

Carbene Complexes

Template Synthesis of a Coordinated
Tetracarbene Ligand with Crown Ether
Topology**

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Nucleophilic attack at the carbon atom of a coordinated isocyanide is one of the oldest methods for the preparation of carbene complexes.^[1] Particularly protic nucleophiles like alcohols and primary amines have been useful in this reaction. They give in good yield carbene complexes in which the carbene ligand has a H substituent at the N-position.^[2] The use of functionalized isocyanides like 2-hydroxyethyl isocyanide containing both the isocyanide function and the nucleophile in the same molecule leads, when the isocyanide is coordinated to a metal center in a high oxidation state, to complexes with a heterocyclic NH,O-stabilized carbene ligand.^[3]

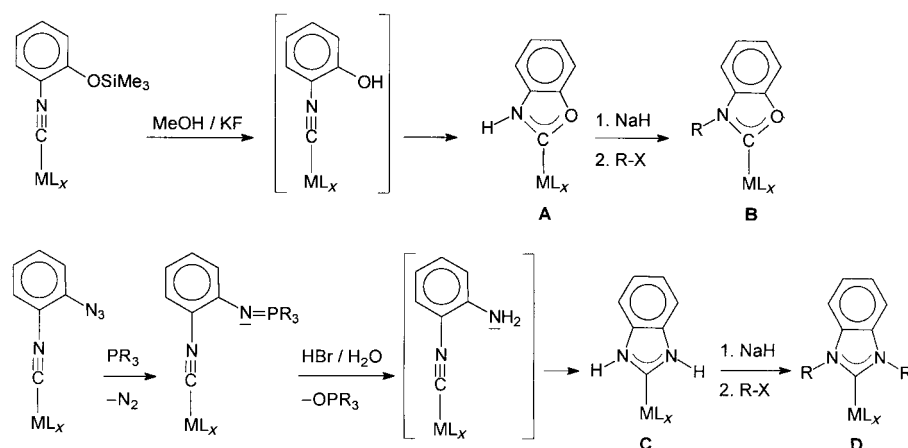
We reported on the template-controlled cyclization of 2-hydroxyphenyl isocyanide, which was obtained from complexes containing 2-(trimethylsiloxy)phenyl isocyanide^[4] by cleavage of the O–Si bond^[5] (Scheme 1). The synthesis of

complexes containing benzannulated NH,NH-stabilized N-heterocyclic carbene ligands was also achieved in a template synthesis.^[6] In this reaction 2-azidophenyl isocyanide was used as a synthon for the unstable 2-aminophenyl isocyanide. 2-Azidophenyl isocyanide, when coordinated to a transition metal, can be activated at the azido function by a Staudinger reaction.^[7] Hydrolysis of the initially obtained iminophosphorane leads to immediate cyclization and formation of the NH,NH-stabilized carbene ligand. Both the NH,O- (in **A**) and the NH,NH-stabilized carbene ligand (in **C**) are easily alkylated at the N-position to form the carbene complexes **B** and **D** (Scheme 1). The carbene ligands in complexes **A–C** are not stable when removed from the metal center. The template-controlled synthesis of **D** offers an alternative to the direct reaction of stable benzannulated carbene ligands^[8,9] and benzimidazolium salts^[10] with transition-metal complexes for the preparation of carbene complexes. Here we report on a modified cyclization reaction of coordinated 2-azidophenyl isocyanide for the synthesis of the tetracarbene complex **[5]**(CF₃SO₃)₂ (Scheme 2) and on a method to bridge the four NH,NH-stabilized carbene ligands in **[5]**²⁺ to give complex **[8]**²⁺, which contains a cyclic tetracarbene ligand with crown ether topology (Scheme 3).

The preparation of a cationic tetracarbene complex of type **[5]**²⁺ (Scheme 2) starting from a cationic square-planar tetrakis(2-azidophenyl isocyanide)metal(II) complex by a fourfold Staudinger reaction, hydrolysis, and cyclization in analogy to the preparation of **C** (Scheme 1) appears initially unproblematic. Homoleptic tetrakis(phenyl isocyanide) complexes of Pd^{II} and Pt^{II} have been described,^[11] while Ni^{II} is known to polymerize isocyanides.^[12] However, the preparation of complexes of type $[M(C\equiv N-Ar)_4]^{2+}$ starting from PdX₂ or PtX₂ (X = Cl, I) requires a tenfold excess of aryl isocyanide and yields, particularly upon stoichiometric application of the aryl isocyanide, often only the diisocyanide complexes^[13] of type $[MX_2(C\equiv N-Ar)_2]^{2+}$. Similar results were obtained in the reaction of 2-azidophenyl isocyanide **2** with PtX₂.

Contrary to this, the more nucleophilic alkyl isocyanides readily form homoleptic complexes^[3e,14] with Pt^{II} and Pd^{II}.

To avoid the problems associated with the preparation of tetrakis(2-phenyl isocyanide) complexes we developed the template-controlled reaction cascade depicted in Scheme 2. First tetrakis(trimethylphosphane)platinum(II) bis(trifluoromethanesulfonate) **[1]**(CF₃SO₃)₂ was treated with four equivalents of ligand **2**. At first only one of the phosphine ligands is replaced by an isocyanide ligand in the formation of complex **[3]**²⁺. No further substitution takes place at this stage. The liberated phosphine ligand can attack the metal center in **[3]**²⁺ to regenerate **[1]**²⁺. An alternative reaction path is the Staudinger reaction of the liberated phosphine with the



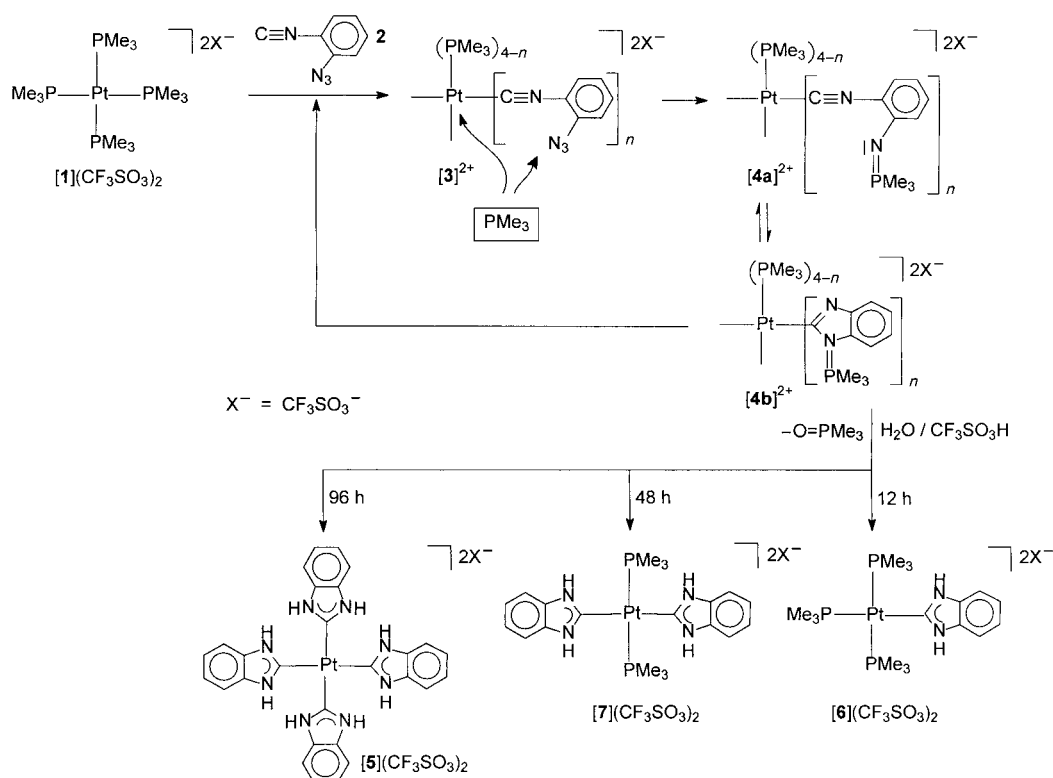
Scheme 1. Template-controlled cyclization of β -functionalized phenyl isocyanides to give N-heterocyclic carbene ligands. $ML_x = W(CO)_5, Mo(CO)_5, Cr(CO)_5$.

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Scheme 2. Synthesis of Pt^{II} carbene complexes **[5](CF₃SO₃)₂**, **[6](CF₃SO₃)₂**, and **[7](CF₃SO₃)₂**.

azido function of the coordinated 2-azidophenyl isocyanide. If the Staudinger reaction proceeds faster than the backreaction to **[1]**²⁺, the competitor for a coordination site at platinum (PMe₃) is consumed and irreversible liberation of N₂ gives the iminophosphorane complex **[4a]**²⁺. This reaction is indeed observed.

For electron-rich transition metals, the chemical equilibrium between the complexes with the open and cyclized forms of the iminophosphorane ligand (**[4a]**²⁺/**[4b]**²⁺) resides mainly on the side of the noncyclized ligand (type **[4a]**²⁺), which has been confirmed crystallographically for the W(CO)₅ complex (Scheme 1).^[6a,15] However, the Pt^{II}-coordinated isocyanide carbon atom in **[4a]**²⁺ is much more strongly activated for the nucleophilic attack of the iminophosphorane nitrogen atom. We therefore postulate that the iminophosphorane ligand in **[4a]**²⁺ cyclizes in an intramolecular fashion to give complex **[4b]**²⁺ as the main product.^[16] This would also explain the subsequent reactions. The formation of an ylide-type heterocycle in **[4b]**²⁺ leads to a strong *trans* effect. The PMe₃ ligand in *trans* position to the ylide in **[4b]**²⁺ is more labile than a PMe₃ ligand *trans* to the phenyl isocyanide in **[4a]**²⁺. Consequently, complex **[4b]**²⁺ reacts by substitution of the *trans* phosphine ligand for an isocyanide ligand **2**, which then again undergoes Staudinger reaction and cyclization. The reaction sequence substitution of a phosphine, Staudinger reaction, and cyclization proceeds a total of four times. The four cyclized iminophosphorane ligands were hydrolyzed after a total reaction time of 96 h with H₂O/CF₃SO₃H giving the tetracarbenes complex **[5](CF₃SO₃)₂** in 57% yield (Scheme 2).

Complex **[5](CF₃SO₃)₂** was characterized by NMR spectroscopy and X-ray diffraction. The ¹H NMR spectrum exhibits the expected low-field resonance^[6] for the amine protons at $\delta = 12.77$ ppm. The protons of the symmetrically substituted aromatic ring give rise to two multiplets at $\delta = 7.56$ ppm and $\delta = 7.38$ ppm. The signal for the carbene carbon was observed in the ¹³C NMR spectrum at $\delta = 168.6$ ppm with pronounced platinum–carbon coupling (¹J_{Pt-C} = 920.7 Hz), which is indicative of carbene coordination to the platinum atom.

Single crystals of **[5](CF₃SO₃)₂·4 THF** for a diffraction study (Figure 1)^[17] were obtained by recrystallization from THF. The structure analysis shows a platinum atom on a crystallographic inversion center with almost perfect square-planar coordination of four carbene ligands. The Pt–C bond lengths (2.025(3) Å and 2.020(3) Å) fall in the range reported for Pt^{II} complexes with acyclic NH,NH-stabilized carbene ligands (2.043(9) Å and 2.041(8) Å).^[14c] They are significantly shorter than those reported for the Pt^{II} complex with a six-membered N-heterocyclic NH,NH-stabilized carbene ligand.^[16] One of the two unique carbene ligands in the asymmetric unit is rotated about the Pt–C bond out of the PtC₄ plane and is oriented almost perpendicular to this plane (angle between the PtC₄ plane and plane C2/N21/C21C22/N22 85.30°). The second carbene ligand is almost coplanar with the PtC₄ plane (angle between PtC₄ plane and plane C1/N11/C11C12/N12 0.73°). A similar rotation of the carbene planes relative to the ML₄ plane (83.06° and 79.84°) has been described for Pd^{II} complexes with benzannulated N-heterocyclic carbenes.^[10]

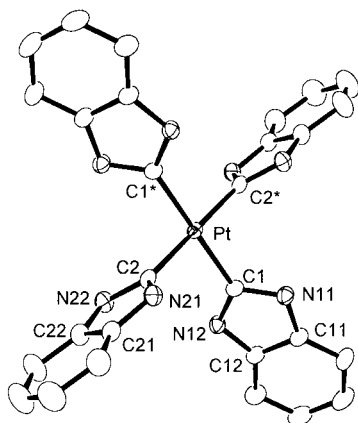


Figure 1. Molecular structure of the dication $[5]^{2+}$ in crystalline $[5]-(\text{CF}_3\text{SO}_3)_2 \cdot 4\text{C}_4\text{H}_8\text{O}$. The asymmetric unit contains one-half of the dication; the platinum atom resides on a crystallographic inversion center. Selected bond lengths [Å] and bond angles [°]: Pt–C1 2.025(3), Pt–C2 2.020(3), N11–C1 1.345(3), N11–C11 1.396(3), N12–C1 1.350(3), N12–C12 1.393(3), C1–Pt–C2* 88.12(10), C1–Pt–C2* 91.88(10), C1–Pt–C1* 180.0, N11–C1–N12 106.0(2), N21–C2–N22 105.2(2).

The complex dication $[5]^{2+}$ is formed in a domino reaction in which each of the trimethylphosphane ligands in $[1]^{2+}$ is replaced in a stepwise manner by an isocyanide ligand, which subsequently reacts with the liberated phosphine to form a cyclic iminophosphorane ligand, thereby generating the conditions for the next phosphine substitution. Because of the sensitivity of the iminophosphorane ligand towards acid, the reaction can be terminated after each cycle by addition of an acid, even before all four iminophosphorane ligands have been formed. This method was used for the preparation of the monocarbene complex $[6]^{2+}$ and the *trans*-dicarbene complex $[7]^{2+}$ (Scheme 2), which were isolated after hydrolysis of the reaction mixture with $\text{CF}_3\text{SO}_3\text{H}/\text{H}_2\text{O}$ after reaction times of 12 h and 48 h, respectively. However, compounds $[6]-(\text{CF}_3\text{SO}_3)_2$ and $[7](\text{CF}_3\text{SO}_3)_2$ obtained this way were contaminated with large amounts of unreacted ligand **2** and were difficult to purify. To obtain X-ray quality crystals, we prepared complexes $[6](\text{CF}_3\text{SO}_3)_2$ and $[7](\text{CF}_3\text{SO}_3)_2$ again from $[1](\text{CF}_3\text{SO}_3)_2$ and stoichiometric amounts of **2**.

The ^{13}C NMR spectrum of the monocarbene complex $[6]^{2+}$ exhibits a resonance for the carbene carbon atom at $\delta = 167.2$ ppm, which is comparable to that observed for the carbene carbons in $[5]^{2+}$. In contrast to the resonance in $[5]^{2+}$ the carbene signal for $[6]^{2+}$ shows $^2J_{\text{P-C}}$ coupling to the phosphorous atoms in *cis* (13.4 Hz) and *trans* (115.6 Hz) positions. Two resonances for the phosphorous atoms at $\delta = -15.2$ ppm (d, Pt satellites, $^2J_{\text{P-P}} = 27.8$ Hz, $^1J_{\text{Pt-P}} = 2143.8$ Hz, 2P *cis* to carbene) and $\delta = -25.2$ (t, Pt satellites, $^2J_{\text{P-P}} = 27.8$ Hz, $^1J_{\text{Pt-P}} = 2143.4$ Hz, P *trans* to carbene) were observed in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum. Similar observations were made for the *trans*-dicarbene complex $[7]^{2+}$, where the resonance for the carbene carbon atoms appears at $\delta = 168.4$ ppm (t, Pt satellites, $^2J_{\text{P-C}} = 12.1$ Hz, $^1J_{\text{Pt-C}} = 854.5$ Hz) in the ^{13}C NMR spectrum.

Single crystals suitable for X-ray diffraction analyses of $[6](\text{CF}_3\text{SO}_3)_2$ and $[7](\text{CF}_3\text{SO}_3)_2 \cdot 2\text{CH}_3\text{OH}$ (Figure 2)^[17] were obtained by recrystallization from methanol. The structure

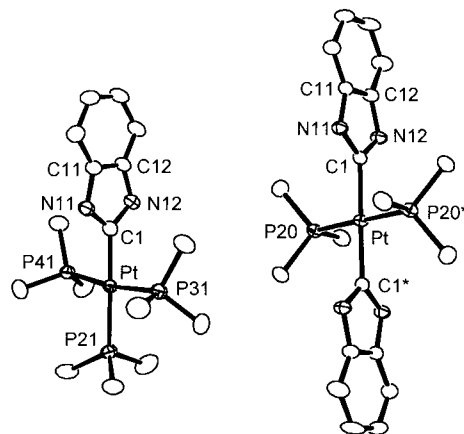
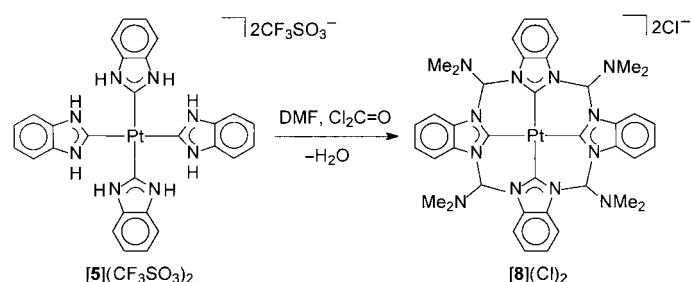


Figure 2. Molecular structures of the dications $[6]^{2+}$ (left) in crystalline $[6](\text{CF}_3\text{SO}_3)_2$ and $[7]^{2+}$ (right) in crystalline $[7](\text{CF}_3\text{SO}_3)_2 \cdot 2\text{CH}_3\text{OH}$. The platinum atom in dication $[7]^{2+}$ resides on a crystallographic inversion center. Selected bond lengths [Å] and bond angles [°] for $[6]^{2+}$: Pt–C1 2.018(4), Pt–P21 2.3309(11), Pt–P31 2.3260(10), Pt–P41 2.3262(10), N11–C1 1.346(6), N11–C11 1.395(5), N12–C1 1.344(5), N12–C12 1.397(5), C1–Pt–P21 178.79(12), C1–Pt–P31 86.11(10), C1–Pt–P41 85.89(10), P21–Pt–P31 93.46(4), P21–Pt–P41 94.58(4), P31–Pt–P41 171.63(4), N11–C1–N12 107.1(4). Selected bond lengths [Å] and bond angles [°] for $[7]^{2+}$: Pt–C1 2.025(2), Pt–P20 2.3012(6), N11–C1 1.339(3), N11–C11 1.385(3), N12–C1 1.354(3), N12–C12 1.396(3), C1–Pt–C1* 180.0, P20–Pt–P20* 180.0, C1–Pt–P20 89.73(7), N11–C1–N12 106.1(2).

analysis of $[6](\text{CF}_3\text{SO}_3)_2$ confirms that the formation of just one NH,NH-stabilized carbene ligand, i.e. the cyclic iminophosphorane precursor, is completed before a second phosphine ligand is substituted. The molecular structure of $[7](\text{CF}_3\text{SO}_3)_2 \cdot 2\text{CH}_3\text{OH}$ shows that the second isocyanide ligand enters and cyclizes in *trans* position to the first carbene ligand.

The bonding parameters in the dications $[6]^{2+}$ and $[7]^{2+}$ are only marginally different from the equivalent parameters in $[5]^{2+}$. Particularly the Pt–C bond lengths are independent of the type of ligand in *trans* position. Both dications are coordinated in a slightly distorted square-planar geometry; the distortions observed in $[6]^{2+}$ are larger than those in $[7]^{2+}$. The carbene planes in both complex cations are oriented almost perpendicular to the PtL_4 plane (angle between planes 87.35° for $[6]^{2+}$ and 75.92° for $[7]^{2+}$).

Attempts to connect the four NH,NH-stabilized carbene ligands in $[5]^{2+}$ by deprotonation and bridging alkylation with dibromomethane or 1,2-dibromoethane to give a cyclic tetracarbene ligand were initially unsuccessful. The removal of eight NH protons from $[5]^{2+}$ using NaH generates a sixfold negatively charged anion that is insoluble and unreactive in all common solvents. Highly charged intermediates are avoided in the reaction of $[5]^{2+}$ with DMF, which also serves also as the solvent for the reaction. Diphosgene is also added to trap the water formed. By this method four $\text{Me}_2\text{N-CH}$ bridges are introduced between the carbene ligands, and complex **[8]**(Cl)₂ is formed in over 60 % yield. Complex cation $[8]^{2+}$ contains a cyclic tetracarbene ligand with a crown ether topology (Scheme 3).



Scheme 3. Template synthesis of $[8]^{2+}$ from $[5]^{2+}$.

The ^{13}C NMR spectrum of $[8](\text{Cl})_2$ (in $[\text{D}_6]\text{DMSO}$) differs only slightly from that of $[5](\text{CF}_3\text{SO}_3)_2$. The bridging alkylation of the N1 and N3 positions at the carbene ligands has little effect on the chemical shift of the atoms within the heterocycle.^[6] Two new resonances were observed for the carbon atoms of the bridging $\text{CH}-\text{N}(\text{CH}_3)_2$ groups.

The X-ray diffraction study (Figure 3)^[17] shows complex $[8]^{2+}$ to contain a platinum atom surrounded in an almost perfect square-planar fashion by four carbene carbon atoms. The Pt–C bond lengths are about 0.05 Å shorter than those in dication $[5]^{2+}$. The bridges between the carbene ligands force in $[8]^{2+}$, in contrast to $[5]^{2+}$, the carbene planes to be almost coplanar with the PtC_4 plane (maximum angle between carbene planes and PtC_4 plane 15.6°).

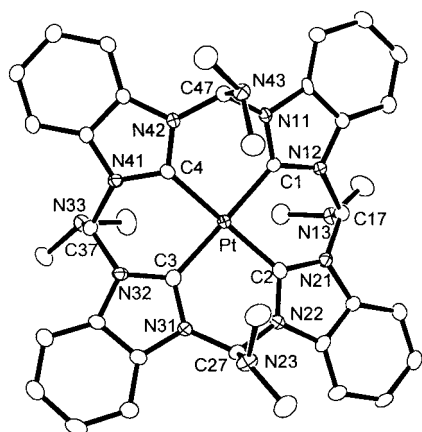


Figure 3. Molecular structure of the dication $[8]^{2+}$ in crystalline $[8](\text{Cl})_2 \cdot 4\text{CH}_3\text{OH}$. Selected bond lengths [Å] and bond angles [°]: Pt–C1 1.980(4), Pt–C2 1.969(4), Pt–C3 1.973(4), Pt–C4 1.978(4); C1–Pt–C2 89.89(14), C1–Pt–C3 179.03(15), C1–Pt–C4 90.19(14), C2–Pt–C3 90.54(15), C2–Pt–C4 178.77(15), C3–Pt–C4 89.40(14).

We have demonstrated that the homoleptic Pt^{II} tetracarbene complex $[5]^{2+}$ can be prepared from the tetrakis(trimethylphosphane)platinum(II) dication $[1]^{2+}$ and 2-azidophenyl isocyanide (**2**) in a template-controlled reaction cascade. Mono- and dicarbene intermediates in this multistep reaction were also isolated. The connection of the four NH, NH -stabilized carbene ligands in $[5]^{2+}$ using the sp^3 carbon atom of a $\text{CH}-\text{NMe}_2$ group as a bridge to yield a coordinated cyclic tetracarbene ligand was achieved by reaction of $[5]^{2+}$ with DMF in the presence of diphosgene. Attempts to introduce an sp^2 -hybridized bridging atom between the carbene ligands

and to remove the platinum atom from the macrocycle are currently underway.

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- [17] X-ray structure determinations: **[5]**(CF₃SO₃)₂·4C₄H₈O (C₄₆H₅₆N₈F₆O₁₀PtS₂): $M_w = 1254.20$, colorless crystal, $0.36 \times 0.28 \times 0.25$ mm, $a = 9.641(4)$, $b = 10.440(4)$, $c = 14.224(5)$ Å, $\alpha = 108.280(12)$, $\beta = 104.839(12)$, $\gamma = 90.715(13)^\circ$, $V = 1307.3(8)$ Å³, $\rho_{\text{calcd}} = 1.593$ g cm⁻³, $\mu = 2.847$ mm⁻¹, ω - and φ -scans, 14742 measured intensities ($3.1^\circ \leq 2\theta \leq 60.0^\circ$), $\lambda = 0.71073$ Å, $T = 153(2)$ K, semiempirical absorption correction ($0.472 \leq T \leq 0.536$), 7367 independent ($R_{\text{int}} = 0.0337$) and 7348 observed ($I \geq 2\sigma(I)$) intensities, $P1$, $Z = 1$, $R = 0.0315$, $wR = 0.0705$, refinement of 379 parameters against $|F^2|$ with H atoms at calculated positions, the asymmetric unit contains 1/2 molecule of the complex and two molecules of THF. **[6]**(CF₃SO₃)₂ (C₁₈H₃₃N₂F₆O₆P₃PtS₂): $M_w = 839.58$, yellow crystal, $0.20 \times 0.20 \times 0.20$ mm, $a = 12.1131(5)$, $b = 13.2949(5)$, $c = 20.3941(8)$ Å, $\beta = 90.5830(10)^\circ$, $V = 3284.1(2)$ Å³, $\rho_{\text{calcd}} = 1.763$ g cm⁻³, $\mu = 4.617$ mm⁻¹, ω - and φ -scans, 37128 measured intensities ($4.0^\circ \leq 2\theta \leq 60.0^\circ$), $\lambda = 0.71073$ Å, $T = 153(2)$ K, semiempirical absorption correction ($0.459 \leq T \leq 0.459$), 9527 independent ($R_{\text{int}} = 0.0343$) and 8001 observed ($I \geq 2\sigma(I)$) intensities, $P2_1/c$, $Z = 4$, $R = 0.0355$, $wR = 0.0903$, refinement of 368 parameters against $|F^2|$ with H atoms at calculated positions, the asymmetric unit contains one molecule of the complex, one of the triflate anions is disordered. **[7]**(CF₃SO₃)₂·2CH₃OH (C₂₄H₃₈N₄F₆O₈P₂PtS₂): $M_w = 945.73$, colorless crystal, $0.45 \times 0.19 \times 0.10$ mm, $a = 9.1125(4)$, $b = 18.1914(7)$, $c = 10.9333(4)$ Å, $\beta = 103.4470(10)^\circ$, $V = 1762.72(12)$ Å³, $\rho_{\text{calcd}} = 1.782$ g cm⁻³, $\mu = 4.270$ mm⁻¹, ω - and φ -scans, 13913 measured intensities ($4.4^\circ \leq 2\theta \leq 50.0^\circ$), $\lambda = 0.71073$ Å, $T = 153(2)$ K, semiempirical absorption correction ($0.250 \leq T \leq 0.675$), 3100 independent ($R_{\text{int}} = 0.0279$) and 2764 observed ($I \geq 2\sigma(I)$) intensities, $P2_1/n$, $Z = 2$, $R = 0.0175$, $wR = 0.0385$, refinement against 290 parameters against $|F^2|$ with H atoms at calculated positions, the asymmetric unit contains 1/2 molecule of the complex and one molecule of methanol. **[8]**Cl₂·4CH₃OH (C₄₄H₆₀N₁₂Cl₂O₄Pt): $M_w = 1087.03$, colorless crystal, $0.35 \times 0.06 \times 0.04$ mm, $a = 16.434(3)$, $b = 14.397(3)$, $c = 19.529(4)$ Å, $\beta = 91.148(4)^\circ$, $V = 4619.8(16)$ Å³, $\rho_{\text{calcd}} = 1.563$ g cm⁻³, $\mu = 3.209$ mm⁻¹, ω - and φ -scans, 52223 measured intensities ($3.2^\circ \leq 2\theta \leq 60.0^\circ$), $\lambda = 0.71073$ Å, $T = 153(2)$ K, semiempirical absorption correction ($0.399 \leq T \leq 0.882$), 13421 independent ($R_{\text{int}} = 0.0684$) and 8268 observed ($I \geq 2\sigma(I)$) intensities, $P2_1/n$, $Z = 4$, $R = 0.0363$, $wR = 0.0710$, refinement of 592 parameters against $|F^2|$ with H atoms at calculated positions, the asymmetric unit contains one molecule of the complex and four molecules methanol. CCDC-237759 ([**5**](CF₃SO₃)₂·4C₄H₈O), CCDC-237760 ([**6**](CF₃SO₃)₂), CCDC-237761 ([**7**](CF₃SO₃)₂·2CH₃OH), and CCDC-256449 ([**8**]Cl₂·4CH₃OH) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.