*, *a* = 23.7702(2), *b* = 15.91890(10), *c* = 24.7746(2) Å, α = 90°, β = 90°, γ = 90°, *V* = 9374.60(12) Å$^3$, *Z* = 8, $\rho_{calc}$ = 1.485 g/cm$^3$, μ = 11.072 mm$^{-1}$, crystal size 0.09 × 0.05 × 0.03 mm$^3$, 2θ range for data collection 7.136–139.994, index range $-24 \le h \le 28$, $-18 \le k \le 19$, $-30 \le l \le 29$, total number of reflections 40871, independent reflections 8877 ($R_{int}$ = 0.0338, $R_{sigma}$ = 0.0276), data/restraints/parameters 8877/0/521, final *R* ($I \ge 2\sigma$ (*I*)) $R_1$ = 0.0450, $wR_2$ = 0.0970, final *R*

**Table 1.** Selected bond lengths (Å) and angles (deg) in compounds **IIa**–**c** and **IIIa**–**c**

| Bonds | IIa | IIb | IIc | IIIa | IIIb | IIIc |
|---|---|---|---|---|---|---|
| | *d*, Å | | | | | |
| Pt–C(1) | 2.002(3) | 1.996(6) | 2.011(3) | 2.003(3) | 2.009(4) | 2.030(3) |
| Pt–C(2) | 1.998(3) | 2.010(6) | 2.008(3) | 2.013(3) | 2.013(4) | 2.025(3) |
| Pt–C(Me) | 2.170(4) | 2.124(6) | 2.119(3) | | | |
| Pt–N(7) | 2.105(3) | 2.129(5) | 2.109(2) | 2.110(2) | 2.122(3) | 2.111(3) |
| Pt–N(8) | 2.148(3) | 2.131(5) | 2.153(2) | 2.157(2) | 2.139(3) | 2.132(3) |
| Pt(1)–I(1) | 2.7661(2) | 2.7546(5) | 2.7471(2) | 2.6472(2) | 2.6529(3) | 2.6503(3) |
| Pt(1)–I(2) | | | | 2.6534(2) | 2.6408(3) | 2.6598(3) |
| Angle | ω, deg | | | | | |
| N(1)C(1)N(3) | 121.0(3) | 120.1(6) | 121.4(2) | 120.5(3) | 121.0(3) | 123.3(3) |
| N(2)C(2)N(4) | 120.4(3) | 122.4(5) | 122.2(3) | 121.2(3) | 122.6(3) | 123.9(3) |

(all data) $R_1 = 0.0490$, $wR_2 = 0.0991$, $\rho_{min}/\rho_{max} = 1.29/-1.35$ e/Å$^3$.

**Complex IIc.** $C_{44}H_{43}N_8Cl_2IPt$, $FW = 1076.75$, triclinic crystal system, space group $P\bar{1}$, $a = 12.26490(10)$, $b = 16.4658(2)$ , $c = 23.69390(10)$ Å, $\alpha = 70.2910(10)°$, $\beta = 88.8960(10)°$, $\gamma = 68.8880(10)°$, $V = 4173.78(7)$ Å$^3$, $Z = 4$, $\rho_{calc} = 1.714$ g/cm$^3$, $\mu = 13.604$ mm$^{-1}$, crystal size $0.18 \times 0.16 \times 0.12$ mm$^3$, 2θ range for data collection 3.988–134.996, index range $-14 \le h \le 14$, $-19 \le k \le 19$, $-28 \le l \le 25$, total number of reflections 66842, independent reflections 15038 ($R_{int} = 0.0389$, $R_{sigma} = 0.0330$), data/restraints/parameters 15038/0/1015, final $R$ ($I \ge 2\sigma(I)$) $R_1 = 0.0229$, $wR_2 = 0.0546$, final $R$ (all data) $R_1 = 0.0252$, $wR_2 = 0.0555$, $\rho_{min}/\rho_{max} = 1.55/-1.11$ e/Å$^3$.

**Complex IIIa.** $C_{45}H_{44}N_8Cl_2I_2Pt$, $FW = 1216.67$, triclinic crystal system, space group $P\bar{1}$, $a = 12.6683(2)$, $b = 18.6496(2)$, $c = 20.9254(2)$ Å, $\alpha = 108.0040(10)°$, $\beta = 98.3940(10)°$, $\gamma = 102.3480(10)°$, $V = 4471.70(10)$ Å$^3$, $Z = 4$, $\rho_{calc} = 1.807$ g/cm$^3$, $\mu = 18.135$ mm$^{-1}$, crystal size $0.4 \times 0.2 \times 0.15$ mm$^3$, 2θ range for data collection 5.182–139.998, index range $-15 \le h \le 15$, $-22 \le k \le 22$, $-25 \le l \le 22$, total number of reflections 65446, independent reflections 16940 ($R_{int} = 0.0437$, $R_{sigma} = 0.0330$), data/restraints/parameters 16940/0/1053, final $R$ ($I \ge 2\sigma(I)$) $R_1 = 0.0261$, $wR_2 = 0.0526$, final $R$ (all data) $R_1 = 0.0315$, $wR_2 = 0.0545$, $\rho_{min}/\rho_{max} = 1.26/-1.07$ e/Å$^3$.

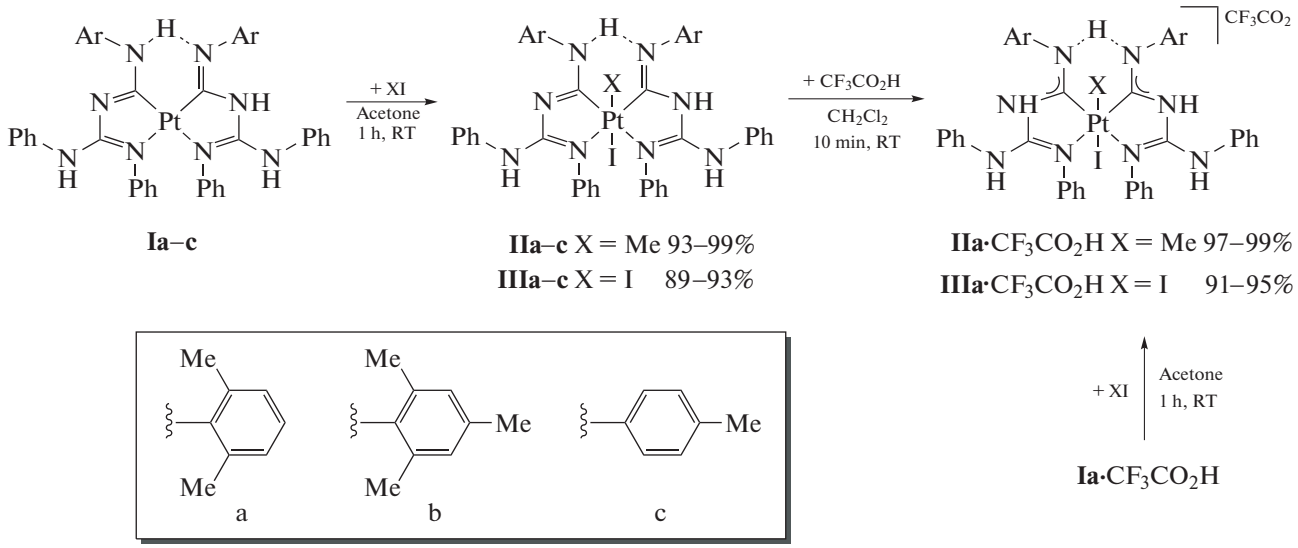
**Complex IIIb.** $C_{46}H_{46}N_8I_2Pt$, $FW = 1159.80$, orthorhombic crystal system, space group *Pbca*, $a = 23.8005(2)$, $b = 16.2553(2)$, $c = 24.5609(2)$ Å, $\alpha = 90°$, $\beta = 90°$, $\gamma = 90°$, $V = 9502.22(16)$ Å$^3$, $Z = 8$, $\rho_{calc} = 1.621$ g/cm$^3$, $\mu = 16.026$ mm$^{-1}$, crystal size $0.41 \times 0.15 \times 0.09$ mm$^3$, 2θ range for data collection 7.198–138.128, index range $-28 \le h \le 28$, $-19 \le k \le 19$, $-29 \le l \le 29$, total number of reflections 43391, independent reflections 8815 ($R_{int} = 0.0440$, $R_{sigma} = 0.0327$), data/restraints/parameters 8815/0/520, final $R$ ($I \ge 2\sigma(I)$) $R_1 = 0.0265$, $wR_2 = 0.0652$, final $R$ (all data) $R_1 = 0.0315$, $wR_2 = 0.0673$, $\rho_{min}/\rho_{max} = 1.88/-1.09$ e/Å$^3$.

**Complex IIIc.** $C_{42}H_{38}N_8I_2Pt$, $FW = 1103.69$, monoclinic crystal system, space group $P2_1/n$, $a = 9.33830(10)$, $b = 18.8275(2)$, $c = 22.5476(2)$ Å, $\alpha = 90°$, $\beta = 95.9800(10)°$, $\gamma = 90°$, $V = 3942.68(7)$ Å$^3$, $Z = 4$, $\rho_{calc} = 1.859$ g/cm$^3$, $\mu = 19.275$ mm$^{-1}$, crystal size $0.13 \times 0.09 \times 0.05$ mm$^3$, 2θ range for data collection 6.13–154.956, index range $-11 \le h \le 11$, $-23 \le k \le 20$, $-27 \le l \le 28$, total number of reflections 32109, independent reflections 8158 ($R_{int} = 0.0404$, $R_{sigma} = 0.0316$), data/restraints/parameters 8158/0/480, final $R$ ($I \ge 2\sigma(I)$) $R_1 = 0.0305$, $wR_2 = 0.0840$, final $R$ (all data) $R_1 = 0.0342$, $wR_2 = 0.0867$, $\rho_{min}/\rho_{max} = 1.07/-1.69$ e/Å$^3$.

## RESULTS AND DISCUSSION

The deprotonated bis(C,N-chelate) diaminocarbene platinum(II) complexes **Ia**–**c** synthesized by the reaction of the isocyanide complexes $[PtCl_2(CNAr)_2]$ (Ar = (**a**) Xyl, (**b**) Mes, and (**c**) *p*Tol) with *N*,*N*-diphenylguanidine [19, 20] engage the oxidative addition of methyl iodide and molecular iodine at room temperature (Scheme 1). The reaction affords platinum(IV) complexes **IIa**–**c** and **IIIa**–**c** in yields of 93–99 and 89–93%, respectively.

The addition of $CF_3CO_2H$ to complex **IIa** or **IIIa** results in the formation of cationic complexes **IIa**·$CF_3CO_2H$ and **IIIa**·$CF_3CO_2H$. Compounds **IIa**·$CF_3CO_2H$ and **IIIa**·$CF_3CO_2H$ can also be prepared by the addition of methyl iodide and molecular iodine to cationic platinum(II) complex **Ia**·$CF_3CO_2H$ (Scheme 1).




**Scheme 1.**

The compounds were isolated as fine crystalline white (**IIa**–**c**, **IIa**·$CF_3CO_2H$) or reddish (**IIIa**–**c**, **IIIa**·$CF_3CO_2H$) powders. The structures of compounds **IIa**–**c**, **IIIa**–**c**, **IIa**·$CF_3CO_2H$, and **IIIa**·$CF_3CO_2H$ were solved using high resolution mass spectrometry with electrospray ionization (ESI HRMS); IR spectroscopy; $^1H$, $^{13}C\{^1H\}$, and $^{19}F\{^1H\}$ NMR spectroscopy (**IIa**·$CF_3CO_2H$, **IIIa**·$CF_3CO_2H$); and $^{195}Pt\{^1H\}$ NMR and elemental analysis (**IIa**–**c**, **IIIa**–**c**) and were proved by single crystal XRD (**IIa**–**c**, **IIIa**–**c**). Compounds **IIa**–**c**, **IIIa**–**c**, and **IIa**·$CF_3CO_2H$ are stable in air ($T_{decomp}$ > 184°C) and soluble in the widely used aprotic solvents ($CH_2Cl_2$, $CHCl_3$, $C_2H_4Cl_2$, and MeCN).

According to the elemental analysis data for **IIa**–**c** and **IIIa**–**c**, the C, H, and N contents are well consistent with the proposed empirical formulas. The mass spectra demonstrate the peaks corresponding to the $[M+H]^+$ (**IIa**–**c**, **IIIa**–**c**) and $[M-CF_3CO_2]^+$ (**IIa**·$CF_3CO_2H$, **IIIa**·$CF_3CO_2H$) ions with the isotopic distribution characteristic for platinum compounds. The intense absorption in a range of 1560–1620 $cm^{-1}$ in the IR spectra of compounds **IIa**–**c** and **IIIa**–**c** indicates the preservation of the diaminocarbene fragments [19, 24]. The presence of $CF_3CO_2H$ in **IIa**·$CF_3CO_2H$ and **IIIa**·$CF_3CO_2H$ confirms the characteristic absorption bands corresponding to stretching vibrations of the C=O (1784–1787 $cm^{-1}$) and C–F (1142–1203 $cm^{-1}$) bonds [25–27].

The $^1H$ and $^{13}C\{^1H\}$ NMR spectra of compounds **IIa**–**c** in the low-frequency range exhibit signals of the methyl substituent coordinated to platinum at $\delta_H$ 1.52–1.69 ppm ($J_{H,Pt}$ = 68.6–69.4 Hz) and $\delta_C$ = 2.88–4.30 ppm ($J_{Pt,C}$ = 554.5–556.4 Hz), which correlates with the published data for the methylated platinum complexes ($\delta_H$ 0.9–2.0 ppm, $J_{Pt,H}$ = 25–75 Hz [6–9, 28–35], $\delta_C$ (–12)–12 ppm, $J_{Pt,C}$ = 500–780 [7, 34, 35]). In comparison with the $^1H$ and $^{13}C\{^1H\}$ NMR spectra of compounds **Ia**–**c** [19, 20], the spectra of complexes **IIa**–**c** exhibit a doubled set of signals due to a decrease in the symmetry of the molecule. The addition of molecular iodine does not qualitatively change the shape of the $^1H$ and $^{13}C\{^1H\}$ NMR spectra of compounds **IIIa**–**c**. The signals of the NH groups in the ranges $\delta_H$ 5.69–5.71, 5.87–5.94, and 12.43–13.00 ppm ($J_{H,Pt}$ = 23.9–40.6 Hz) indicate that the diaminocarbene structure in compounds **IIa**–**c** and **IIIa**–**c** remains unchanged [19].

The addition of one equivalent of $CF_3CO_2H$ to a solution of complex **IIa** in $CDCl_3$ decreases the number of signals in the $^1H$ and $^{13}C\{^1H\}$ NMR spectra due to symmetrization of the structure upon the protonation of the endocyclic nitrogen atom (compound **IIa**·$CF_3CO_2H$). The further addition of the acid does not result in a qualitative change in the spectra, and chemical shifts of the signals change insignificantly.

Signal assignment for compounds **IIa**·$CF_3CO_2H$ in the $^1H$ and $^{13}C\{^1H\}$ NMR spectra was performed using 2D correlation NMR spectroscopy ($^1H$,$^1H$ COSY, $^1H$,$^1H$ NOESY, $^1H$,$^{13}C$ HSQC, $^1H$,$^{13}C$ HMBC, $^1H$,$^{15}N$ HSQC, and $^1H$,$^{15}N$ HMBC). The diaminocarbene carbon atoms are known to resonate at $\delta_C$ 160–224 ppm [36]. The $^{13}C\{^1H\}$ NMR spectrum of compound **IIa**·$CF_3CO_2H$ contains the signal $\delta_C$ 151.87 ppm, and a high value of $J_{C,Pt}$ (1014 Hz) of the satellite doublet indicates the direct coordination of this carbon atom to platinum [37, 38]. In addition, in the $^1H$,$^{13}C$ HMBC NMR spectrum of compound

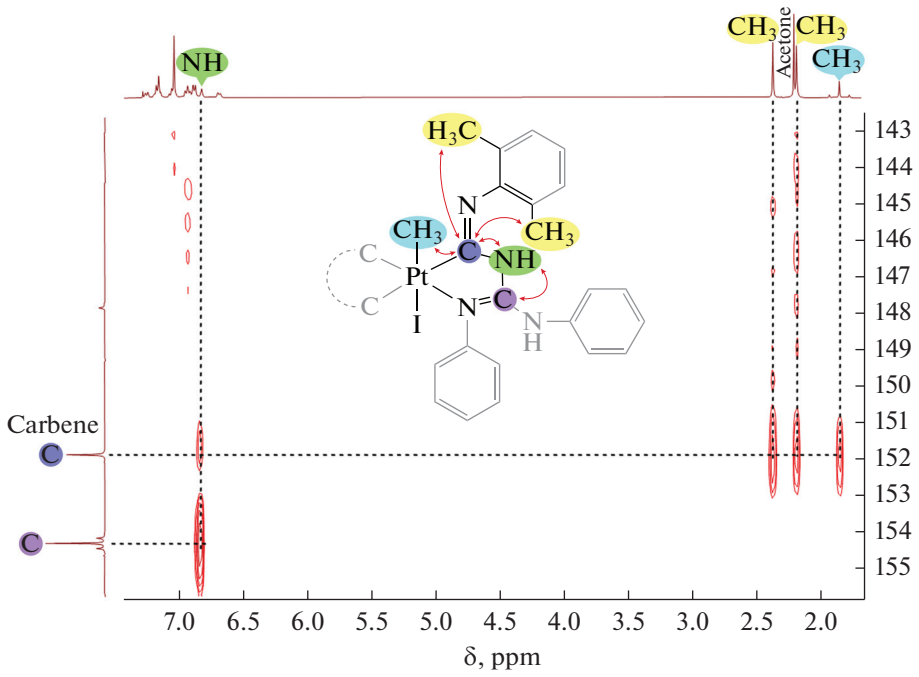



**Fig. 1.** Fragment of the $^{1}H,^{13}C$ HMBC NMR spectrum of compound **IIa**·$CF_3CO_2H$.

**IIa**·$CF_3CO_2H$, the signal $\delta_C$ 151.87 ppm has a cross peak with the protons of the methyl substituent coordinated to platinum(IV) ($\delta_H$ 1.84 ppm) (Fig. 1). This suggests that the signal $\delta_C$ 151.87 ppm in compound **IIa**·$CF_3CO_2H$ belongs to the diaminocarbene carbon atom. The $^{13}C\{^{1}H\}$ NMR spectrum of complex **IIa** exhibits two signals with high $J_{C,Pt}$ at $\delta_C$ 144.25 and 167.40 ppm ($J_{C,Pt}$ = 1045.2 and 925.1 Hz, respectively) attributed to the carbene carbon atoms. As compared to compounds **Ia**–**c** [19, 20], the signals of the carbene carbon atoms in complexes **IIa**–**c** and **IIIa**–**c** shift to low frequencies by 20–30 ppm. Similar low-frequency shifts $\delta_C$ of the carbene carbon atoms were earlier observed in the spectra of the bis(C,N-chelate) NHC platinum complexes when oxidizing from +2 to +4 [39].

The $^{195}Pt\{^{1}H\}$ chemical shifts depend on the shielding and different donor abilities of the ligand environment in the platinum complexes [32]. According to published data, the oxidative addition of methyl iodide or molecular iodine to the platinum(II) complexes is accompanied by the high-frequency shift of $\delta_{Pt}$ by $\Delta\delta_{Pt}$ = 350–883 ppm in the case of methyl iodide [7, 9, 12, 32, 40–44] or $\Delta\delta_{Pt}$ = 217–283 ppm in the case of molecular iodine [45–47]. In our case, a stronger shift in the $^{195}Pt\{^{1}H\}$ NMR spectra of compounds **IIa**–**c** is observed ($\delta_{Pt}$ from –2585 to –2512 ppm), which has $\Delta\delta_{Pt}$ in a range of 1117–1146 ppm compared to the signals of complexes **Ia**–**c** ($\delta_{Pt}$ from –3682 to –3629 ppm). For complexes **IIIa**–**c**, $\delta_{Pt}$ ranges from –3327 to –3326 ppm. On going from **Ia** to **Ic**, $\Delta\delta_{Pt}$ = 303–355 ppm, which lies in the range described for other types of the complexes. The protonation of complex **IIa** exerts almost no effect on $\delta_{Pt}$ ($\delta_{Pt}$ –2536 ppm in **IIa** and $\delta_{Pt}$ –2585 ppm in **IIa**·$CF_3CO_2H$).

A possibility of the thermal elimination of methyl iodide and iodine in complexes **IIa**–**c**, **IIa**·$CF_3CO_2H$, and **IIIa**–**c** was studied by gravimetric analysis [48]. The heating of compound **IIa**·$CF_3CO_2H$ leads to ~10% mass loss in a range of 184–203°C, which corresponds to the elimination of the $CF_3CO_2H$ molecule. The further heating of compounds **IIa**·$F_3CO_2H$, **IIa**–**c**, and **IIIa**–**c** is accompanied by 50–60% mass loss in the range above the temperature of decomposition onset (**IIa**–**c**: 200–233°C, **IIIa**–**c**: 245–260°C). The observed mass loss exceeds the calculated mass loss upon the elimination of methyl iodide or molecular iodine (13–14% for MeI or 22–23% for $I_2$), which suggests that organometallic framework destruction occurs on heating.

Single crystal XRD was used to prove the structures of compounds **IIa**–**c** and **IIIa**–**c** in the solid phase. The key parameters of bonds and angles are listed in Table 1. The molecular structures for each series are given in Fig. 2.

According to the XRD results, compounds **IIa**–**c** and **IIIa**–**c** are electroneutral molecules. The octahedral coordination sphere is formed by two deproton-

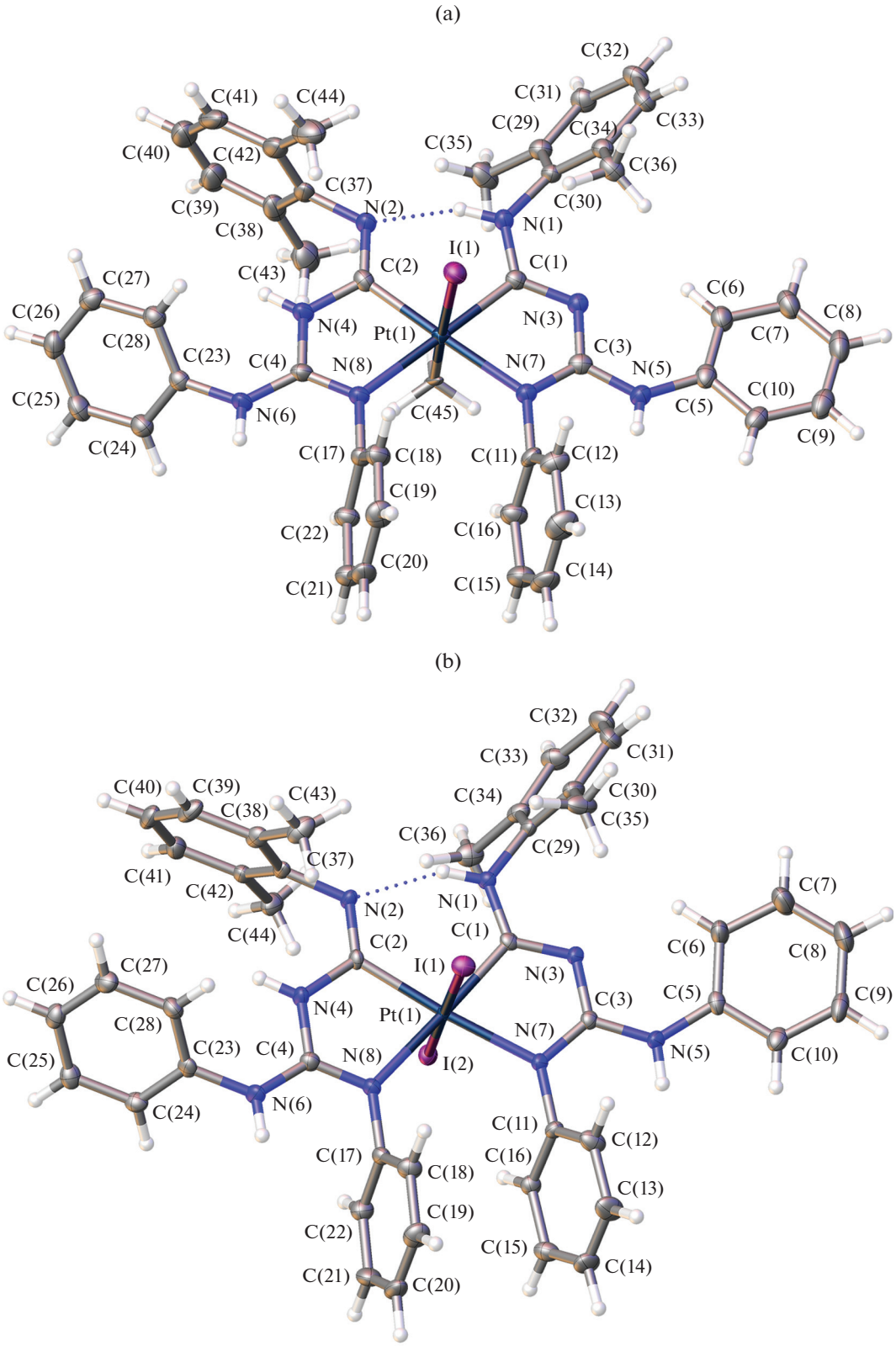



**Fig. 2.** Molecular structures of (a) **IIa**·$(CH_3)_2CO$ and (b) **IIIa**·$CH_2Cl_2$ in thermal ellipsoids of 50% probability. Solvent molecules are hidden.

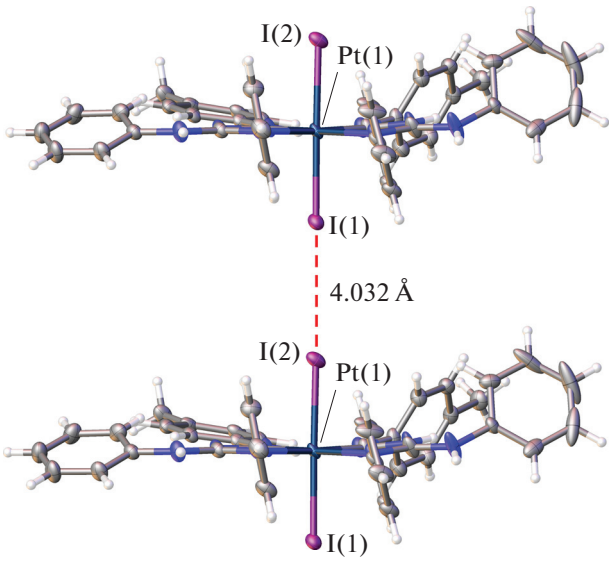



**Fig. 3.** Supramolecular structure of compound **IIIc** in thermal ellipsoids of 50% probability.

ated diaminocarbene C,N-chelate substituents and iodine and methyl (**IIa**–**c**) or two iodine atoms (**IIIa**–**c**) localized in the apical positions. The Pt–$C_{carbene}$ (1.996(6)–2.030(3) Å) and Pt–N (2.105(3)–2.157(2) Å) distances in compounds **IIa**–**c** and **IIIa**–**c** are longer than those in compounds **Ia**, **b** (Pt–$C_{carbene}$, 1.964(2)–1.981(6) Å, Pt–N, 2.0925(18)–2.121(5) Å) [19, 20] and shorter than those in the known NHC platinum(IV) complexes (2.015–2.079 Å) [13, 35]. The $NC_{carbene}N$ angles (120.1(6)°–123.9(5)°) in complexes **IIa**–**c** and **IIIa**–**c** are unsubstantially larger than those in complexes **Ia**, **b** (116.9(2)°–119.7(5)°) [19, 20]. The C–N bond lengths and $NC_{carbene}N$ angles lie in the characteristic range for diaminocarbene complexes [15, 36]. The angles between the chelate plane and I or Me in complexes **IIa**–**c** and **IIIa**–**c** are close to right angles (84.75(13)–95.06(9) Å), and the Pt–I and Pt–Me distances in complexes **IIa**–**c** and **IIIa**–**c** (2.6472(2)–2.7661(2) and 2.119(3)–2.170(4) Å, respectively) resemble those in the methylated platinum(IV) complexes [13, 28, 29, 35, 49]. The Pt–$C_{carbene}$ bond is by 0.128–0.140 Å shorter than Pt–Me, which is due to the partially double character of the metal–carbene bond [50]. The Pt–I bond in complexes **IIa**–**c** is longer than that in **IIIa**–**c** because of a high *trans*-effect of the carbon atom of the methyl group compared to the iodide ligand [28]. The Pt–I (2.6472(2)–2.6598(3) Å) bond lengths in complexes **IIIa**–**c** are comparable with those in other Pt(IV) complexes with the *trans*-iodide geometry [28].

A short intermolecular contact between the iodide substituents was observed in the structure of compound **IIIc** (Fig. 3). The I(1)···I(2) distance (4.032(3) Å) is comparable with the dismissed van der Waals radii proposed by Bondi (101.8% of the sum) [51]. The close Pt(1)I(1)I(2) and Pt(1)I(2)I(1) angles (176.5°–178.1°) suggests that this contact is a halogen–halogen nonpolar contact of type I [52].

To conclude, the oxidative addition of methyl iodide or molecular iodine to the bis(C,N-chelate) deprotonated diaminocarbene platinum(II) complexes affords the octahedral platinum(IV) complexes. In both cases, the reaction proceeds with the preservation of the diaminocarbene fragment. The compounds are thermally stable up to 200–260°C, and above this temperature the decomposition with the destruction of the organometallic framework occurs.

## SUPPLEMENTARY INFORMATION

The online version contains supplementary material available at https://doi.org/10.1134/S107032842360153X.

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## CONFLICT OF INTEREST

The authors of this work declare that they have no conflicts of interest.

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