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Unusual $[Pt\{\kappa^2(C,N)\}]^+ \rightarrow [Pt\{\kappa^2(N,N)\}]^+$ Coordination Mode Flip of the Guanidinate(1−) Ligand in Cationic *N,N′,N″*-Tris(3,5-xylyl)guanidinatoplatinum(II) Bis(phosphine) Complexes. Syntheses, Structural and Theoretical Studies

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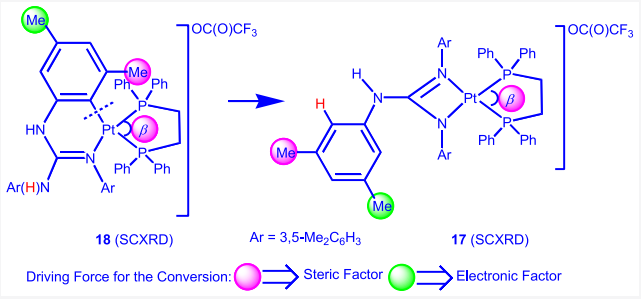
ABSTRACT: Separate reactions of $[Pt\{\kappa^2(C,N)\}X(S(O)Me_2)]$ ($\kappa^2(C,N)$ = *N,N′,N″*-triarylguanidinate(1−); Ar = 2-$(MeO)C_6H_4$ (**3**), 2-MeC_6H_4 (**4**), 4-MeC_6H_4 (**5**), 2,4-$Me_2C_6H_3$ (**6**), 2,5-$Me_2C_6H_3$ (**7**), and 3,4-$Me_2C_6H_3$ (**8**); X = Cl (**3**), $OC(O)CF_3$ (**4**−**8**)) with 1,1-bis(diphenylphosphino)methane (dppm) afforded the respective cationic complexes $[Pt\{\kappa^2(C,N)\}\{\kappa^2(dppm)\}][X]$ (**10**−**15**) in high yields. In contrast, the separate reactions of $[Pt\{\kappa^2(C,N)\}(OC(O)CF_3)(S(O)Me_2)]$ ($\kappa^2(C,N)$ = *N,N′,N″*-tris(3,5-xylyl)guanidinate(1−); **9**) with dppm and 1,2-bis(diphenylphosphino)ethane (dppe) afforded the cationic guanidinatoplatinum(II) complexes $[Pt\{\kappa^2(N,N)\}\{\kappa^2(P,P)\}][OC(O)CF_3]$ (*P,P* = dppm (**16**), dppe (**17**), respectively) in high yields. Further, the separate reactions of **9** with dppe and 1,3-bis(diphenylphosphino)propane (dppp) afforded the cationic complexes $[Pt\{\kappa^2(C,N)\}\{\kappa^2(P,P)\}][OC(O)CF_3]$ (*P,P* = dppe (**18**), dppp (**19**), respectively) in high yields. The salt metathesis reaction of **19** with an excess of NH_4PF_6 afforded the cationic complex $[Pt\{\kappa^2(C,N)\}\{\kappa^2(dppp)\}][PF_6]$ (**20**) in good yield. The new Pt(II) complexes were characterized by elemental analyses, mass spectrometry, IR, multinuclear (^{195}Pt, ^{31}P, ^{1}H, ^{13}C, and ^{19}F) NMR spectroscopy, and conductivity measurements. Further, the molecular structures of **10**·$CHCl_3$, **11**·$CHCl_3$, **12**·CH_2Cl_2, **14**·1.5C_7H_8, **15**·CH_2Cl_2, **16**, **17**, **18**·0.5C_7H_8, **19**·$C_4H_{10}O$, and **20**·C_7H_8 were determined by single-crystal X-ray diffraction. To the best of our knowledge, **17** and **18**·0.5C_7H_8 represent the first pair of crystallographically characterized metallacyclic structural isomers to be reported. The reactions of **9** with dppm and dppe carried out separately in $CDCl_3$ at RT were monitored by variable-time ^{31}P NMR spectroscopy, which revealed the formation of a transient species, $[Pt\{\kappa^2(C,N)\}\{\kappa^2(dppm)\}][OC(O)CF_3]$ (**22**), and **18** before finally forming the end products **16** and **17**, respectively. The contributions of various factors in dictating the coordination flip of the guanidinate(1−) ligand from $\kappa^2(C,N)$ in **22** and **18** to $\kappa^2(N,N)$ in **16** and **17**, respectively, were unraveled. The mechanism associated with the coordination flip of the guanidinate(1−) ligand was mapped with the aid of DFT calculations on a model complex, $[Pt\{\kappa^2(C,N)\}\{\kappa^2(P,P)\}][OC(O)CF_3]$ (**22′**), which revealed a pathway involving a Wheland intermediate, **F**, and further point out that the product, $[Pt\{\kappa^2(N,N)\}\{\kappa^2(P,P)\}][OC(O)CF_3]$ (**16′**), is a kinetically controlled product.



INTRODUCTION

Cycloplatinated imine, oxime, ketimine, and related *N*-donor complexes have been extensively studied in the literature due to their relevance in Pt(II)-mediated C−H activation and their utility as luminescent materials and metallomesogens.[1−6] The mechanism of C−H activation involving Pt(II) salts/precursors and an appropriate *N*-donor ligand was shown to critically depend upon various factors such as the nature of the Pt(II) precursors, the steric, electronic, and conformational properties of the *N*-donor ligands, and the nature of the external base and solvent.[1,7] One of the simplest methods to cycloplatinate the *N*-donor ligands is to use *cis*-$[PtCl_2(S(O)Me_2)_2]$ as the Pt(II) precursor in the presence of NaOAc as an external base in methanol or a methanol/toluene mixture under heating conditions. In this method, the role of NaOAc was thoroughly scrutinized and the OAc^- group was shown to enter into the coordination sphere of the Pt(II) atom during the course of the cycloplatination reaction.[1,7a,8,9]

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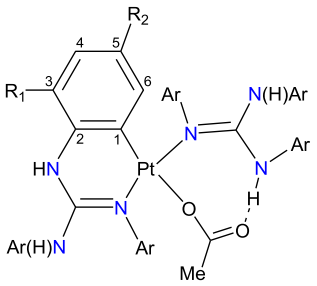
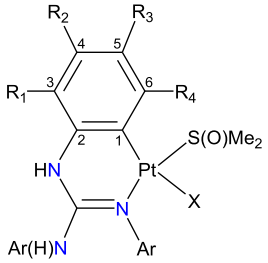




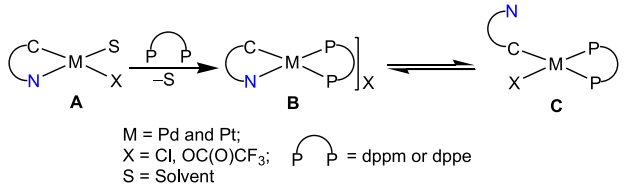
	Ar	R_1	R_2		Ar	R_1	R_2	R_3	R_4
1	2-MeC_6H_4	Me	H	**3**	2-$(MeO)C_6H_4$	OMe	H	H	H
2	2,4-$Me_2C_6H_3$	Me	Me	**4**	2-MeC_6H_4	Me	H	H	H
				5	4-MeC_6H_4	H	H	Me	H
				6	2,4-$Me_2C_6H_3$	Me	H	Me	H
				7	2,5-$Me_2C_6H_3$	Me	H	H	Me
				8	3,4-$Me_2C_6H_3$	H	Me	Me	H
				9	3,5-$Me_2C_6H_3$	H	Me	H	Me

Figure 1. List of known platinacycles **1**−**6** and new platinacycles **7**−**9**: X = Cl (**3**), $OC(O)CF_3$ (**4**−**9**).

Transition-metal complexes of *N*-substituted guanidines have been extensively studied in the literature due to their rich structural chemistry, their diverse reactivity patterns, and their promising role as catalysts in organic transformations.[10−13] During the course of the reactions of sym-*N*,*N*′,*N*″-triarylguanidines, $[(ArNH)_2C{=}NAr]$ (sym = symmetrical; Ar = tolyl, xylyl, anisyl) with *cis*-$[PtCl_2(S(O)Me_2)_2]$, we were able to identify how factors such as the conformations of the guanidines and the coordinating ability of OAc^- from the external base NaOAc influence the course of Pt(II)-mediated C−H activation.[8] Further, we have also shown that the reactions of *cis*-$[PtCl_2(S(O)Me_2)_2]$ in the presence of NaOAc or the reactions of $[Pt(OC(O)R)_2(S(O)Me_2)_2]$ (R = Me, CF_3) in the absence of base with sym-*N*,*N*′,*N*″-triarylguanidines afforded the chelate hemichelate platinacycles **1** and **2** and chelate platinacycles **3**−**6**, as illustrated in Figure 1.[8,14]

The reactions of five-membered cyclometalated imine complexes **A** with bisphosphines such as 1,1-bis(diphenylphosphino)methane (dppm) and 1,2-bis(diphenylphosphino)ethane (dppe) have been studied in the literature to probe the lability of the M−N bond in the substrate, **A**. Such reactions are known to produce cationic metallacycles **B**, neutral organometallic complexes **C**, or a equilibrated mixture of these products (see Scheme 1).[15] The exact nature of the products was shown to depend upon the basicity of the N atom, the endocyclic or exocyclic nature of the >C=N double bond inside the $[Pt\{\kappa^2(C,N)\}]$ ring, and the bite angle of the bisphosphines. The Pd−N bond in six-membered cyclopalladated *N*,*N*′,*N*″-tri(2-tolyl)guanidine and *N*,*N*′,*N*″-tris(2-anisyl)guanidine complexes $[Pd\{\kappa^2(C,N)\}(\mu\text{-}NCS)]_2$ was cleaved smoothly by treating these palladacycles with an excess of PMe_3 to afford *trans*-$[Pd(\kappa^1C\text{-guanidinate-}(1-))(NCS)(PMe_3)_2]$.[16]

Scheme 1. Reactivity of Metallacycles with Chelating Bisphosphines



We wished to study the reactions of **3**−**6**[8,14] and **7**−**9** with dppm, dppe, and 1,3-bis(diphenylphosphino)propane (dppp) to investigate the influence of steric and electronic properties of the guanidinate(1−) ligands in these platinacycles and the variation of natural bite angles β in dppm (β = 72°), dppe (β = 85°), and dppp (β = 91°)[17] upon the lability of the Pt−N bond in the platinacycles. In this endeavor, we were able to isolate the anticipated cationic platinacycles **10**−**15**, **18**, and **19** and the pair of unanticipated cationic guanidinatoplatinum(II) complexes **16** and **17** in high yields (see below). The results pertinent to the syntheses and complete characterization of both types of cationic Pt(II) complexes are reported in this paper. The structural isomers **17** and **18** have been successfully isolated and structurally characterized for the first time. A plausible mechanism outlining the transformations of **22** to **16** was mapped with **22**′ and **16**′ via two pathways, and the factors responsible for the transformation are also outlined.

RESULTS AND DISCUSSION

Syntheses and Reactivity Studies. sym-*N*,*N*′,*N*″-tris(3,4-xylyl)guanidine, $[(ArNH)_2C{=}NAr]$ (Ar = 3,4-$(CH_3)_2C_6H_3$; $\mathbf{LH_2}^{\mathbf{3,4\text{-}xylyl}}$), was prepared from the reaction of sym-*N*,*N*′-bis(3,4-xylyl)thiourea and 3,4-xylidine in the presence of 100% aqueous KOH solution in nitrobenzene in 93%

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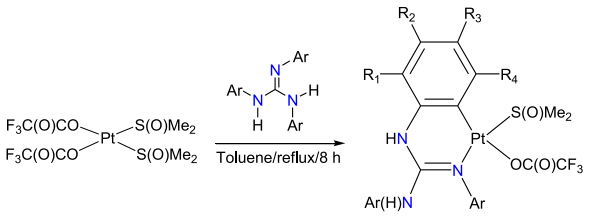
yield following the literature procedure reported for the other sym-*N*,*N*′,*N*″-triarylguanidines.[18] The separate reactions of *cis*-$[Pt(OC(O)CF_3)_2(S(O)Me)_2]$ with sym-*N*,*N*′,*N*″-triarylguanidines $[(ArNH)_2C{=}NAr]$ (Ar = 2,5-$Me_2C_6H_3$ (**$LH_2^{2,5\text{-xylyl}}$**), 3,4-$Me_2C_6H_3$ (**$LH_2^{3,4\text{-xylyl}}$**) and 3,5-$Me_2C_6H_3$ (**$LH_2^{3,5\text{-xylyl}}$**)) in toluene under reflux conditions for 8 h afforded **7**−**9** in 83%, 64%, and 78% yields, respectively, following the literature procedure reported by us for **4**−**6** (see Scheme 2).[14,19]

Scheme 2. Syntheses of Platinacycles 7−9



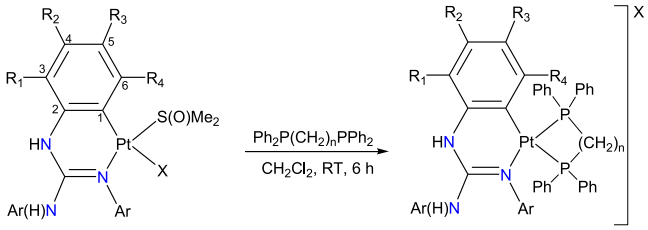
	Ar	R_1	R_2	R_3	R_4
7[19]	2,5-$Me_2C_6H_3$	Me	H	H	Me
8	3,4-$Me_2C_6H_3$	H	Me	Me	H
9[19]	3,5-$Me_2C_6H_3$	H	Me	H	Me

Cyclopalladation of the imine ligands ArCH=NAr′ (Ar = 2,5-$Me_2C_6H_3$; Ar′ = Ph, 2,4,6-$Me_3C_6H_2$) was shown to be solvent- and temperature-dependent.[20,21] Thus, cyclopalladation of ArCH=NPh (Ar = 2,5-$Me_2C_6H_3$) with $Pd(OAc)_2$ in AcOH was unsuccessful even under reflux conditions while the analogous reaction with ArCH=NAr′ (Ar = 2,5-$Me_2C_6H_3$ and Ar′ = 2,4,6-$Me_3C_6H_2$) in toluene at 60 °C for 24 h was shown to afford the five-membered dinuclear palladacycle $[Pd\{\kappa^2(C,N)(\mu\text{-}OAc)\}]_2$. Our attempts to cyclopalladate the guanidine **$LH_2^{2,5\text{-xylyl}}$** with $Pd(OAc)_2$ was unsuccessful in toluene at elevated temperature, which was ascribed to the steric hindrance posed by the methyl substituent on the C5 carbon atom of one the N(H)Ar units.[22] To our surprise, we were able to smoothly cycloplatinate both **$LH_2^{2,5\text{-xylyl}}$** and **$LH_2^{3,5\text{-xylyl}}$** with electrophilic *cis*-$[Pt(OC(O)CF_3)_2(S(O)Me)_2]$ to afford **7** and **9**, respectively, as illustrated in Scheme 2.

The reactions of cycloplatinated *N*-donor complexes of the type $[Pt\{\kappa^2(C,N)\}X(S(O)Me_2)]$ (X = Cl, $OC(O)CF_3$) with bisphosphines such as dppm, dppe, and 1,1′-bis-(diphenylphosphino)ferrocene are known to produce the corresponding cationic platinacycles of the type $[Pt\{\kappa^2(C,N)\}\{\kappa^2(P,P)\}][X]$.[15b,c,23−27] The separate reactions of **3**−**8** with dppm in CH_2Cl_2 at RT for 6 h afforded cationic platinacycles **10**−**15**, respectively, in 90%−95% yields (see Scheme 3). Separate reactions of **9** with dppm and dppe in CH_2Cl_2 at RT for 6 and 24 h afforded the unanticipated cationic guanidinatoplatinum(II) complexes **16** and **17** in 95% and 91% yields, respectively (see Scheme 4). Separate reactions of **9** carried out with dppe and dppp in CH_2Cl_2 at RT for 6 h afforded the cationic platinacycles **18** and **19** in 91% and 84% yields, respectively (see Scheme 3).

The compositions of **17** and **18** are identical, but the coordination modes of the guanidinate(1−) ligands are $\kappa^2(N,N)$ and $\kappa^2(C,N)$, respectively, and thus these two complexes can be considered as structural or linkage isomers. To the best of our knowledge, this type of isomerism is unprecedented in metal guanidinate and metallacyclic

Scheme 3. Syntheses of 10−15, 18, and 19[a]



	Ar	R_1	R_2	R_3	R_4	n	
3	2-(MeO)C_6H_4	OMe	H	H	H	1	**10**
4	2-MeC_6H_4	Me	H	H	H	1	**11**
5	4-MeC_6H_4	H	H	Me	H	1	**12**
6	2,4-$Me_2C_6H_3$	Me	H	Me	H	1	**13**
7	2,5-$Me_2C_6H_3$	Me	H	H	Me	1	**14**
8	3,4-$Me_2C_6H_3$	H	Me	Me	H	1	**15**
9	3,5-$Me_2C_6H_3$	H	Me	H	Me	2	**18**
9	3,5-$Me_2C_6H_3$	H	Me	H	Me	3	**19**

[a]X = Cl (**10**) and $OC(O)CF_3$ (**11**−**15**, **18**, and **19**).

chemistry. Platinacycle **19** was subjected to a metathesis reaction with an excess of NH_4PF_6 in CH_2Cl_2 at RT for 24 h with the aim of obtaining **21**, as PF_6^- is more noncoordinating anion in comparison with $OC(O)CF_3^-$, but only platinacycle **20** was formed in 79% yield, as outlined in Scheme 5 (see also Figure 2). Thus, our attempt to isolate **21** by carrying out a salt metathesis reaction on **19** with NH_4PF_6 was not successful; rather, we were able to isolate only **20** from the aforementioned reaction.

The reaction of **9** with dppm was monitored by ^{31}P NMR spectroscopy, which revealed the formation of the reactive intermediate **22**, as illustrated in Figure 3, before forming **16** (see below). From the fact that we were able to experimentally detect or isolate both types of structural isomers, namely **22**/**16** and **18**/**17**, we summarize the following three criteria which all need to be fulfilled for the smooth isomeric transformations. Platinacyclic precursors $[Pt\{\kappa^2(C,N)\}\{\kappa^2(P,P)\}][OC(O)CF_3]$ should possess (i) short-bite-angle phosphines such as dppm and dppe, (ii) a protruding Me substituent on the carbon atom adjacent to the Pt−C bond in the platinated aryl ring, and (iii) the Me substituent *para* to the Pt−C bond in the platinated aryl ring. Thus, platinacycles **22** and **18** simultaneously satisfy all three criteria mentioned above and transform to **16** and **17**, respectively while **13**−**15** satisfy only criterion i, criteria i and ii, and criteria i and iii, respectively, and thus these platinacycles are unable to transform to their respective $\kappa^2(N,N)$ counterparts such as **16** and **17**. The faster transformation of **22** to **16** in comparison to the transformation of **18** to **17** is ascribed to the smaller bite angle of dppm in **22** than that of dppe in **18**. In other words, **22** is more destabilized than **18** due to the presence of a four-membered $[Pt\{\kappa^2(dppm)\}]$ ring in the former complex and this could provide a lower energy pathway for the former platinacycle to undergo a faster transformation.[28] One can invoke a combination of several factors for the smooth transformations of **22** to **16** or **18** to **17** such as steric factors and an antisymbiosis or transphobia effect.[29] The square-planar Pd(II)

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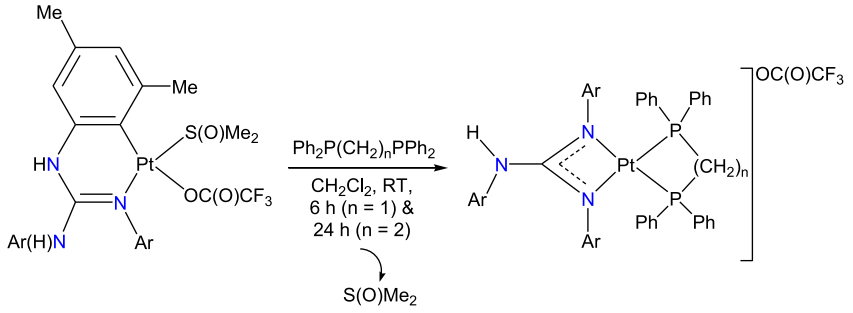
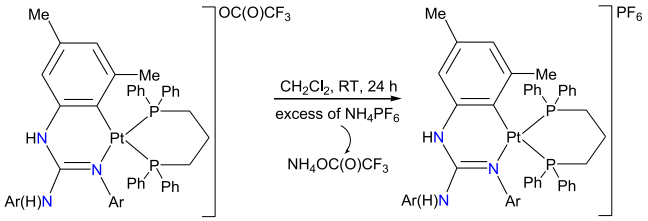
Scheme 4. Syntheses of 16 (n = 1) and 17 (n = 2)

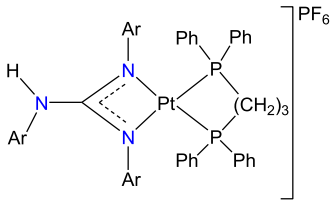


9 Ar = 3,5-$Me_2C_6H_3$ **16** and **17**

Scheme 5. Synthesis of 20 via a Metathesis Reaction of 19 with NH_4PF_6

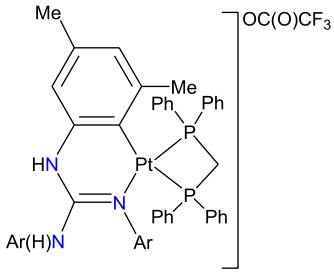


19 Ar = 3,5-$Me_2C_6H_3$ **20**



Ar = 3,5-$Me_2C_6H_3$ (**21**)

Figure 2. Hitherto unknown guanidinatoplatinum(II) complex **21** anticipated from the transformation illustrated in Scheme 5.



Ar = 3,5-$Me_2C_6H_3$ (**22**)

Figure 3. ^{31}P NMR spectroscopically detected transient intermediate formed upon mixing **9** with dppm in $CDCl_3$.

complexes that contain aryl and phosphine ligands in *trans* positions are destabilized due to a antisymbiosis or transphobia effect, as these two ligands are soft in nature and thus compete with each other for metal electrons. The phosphine and aryl ligands are *trans* to each other around the Pt(II) atom in **19**, and its reactivity was further increased by replacing $OC(O)CF_3^-$ with PF_6^-, which allowed us to isolate only **20**, as illustrated in Scheme 5, but not **21** (see Figure 2). This can likely be attributed to the absence of a short-bite-angle phosphine in **19** and **20** and thus criterion i is not fulfilled.

Molecular Structures. The molecular structures of **10**·$CHCl_3$, **11**·$CHCl_3$, **12**·CH_2Cl_2, **14**·1.5C_7H_8, **15**·CH_2Cl_2, **16**, **17**, **18**·0.5C_7H_8, **19**·$C_4H_{10}O$, **20**·C_7H_8, and $\mathbf{LH_2}^{3,4\text{-xylyl}}$ were determined by single-crystal X-ray diffraction. Molecular structures of the aforementioned complexes are illustrated in Figures 4−8, and that of $\mathbf{LH_2}^{3,4\text{-xylyl}}$ is illustrated in Figure S1 in the Supporting Information. Salient structural features of the aforementioned complexes are given in Tables 1−5.

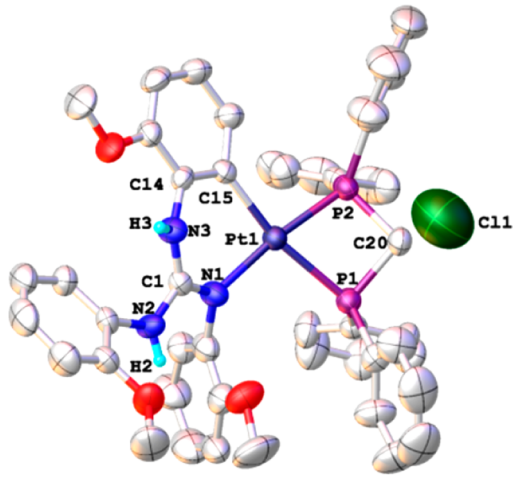


Figure 4. Molecular structure of **10**·$CHCl_3$. Solvent molecules and all hydrogen atoms except those on the amino nitrogen atoms are removed for clarity.

The Pt(II) atom in $[Pt\{\kappa^2(C,N)\}\{\kappa^2(P,P)\}][X]$ is surrounded by the chelating guanidinate(1−) ligand and chelating dppm (**10**·$CHCl_3$, **11**·$CHCl_3$, **12**·CH_2Cl_2, **14**·1.5C_7H_8, **15**·CH_2Cl_2), dppe (**18**·0.5 C_7H_8), or dppp (**19**·$C_4H_{10}O$ and **20**·C_7H_8) ligand. The Pt−P bond that is *trans* to the Pt−C bond is uniformly longer than the Pt−P bond that is *trans* to the Pt−N bond in the aforementioned platinacycles, a feature typical of cationic platinacycles of this type reported in the literature (see Table 1).[23−26,30−32] The N1−Pt1−C15 bond angle in **10**·$CHCl_3$ (89.4(3)°), **11**·$CHCl_3$ (87.6(3)°), **12**·CH_2Cl_2 (88.7(4)°), and **15**·CH_2Cl_2 (87.1(3)°) are wider than the corresponding angle in **14**·1.5C_7H_8 (84.4(3)°) due to the presence of a protruding Me substituent on the carbon atom adjacent to the Pt−C bond in the last complex. The bite angles

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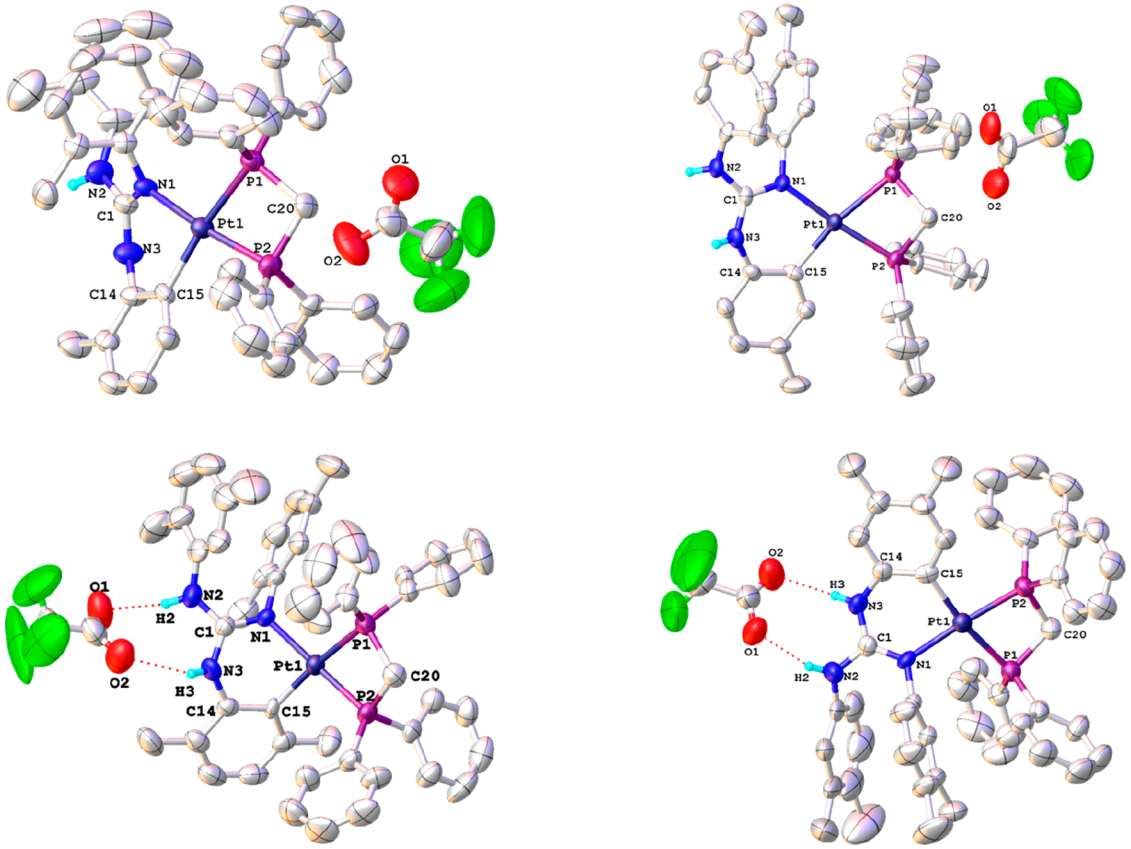

Figure 5. Molecular structures of **11**·$CHCl_3$, **12**·CH_2Cl_2, **14**·1.5C_7H_8, and **15**·CH_2Cl_2. Solvent molecules and all hydrogen atoms except those on the amino nitrogen atoms are removed for clarity.

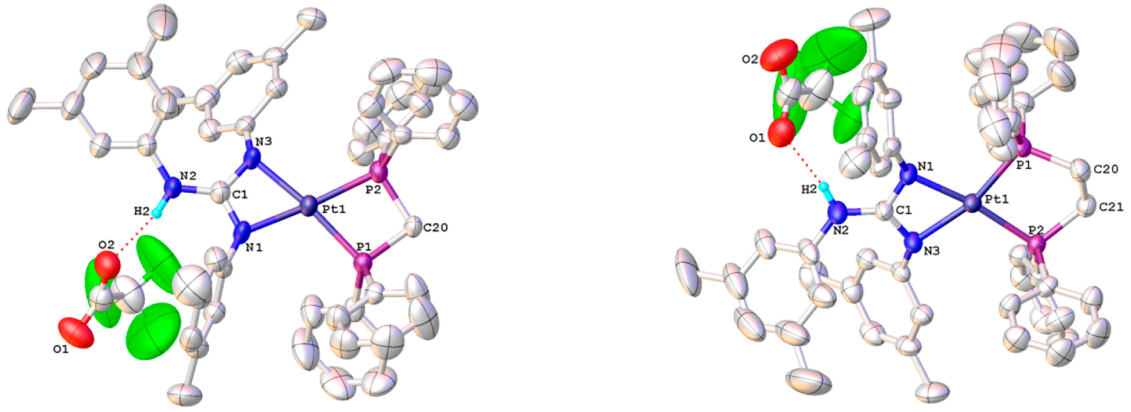

Figure 6. Molecular structures of **16** and **17**. All hydrogen atoms except those on the amino nitrogen atoms are removed for clarity.

of dppp in **19**·$C_4H_{10}O$ (89.78(6)°) and **20**·C_7H_8 (89.76(4)°) as indicted by the P1−Pt1−P2 angles are wider, and hence the N1−Pt1−C15 bond angles, 82.6(2)° (**19**·$C_4H_{10}O$) and 82.0(2)° (**20**·C_7H_8), become smaller; this trend is opposite to the trend observed with solvated **10**−**12**, **14**, and **15**. As the P1−Pt1−P2 angle increases in the sequence **10**·$CHCl_3$, **11**·$CHCl_3$, **12**·CH_2Cl_2, **14**·1.5 C_7H_8, **15**·CH_2Cl_2 > **18**·0.5 C_7H_8 > **19**·$C_4H_{10}O$ and **20**·C_7H_8, the P2−Pt1−C15 and P1−Pt1−N1 angles decrease due to an increase in steric factors imparted by the Ph substituents of bisphosphines.[17b]

The six-membered [Pt{κ^2(*C*,*N*)}] ring in the platinacycles revealed a pseudoboat conformation with the Pt1 atom and an endocyclic N3 atom occupying the flagpole positions while the remaining C1, N1, C14, and C15 atoms occupy the basal plane, as shown in Table 3. The Pt1 atom revealed a distorted-square-planar geometry, as reflected in the value of θ_1. The magnitude of distortion, θ_1, is largely influenced by the degree of steric factors associated with the Ar substituent of the ═NAr unit. The folding along the N1···C15 vector of the six-membered [Pt{κ^2(*C*,*N*)}] ring, denoted θ_2, decreases in the following order. **14**·1.5C_7H_8 ≫ **11**·$CHCl_3$ > **15**·CH_2Cl_2 > **10**·$CHCl_3$ ≈ **12**·CH_2Cl_2. The greater folding of the six-membered [Pt{κ^2(*C*,*N*)}] ring in **14**·1.5C_7H_8 in comparison to that in **11**·$CHCl_3$ clearly suggests a significant role of the protruding Me substituent present adjacent to the Pt−C bond in the former complex. The role of steric factor associated with the ═NAr unit in **10**·$CHCl_3$ and the presence of a pair of inter- and intramolecular N−H···O hydrogen bonds in **12**·CH_2Cl_2 and

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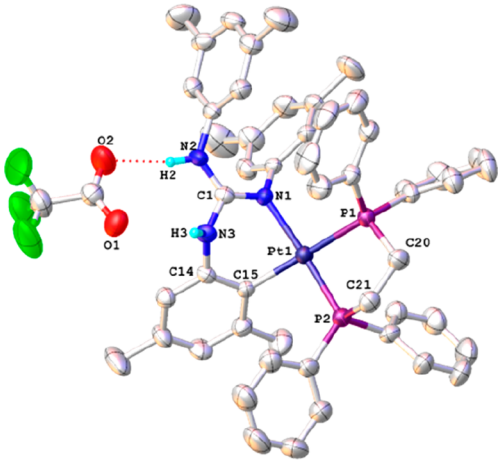


Figure 7. Molecular structure of **18**·0.5C_7H_8. Solent molecules and all hydrogen atoms except those on the amino nitrogen atoms are removed for clarity.

15·CH_2Cl_2, respectively, can be invoked together to explain the trend associated with θ_2 in these platinacycles. The greater folding of the six-membered [Pt{κ^2(*C*,*N*)}] ring along the N1···C15 vector in **18**·0.5C_7H_8, **19**·$C_4H_{10}O$, and **20**·C_7H_8 in comparison to that in the remaining cationic platinacycles can be correlated to the greater degree of steric pressure exerted by Ph substituents of dppe and dppp in the former complexes upon the six-membered [Pt{κ^2(*C*,*N*)}] ring in comparison to the Ph substituents of dppm in the latter complexes.[17b]

The degree of folding of the four-membered [Pt{κ^2(*P*,*P*)}] ring along the P···P vector was reflected in the value of θ_3, which is greater for **10**·$CHCl_3$ and **12**·CH_2Cl_2 than for of **11**·$CHCl_3$, **14**·1.5C_7H_8, and **15**·CH_2Cl_2. This trend is somewhat inversely related to the trend observed with θ_2, with the exception being **14**·1.5C_7H_8. Thus, a subtle balance is observed between folding along the N1···C15 vector of the six-membered [Pt{κ^2(*C*,*N*)}] ring and the P···P vector of the four-membered [Pt{κ^2(*P*,*P*)}] ring to maintain the distorted-square-planar geometry of the Pt(II) atom. In the case of **19**·$C_4H_{10}O$ and **20**·C_7H_8, the six-membered [Pt{κ^2(dppp)}] ring exhibits a chair conformation with the Pt1 and C21 atoms occupying the tip and bottom of the chair while P1, P2, C20, and C22 occupy the basal plane.

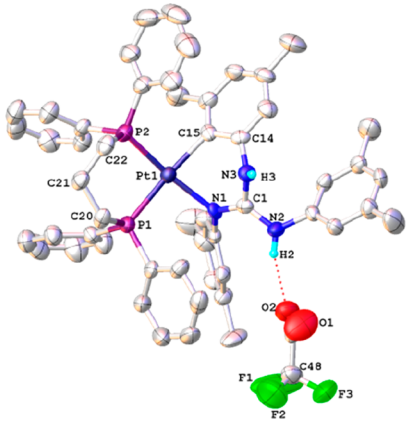
Table 1. Selected Bond Distances (Å) in [Pt{κ^2(*C*,*N*)}{κ^2(*P*,*P*)}][X]

	Pt1−N1	Pt1−C15	Pt1−P1	Pt1−P2
10·$CHCl_3$	2.076(7)	2.042(7)	2.370(2)	2.244(2)
11·$CHCl_3$	2.091(7)	2.041(9)	2.370(2)	2.243(2)
12·CH_2Cl_2	2.088(9)	2.045(12)	2.355(4)	2.243(4)
14·1.5C_7H_8	2.080(7)	2.060(9)	2.330(3)	2.249(2)
15·CH_2Cl_2	2.080(8)	2.033(9)	2.336(3)	2.249(2)
18·0.5C_7H_8	2.095(3)	2.065(4)	2.320(1)	2.228(1)
19·$C_4H_{10}O$	2.099(5)	2.069(6)	2.328(2)	2.235(2)
20·C_7H_8	2.090(5)	2.063(4)	2.334(1)	2.244(1)

The overlap of the lone pair of the amino N atoms with the C═N π^* orbitals of the CN_3 unit in the guanidinate(1−) ligand in the six-membered [M{κ^2(*C*,*N*)}] (M = Pd, Pt) unit of pallada- and platinacycles is known as n−π conjugation, and this stabilizing effect can be quantified from the ρ value.[33] A ρ value of 1.0 indicates a maximum n−π conjugation and a ρ value of 0.0 indicates a no n−π conjugation. In general, n−π conjugation in six-membered cyclometalated guanidine complexes are greater than that in their respective uncoordinated guanidine ligands.[8,14,16,18] This trend was also observed in the structurally characterized platinacycles [Pt{κ^2(*C*,*N*)}{κ^2(*P*,*P*)}][X] reported in the present investigation (see the Supporting Information for ρ value of platinacycles and the respective guanidine ligands).

The Pt(II) atom is simultaneously chelated by the guanidinate(1−) ligand in a κ^2(*N*,*N*) coordination mode on one side and dppm (**16**) or dppe (**17**) in a κ^2(*P*,*P*) coordination mode on the opposite side and thus becomes a part of the four-membered [Pt{κ^2(*N*,*N*)}] ring and the four-membered [Pt{κ^2(dppm)}] ring in **16**, while in **17**, the Pt(II) atom is part of the four-membered [Pt{κ^2(*N*,*N*)}] ring and the five-membered [Pt{κ^2(dppe)}] ring. In both **16** and **17**, the Pt(II) atom revealed a distorted-square-planar geometry, as reflected in the θ_1 value (see Table 5). The N−Pt−P bond angles in **16** (111.0(1) and 112.5(1)°) are greater than the corresponding angles in **17** (102.54(9) and 109.36(9)°), as the bite angle of dppm (72.82(5)°) in the former complex is smaller than the bite angle of dppe (84.85(4)°) in the latter.

We have shown that for [(η^6-*p*-cymene)Ru(PTA)(κ^2(*N*,*N*′)-{$(ArN)_2CN(H)Ar$}][OTf] (Ar = 2-MeC_6H_4; PTA = 1,3,5-triaza-7-phosphaadamantane) the lone pair on the N atoms of



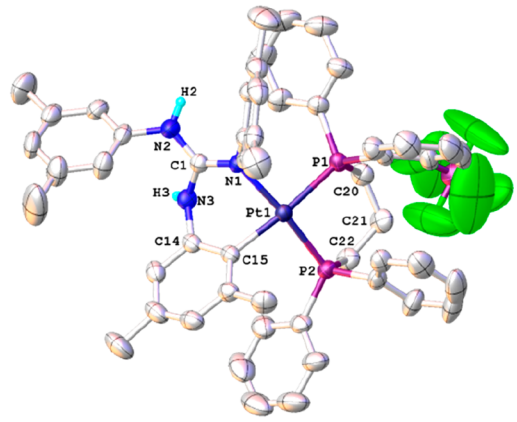


Figure 8. Molecular structures of **19**·$C_4H_{10}O$ and **20**·C_7H_8. Solvent molecules and all hydrogen atoms except those on the amino nitrogen atoms are removed for clarity.

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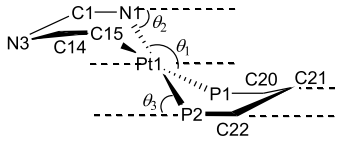
Table 2. Selected Bond Angles (deg) in $[Pt\{\kappa^2(C,N)\}\{\kappa^2(P,P)\}][X]$

	N1−Pt1−C15	P2−Pt1−C15	P1−Pt1−P2	P1−Pt1−N1	P1−Pt1−C15	N1−Pt1−P2
10·$CHCl_3$	89.4(3)	97.9(2)	70.84(7)	102.0(2)	167.7(2)	172.7(2)
11·$CHCl_3$	87.6(3)	96.8(3)	73.16(9)	102.9(2)	168.7(3)	173.1(2)
12·CH_2Cl_2	88.7(4)	97.1(4)	71.6(1)	102.7(3)	168.4(3)	173.3(3)
14·1.5C_7H_8	84.4(3)	100.0(2)	73.24(9)	101.7(2)	171.5(2)	171.7(2)
15·CH_2Cl_2	87.1(3)	98.0(3)	73.11(9)	101.8(2)	171.1(3)	174.3(2)
18·0.5C_7H_8	83.8(1)	94.7(1)	83.94(4)	96.49(9)	172.4(1)	172.05(9)
19·$C_4H_{10}O$	82.6(2)	92.7(2)	89.78(6)	94.2(1)	174.1(2)	170.5(1)
20·C_7H_8	82.0(2)	93.4(1)	89.76(4)	94.2(1)	172.8(1)	173.2(1)

Table 3. Key Structural Parameters Illustrating the Distortion of the $[Pt\{\kappa^2(C,N)\}]$ Ring and the Pt(II) Atom in $[Pt\{\kappa^2(C,N)\}\{\kappa^2(P,P)\}][X]$



	θ_1 (deg)[a]	θ_2 (deg)[b]	θ_3 (deg)[c]
10·$CHCl_3$	5.3(36)	21.72(47)	31.86(34)
11·$CHCl_3$	7.99(30)	26.46(46)	14.31(32)
12·CH_2Cl_2	4.39(26)	21.67(31)	28.60(74)
14·1.5C_7H_8	8.10(43)	42.21(44)	13.65(71)
15·CH_2Cl_2	2.59(18)	23.79(20)	15.00(57)
18·0.5C_7H_8	10.38(18)	44.64(16)	27.36(16)
19·$C_4H_{10}O$	9.64(32)	48.90(29)	42.05(12)
20·C_7H_8	7.92(26)	46.64(23)	43.50(11)

[a]θ_1 is the angle between the mean plane defined by the N1Pt1C15 and P1Pt1P2 planes. [b]θ_2 is the angle between the mean plane defined by the N1Pt1C15 and N1C1C14C15 planes. [c]θ_3 is the angle between the mean plane defined by the P1C20P2 and P1Pt1P2 planes (**10**·$CHCl_3$, **11**·$CHCl_3$, **12**·CH_2Cl_2, **14**·1.5 C_7H_8, **15**·CH_2Cl_2), the angle between the mean plane defined by the P1C20C21P2 and P1Pt1P2 planes (**18**·0.5C_7H_8), and the angle between the mean plane defined by the P1C20C22P2 and P1Pt1P2 planes (**19**·$C_4H_{10}O$ and **20**·C_7H_8).

the CN_3 unit overlaps with the antibonding orbital of the central C atom to different extents, with the order of overlap being N1 (*syn* to H atom of NH(Ar) unit) > N3 (exocyclic N atom of N(H)Ar unit) > N2 (*anti* to H atom of NH(Ar) unit).[34] There was a small but significant overlap of the lone pair on the N3 with the antibonding orbital of the tolyl ring. A perusal of the C−N distances of the CN_3 unit in the guanidinate(1−) ligands of **16** and **17** suggests a bonding pattern analogous to that observed in the aforementioned guanidinatoruthenium(II) complex, although the angle sums around the N1 and N3 atoms differ more widely in **16**. This stereochemical difference arises due to the difference in the bite angle of dppe (84.85(4)°) in **17** with that of dppm (72.82(5)°) in **16**. The H atom of the exocyclic −N(H)Ar unit

Table 5. Key Structural Parameters of the Guanidinate(1−) Ligands in 16 and 17

structural param	16	17
θ_1 (deg)[a]	6.9(3)	7.9(1)
θ_2 (deg)[b]	0.5(8)	3.8(4)
θ_3 (deg)[c]	20.4(7)	13.9(4)
Δ_{CN} (Å)	0.036(5)	0.002(3)
Δ_{CN}' (Å)	0.053(5)	0.009(3)
∑N1 (deg)	343	352
∑N2 (deg)	360	360
∑N3 (deg)	354	349

[a]θ_1 is the angle between the mean plane defined by the N1Pt1N3 and P1Pt1P2 planes. [b]θ_2 is the angle between the mean plane defined by the N1Pt1N3 and N1C1N3 planes. [c]θ_3 is the angle between the mean plane defined by the N1C1N3 and C8N2H2 planes.

in both **16** and **17** is involved in intramolecular N−H···O hydrogen bonding with the $OC(O)CF_3$ anion. Further, the bond parameters associated with the CN_3 unit of the guanidinate(1−) ligand in **16** and **17** closely match with the corresponding bond parameters reported for the guanidinate(1−) ligand in $[Pt\{\kappa^2(N,N)[(PhN)_2C{-}N(H)Ph]\}_2]$ (Δ_{CN} = 0.025(5) Å, Δ_{CN}' = 0.050(5) Å; ∑N = 343, 356, 360°).[35]

Solution Studies. The new complexes were characterized by conductivity measurements and multinuclear (^{31}P, ^{195}Pt, ^{1}H, ^{13}C, and ^{19}F) NMR spectroscopy. The molar conductance (Λ_M) values of cationic platinacycles prepared in the present investigation fall in the range 68.4−116.0 Ω^{-1} cm^2 mol^{-1} (10^{-3} M) anticipated for 1:1 electrolytes reported in the literature.[36] ^{31}P NMR spectra of **10**−**15** revealed a pair of doublets with each doublet flanked by ^{195}Pt satellites assignable to two distinct P nuclei of dppm. The $\delta(^{31}P)$ shifts of **10**−**15** and **18**−**20** are given in Table 6. Platinacycles **10**−**15** revealed one doublet in the range $\delta(^{31}P_N)$ −37.8 to −43.9 ppm ($^1J_{P-Pt}$ = 3388−3448 Hz; $^1J_{P-P}$ = 35−39 Hz) assignable to the P nucleus located *trans* to the N atom of the $[Pt\{\kappa^2(C,N)\}]$ chelate and one doublet in the range $\delta(^{31}P_C)$ −31.9 to −34.0 ppm ($^1J_{P-Pt}$ = 1463−1504 Hz; $^1J_{P-P}$ = 35−43 Hz) assignable to the P nucleus located *trans* to the C atom. The more upfield $\delta(^{31}P_N)$ shift value in comparison to the $\delta(^{31}P_C)$ shift and greater $^1J_{P-Pt}$

Table 4. Selected Bond Distances (Å) and Bond Angles (deg) in 16 and 17

	16	17		16	17
Pt1−N1	2.104(4)	2.107(3)	N1−Pt1−N3	63.9(2)	63.7(1)
Pt1−N3	2.073(4)	2.073(3)	N3−Pt1−P1	175.8(1)	171.4(1)
Pt1−P1	2.242(1)	2.238(1)	P1−Pt1−P2	72.82(5)	84.85(4)
Pt1−P2	2.234(1)	2.226(1)	N1−Pt1−P1	112.5(1)	109.36(9)
			N1−Pt1−P2	172.5(1)	165.23(9)
			N3−Pt1−P2	111.0(1)	102.54(9)

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Table 6. $^{31}P\{^{1}H\}$ (161.8 MHz, $CDCl_3$) NMR Chemical Shifts and Coupling Constants for $[Pt\{\kappa^2(C,N)\}\{\kappa^2(P,P)\}][X]$

	$\delta(^{31}P)$ (ppm)		Δ[a]		$^{1}J_{P-Pt}$ (Hz)		$^{1}J_{P-P}$ (Hz)	
platinacycle	P *trans* to N	P *trans* to C	P *trans* to N	P *trans* to C	P *trans* to N	P *trans* to C	P *trans* to N	P *trans* to C
10	−37.8	−34.0	−14.2	−10.4	3422	1504	39	39
11	−37.9	−33.6	−14.3	−10.0	3433	1463	35	39
12	−37.8	−31.9	−14.2	−8.3	3388	1468	35	35
13	−38.2	−33.6	−14.6	−10.0	3448	1463	37	37
14	−43.9	−32.6	−20.3	−9.0	3409	1463	39	43
15	−38.1	−32.4	−14.5	−8.8	3388	1492	35	35
18	32.4	36.2	44.9	48.7	3784	1872		
19	−4.40	−0.50	12.9	16.8	3675	1696	30	26
20[b]	−0.45	−4.50	16.85	12.8	3698	1714	30	28

[a] $\Delta = \delta(^{31}P)_{complex} - \delta(^{31}P)_{bis(phosphine)}$; $\delta(^{31}P)$ −23.6 ppm (dppm), −12.5 ppm (dppe), and −17.3 ppm (dppp).[37] [b] δ −143.53 (sept, $^{1}J_{P-F}$ = 713 Hz) was also observed for PF_6^-.

value associated with the former P nucleus in the aforementioned complexes are in line with the literature trend reported for the related $[Pt\{\kappa^2(C,N)\}\{\kappa^2(P,P)\}][X]$ type platinacycles.[15b,c,23−27,31,32] This spectral pattern is ascribed to a greater *trans* influence of the platinated carbon in comparison to that of the imine N atom in this type of platinacycles. The slightly greater coordination chemical shift,[37] Δ = −20.3 ppm, observed for the P located *trans* to the N atom in **14** is ascribed to the influence of steric factors imparted by the Me substituent on the carbon atom adjacent to the Pt−C bond in the platinated xylyl ring.

The $\delta(^{31}P)$ shifts and $^{1}J_{P-Pt}$ values observed for **10**−**15** and **18** compare favorably with the $\delta(^{31}P)$ shifts and $^{1}J_{P-Pt}$ values reported for the six-membered cycloplatinated 2-benzylpyridine complex $[Pt\{\kappa^2(C,N)\}\{\kappa^2(dppm)\}][BF_4]$[38] and the six-membered cyloplatinated amine,[27] 6-alkyl-2,2′-bipyridine,[32] benzylpyridine,[38] and pyridylphosphane oxide[39] complexes of the type $[Pt\{\kappa^2(C,N)\}\{\kappa^2(dppe)\}][Cl]$, respectively. Platinacycles **19** and **20** revealed ^{31}P NMR spectral patterns analogous to those revealed by **13**−**15**; however, $\delta(^{31}P)$ shifts are shifted less upfield in the former platinacycles. The trend associated with the coordination chemical shift, Δ for **18** > **19** and **20** > **13**−**15**, parallels that known for *cis*-$M(CO)_4\{\kappa^2(P,P)\}$ ($\kappa^2(P,P)$ = dppm, dppe, dppp; M = Cr, Mo, W).[37] ^{31}P NMR spectra of **16** and **17** revealed a singlet at $\delta(^{31}P)$ −58.6 ppm ($^{1}J_{P-Pt}$ = 2782 Hz) and $\delta(^{31}P)$ 38.2 ppm ($^{1}J_{P-Pt}$ = 3277 Hz), respectively, with both singlets flanked by ^{195}Pt satellite peaks. The coordination chemical shift observed for **17** (Δ = 50.7 ppm) is greater than that of **16** (Δ = −35.0 ppm), as anticipated.[37]

^{195}Pt NMR spectroscopy is a useful technique to probe the environment around the square-planar Pt(II) complexes.[8,14,40−44] $\delta(^{195}Pt)$ values of platinacycles prepared in the present investigation except for the shift of **20** were measured and are given in Table 7. ^{195}Pt NMR spectra of **10**−**15** revealed a doublet of doublets in the range $\delta(^{195}Pt)$ −3755 to −3917 ppm ($^{1}J_{Pt-P}$ = 3400−3448 and 1438−1499 Hz) due to coupling with two distinct P nuclei. The more shielded $\delta(^{195}Pt)$ values observed for **18** and **19** in comparison to those observed for **13**−**15** is in line with the literature trend published for thes types of platinacyles.[23,27,45] Remarkably, the $\delta(^{195}Pt)$ shift observed for **14** is more shielded than the shifts observed for **10**−**13** and **15**, and this spectral feature is ascribed to the more sterically hindered environment around the Pt(II) atom in the former complex (see Table 7). ^{195}Pt NMR spectra of **16** and **17** revealed a triplets at $\delta(^{195}Pt)$ −3716 ppm ($^{1}J_{Pt-P}$ = 2799 Hz) and $\delta(^{195}Pt)$ −4356 ppm ($^{1}J_{Pt-P}$ = 3277 Hz), respectively.

Table 7. δ_{Pt} (85.78 MHz, $CDCl_3$) and $^{1}J_{Pt-P}$ Values for $[Pt\{\kappa^2(C,N)\}\{\kappa^2(P,P)\}][X]$

		$^{1}J_{Pt-P}$ (Hz)[a]	
	$\delta(^{195}Pt)$ (ppm)	P *trans* to N	P *trans* to C
10	−3819	3430	1499
11	−3786	3417	1438
12	−3789	3401	1467
13	−3755	3448	1465
14	−3917	3411	1481
15	−3790	3400	1465
18	−4546	3780	1874
19	−4519	3701	1720

[a] A standard deviation of up to ∼26 Hz was noted in the $^{1}J_{Pt-P}$ values for certain complexes, and this error is acceptable considering the wide range of about 15000 ppm known in ^{195}Pt NMR.[40]

^{31}P NMR Monitoring Experiments. The separate reactions of **9** with dppm and dppe in $CDCl_3$ at RT were monitored with time by ^{31}P NMR spectroscopy in order to investigate the nature of the intermediates formed prior to the formation of **16** and **17**, respectively. The ^{31}P NMR stack plot for the reaction involving **9** and dppm in $CDCl_3$ is illustrated in Figure 9. The ^{31}P NMR spectrum of the reaction mixture recorded immediately after mixing the reactants revealed the formation of a pair of doublets at $\delta(^{31}P_C)$ −31.8 ($^{1}J_{Pt-P}$ = 1440 Hz) and $\delta(^{31}P_N)$ −42.8 ppm ($^{1}J_{Pt-P}$ = 3406 Hz), $^{1}J_{P-P}$ = 39 Hz, as indicated by blue ● and red ● symbols, respectively. We assign these signals to a highly reactive species, **22**, on the basis of a comparison of the aforementioned ^{31}P NMR shifts and coupling constants with those shifts and coupling constants of **13**−**15**. A minor singlet represented with an orange ▼ symbol was also observed at $\delta(^{31}P)$ −58.8 ppm. The intensity of this singlet and the associated ^{195}Pt satellites ($^{1}J_{Pt-P}$ = 2783 Hz) grew after 2 h, and this signal was thus assigned to the P nucleus of dppm in **16**. The ^{31}P NMR spectrum of the reaction mixture recorded after 6 h revealed the complete disappearance of signals attributed to **22** and the presence of the signals exclusively attributable to **16**.

The reaction of **9** with dppe in $CDCl_3$ was much slower, as revealed by the ^{31}P NMR stack plot illustrated in Figure 10, possibly due to the greater bite angle of dppe (β = 85°) in comparison to that of dppm (β = 72°).[17] The ^{31}P NMR spectrum of the reaction mixture containing **9** and dppe in $CDCl_3$ recorded after 6 h revealed the formation of **18**

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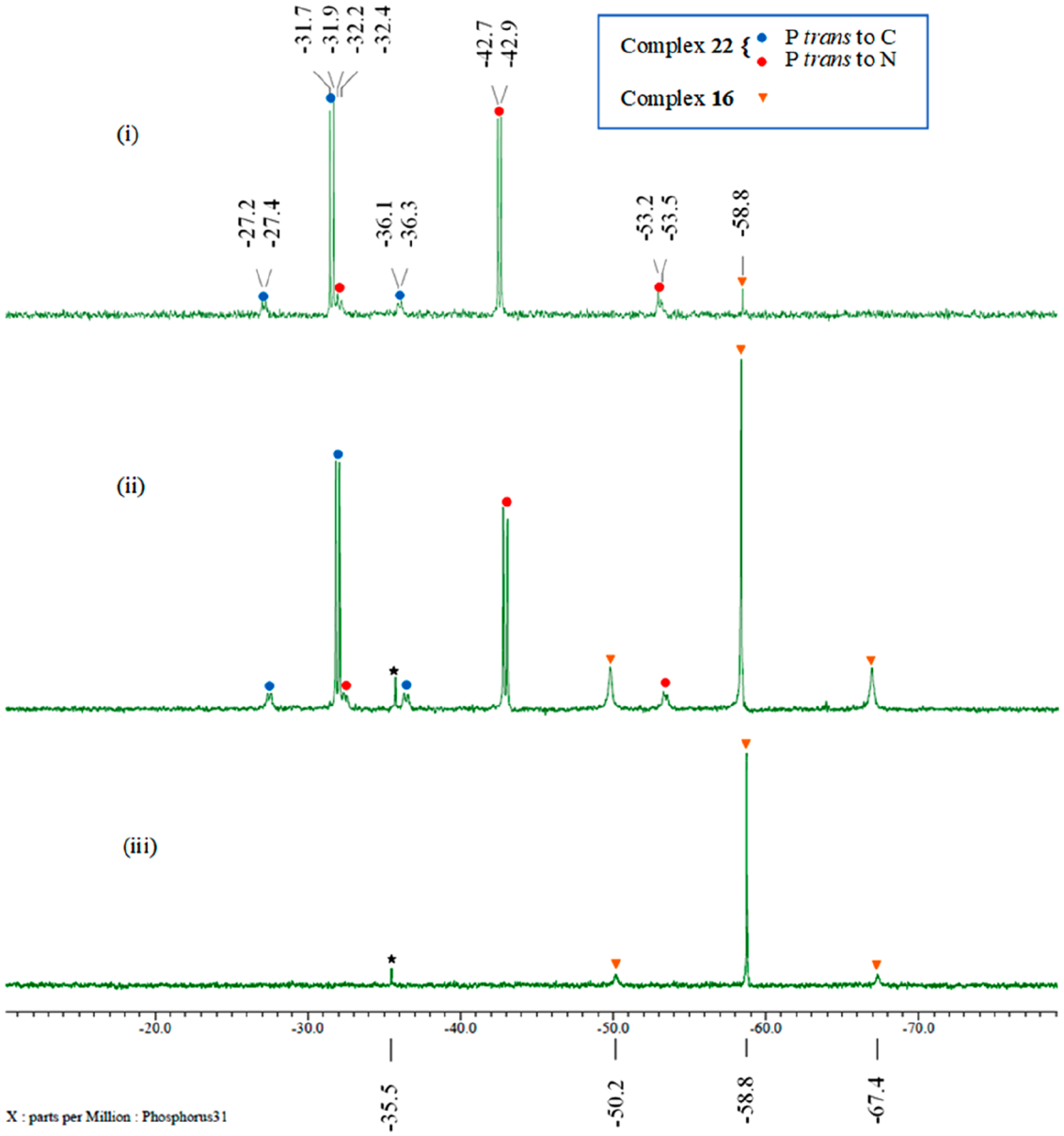

Figure 9. VT $^{31}P\{^{1}H\}$ (161.8 MHz, $CDCl_3$) NMR spectra of an equimolar mixture of **9** and dppm measured (i) immediately, (ii) after 2 h, and (iii) after 6 h. The blue ● and red ● symbols represent signals of two distinct P nuclei of **22**. The asterisks represent the signal of an as yet unidentified species.

exclusively, as indicated by blue ● and red ● symbols, and after 12 h the intensity of ^{31}P NMR signals of **18** decreases with the concomitant growth of ^{31}P NMR signals of **17**, as indicated by an orange ▼ symbol, with the major species being the former complex. The intensity of ^{31}P NMR signals of **17** grew gradually at the expense of ^{31}P NMR signals of **18** after 12 and 18 h. The ^{31}P NMR signals of **18** completely disappeared, and those of **17** appeared exclusively after 24 h. Thus, the variable-time (VT) ^{31}P NMR studies discussed above point out that **22** and **18** are some of the possible intermediates formed transiently before the final products **16** and **17**, respectively, are formed.

DFT Studies on the Transformation of [Pt{κ^2(*C*,*N*)}{κ^2(*P*,*P*)}][OC(O)CF_3] to [Pt{κ^2(*N*,*N*)}{κ^2(*P*,*P*)}][OC(O)CF_3]. DFT calculations were carried out on the model complexes **22′** and **16′** and the possible intermediates formed between these two model complexes to illuminate the driving force responsible for the conversions of **22** to **16** and of **18** to **17** discussed in the previous sections. In the proposed mechanism illustrated in Scheme 6, the guanidinate(1−) ligand in **22′** undergoes amine−imine tautomerism to afford **D**, and this transformation was calculated to be endergonic in nature by 15.3 kcal/mol. The conversion of **D** to **E** proceeds by the deprotonation of the coordinated amine by the weakly basic trifluoroacetate anion, and this step was calculated to be slightly exergonic in nature by 0.9 kcal/mol; thus, this step can be considered almost thermoneutral. We have recently shown that the guanidinate(2−) ligand with the anionic charges residing on the N and the C atoms such as that found in **E** in the coordination sphere of Pt(II) could be isolated and structurally characterized.[44] Further, the trifluoroacetic acid released during the formation of **E** protonates the platinated carbon atom of the guanidinate(1−) ligand to afford the Wheland intermediate **F**. The formation of **F** was calculated to

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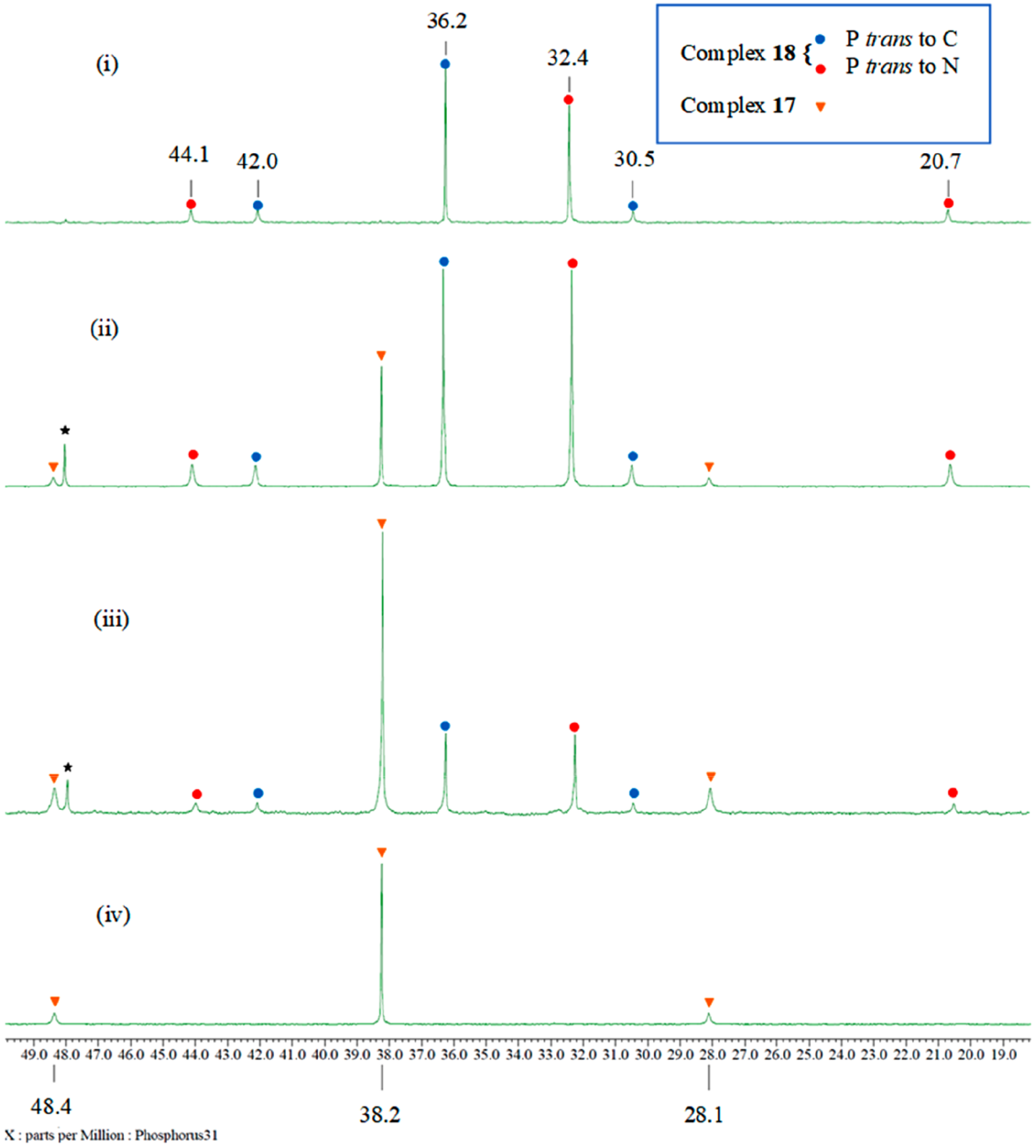

Figure 10. VT $^{31}P\{^{1}H\}$ (161.8 MHz, $CDCl_3$) NMR spectra of an equimolar mixture of **9** and dppe measured after (i) 6 h, (ii) 12 h, (iii) 18 h, and (iv) 24 h. Asterisks represent the signal of an as yet unidentified species.

be slightly endergonic in nature by 3.0 kcal/mol. In other words, the intermediate **E** is said to be in a rapid equilibrium with **D** on one side and **F** on the other side in solution at any moment. Finally, the Wheland intermediate **F** converts into **16′**, and this transformation was calculated to be exergonic by 15.3 kcal/mol.

Protonation of the Pt−C bond in organoplatinum complexes and mechanistic aspects pertinent to this subject has been extensively discussed in the literature. Protonation of the Pt−C bond in organoplatinum complexes can occur via (i) a concerted S_E2 pathway and (ii) stepwise oxidative addition to the Pt(II) atom followed by reductive elimination, an S_Eox pathway.[26,46−50] Thus, the protonation of the intermediate **E** with trifluoroacetic acid can occur via oxidative addition to afford the cationic Pt^{IV}-hydride species **G**, and this transformation was calculated to be more exergonic in nature by 63.8 kcal/mol; nevertheless, the formation of **16′** from **G** via **H** is not feasible (see Scheme 7). Probably, the Pt(II) atom in the model complex **22′** is much less crowded than that in **22** and thus protonation of the former complex becomes easier and as a result this step is more exergonic in our calculations. Thus, the formation of **16′** from the cationic Pt^{IV}-hydride species **G** via the agostic species **H** is not feasible due to over-simplification of steric factors in the models **22′**, **D**, and **E**. The facile protonation of the platinated C atom in the intermediate **E** by trifluoroacetic acid to afford **F** is likely due to the transphobia effect,[29] as both the platinated C atom and the P atom which is located *trans* to the platinated C atom are soft in nature. Thus, the platinated C atom could be nucleophilic enough for fast protonation and as a result the formation of **16′** is controlled by kinetics. The fact that we were able to isolate both **16** and **17** only when the platinated aryl ring in their respective precursors contains Me substituents in 4,6-positions and not in 3,5-, 3,6-, and 4,5-positions suggests

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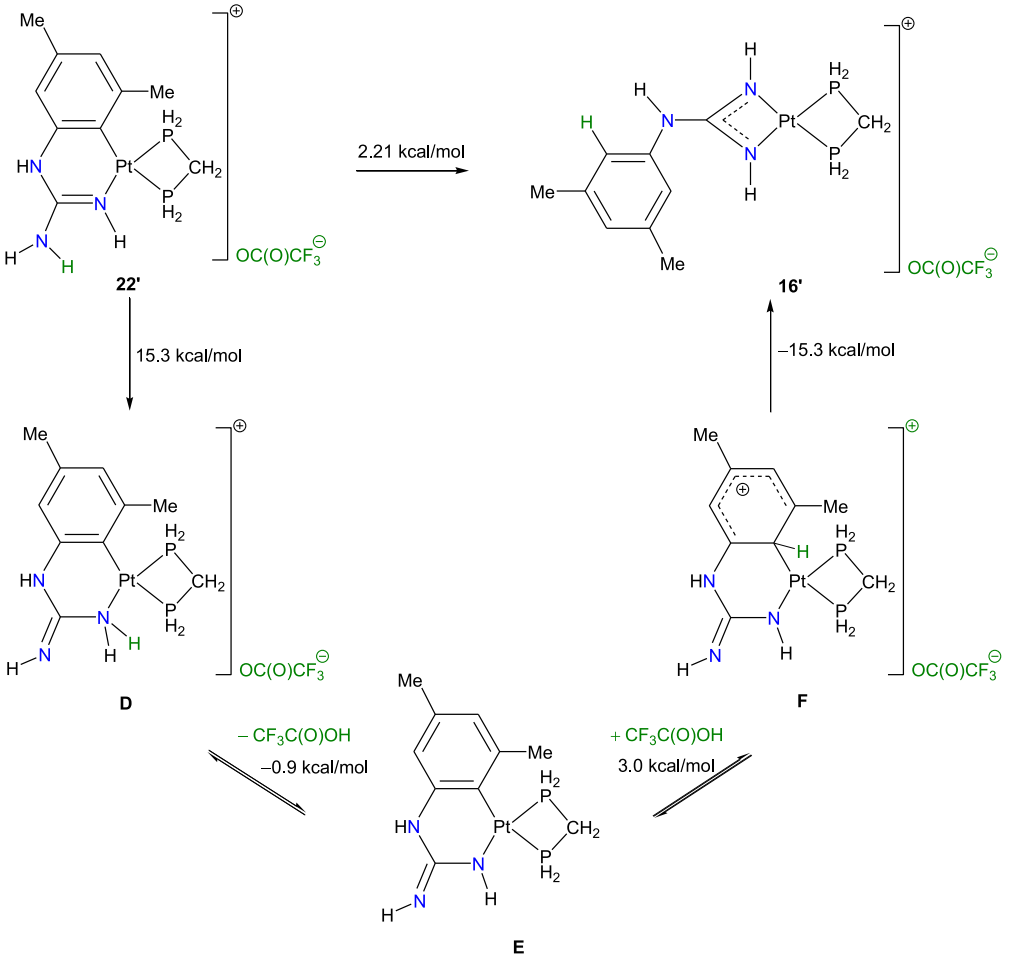
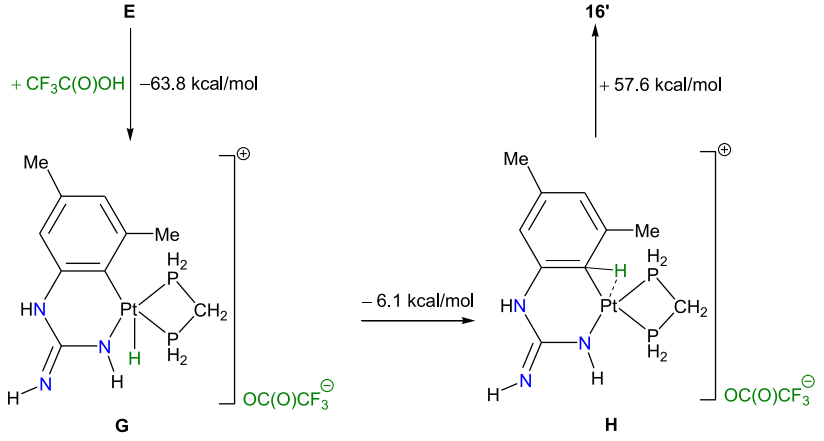
Scheme 6. DFT Studied Transformation of 22′ to 16′ via the Wheland Intermediate F



Scheme 7. DFT Studied Transformation of 22′ to 16′ via the Pt^{IV}-Hydride Species G



the pathway illustrated in Scheme 6 (see Figure 1). The formations of a Wheland intermediate such as **F** and an agostic complex such as **H** have been invoked as intermediates in the protonation of organoplatinum(II) phosphine complexes.[49,51]

CONCLUSION

Two types of cationic guanidinatoplatinum(II) complexes, namely $[Pt\{\kappa^2(C,N)\}\{\kappa^2(P,P)\}][X]$ and $[Pt\{\kappa^2(N,N)\}\{\kappa^2(P,P)\}][X]$, were isolated in high yields and fully characterized by analytical, IR, and multinuclear NMR spectroscopic techniques and conductivity measurements. The molecular structures of representative complexes from both types of complexes were determined by single-crystal X-ray diffraction (SCXRD). The structural or linkage isomers **17** and **18** are stable enough for isolation and complete characterization by analytical, spectral, and SCXRD studies, while **22** was only formed transiently in solution, as inferred from VT ^{31}P NMR spectroscopy, before forming the stable and crystallographically characterized complex **16**. We have identified three factors responsible for the **22** to **16** and **18**

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to **17** transformations: namely, steric factors imparted by a Me substituent *ortho* to the Pt−C bond, electronic factors imparted by a Me substituent *para* to the Pt−C bond to labilize the Pt−C bond in the six-membered [Pt{κ^2(*C*,*N*)}] ring of respective Pt(II) substrates, and a greater level of ground-state destabilization of **22** in comparison to that of **18** due to the greater steric nature of dppm in the former complex in comparison to that of dppe in the latter. The transformation of **22′** to **16′** was investigated through DFT calculations, which point out the possibility of the formation of the Wheland intermediate **F**, rather than the frequently reported Pt^{IV}−H intermediate, as one of the key intermediates.

EXPERIMENTAL SECTION

[Pt{κ^2(*C*,*N*)-$C_6H_2Me_2$-4,5-(NHC(NHAr)(=NAr))-2}(OC(O)CF_3)(S(O)Me_2)] (Ar = 3,4-$Me_2C_6H_3$; 8). *cis*-[Pt(OC(O)CF_3)$_2$(S(O)Me_2)$_2$] (50.6 mg, 0.087 mmol) and $LH_2^{3,4\text{-xylyl}}$ (32.5 mg, 0.087 mmol) were placed in a 25 mL round-bottom (RB) flask and dispersed in toluene (10 mL). The RB flask was fitted with a double surface condenser capped with a freshly prepared anhydrous $CaCl_2$ guard tube and the reaction mixture refluxed for 8 h and filtered. The volume of the filtrate was reduced to about one-third of its original volume and stored at RT for 2 days to afford **8** as colorless crystals. Yield: 64% (42.8 mg, 0.056 mmol). Mp: 207.6 °C. ATR-IR (cm^{-1}): ν(N−H) 3366 (m); ν_a(OCO) 1672 (s); ν(C=N) 1640 (m); ν_s(OCO) 1317 (m); ν(S=O) 1138 (s). Anal. Calcd for $PtC_{29}H_{34}O_3N_3F_3S$ (M_w: 756.7482 g/mol): C, 46.03; H, 4.53; N, 5.55; S, 4.24. Found: C, 45.83; H, 4.34; N, 5.42; S, 4.20. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.17 (s, 3 H, CH_3), 2.23 (br, s, 2 × 3 H, CH_3), 2.24, 2.27, 2.29 (each s, 3 × 3 H, CH_3), 3.14 (s, 2 × 3 H, $(CH_3)_2S(O)$), 6.25, 6.50 (each s, 2 × 1 H, NH), 6.55 (s, 1 H, Ar*H*), 6.82 (d, J_{HH} = 8.0 Hz, 1 H, Ar*H*), 6.86 (s, 1 H, Ar*H*), 6.94 (d, J_{HH} = 7.6 Hz, 1 H, Ar*H*), 6.99 (s, 1 H, Ar*H*), 7.12 (d, J_{HH} = 8.0 Hz, 1 H, Ar*H*), 7.19 (d, J_{HH} = 8.0 Hz, 1 H, Ar*H*), 7.72 (s, J_{Pt-H} = 30.8 Hz, 1 H, Ar*H*). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.5 MHz): δ 19.23, 19.31, 19.36, 19.49, 19.88, 19.90 (CH_3), 45.58 ($(CH_3)_2S(O)$), 105.01 (ArCH/ArC), 117.02 (q, $^1J_{C-F}$ = 292.8 Hz, CF_3), 115.97, 123.36, 124.38, 127.26, 128.00, 130.93, 131.38, 131.90, 133.08, 133.64, 135.40, 135.70, 136.75, 138.34, 139.19, 140.37 (ArCH/ArC), 148.67 (CN_3), 161.56 (q, $^2J_{C-F}$ = 35.6 Hz, OC(O)). ^{19}F{^{1}H} NMR ($CDCl_3$, 376.31 MHz): δ −74.9. ^{195}Pt{^{1}H} NMR ($CDCl_3$, 85.78 MHz): δ −3664. ESI mass *m*/*z* [ion]: 643.2100 [M − OC(O)CF_3]$^+$.

[Pt{κ^2(*C*,*N*)-C_6H_3(OMe)-3-(NHC(NHAr)(=NAr))-2}(κ^2(*P*,*P*)-dppm)]Cl (Ar = 2-(MeO)C_6H_4; 10). Platinacycle **3** (50.3 mg, 0.073 mmol) and dppm (28.2 mg, 0.073 mmol) were dispersed in freshly distilled CH_2Cl_2 (15 mL) in a 25 mL RB flask, and the flask was capped with a freshly prepared anhydrous $CaCl_2$ guard tube. The contents in the flask were stirred at RT for 24 h and the volatiles removed under reduced pressure to afford a light yellow sticky solid. The solid was triturated with diethyl ether (10 mL) to afford a free-flowing pale yellow solid. The solid was dissolved in $CHCl_3$ (2 mL), layered with toluene (2 mL), and stored at RT for about 5 days to afford **10**·$CHCl_3$ as light yellow crystals suitable for SCXRD. Yield: 93% (68.4 mg, 0.068 mmol). Mp: 162.2 °C. Anal. Calcd for $PtC_{47}H_{44}O_3P_2N_3Cl\cdot 1/3CHCl_3$ (M_w 991.3685 + 39.392 g/mol): C, 55.15; H, 4.34; N, 4.08. Found: C, 55.32; H, 4.62; N, 4.19. ATR-IR (cm^{-1}): ν(N−H) 3368 (m), ν(C=N) 1607 (m), ν(P−C_6H_5) 1101 (m). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.52, 3.75, 3.81 (each s, 3 × 3 H, OCH_3), 4.00−4.09 (m, 1 H, CH_2, dppm), 4.23−4.32 (m, 1 H, CH_2, dppm), 6.40 (d, J_{HH} = 8.4 Hz, 1 H, Ar*H*), 6.48−6.53 (m, 2 H, Ar*H*), 6.64−6.66 (m, 2 H, Ar*H* (1 H), N*H* (1 H)), 6.72 (t, J_{HH} = 8.0 Hz, 1 H, Ar*H*), 6.86−6.91 (m, 1 H, Ar*H*), 6.94−7.01 (m, 3 H, Ar*H*), 7.14−7.17 (m, 1 H, Ar*H*), 7.20 (d, J_{HH} = 6.4 Hz, 1 H, Ar*H*), 7.28−7.36 (m, 5 H, P(C_6H_5)$_2$), 7.42−7.43 (m, 4 H, P(C_6H_5)$_2$), 7.49−7.62 (m, 9 H, P(C_6H_5)$_2$), 7.81−7.86 (m, 2 H, P(C_6H_5)$_2$), 8.48 (s, 1 H, N*H*). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.5 MHz): δ 47.67 (dd, $^1J_{C-P}$ = 26.9 and 27.9 Hz, CH_2, dppm), 55.18, 55.77, 56.03 (OCH_3), 107.71, 111.37, 111.81, 120.91, 121.15, 122.97, 123.04, 123.10, 123.64, 124.92 (d, $^1J_{C-P}$ = 3.9 Hz, P(C_6H_5)$_2$, *ipso*-*C*), 125.17, 125.49 (d, $^1J_{C-P}$ = 4.7 Hz, P(C_6H_5)$_2$, *ipso*-*C*), 125.71, 126.23 (d, $^1J_{C-P}$ = 4.8 Hz, P(C_6H_5)$_2$, *ipso*-*C*), 126.61, 127.05, 127.29, 127.42, 128.40, 128.50, 128.55, 128.66, 129.03, 129.16, 129.28, 129.49, 129.61, 130.25, 130.96, 131.01, 131.05, 131.42, 131.85, 132.00, 132.26, 132.59, 132.80, 132.92, 133.45, 133.50, 133.56, 133.61, 133.70, 133.88, 134.01, 137.24, 137.29, 145.59, 146.87, 146.95, 151.51 (ArCH/ArC), 151.92 (CN_3). ESI mass *m*/*z* [ion]: 955.2504 [M − Cl]$^+$. Λ_M (Ω^{-1} cm^2 mol^{-1}, MeCN) = 74.7 (10^{-3} M).

[Pt{κ^2(*C*,*N*)-C_6H_3Me-3-(NHC(NHAr)(=NAr))-2}(κ^2(*P*,*P*)-dppm)][OC(O)CF_3] (Ar = 2-MeC_6H_4; 11). Platinacycle **11** was prepared from platinacycle **4** (40.0 mg, 0.056 mmol) and dppm (21.7 mg, 0.056 mmol) in freshly distilled CH_2Cl_2 (15 mL) and purified as described previously for platinacycle **10**. The solid obtained from the reaction mixture was dissolved in $CHCl_3$ (2 mL), layered with toluene (2 mL), and stored at RT for 4 days to afford **11**·$CHCl_3$ as transparent colorless crystals suitable for SCXRD. Yield: 95% (54.9 mg, 0.053 mmol). Mp: 208.4 °C. Anal. Calcd for $PtC_{49}H_{44}O_2P_2N_3F_3\cdot 1/5CHCl_3$ (M_w 1020.9367 + 23.8738 g/mol): C, 56.56; H, 4.26; N, 4.02. Found: C, 56.77; H, 4.49; N, 4.14. ATR-IR (cm^{-1}): ν(N−H) 3402 (w), ν_a(OCO) 1686 (s), ν(C=N) 1616 (m), ν_s(OCO) 1331(m), ν(P−C_6H_5) 1103 (s). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.95, 2.00, 2.18 (each s, 3 × 3 H, CH_3), 3.96−4.05 (m, 1 H, CH_2, dppm), 4.15−4.24 (m, 1 H, CH_2, dppm), 6.39 (t, J_{HH} = 7.4 Hz, 1 H, Ar*H*), 6.43−6.45 (m, 1 H, Ar*H*), 6.52 (t, J_{HH} = 7.4 Hz, 1 H, Ar*H*), 6.67 (t, J_{HH} = 7.4 Hz, 1 H, Ar*H*), 6.85−6.91 (m, 3 H, Ar*H*), 7.02−7.06 (m, 1 H, Ar*H*), 7.08−7.14 (m, 3 H, Ar*H* (2 H), N*H* (1 H)), 7.21 (t, J_{HH} = 7.8 Hz, 1 H, Ar*H*), 7.36−7.47 (m, 7 H, P(C_6H_5)$_2$), 7.52−7.59 (m, 8 H, P(C_6H_5)$_2$), 7.63−7.71 (m, 5 H, P(C_6H_5)$_2$), 7.95 (s, 1 H, N*H*). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.5 MHz): δ 17.68 18.01, 18.49 (CH_3), 47.31 (dd, $^1J_{C-P}$ = 27.0 and 28.0 Hz, CH_2, dppm), 117.46 (q, $^1J_{C-F}$ = 296.6 Hz, CF_3), 122.84, 122.90, 122.96, 123.61, 123.67 (ArCH/ArC), 124.98 (d, $^1J_{C-P}$ = 6.7 Hz, P(C_6H_5)$_2$, *ipso*-*C*, dppm), 125.53 (d, $^1J_{C-P}$ = 6.7 Hz, P(C_6H_5)$_2$, *ipso*-*C*, dppm), 125.74, 126.02, 126.41, 126.55, 126.90, 127.56, 128.34, 128.50, 128.69, 129.01, 129.11, 129.18, 129.29, 129.43, 129.54, 130.47, 131.39, 131.45, 131.57, 132.16, 132.25, 132.45, 132.84, 132.96, 133.49, 133.55, 133.62, 133.71, 134.78, 135.90, 136.07, 139.96, 140.11, 148.17, 148.23 (ArCH/ArC), 148.28 (CN_3), 161.26 (q, $^2J_{C-F}$ = 32.8 Hz, OC(O)). ^{19}F{^{1}H} NMR ($CDCl_3$, 376.31 MHz): δ −74.8. ESI mass *m*/*z* [ion]: 907.2687 [M − OC(O)CF_3]$^+$. Λ_M (Ω^{-1} cm^2 mol^{-1}, MeCN) = 103.7 (10^{-3} M).

[Pt{κ^2(*C*,*N*)-C_6H_3Me-5-(NHC(NHAr)(=NAr))-2}(κ^2(*P*,*P*)-dppm)][OC(O)CF_3] (Ar = 4-MeC_6H_4; 12). Platinacycle **12** was prepared from platinacycle **5** (50.0 mg, 0.070 mmol) and dppm (26.9 mg, 0.070 mmol) in CH_2Cl_2 (15 mL) and purified as described previously for platinacycle **10**. The solid obtained from the reaction mixture was dissolved in CH_2Cl_2 (2 mL), layered with toluene (2 mL) and stored at RT for about 3 days to afford **12**·CH_2Cl_2 as colorless transparent crystals suitable for SCXRD. Yield: 90% (65.1 mg, 0.063 mmol). Mp: 234.9 °C. Anal. Calcd for $PtC_{49}H_{44}O_2P_2N_3F_3\cdot 0.20\ CH_2Cl_2$ (M_w 1020.9367 + 23.8738 g/mol): C, 56.94; H, 4.31; N, 4.05. Found: C, 57.01; H, 4.48; N, 4.02. ATR-IR (cm^{-1}): ν(N−H) 3051 (w), ν_a(OCO) 1672 (s), ν(C=N) 1638 (m), ν_s(OCO) 1354 (m), ν(P−C_6H_5) 1101 (s). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.76, 2.03, 2.20, (each s, 3 × 3 H, CH_3), 4.11 (t, $^2J_{PH}$ = 9.8 Hz, 2 H, CH_2, dppm) 6.47−6.51 (m, 4 H, Ar*H*), 6.76−6.78 (m, 2 H, Ar*H*), 6.83−6.85 (m, 3 H, Ar*H*), 6.91−6.94 (m, 1 H, Ar*H*), 7.01−7.04 (m, 1 H, Ar*H*), 7.32−7.41 (m, 12 H, P(C_6H_5)$_2$), 7.48−7.58 (m, 8 H, P(C_6H_5)$_2$), 8.03, 9.47 (each s, 2 × 1 H, N*H*). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.5 MHz): δ 20.24, 20.77, 20.99, (CH_3), 47.47 (dd, $^1J_{C-P}$ = 34.7 and 35.7 Hz, CH_2, dppm), 117.37 (q, $^1J_{C-F}$ = 295.0 Hz, CF_3), 116.93, 116.98, 124.24, 124.58, 124.80, 124.99 (ArCH/ArC), 125.57 (d, $^1J_{C-P}$ = 5.8 Hz, P(C_6H_5)$_2$, *ipso*-*C*, dppm), 126.12 (d, $^1J_{C-P}$ = 4.8 Hz, P(C_6H_5)$_2$, *ipso*-*C*, dppm), 126.29, 126.46, 126.87, 127.54 (ArCH/ArC), 127.80 (d, $^1J_{C-P}$ = 4.8 Hz, P(C_6H_5)$_2$, *ipso*-*C*, dppm), 128.17 (d, $^1J_{C-P}$ = 4.8 Hz, P(C_6H_5)$_2$, *ipso*-*C*, dppm), 128.50, 128.75, 129.01, 129.13, 129.23, 129.31, 129.36, 129.48, 129.87, 130.16, 131.71, 132.26, 133.07, 133.12, 133.18, 133.44, 133.52, 133.56, 133.63, 135.42, 135.46, 135.58, 136.16, 141.33, 141.47, 147.86, 147.91

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(ArCH/ArC), 149.27 (CN_3), 161.77 (q, $^2J_{C-F}$ = 35.0 Hz, OC(O)). $^{19}F\{^1H\}$ NMR ($CDCl_3$, 376.31 MHz): δ −74.8. ESI mass m/z [ion]: 907.2639 $[M - OC(O)CF_3]^+$. Λ_M (Ω^{-1} cm^2 mol^{-1}, MeCN) = 86.9 (10^{-3} M).

[Pt{κ^2(*C*,*N*)-$C_6H_2Me_2$-3,5-(NHC(NHAr)(=NAr))-2}(κ^2(*P*,*P*)-dppm)][OC(O)CF_3] (Ar = 2,4-C_6H_3; 13). Platinacycle **13** was prepared from platinacycle **6** (50.0 mg, 0.066 mmol) and dppm (25.4 mg, 0.066 mmol) in freshly distilled CH_2Cl_2 (15 mL) and purified as described previously for platinacycle **10**. The solid obtained from the reaction mixture was dissolved in CH_2Cl_2 (2 mL), layered with toluene (2 mL), and stored at RT for 2 days to afford **13** as a white crystalline material. Yield: 95% (67.0 mg, 0.063 mmol). Mp: 148.3 °C. Anal. Calcd for $PtC_{52}H_{50}O_2P_2N_3F_3$ (M_w 1063.0177 g/mol): C, 58.75; H, 4.74; N, 3.95. Found: C, 58.85; H, 4.61; N, 3.83. ATR-IR (cm^{-1}): ν(N−H) 3402 (w), ν_a(OCO) 1686 (s), ν(C=N) 1605 (m), ν_s(OCO) 1348 (m), ν(P−C_6H_5) 1103 (s). ^1H NMR ($CDCl_3$, 400 MHz): δ 1.70, 1.75, 2.04, 2.08, 2.22, 2.31, (each s, 6 × 3 H, CH_3), 4.02−4.11 (m, 1 H, CH_2, dppm), 4.16−4.25 (m, 1 H, CH_2, dppm) 6.16 (s, 1 H, N*H*), 6.51−6.53 (m, 2 H, Ar*H*), 6.65 (d, J_{HH} = 8.0 Hz, 1 H, Ar*H*), 6.67 (s, 1 H, Ar*H*), 6.89 (d, J_{HH} = 7.2 Hz, 1 H, Ar*H*), 6.92 (d, J_{HH} = 7.6 Hz, 1 H, Ar*H*), 7.04−7.06 (m, 2 H, Ar*H*), 7.16 (s, 1 H, N*H*), 7.22−7.24 (m, 2 H, P(C_6H_5)$_2$), 7.31−7.36 (m, 2 H, P(C_6H_5)$_2$), 7.40−7.46 (m, 3 H, P(C_6H_5)$_2$), 7.48−7.63 (m, 9 H, P(C_6H_5)$_2$), 7.72−7.83 (m, 4 H, P(C_6H_5)$_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.5 MHz): δ 17.58, 17.64, 18.58, 19.88, 20.72, 21.10 (CH_3), 47.05 (dd, $^1J_{C-P}$ = 26.9 and 27.9 Hz, CH_2, dppm), 117.55 (q, $^1J_{C-F}$ = 297.3 Hz, CF_3), 122.25, 122.31, 124.91, 125.40 (d, $^1J_{C-P}$ = 4.8 Hz, P(C_6H_5)$_2$, *ipso-C*, dppm), 125.87 (d, $^1J_{C-P}$ = 5.8 Hz, P(C_6H_5)$_2$, *ipso-C*, dppm), 126.24 (d, $^1J_{C-P}$ = 5.8 Hz, P(C_6H_5)$_2$, *ipso-C*, dppm), 126.61 (d, $^1J_{C-P}$ = 5.8 Hz, P(C_6H_5)$_2$, *ipso-C*, dppm), 127.56, 127.72, 127.96, 128.20, 128.58, 128.65, 128.75, 129.09, 129.20, 129.36, 129.49, 129.61, 130.86, 131.09, 131.38, 131.44, 131.50, 132.14, 132.26, 132.40, 132.50, 132.97, 133.32, 133.44, 133.50, 133.61, 134.15, 134.28, 136.08, 137.01, 139.46, 141.17, 141.34, 145.89, 145.95 (ArCH/ArC), 146.99 (CN_3) 160.83 (q, $^2J_{C-F}$ = 31.8 Hz, OC(O)). $^{19}F\{^1H\}$ NMR ($CDCl_3$, 376.31 MHz): δ −74.9. ESI mass m/z [ion]: 949.3534 $[M - OC(O)CF_3]^+$. Λ_M (Ω^{-1} cm^2 mol^{-1}, MeCN) = 116.0 (10^{-3} M).

[Pt{κ^2(*C*,*N*)-$C_6H_2Me_2$-3,6-(NHC(NHAr)(=NAr))-2}(κ^2(*P*,*P*)-dppm)][OC(O)CF_3] (Ar = 2,5-$Me_2C_6H_3$; 14). Platinacycle **14** was prepared from platinacycle **7** (45.1 mg, 0.059 mmol) and dppm (22.8 mg, 0.059 mmol) in freshly distilled CH_2Cl_2 (15 mL) and purified as described previously for platinacycle **10**. The solid obtained from the reaction mixture was dissolved in CH_2Cl_2 (2 mL), layered with toluene (2 mL), and stored at RT for about 7 days to afford **14**·1.5(toluene) as colorless crystals suitable for SCXRD. Yield: 93% (58.4 mg, 0.055 mmol). Mp: 138.3 °C. Anal. Calcd for $PtC_{52}H_{50}O_2P_2F_3N_3 \cdot 1/2C_7H_8$ (M_w 1063.0177 + 46.0705 g/mol): C, 60.10; H, 4.91; N, 3.79. Found: C, 60.40; H, 5.20; N, 3.98. ATR-IR (cm^{-1}): ν(N−H) 3051 (w), ν_a(OCO) 1682 (s), ν(C=N) 1605 (m), ν_s(OCO) 1435 (m), ν(P−C_6H_5) 1167 (s). ^1H NMR ($CDCl_3$, 400 MHz): δ 1.67, 1.84, 1.95, 1.97 (each s, 4 × 3 H, CH_3), 2.25 (br, s, 2 × 3 H, CH_3), 3.72−3.84 (m, 1 H, CH_2, dppm), 4.60−4.69 (m, 1 H, CH_2, dppm), 5.77 (s, 1 H, N*H*), 6.61 (d, J_{HH} = 6.4 Hz, 1 H, Ar*H*), 6.75 (d, J_{HH} = 7.2 Hz, 1 H, Ar*H*), 6.83−6.88 (m, 4 H, Ar*H* (3 H), N*H* (1 H)), 7.03−7.10 (m, 1 H, Ar*H*), 7.16−7.18 (m, 2 H, Ar*H*), 7.28−7.38 (m, 12 H, P(C_6H_5)$_2$), 7.45−7.54 (m, 4 H, P(C_6H_5)$_2$), 7.57−7.64 (m, 4 H, P(C_6H_5)$_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.5 MHz): δ 19.47, 20.00, 20.23, 20.34, 20.83, 21.04 (CH_3), 47.13 (dd, $^1J_{P-C}$ = 27.3 Hz, CH_2, dppm), 117.07 (q, $^1J_{C-F}$ = 295.8 Hz, CF_3), 116.18, 116.25, 117.01, 117.05, 124.28, 125.02 (ArCH/ArC), 125.28 (d, $^1J_{P-C}$ = 5.7 Hz, P(C_6H_5)$_2$, *ipso-C*, dppm), 125.67, 125.81, 125.85, 126.31, 126.78, 127.54, 127.87, 128.34, 128.42, 128.51, 128.78, 129.12, 129.29, 129.39, 129.88, 130.89, 131.42, 131.87, 132.41, 132.66, 132.70, 132.76, 133.57, 133.61, 133.69, 133.81, 135.16, 135.20, 135.86, 135.89, 147.58 (ArCH/ArC), 149.07 (CN_3), 161.41 (q, $^2J_{C-F}$ = 32.6 Hz, OC(O)). $^{19}F\{^1H\}$ NMR ($CDCl_3$, 376.31 MHz): δ −74.8. ESI mass m/z [ion]: 949.3146 $[M - OC(O)CF_3]^+$. Λ_M (Ω^{-1} cm^2 mol^{-1}, MeCN) = 95.0 (10^{-3} M).

[Pt{κ^2(*C*,*N*)-$C_6H_2Me_2$-4,5-(NHC(NHAr)(=NAr))-2}(κ^2(*P*,*P*)-dppm)][OC(O)CF_3] (Ar = 3,4-$Me_2C_6H_3$; 15). Platinacycle **15** was prepared from platinacycle **8** (50.5 mg, 0.066 mmol) and dppm (25.6 mg, 0.066 mmol) in freshly distilled CH_2Cl_2 (15 mL) and purified as described previously for platinacycle **10**. The solid obtained from the reaction mixture was dissolved in CH_2Cl_2 (2 mL), layered with toluene (2 mL), and stored at RT for 5 days to afford **15**·CH_2Cl_2 as colorless crystals suitable for SCXRD. Yield: 92% (64.8 mg, 0.061 mmol). Mp: 241.5 °C. Anal. Calcd for $PtC_{52}H_{50}O_2P_2N_3F_3 \cdot 1/4CH_2Cl_2$ (M_w 1063.0177 + 21.2318 g/mol): C, 57.88; H, 4.69; N, 3.88. Found: C, 58.24; H, 4.94; N, 4.02. ATR-IR (cm^{-1}): ν(N−H) 2918 (w), ν_a(OCO) 1674 (s), ν(C=N) 1578 (m), ν_s(OCO) 1342 (m), ν(P−C_6H_5) 1111 (s). ^1H NMR ($CDCl_3$, 400 MHz): δ 1.60, 1.65, 1.93, 2.08, 2.11, 2.15 (each s, 6 × 3 H, CH_3), 4.08 (t, J_{PH} = 9.8 Hz, 2 H, CH_2, dppm), 6.38 (s, 1 H, N*H*), 6.48−6.50 (m, 1 H, Ar*H*), 6.55−6.57 (m, 1 H, Ar*H*), 6.70−6.76 (m, 3 H, Ar*H*), 6.87−7.00 (m, 2 H, Ar*H*), 7.31 (s, 1 H, Ar*H*), 7.35−7.43 (m, 13 H, P(C_6H_5)$_2$), 7.49−7.53 (m, 3 H, P(C_6H_5)$_2$), 7.58−7.62 (m, 4 H, P(C_6H_5)$_2$), 8.66 (m, 1 H, N*H*). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.5 MHz): δ 19.78, 20.31, 20.54, 20.66, 21.14, 21.35 (CH_3), 47.45 (dd, $^1J_{P-C}$ = 27.3 Hz, CH_2, dppm), 117.39 (q, $^1J_{C-F}$ = 295.8 Hz, CF_3), 116.49, 116.57, 117.32, 117.37, 124.60, 125.34 (ArCH/ArC), 125.60 (d, $^1J_{P-C}$ = 5.7 Hz, P(C_6H_5)$_2$, *ipso-C*, dppm), 125.99, 126.12, 126.17, 126.63, 127.11, 127.86, 128.18, 128.66, 128.73, 128.83, 129.10, 129.44, 129.60, 129.71, 130.19, 131.20, 131.74, 132.18, 132.73, 132.98, 133.01, 133.07, 133.88, 133.92, 134.01, 134.12, 135.47, 135.51, 136.17, 136.21, 147.90 (ArCH/ArC), 149.38 (CN_3), 161.73 (q, $^2J_{C-F}$ = 32.6 Hz, OC(O)). $^{19}F\{^1H\}$ NMR ($CDCl_3$, 376.31): δ −75.0. ESI mass m/z [ion]: 949.3201 $[M - OC(O)CF_3]^+$. Λ_M (Ω^{-1} cm^2 mol^{-1}, MeCN) = 83.2 (10^{-3} M).

[Pt{κ^2(*N*,*N*)[$(ArN)_2C(NHAr)$]}(κ^2(*P*,*P*)-dppm)][OC(O)CF_3] (Ar = 3,5-$Me_2C_6H_3$; 16). Platinacycle **16** was prepared from platinacycle **9** (50.3 mg, 0.066 mmol) and dppm (25.5 mg, 0.066 mmol) in freshly distilled CH_2Cl_2 (15 mL) and purified as described previously for platinacycle **10**. The solid obtained from the reaction mixture was dissolved in CH_2Cl_2 (2 mL), layered with toluene (2 mL), and stored at RT for about 4 days to afford **16** as bright yellow transparent crystals suitable for SCXRD. Yield: 95% (67.3 mg, 0.063 mmol). Mp: 232.5 °C. Anal. Calcd for $PtC_{52}H_{50}O_2P_2F_3N_3$ (M_w 1063.0177 g/mol): C, 58.75; H, 4.74; N, 3.95. Found: C, 58.45; H, 4.35; N, 3.60. ATR-IR (cm^{-1}): ν(N−H) 3053 (w), ν_a(OCO) 1676 (s), ν(C=N) 1572 (m), ν_s(OCO) 1335 (m), ν(P−C_6H_5) 1109 (s). ^1H NMR ($CDCl_3$, 400 MHz): δ 1.92 (s, 4 × 3 H, CH_3), 2.01 (s, 2 × 3 H, CH_3), 5.08 (t, $^2J_{P-H}$ = 11.4 Hz, 2 H, CH_2, dppm), 6.31 (br, 4 H, N*H* (1H), Ar*H* (3H)), 6.41−6.46 (m, 6 H, Ar*H*), 7.34−7.41 (m, 7 H, P(C_6H_5)$_2$), 7.50−7.56 (m, 13 H, P(C_6H_5)$_2$). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 161.8 MHz): δ −58.6 ($^1J_{Pt-P}$ = 2782 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.5 MHz): δ 20.94 (CH_3), 21.04 (CH_3), 44.81 (t, $^1J_{C-P}$ = 34.7 Hz, CH_2, dppm), 117.56 (q, $^1J_{C-F}$ = 297.3 Hz, CF_3), 120.30, 121.75, 122.72, 124.08, 125.24, 125.55, 125.80, 126.32, 126.76, 126.98, 129.00, 129.11, 129.46, 129.51, 129.57, 132.74, 132.96, 133.01, 133.08, 135.79, 137.16, 138.05, 138.26, 138.53, 138.61, 138.89, 140.72, 144.61, 144.97, 147.45, 150.94 (ArCH/ArC), 161.19 (q, $^1J_{C-F}$ = 32.4 Hz, OC(O)), 165.54 (CN_3). $^{19}F\{^1H\}$ NMR ($CDCl_3$, 376.31): δ −74.6. $^{195}Pt\{^1H\}$ NMR ($CDCl_3$, 85.78 MHz): δ −3716 (t, $^1J_{Pt-P}$ = 2799 ± 17 Hz). ESI mass m/z [ion]: 949.3153 $[M - OC(O)CF_3]^+$. Λ_M (Ω^{-1} cm^2 mol^{-1}, MeCN) = 68.4 (10^{-3} M).

[Pt{κ^2(*N*,*N*)[$(ArN)_2C(NHAr)$]}(κ^2(*P*,*P*)-dppe)][OC(O)CF_3] (Ar = 3,5-$Me_2C_6H_3$; 17). Platinacycle **17** was prepared from platinacycle **9** (50.2 mg, 0.066 mmol) and dppe (26.4 mg, 0.066 mmol) in freshly distilled CH_2Cl_2 (15 mL) in a 25 mL RB flask which was fitted with a guard tube. The contents in the RB flask were stirred at RT continuously for 2 days. Subsequently, the volatiles were completely removed under reduced pressure to afford a light green solid, which was dissolved in CH_2Cl_2 (2 mL), layered with toluene (2 mL), and stored at RT for about 7 days to afford **17** as light green transparent crystals suitable for SCXRD. Yield: 91% (65.1 mg, 0.060 mmol). Mp: 229.2 °C. Anal. Calcd for $PtC_{53}H_{52}O_2P_2F_3N_3$ (M_w 1077.045 g/mol): C, 59.10; H, 4.87; N, 3.90. Found: C, 58.81; H, 5.17; N, 3.75. ATR-IR (cm^{-1}): ν(N−H) 2916 (w), ν_a(OCO) 1682 (s), ν(C=N) 1597 (m), ν_s(OCO) 1327 (m), ν(P−C_6H_5) 1111 (s). ^1H NMR ($CDCl_3$, 400 MHz): δ 1.86 (s, 4 × 3 H, CH_3), 1.96 (s, 2 × 3 H, CH_3), 2.43−2.56

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(m, 2 × 2 H, CH_2, dppe), 6.07 (br, s, 4 H, ArH), 6.10 (s, 1 H, NH), 6.32−6.34 (m, 4 H, ArH), 6.38 (s, 1 H, ArH), 7.39−7.44 (m, 7 H, P(C_6H_5)$_2$), 7.50−7.55 (m, 13 H, P(C_6H_5)$_2$). ^{31}P{^{1}H} NMR ($CDCl_3$, 161.8 MHz): δ 38.2 ($^1J_{Pt-P}$ = 3277 Hz). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.5 MHz): δ 20.90 (CH_3), 21.01 (CH_3), 28.50 (d, $^1J_{C-P}$ = 6.7 Hz, CH_2, dppe), 28.94 (d, $^1J_{C-P}$ = 6.7 Hz, CH_2, dppe), 117.68 (q, $^1J_{C-F}$ = 297.6 Hz, CF_3), 120.64, 123.19, 125.32, 125.93, 126.23, 129.29, 129.35, 129.41, 132.55, 133.17, 133.23, 133.28, 135.25, 137.94, 138.14, 143.22, (ArCH/ArC), 160.98 (q, $^2J_{C-F}$ = 29.9 Hz, OC(O)), 167.52 (CN_3). ^{19}F{^{1}H} NMR ($CDCl_3$, 376.31): δ −74.5. ^{195}Pt{^{1}H} NMR ($CDCl_3$, 85.78 MHz): δ −4356 (t, $^1J_{Pt-P}$ = 3277 Hz). ESI mass m/z [ion]: 963.3280 [M − OC(O)CF_3]$^+$. Λ_M (Ω^{-1} cm^2 mol^{-1}, MeCN) = 69.7 (10^{-3} M).

[Pt{κ^2(*C*,*N*)-($C_6H_2Me_2$-4,6-(NHC(NHAr)(=NAr))-2}(κ^2(*P*,*P*)-dppe)][OC(O)CF_3] (Ar = 3,5-$Me_2C_6H_3$; 18). Platinacycle **18** was prepared from platinacycle **9** (50.1 mg, 0.066 mmol) and dppe (26.4 mg, 0.066 mmol) in freshly distilled CH_2Cl_2 (15 mL) and purified as described previously for platinacycle **10**. The solid obtained from the reaction mixture was dissolved in CH_2Cl_2 (2 mL), layered with toluene (2 mL), and stored at RT for about 3 days to afford **18**·1/2(toluene) as colorless crystals suitable for SCXRD. Yield: 91% (65.1 mg, 0.060 mmol). Mp: 224.6 °C. Anal. Calcd for $PtC_{53}H_{52}O_2P_2F_3N_3$·1/4$C_7H_8$ (M_w 1077.045 + 23.035 g/mol): C, 59.78; H, 4.95; N, 3.82. Found: C, 59.96; H, 4.97; N, 4.01. ATR-IR (cm^{-1}): ν(N−H) 3015 (w), ν_a(OCO) 1684 (s), ν(C═N) 1467 (m), ν_s(OCO) 1373 (m), ν(P−C_6H_5) 1107 (s). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.73 (s, 3 H, CH_3), 1.82 (s, 2 × 3 H, CH_3), 1.86, 1.96 (each s, 2 × 1 H, CH_2, dppe), 2.07 (s, 2 × 3 H, CH_3), 2.13 (s, 3 H, CH_3), 2.38−2.51 (m, 2 H, CH_2, dppe), 5.96 (s, 2 H, ArH), 6.20 (s, 1 H, ArH), 6.28 (s, 2 H, ArH), 6.41 (s, 1 H, ArH), 6.62 (s, 1 H, ArH), 6.69 (s, 1 H, ArH), 7.28−7.37 (m, 8 H, P(C_6H_5)$_2$), 7.46−7.56 (m, 7 H, P(C_6H_5)$_2$), 7.65−7.66 (m, 3 H, P(C_6H_5)$_2$), 7.73−7.75 (m, 2 H, P(C_6H_5)$_2$), 8.53, 8.77 (each s, 2 × 1 H, NH). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.5 MHz): δ 20.59, 21.00, 21.18 (CH_3), 26.85 (dd, $^1J_{C-P}$ = 32.8 Hz, $^2J_{C-P}$ = 7.7 Hz, CH_2, dppe, *trans* to C), 32.00 (dd, $^1J_{C-P}$ = 41.9 Hz, $^2J_{C-P}$ = 14.0 Hz, CH_2, dppe, *trans* to N), 117.62 (q, $^1J_{C-F}$ = 296.3 Hz, CF_3), 114.31, 114.33, 122.53, 123.19, 123.57 (ArCH/ArC), 126.62 (d, $^1J_{C-P}$ = 6.7 Hz, P(C_6H_5)$_2$, *ipso*-C, dppm), 126.88 (ArCH/ArC), 127.35 (d, $^1J_{C-P}$ = 8.6 Hz, P(C_6H_5)$_2$, *ipso*-C, dppm), 127.64, 127.75, 128.07, 128.47, 128.59, 128.85, 128.96, 129.19, 129.67, 129.77, 131.08, 131.20, 131.51, 131.71, 131.84, 132.19, 132.46, 132.61, 132.73, 132.87, 133.91, 134.03, 134.46, 134.57, 135.06, 136.86, 138.50, 138.66, 140.69, 143.64, 146.40 (ArCH/ArC), 151.83 (CN_3), 161.63 (q, $^2J_{C-F}$ = 32.7 Hz, OC(O)). ^{19}F{^{1}H} NMR ($CDCl_3$, 376.31): δ −74.7. ESI mass m/z [ion]: 963.3311 [M − OC(O)CF_3]$^+$. Λ_M (Ω^{-1} cm^2 mol^{-1}, MeCN) = 77.7 (10^{-3} M).

[Pt{κ^2(*C*,*N*)-($C_6H_2Me_2$-4,6-(NHC(NHAr)(=NAr))-2}(κ^2(*P*,*P*)-dppp)][OC(O)CF_3] (Ar = 3,5-$Me_2C_6H_3$; 19). Platinacycle **19** was prepared from platinacycle **9** (56.5 mg, 0.074 mmol) and dppp (30.8 mg, 0.074 mmol) in freshly distilled CH_2Cl_2 (15 mL) in a 25 mL RB flask which was fitted with a guard tube. The contents in the RB flask were stirred at RT for 24 h. Subsequently, the volatiles were completely removed under reduced pressure to afford a colorless sticky solid. The solid was dissolved in CH_2Cl_2 (2 mL), layered with diethyl ether (15 mL), and stored at RT for 7 days to afford **19**·$C_4H_{10}O$ as colorless transparent crystals suitable for SCXRD. Yield: 84% (67.9 mg, 0.062 mmol). Mp: 218.8 °C. Anal. Calcd for $PtC_{54}H_{54}O_2P_2F_3N_3$ (M_w 1091.072 g/mol): C, 59.45; H, 4.99; N, 3.85. Found: C, 59.83; H, 5.12; N, 3.52. ATR-IR (cm^{-1}): ν(N−H) 2916 (w), ν_a(OCO) 1686 (s), ν(C═N) 1574 (m), ν_s(OCO) 1360 (m), ν(P−C_6H_5) 1105 (s). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.28−1.41 (m, 1 H, CH_2, dppp), 1.93 (s, 3 H, CH_3), 2.02 (br, 1 H, CH_2, dppp), 2.05 (s, 2 × 3 H, CH_3), 2.07 (s, 3 H, CH_3), 2.09−2.22 (m, 1 H, CH_2, dppp), 2.25 (s, 2 × 3 H, CH_3), 2.47−2.67 (m, 3 H, CH_2, dppp), 5.65 (s, 2 H, ArH), 5.94 (s, 1 H, NH), 6.51 (s, 2 H, ArH), 6.71 (s, 1 H, ArH), 6.73−6.76 (m, 2 H, ArH), 6.84 (s, 1 H, ArH), 6.91−6.99 (m, 4 H, P(C_6H_5)$_2$), 7.09−7.21 (m, 7 H, P(C_6H_5)$_2$), 7.31−7.43 (m, 4 H, P(C_6H_5)$_2$), 7.63−7.73 (m, 5 H, P(C_6H_5)$_2$), 7.93 (s, 1 H, NH). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.5 MHz): δ 19.46, 20.32, 21.22, 21.30, (CH_3), 27.15 (d, $^1J_{C-P}$ = 30.9 Hz, CH_2, dppp *trans* to C), 27.72 (CH_2, dppp), 29.53 (d, $^1J_{C-P}$ = 40.4 Hz, CH_2, dppp *trans* to N), 117.69 (q, $^1J_{C-F}$ = 297.3 Hz, CF_3), 113.64, 122.60, 124.01, 125.04, 126.00, 126.61, 126.68, 126.92, 127.37, 127.48, 127.70, 128.37, 128.49, 128.87, 128.98, 129.04, 129.13, 129.27 (ArCH/ArC), 130.00 (d $^1J_{C-P}$ = 3.8 Hz, P(C_6H_5)$_2$, *ipso*-C, dppp), 131.03, 131.08, 131.31, 132.08, 132.47, 132.51, 132.62, 132.76, 132.88, 132.92, 134.86, 136.17, 136.34, 138.96, 139.64 (ArCH/ArC), 139.97 (d $^1J_{C-P}$ = 2.9 Hz, P(C_6H_5)$_2$, *ipso*-C, dppp), 140.58 (d $^1J_{C-P}$ = 2.9 Hz, P(C_6H_5)$_2$, *ipso*-C, dppp), 142.89, 145.21 (ArCH/ArC), 151.30 (CN_3), 161.09 (q, $^2J_{C-F}$ = 32.8 Hz, OC(O)). ^{19}F{^{1}H} NMR ($CDCl_3$, 376.31): δ −74.4. ESI mass m/z [ion]: 977.3485 [M − OC(O)CF_3]$^+$. Λ_M (Ω^{-1} cm^2 mol^{-1}, MeCN) = 81.4 (10^{-3} M).

[Pt{κ^2(*C*,*N*)-($C_6H_2Me_2$-4,6-(NHC(NHAr)(=NAr))-2}(κ^2(*P*,*P*)-dppp)][PF_6] (Ar = 3,5-$Me_2C_6H_3$; 20). Platinacycle **19** (15.7 mg, 0.014 mmol) was stirred with a large excess of NH_4PF_6 (15.2 mg, 0.093 mmol) in freshly distilled CH_2Cl_2 (15 mL) for 24 h at RT in a 25 mL RB flask which was fitted with a freshly prepared anhydrous $CaCl_2$ guard tube. The reaction mixture was filtered off with Whatman filter paper to remove $NH_4OC(O)CF_3$ and unreacted NH_4PF_6. The filtrate was stored at RT over a period of 3 days to afford **20**·(toluene) as colorless transparent crystals suitable for SCXRD. Yield: 79% (13.2 mg, 0.011 mmol). Mp: 189.7 °C. Anal. Calcd for $PtC_{52}H_{54}P_3F_6N_3$ (M_w 1121.0047 g/mol): C, 55.71; H, 4.68; N, 3.75. Found: C, 55.45; H, 5.01; N, 3.86. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.26−1.35 (m, 1 H, CH_2, dppp), 1.96, 2.04 (each s, 2 × 3 H, CH_3), 2.10 (s, 2 × 3 H, CH_3), 2.15−2.30 (m, 2 H, CH_2, dppp), 2.34 (s, 2 × 3 H, CH_3), 2.41−2.60 (m, 3 H, CH_2, dppp), 5.64 (s, 2 H, ArH), 5.94, 6.29 (each s, 2 × 1 H, NH), 6.55 (s, 1 H, ArH), 6.64 (s, 2 × 1 H, ArH), 6.70−6.75 (s, 3 H, ArH), 6.95−7.02 (m, 6 H, P(C_6H_5)$_2$), 7.11−7.22 (m, 5 H, P(C_6H_5)$_2$), 7.33−7.43 (m, 4 H, P(C_6H_5)$_2$), 7.59−7.73 (m, 5 H, P(C_6H_5)$_2$). ^{19}F{^{1}H} NMR ($CDCl_3$, 376.31): δ −73.0 (d, $^1J_{P-F}$ = 715.0 Hz). Λ_M (Ω^{-1} cm^2 mol^{-1}, MeCN) = 84.6 (10^{-3} M). Platinacycle **20** was sparingly soluble in $CDCl_3$ and CD_3CN, which hampered our attempts to record ^{195}Pt and ^{13}C NMR spectra with an acceptable signal to noise ratio.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.0c00408.

General considerations, syntheses and complete characterization of $LH_2^{3,4\text{-xylyl}}$, NMR (^{1}H, ^{13}C, ^{31}P, ^{195}Pt, and ^{19}F) and mass spectra of all new compounds wherever applicable, crystal acquisition, and refinement SCXRD data for the structurally characterized compounds **10**·$CHCl_3$, **11**·$CHCl_3$, **12**·CH_2Cl_2, **14**·1.5C_7H_8, **15**·CH_2Cl_2, **16**, **17**, **18**·0.5C_7H_8, **19**·$C_4H_{10}O$, **20**·C_7H_8, $LH_2^{3,4\text{-xylyl}}$ and details pertinent to DFT studies, namely figures of the optimized structures of **22**′, **D**−**H**, and **16**′ (PDF)

Cartesian coordinates of the calculated structures (XYZ)

Accession Codes

CCDC 2003713−2003723 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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