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Synthesis and reactivity of platinum vinylcarbene complexes prepared from activation of propargyl alcohols

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Dedicated to Professor Richard J. Puddephatt on the Occasion of His 75th Birthday

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ABSTRACT

Platinum vinylcarbene complexes are potentially useful for organometallic synthesis and catalysis, but have been rarely studied. This work reports a convenient route to make platinum vinylcarbene complexes. Treatment of $[PtCl_2(PPh_3)]_2$ with propargyl alcohols HC≡CC(OH)RR' (RR' = Ph_2, *cyclo*-C_6H_{10}(OH), (*i*Pr)(C≡CTMS) and (H)(Ph)) in the presence of EtOH produced the vinylcarbene complexes *trans*-$PtCl_2\{=C(OEt)\text{-}CH{=}CRR'\}(PPh_3)$. Under similar condition, $[PtCl_2(PPh_3)]_2$ reacted with $HC{\equiv}CC(OH)Me_2$ to give *cis*-$PtCl_2\{=C(OEt)\text{-}CH{=}CMe_2\}(PPh_3)$. Complex *trans*-$PtCl_2\{=C(OEt)\text{-}CH{=}CPh_2\}(PPh_3)$ readily undergo a metathesis reaction with NaI to give *trans*-$PtI_2\{=C(OEt)\text{-}CH{=}CPh_2\}(PPh_3)$ which can isomerize to *cis*-$PtI_2\{=C(OEt)\text{-}CH{=}CPh_2\}(PPh_3)$. Complex *trans*-$PtCl_2\{=C(OEt)\text{-}CH{=}CPh_2\}(PPh_3)$ reacted with PPh_3 to give EtCl and the acyl complex *trans*-$PtCl\{C(O)CH{=}CPh_2\}(PPh_3)_2$, which can undergo a decarbonylation reaction to give $PtCl(CH{=}CPh_2)(PPh_3)_2$.

1. Introduction

Vinylcarbene complexes are an interesting class of organometallic compounds that can play an important role in catalysis and organic and organometallic synthesis. For example, $RuCl_2(=CH\text{-}CH{=}CPh_2)(PR_3)_2$ (PR_3 = PPh_3, PCy_3) are catalytically active for olefin metathesis [1], $M\{=C(OR)\text{-}CH{=}CR_2\}(CO)_5$ (M = Cr, Mo, and W) can be used as starting materials to synthesize a variety of organic compounds [2], $[Cp^*Ir\{=C(OMe)CH{=}CPh_2\}(L)]PF_6$ (L = PPh_2Me, PMe_3) can be used to prepare metallabenzenes [3].

While many transition metal vinylcarbene complexes (especially those of group 6–9 metals) [2,4] and platinum carbene complexes [5–9] are known, well-characterized platinum vinylcarbene complexes are still rare. Reported platinum vinylcarbene complexes are mainly those derived from transmetallation reactions of group 6 Fischer vinylcarbene complexes (e.g. **2** from the reactions of **1** with $PtCl_2(PhCN)_2$ [10,11]) (Scheme 1). The transmetallation reactions have been explored for organometallic synthesis [12] and organic synthesis using group 6 Fischer carbene complexes as starting materials and group 10 metal complexes as catalysts [4f,13]. There has also been much interest in developing catalytic reactions involving reactive vinylcarbene intermediates generated from reactions of other substrates with platinum complexes, for example, vinylcarbenes **4** from propargyl derivatives **3** [14] and 2-furylcarbenes **6** from ene-yne-ketones **5** [15]. In view of the rarity of isolated platinum vinylcarbene complexes and their potential applications in organometallic synthesis and catalysis, it is desirable to search for alternative routes to make such complexes and to study their reactivity.

We herein report the synthesis and reactivity of platinum vinylcarbene complexes of the type $PtCl_2\{=C(OR'')\text{-}CH{=}CRR'\}(PPh_3)$ made from the reactions of readily available propargylic alcohols HC≡CC(OH)RR′ with $[PtCl_2(PPh_3)]_2$ in the presence of R″OH.

2. Results and discussion

2.1. Reactions of $[PtCl_2(PPh_3)]_2$ with propargyl alcohols HC≡CC(OH)RR'

Reactions of terminal alkynes HC≡CR with Pt(II) complexes in the presence of alcohols (ROH) represent one of the most convenient routes to prepare platinum carbene complexes $L_nPt{=}C(OR)CH_2R$ [16–22]. The reactions presumably proceed through the

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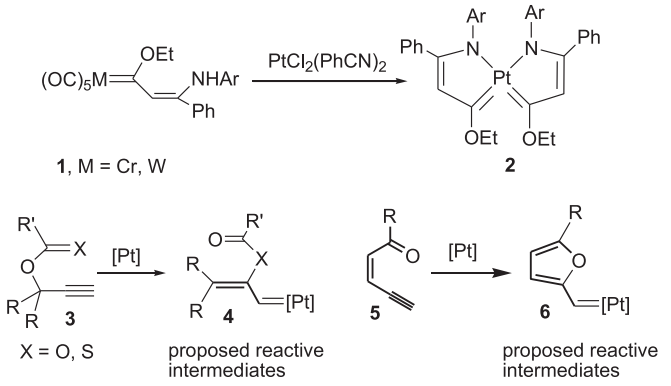
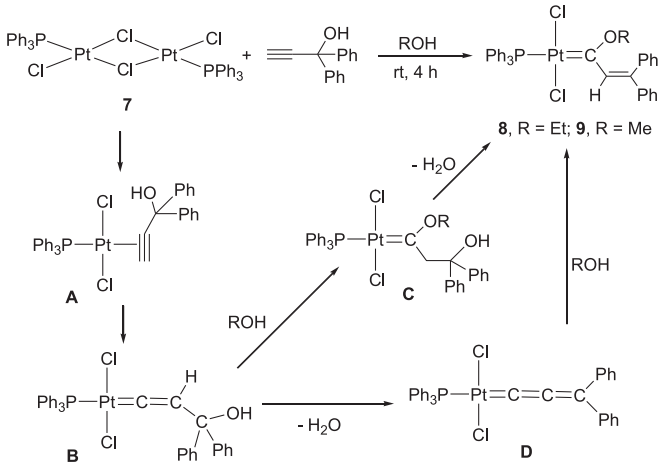


Scheme 1. Vinylcarbene platinum complexes.

addition reactions of alcohols with vinylidene intermediates $L_nPt=C=CHR$. We envisioned that reactions of terminal propargyl alcohols with Pt(II) complexes in the presence of alcohols may proceed similarly to give hydroxyvinylidene complexes which could undergo dehydration and addition of alcohols to give desired platinum vinylcarbene complexes.

To test the hypothesis, we first carried out the reaction of $HC{\equiv}CC(OH)Ph_2$ with the dimeric complex $[PtCl_2(PPh_3)]_2$ (**7**) in a mixed solvent of EtOH and $CHCl_3$ (1:6 V/V). To our delight, the reaction proceeded smoothly to give the vinylcarbene complex *trans*-$PtCl_2\{=C(OEt)\text{-}CH{=}CPh_2\}(PPh_3)$ (**8**) (Scheme 2). The reaction was completed at room temperature within 4 h and complex **8** can be isolated as a yellow solid in 90% yield. Under similar condition, the reaction in a mixture of MeOH and CH_2Cl_2 (3:10 V/V) produced the analogous complex *trans*-$PtCl_2\{=C(OMe)\text{-}CH{=}CPh_2\}(PPh_3)$ (**9**).

The structures of complexes **8** and **9** have been confirmed by X-ray diffraction. The molecular structures of **8** and **9** are shown in Figs. 1 and 2, respectively. The two complexes have very similar structural features. Both adopt a distorted square-planar geometry with two mutually *trans* chloride ligands and a carbene ligand trans to PPh_3. The carbene carbon has a planar geometry. The O(1)-C(1)-C(2) plane is almost perpendicular to the plane formed by Pt, Cl(1), Cl(2) and P(1) atoms. The Pt-C(1) bond lengths [1.997(3) Å for **8**, 1.985(2) Å for **9**] are comparable to those found for cationic alkyl(alkoxy)carbenes such as *trans*-$[Pt(Me)\{C(OMe)Me\}(PMe_2Ph)_2][PF_6]$ (2.13(1) Å) [23] and *trans*-$[Pt(Me)\{COCH_2CH_2CH_2\}(PMe_2Ph)_2][PF_6]$ (2.00(2) Å) [24]. It is however longer than that reported for the neutral carbene complex *cis*-$PtC1_2\{C(OEt)(CH_2Ph)\}(PMe_2Ph)$ (1.920(9) Å) [16b], in which the carbene ligand is *trans* to a chloride ligand.



Scheme 2. Preparation of vinylcarbene complexes **8** and **9**.

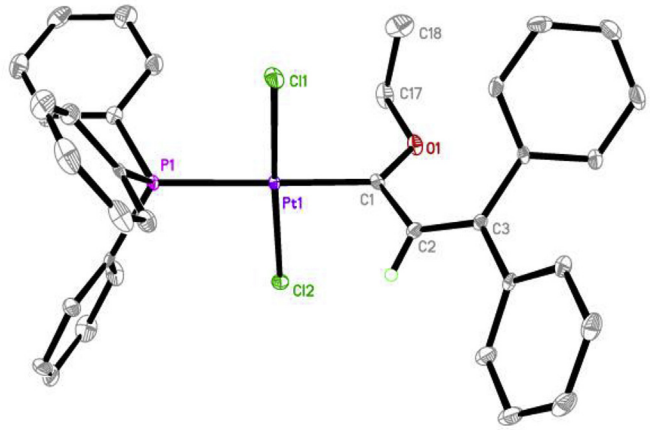


Fig. 1. The X-ray crystal structure of complex **8** (at 30% probability level of the thermal ellipsoid). Except the hydrogen on C2, all the hydrogen atoms are omitted for clarity. Selected bond distances (Å): Pt(1)-C(1) 1.997(3), Pt(1)-P(1) 2.3412(7), Pt(1)-Cl(1) 2.3061(8), Pt(1)-Cl(2) 2.3022(8), C(1)-C(2) 1.448(4), C(2)-C(3) 1.363(4), C(1)-O(1) 1.289(4).

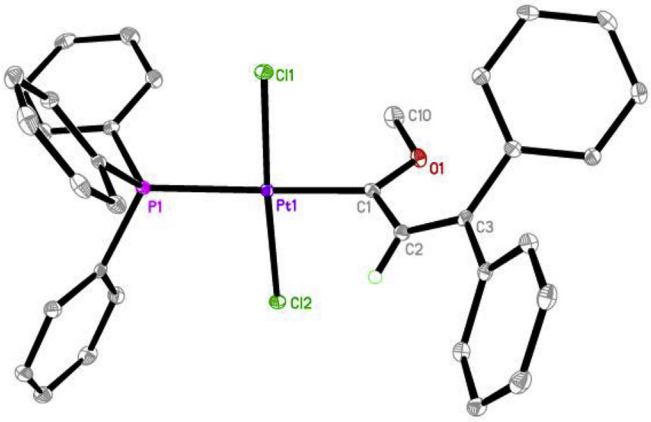


Fig. 2. X-ray crystal structure of complex **9** (at 30% probability level of the thermal ellipsoid). Except the hydrogen on C2, all the hydrogen atoms are omitted for clarity. Selected bond distances (Å): Pt(1)-C(1) 1.985(2), Pt(1)-P(1) 2.3411(6), Pt(1)-Cl(1) 2.3124(5), Pt(1)-Cl(2) 2.3012(5), C(1)-C(2) 1.460(3), C(2)-C(3) 1.364(3), C(1)-O(1) 1.295(3).

The solid-state structures are supported by their solution NMR data. For example, the $^{31}P\{^1H\}$ NMR spectrum of **8** showed a singlet peak at 10.6 ppm flanked by ^{195}Pt satellite signals with a $^2J_{PtP}$ coupling constant of 2090 Hz. The $^{13}C\{^1H\}$ NMR spectrum showed the characteristic signal of $Pt=C$ at 271.3 ppm with a $^2J_{PC}$ coupling constant of 146.7 Hz, the $=CH$ signal at 133.8 ppm and the CPh_2 signal at 161.9 ppm. In the ^1H NMR spectrum, the OCH_2CH_3 signals were observed at 5.54 (CH_2) and 1.34 (CH_3) ppm.

Scheme 2 shows two plausible paths for the formation of complexes **8** and **9**. The reaction of the dimeric complex **7** with $HC{\equiv}CC(OH)Ph_2$ may initially produce the η^2-alkyne complex **A**, which can isomerize to the vinylidene complex **B**. The vinylidene complex **B** could react with ROH to give the hydroxycarbene complexes **C** which undergo dehydration reactions to give complexes **8** and **9**. Alternatively, the vinylidene complex **B** could undergo a dehydration reaction first to give the allenylidene complex **D**, which undergoes addition reactions with ROH to give complexes **8** and **9**. Unfortunately, we have failed to detect the reaction

intermediates. As monitored by in situ NMR spectroscopy, no reaction between **7** and HC≡CC(OH)Ph_2 was observed in the absence of EtOH or MeOH even after overnight. In the presence of EtOH or MeOH, the in situ NMR spectra only showed signals of the starting dimeric complex **7** and the products.

In the presence of EtOH, the dimeric complex **7** also reacted with the alkyl-substituted terminal propargyl alcohol 1-ethynylcyclohexanol and the ethynyl-substituted terminal propargyl alcohol HC≡CC(OH)(*i*Pr)C≡CTMS to give analogous vinylcarbene complexes **10** and **11**, respectively (Scheme 3). Secondary propargyl alcohols behaved similarly. For example, HC≡CCH(OH)Ph reacted with **7** in the presence of EtOH to give complex *trans*-$PtCl_2$(=C(OEt)-CH=CHPh)(PPh_3) (**12**). Interestingly, the dimeric complex **7** reacted with HC≡CC(OH)Me_2 in the presence of EtOH to give *cis*-$PtCl_2$(=C(OEt)-CH=CMe_2)(PPh_3) (**13**) rather than the trans isomer. We noted that complexes *cis*-PtX_2{ = C(OR′)(CH_2R)}(L) (X = Cl, Br, I; L = PMe_2Ph or PEt_3) were produced from the reactions of the halide-bridged dimeric complexes $[PtX_2L]_2$ with terminal acetylenes RC≡CH (R = Ph, Me, or Et) and alcohols R'OH (R' = Me, Et, Pr) [16a,b].

The coordination sphere of complexes **10**–**12** must be the same as those of complexes **8**–**9**, as indicated by their NMR data. In particular, the $^{31}P\{^1H\}$ NMR spectra of these complexes showed a singlet at ca. 11 ppm with a $^1J_{PtP}$ coupling constant of ca. 2150 Hz. The $^{13}C\{^1H\}$ NMR spectra showed a carbene signal at ca. 270 ppm with a $^2J_{PC}$ coupling constant of ca. 150 Hz.

The NMR data of **13** is significantly different from those of **8**–**12**. The $^{31}P\{^1H\}$ NMR spectrum showed a singlet peak at 8.0 ppm with a $^2J_{PtP}$ coupling constant of 4105.0 Hz, which is significantly larger than those of **8**–**12** (ca. 2150 Hz). The $^{13}C\{^1H\}$ NMR spectrum showed the Pt = *C* signal at 247.6 ppm with a $^2J_{PC}$ coupling constant of 4.2 Hz, which is significantly smaller than those of **8**–**12** (ca. 150 Hz). In the ^1H NMR spectrum, the OCH_2 group displayed two signals at 5.60 and 4.94 ppm, indicating that complex has an unsymmetrical structure. The NMR data suggest that the phosphine and carbene ligands in **13** are cis to each other.

The structure of **13** has been confirmed by an X-ray diffraction study. As shown in Fig. 3, complex adopts a square-planar geometry around Pt with two mutually cis chloride ligands. As expected, the Pt-P bond (2.2431(19) Å) and Pt-C(carbene) (1.926(10) Å) distances are appreciably shorter than the corresponding bonds in complexes **8** and **9**. The difference is understandable as the phosphine and carbene ligands are mutually *trans* to each other in **8** and **9**, but are trans to a chloride ligand in **13**. Chloride is a weaker trans influence ligand than phosphine and carbene ligands.

It is interesting to note that the vinylcarbene complex obtained from the reaction of HC≡CC(OH)Me_2 adopts a cis geometry while those from other tested propargyl alcohols adopt a trans geometry.

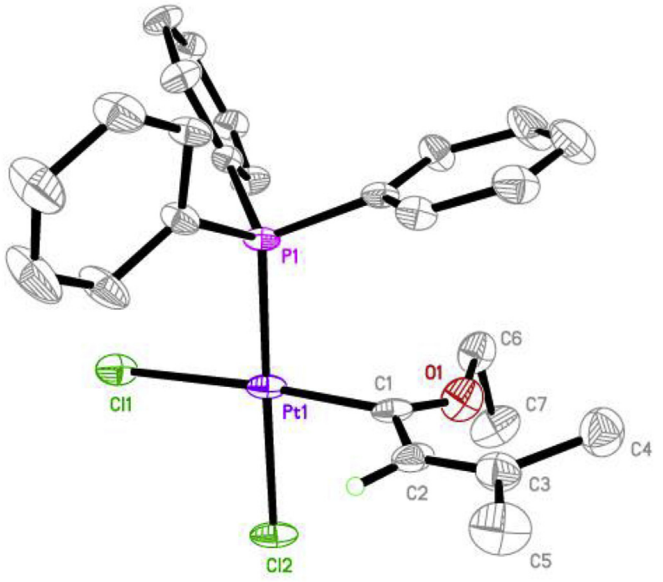
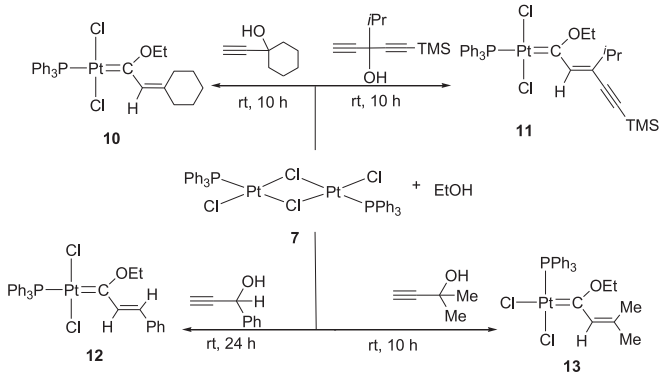


Fig. 3. X-ray crystal structure of complex **13** (at 30% probability level of the thermal ellipsoid). Except the hydrogen on C2, all the hydrogen atoms are omitted for clarity. Selected bond distances (Å): Pt(1)-C(1) 1.926(10), Pt(1)-P(1) 2.2431(19), Pt(1)-Cl(1) 2.367(2), Pt(1)-Cl(2) 2.359(2), C(1)-C(2) 1.433(13), C(2)-C(3) 1.333(14), C(1)-O(1) 1.295(16).

Our computational work confirms that the cis isomer is thermodynamically slightly more stable than the trans isomer for both $PtCl_2${ = C(OEt)-CH=CPh_2}(PPh_3) and $PtCl_2${ = C(OEt)-CH=CMe_2} (PPh_3) as shown in Fig. 4. Thus, complexes **8**–**13** are the kinetic products, although it is not clear to us the cause for the difference in the kinetic preferences. We have tried to convert complex trans-$PtCl_2$(=C(OEt)-CH=CPh_2)(PPh_3) (**8**) to its cis isomer by heating. It was found that complex decomposed to a mixture of several un-identified species along with complex **7** after refluxing in THF or chloroform overnight.

We also carried out the reactions of **7** with HC≡CC(OH)Ph_2 in the presence of *t*BuOH, $PhCH_2OH$, HOAc and $^iPr_2NH$. As indicated by in situ $^{31}P(^1H)$ NMR spectroscopy, the reactions of *t*BuOH and $PhCH_2OH$ also produced analogous vinylcarbene complexes. However, the reactions are not clean and also produced other un-identified complexes. We have failed to obtain pure samples of these vinylcarbene complexes. In the case of HOAc, no reaction was observed even after 24 h. In the case of $^iPr_2NH$, the expected vinylcarbene complex was not observed. Instead, the reaction produced the amine complex *trans*-$PtCl_2(PPh_3)(^iPr_2NH)$ [25].



Scheme 3. Preparation of vinylcarbene complexes **10**–**13**.

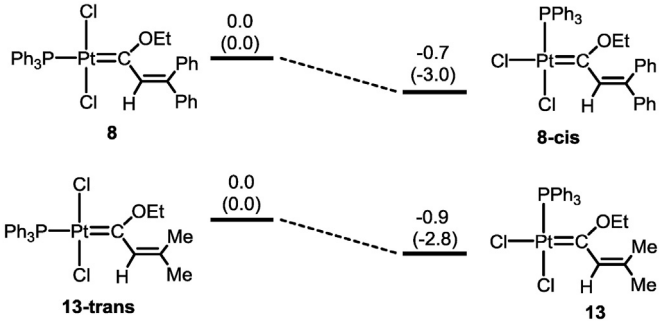


Fig. 4. The relative stability of isomers of $PtCl_2${ = C(OEt)-CH=CPh_2}(PPh_3) and $PtCl_2${ = C(OEt)-CH=CMe_2}Cl_2(PPh_3). The relative free energies and electronic energies (in parentheses) are given in kcal/mol.

2.2. Reactivity of *trans*-$PtCl_2$(=C(OEt)-CH=CPh_2)(PPh_3) (8)

One of the interesting transformations of haloplatinum alkoxycarbene complexes of the type [Pt]X{ = C(OR)R'} is the elimination of RX to give platinum acyl complexes [Pt][= C(O)R']. The reactions can be promoted by halides or neutral ligands such as phosphines and pyridine. For example, *trans*-[PtCl(=C(OMe)Me)(PMe_2Ph)$_2$]PF_6 reacted NaI to give *trans*-PtX(COMe)(PMe_2Ph)$_2$ (X = Cl, I) [26], *cis*-$PtBr_2${C(OMe)(Me)}$_2$ reacted with PPh_3 to give *trans*-PtBr(COMe){C(OMe)(Me)}(PPh_3) and MeBr [27], *cis*-$PtCl_2${C(OMe)(Et)}(PMe_2Ph) reacted with PMe_2Ph to give *trans*-PtCl(COEt)(PMe_2Ph)$_2$ and MeCl [16c]. Complexes *cis*-$PtCl_2${ = C(OMe)(R)}(PMe_2Ph) (R = Et, CH_2Ph) were also reported to slowly evolve to the acyl complex [PtCl(COR)(PMe_2Ph)]$_2$ in $CHCl_3$ and the reaction is facilitate by addition of Et_4NCl [16c].

We have carried out experiments to see if our vinylcarbene complex *trans*-$PtCl_2$(=C(OEt)-CH=CPh_2)(PPh_3) (**8**) behaves similarly. Complex $PtCl_2$(=C(OEt)-CH=CPh_2)(PPh_3) (**8**) was found to remain unchanged in dichloromethane, chloroform or THF even after 20 h. It decomposed completely to a mixture of un-identified species after its THF solution was allowed to stand at room temperature for 7 h in the presence of four equiv. of LiCl or Bu_4NCl.

Interestingly complex **8** in THF reacted rapidly with NaI to give the diiodo-vinylcarbene complex *trans*-PtI_2{ = C(OEt)-CH=CPh_2}(PPh_3) (**14A**) (Scheme 4), which can be isolated as a yellow solid in 95% yield from the reaction of **8** with 10 equiv. of NaI at room temperature for 5 min. If the reaction was carried out in refluxing THF for 2.5 h, the reaction produced complex **14A** along with the isomeric complex *cis*-PtI_2(=C(OEt)-CH=CPh_2)(PPh_3) (**14B**) in a molar ratio of 1: 0.23. Complex **14B** is the only product if the reaction mixture was refluxed for two days. Complex **14B** is presumably formed from isomerization of complex **14A**. Indeed, upon heating in THF for two days, isolated isomer **14A** was converted completely to the isomer **14B**.

The compositions of the two isomers of complex **14** have been confirmed by their analytical and NMR spectroscopic data. The stereochemistry of the two isomers can be assigned based on the NMR data. In complex **14A**, the phosphine ligand is *trans* to the carbene ligand. In complex **14B**, the phosphine ligand is *trans* to an iodide ligand and *cis* to the carbene ligand. In agreement with the stereochemistry, the $^1J_{PtP}$ coupling constant of **14A** (2118.8 Hz) is smaller than that of **14B** (3924.2 Hz). In addition, the ^{1}H NMR spectrum of **14A** showed only one CH_2 signal at 5.04 ppm due to the symmetrical feature of the structure while that of **14B** showed two CH_2 signals at 4.97 and 4.35 ppm due to the unsymmetrical feature of the structure.

Complex **8** in THF reacted with PPh_3 immediately at room temperature to produce the acyl complex *trans*-PtCl{C(O)CH=CPh_2}(PPh_3)$_2$ (**15**) along with EtCl, which was identified by NMR spectroscopy (Scheme 5). Complex **15** can be isolated as a yellow solid in 90% yield from the reaction of **8** with ca. 4 equiv. of PPh_3 in THF for 15 min.

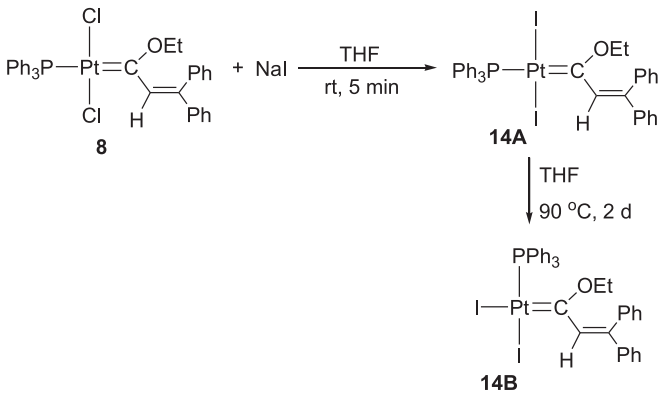
If the reaction was carried out in refluxing THF for 20 min, the reaction produced the acyl complex **15** along with the vinyl complex $PtCl_2$(CH=CPh_2)(PPh_3) (as a mixture of the cis isomer **16A** and the trans isomer **16B** in a molar ratio of 1: 3) in a molar ratio of 1: 14. Complex **16** is presumably formed from decarbonylation of **15**. Subsequent experiments confirmed that the isolated acyl complex **15** can indeed undergo a decarbonylation reaction in both solid state and solutions. In refluxing dichloromethane, the decarbonylation reaction was completed within 20 h to give a mixture of the *cis*- and *trans* isomers of the vinyl complex **16** (**16A** and **16B** are in a molar ratio of 1:7). Refluxing a solution of **15** in chloroform for one h produced cleanly only the *trans* isomer **16B**. The observations may suggest that the decarbonylation reaction initially produced isomer **16A**, which can isomerize to the thermodynamically more stable isomer **16B**. In agreement of the proposition, isolated isomer **16A** could be converted to isomer **16B** on refluxing in chloroform for 4 h. Similar decarbonylation reactions have been reported for *trans*-Pt(COMe)Cl(PR_3)$_2$ (PR_3 = PPh_3, P(4-FC_6H_4)$_3$, $PMePh_2$, PMe_2Ph and PBu_3) [28].

The identity of the acyl complex **15** is supported by the NMR data. In particular, the $^{31}P\{^1H\}$ NMR spectrum showed a singlet peak at 19.8 ppm with a $^2J_{PtP}$ coupling constant of 3532.1 Hz, suggesting that the two phosphine ligands are equivalent and must be trans to each other. The $^{13}C\{^1H\}$ NMR spectrum showed the characteristic signal of Pt*C*(O) signal at 205.7 ppm with a small $^2J_{PC}$ coupling constant of 5.3 Hz, the = *C*H signal at 136.3 ppm and the *C*Ph_2 signal at 143.4 ppm. In the ^{1}H NMR spectrum, the vinyl = *CH* signal was observed at 6.68 ppm.

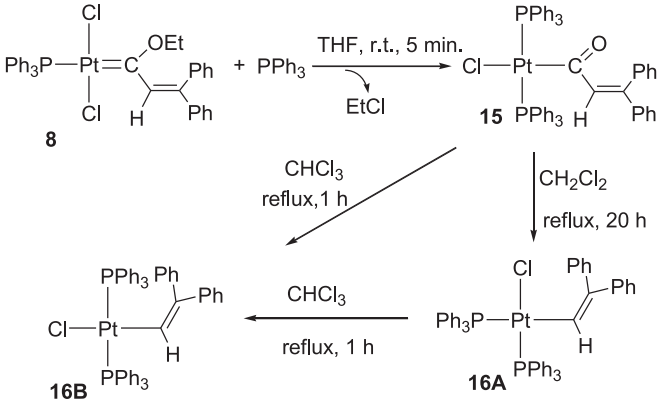
The two isomers of Complex **16** have been characterized by elemental analysis and NMR spectroscopy The structure of **16B** has also been confirmed by X-ray diffraction. As shown Fig. 5, complex **16B** adopts a square planar geometry with two trans-disposed PPh_3 ligands. Consistent with the solid state structure, the $^{31}P\{^1H\}$ NMR spectrum of **16B** showed a singlet peak at 24.4 ppm with a $^2J_{PtP}$ coupling constant of 3122.5 Hz. The $^{13}C\{^1H\}$ NMR spectrum showed a triplet signal of Pt-CH at 136.1 ppm with a $^2J_{PC}$ coupling constant of 9.6 Hz, and the = *C*Ph_2 signal at 139.5 ppm.

Consistent with the *cis*-geometry, complex **16A** showed two $^{31}P\{^1H\}$ signals at 21.1 and 16.2 ppm. The $^{13}C\{^1H\}$ NMR spectrum showed a triplet signal of Pt-*C*H at 149.7 ppm with a $^2J_{PC}$ coupling constant of 114.1 Hz, which is typical for coupling between trans-disposed phosphine and vinyl ligands.

Carbene complexes can be oxidized to give carbonyl derivatives [29]. We found that complex **8** can undergo similar reactions. For



Scheme 4. The reaction of the vinylcarbene complex **8** with NaI.



Scheme 5. Reactions of the vinylcarbene complex **8** with PPh_3.

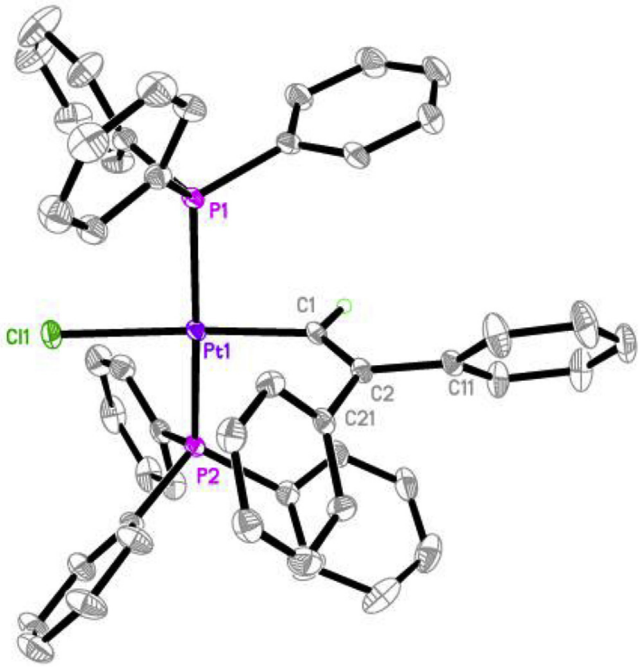


Fig. 5. The X-ray crystal structure of complex **16B** (at 30% probability level of the thermal ellipsoid). Except the hydrogen on C1, all the hydrogen atoms are omitted for clarity. Selected bond distances (Å): Pt(1)-C(1), Pt(1)-P(1), Pt(1)-P(2), Pt(1)-Cl(1), Pt(1)-C)1), C(1)-C(2).

example, it reacted with PhIO or Me_3NO in $CHCl_3$ to give the ester $Ph_2C=CHCO_2Et$ (**17**) (eq. 1). As indicated by in situ NMR spectroscopy, the reaction also produced phosphine oxide $Ph_3P=O$ and other unidentified products. We have carried out experiments to test whether the dimeric complex $[PtCl_2(PPh_3)]_2$ can catalyze the reaction of $HC{\equiv}CC(OH)Ph_2$ with PhIO and EtOH to give the ester **17**. Experimentally, **17** was indeed formed after a mixture of $HC{\equiv}CC(OH)Ph_2$, PhIO (or Me_3NO) and EtOH (in 1:1:1 molar ratio) was refluxed in $CHCl_3$ overnight in the presence of 10 mol% of $[PtCl_2(PPh_3)]_2$. Unfortunately, only a conversion of 10% was achieved.

In summary, platinum vinylcarbene complexes $PtCl_2(=C(OR'')\text{-}CH{=}CRR')(PPh_3)$ can be conveniently prepared from the reactions of $[PtCl_2(PPh_3)]_2$ with propargyl alcohols $HC{\equiv}CC(OH)RR'$ in the presence of alcohols R″OH. Complex *trans*-$PtCl_2(=C(OEt)\text{-}CH{=}CPh_2)(PPh_3)$ readily undergo a metathesis reaction with NaI to give *trans*-$PtI_2(=C(OEt)\text{-}CH{=}CPh_2)(PPh_3)$, which can isomerize to *cis*-$PtI_2(=C(OEt)\text{-}CH{=}CPh_2)(PPh_3)$. Complex *trans*-$PtCl_2(=C(OEt)\text{-}CH{=}CPh_2)(PPh_3)$ reacted with PPh_3 to give EtCl and the acyl complex *trans*-$PtCl\{C(O)CH{=}CPh_2\}(PPh_3)_2$, which can undergo a decarbonylation reaction to give $PtCl(CH{=}CPh_2)(PPh_3)_2$.

3. Experimental section

General Procedures. All reactions were carried out in oven-dried glassware under an atmosphere of argon with the rigid exclusion of air and moisture using standard Schlenk techniques or in a glovebox under N_2 unless otherwise specified. Diethyl ether, *n*-hexane, *n*-pentane and tetrahydrofuran were distilled from sodium benzophenone ketyl, toluene was distilled from sodium, and dichloromethane was distilled from calcium hydride. $[PtCl_2(PPh_3)]_2$ (**7**) was prepared according to a reported procedure [30]. All other chemicals were purchased from either Aldrich or Acros Chemical Co. and used as received unless otherwise specified. ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker DPX 400 spectrometer at 400 MHz, 100 MHz and 162 MHz, respectively. All signals are reported in δ unit with references to the residual solvent resonances of the deuterated solvents for proton and carbon chemical shifts, and to external 85% H_3PO_4 for phosphorus chemical shifts. Microanalyses were performed in M-H-W Laboratories (Phoenix, AZ, USA).

Synthesis of 8. To a solution of $[PtCl_2(PPh_3)]_2$ (**7**) (1.00 g, 0.946 mmol) in $CHCl_3$ (60 mL) was added 1,1-diphenylprop-2-yn-1-ol (788 mg, 3.78 mmol) and ethanol (10 mL). The reaction mixture was stirred for 4 h at room temperature to give a clear yellow solution. All volatiles of the reaction mixture were removed under vacuum. The residue was washed with *n*-hexane (15 mL × 2), ether (10 mL) and dried under reduced pressure to provide complex **8** as a yellow solid. Yield, 90% (1.31 g, 1.71 mmol). ^1H NMR (400 MHz, $CDCl_3$): δ 7.59–7.32 (m, 26H), 5.54 (q, $J = 7.1$ Hz, 2H, CH_2), 1.34 (t, $J = 7.1$ Hz, 3H, CH_3). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 10.6 (s, $J_{PtP} = 2090.0$ Hz). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 271.3 (d, $J_{PC} = 146.7$ Hz, Pt = *C*), 161.9 (HC=*C*Ph_2), 140.9 (*ipso*-CPh_2), 139.0 (*ipso*-CPh_2), 134.8 (d, $J = 10.9$ Hz, *o*- or *m*-PPh_3), 133.8 (d, $J_{PC} = 9.9$ Hz, HC=CPh_2), 131.2, 131.0, 130.3 (br, *p*-PPh_3), 129.8, 129.4 (d, $J_{PC} = 48.2$ Hz, *ipso*-PPh_3), 129.1, 128.5, 128.0 (d, $J = 10.0$ Hz, *o*- or *m*-PPh_3), 127.9, 78.9 (d, $J_{PC} = 3.6$ Hz, CH_2), 14.0 (CH_3). Anal. Calcd. for $C_{35}H_{31}Cl_2OPPt$: C, 54.98, H, 4.09. Found: C, 54.67, H, 4.08.

Synthesis of 9. To a solution of $[PtCl_2(PPh_3)]_2$ (200 mg, 0.189 mmol) in CH_2Cl_2 (10 mL) was added 1,1-diphenylprop-2-yn-1-ol (198 mg, 0.951 mmol) and ethanol (3 mL). The reaction mixture was stirred for 4 h at room temperature to give a clear yellow solution. All volatiles of the reaction mixture were removed under vacuum. The residue was washed with *n*-hexane (5 mL × 2), ether (3 mL) and dried under reduced pressure to provide complex **9** as a yellow solid. Yield, 75% (214 mg, 0.284 mmol). ^1H NMR (400 MHz, $CDCl_3$): δ 7.56–7.29 (m, 26H), 4.99 (s, 3H, CH_3). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 9.9 (s, $J = 2114.4$ Hz). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 271.7 (d, $J = 146.2$ Hz, Pt = *C*), 165.3 (HC=*C*Ph_2), 140.6 (*ipso*-CPh_2), 138.3 (*ipso*-CPh_2), 134.1 (d, $J = 10.2$ Hz, *o*- or *m*-PPh_3), 133.6 (d, $J = 10.6$ Hz, HC=CPh_2), 131.3, 130.6, 129.6 (br, *p*-PPh_3), 129.3129.0, 128.7 (d, $J = 49.1$ Hz, *ipso*-PPh_3), 127.8, 127.3 (d, $J = 10.6$ Hz, *o*- or *m*-PPh_3), 127.2, 67.5 (d, $J = 2.8$ Hz, OCH_3). Anal. Calcd. for $C_{34}H_{29}Cl_2OPPt$: C, 54.41, H, 3.89. Found: C, 54.61, H, 3.93.

Synthesis of 10. To a solution of $[PtCl_2(PPh_3)]_2$ (300 mg, 0.283 mmol) in $CHCl_3$ (25 mL) was added 1-ethynylcyclohexan-1-ol (720 mg, 5.80 mmol) and ethanol (4 mL). The reaction mixture was stirred for 10 h at room temperature to give a clear yellow solution. All volatiles of the reaction mixture were removed under vacuum. The residue was washed with cold pentane (5 mL × 2), then purified by column chromatography on SiO_2 using dichloromethane as the eluent. The yellow band was collected, then recrystallized from Et_2O to provide complex **10** as a yellow solid. Yield, 35% (138 mg, 0.198 mmol). ^1H NMR (400 MHz, CD_2Cl_2): δ 7.67–7.72 (m, 6H), 7.45–7.53 (m, 9H), 6.53 (d, $J = 8.1$ Hz, 1H, C*H*=Cy), 5.83 (q, $J = 7.1$ Hz, 2H, OCH_2), 4.44 (t, $J = 6.0$ Hz, 2H, CH_2), 2.48 (t, $J = 5.8$ Hz, 2H, CH_2), 1.94–1.97 (m, 2H, CH_2), 1.83–1.86 (m, 2H, CH_2), 1.70–1.76 (m, 5H, CH_2, OCH_2CH_3). $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2): δ 12.3 (s, $J_{PtP} = 2136.3$ Hz). $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2): δ 268.8 (d, $J = 145.9$ Hz, Pt = *C*), 183.1 (HC=*C*R_2), 134.0 (d, $J = 10.1$ Hz, *o*- or *m*-PPh_3),132.1 (d, $J = 11.2$ Hz, HC=Cy), 129.7 (d, $J = 2.1$ Hz, *p*-PPh_3), 128.9 (d, $J = 49.5$ Hz, *ipso*-PPh_3), 127.4 (d, $J = 10.4$ Hz, *o*- or *m*-PPh_3), 78.6 (d, $J = 2.6$ Hz, OCH_2), 39.6 (CH_2), 35.1 (CH_2), 28.9 (CH_2), 28.0 (CH_2), 25.3 (CH_2),13.8 (CH_3). Anal. Calcd. for $C_{28}H_{31}Cl_2OPPt$: C, 49.42, H, 4.59. Found: C, 49.74, H, 4.49.

Synthesis of 11. To a solution of $[PtCl_2(PPh_3)]_2$ (200 mg, 0.189 mmol) in $CHCl_3$ (15 mL) was added 3-isopropyl-1-(trimethylsilyl)penta-1,4-diyn-3-ol (150 mg, 0.772 mmol) and ethanol (4 mL). The reaction mixture was stirred for 10 h at room

temperature to give a clear yellow solution. All volatiles of the reaction mixture were removed under vacuum. The residue was washed with cold *n*-pentane (2 mL × 2) and dried under vacuum, then purified by column chromatography on SiO_2 using mixtures of ethyl acetate: *n*-hexane (= 1: 30), and then methanol: dichloromethane (= 1: 100) as the eluents. A yellow-green band was collected. The solvents were removed under reduced pressure to provide complex **11** as a yellow solid. Yield, 30% (85.5 mg, 0.113 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62–7.67 (m, 6H), 7.38–7.46 (m, 9H), 6.70 (d, J = 7.6 Hz, 1H, C*H*=CR$_2$), 6.57 (sept, J = 6.6 Hz, 1H, C*H*Me$_2$), 5.80 (q, J = 7.1 Hz, 1H, OC*H*$_2$), 1.68 (t, J = 7.2 Hz, 3H, OCH$_2$C*H*$_3$), 1.26 (d, J = 6.6 Hz, 6H, CH*Me*$_2$), 0.23 (s, 9H, Si*Me*$_3$). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 11.8 (s, J = 2145.0 Hz). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 269.3 (d, J = 147.2 Hz, Pt = *C*), 161.4 (HC=*C*R$_2$), 139.4 (d, J = 11.4 Hz, H*C*=CR$_2$), 134.0 (d, J = 10.7 Hz, *o*- or *m*-PPh$_3$), 129.7 (*p*-PPh$_3$), 128.7 (d, J = 50.0 Hz, *ipso*-PPh$_3$), 127.4 (d, J = 10.0 Hz, *o*- or *m*-PPh$_3$), 110.9 (C≡CTMS), 103.4 (C≡*C*TMS), 79.2 (d, J = 3.2 Hz, O*C*H$_2$), 32.8 (*C*HMe$_2$), 20.7 (CH*Me*$_2$),13.9 (OCH$_2$*C*H$_3$), −1.08 (Si*Me*$_3$). Anal. Calcd. for $C_{31}H_{37}Cl_2OPPtSi$: C, 49.60, H, 4.97. Found: C, 49.72, H, 4.82.

Synthesis of 12. To a solution of $[PtCl_2(PPh_3)]_2$ (150 mg, 0.142 mmol) in $CHCl_3$ (15 mL) was added 1-phenylprop-2-yn-1-ol (370 mg, 2.80 mmol) and ethanol (3 mL). The reaction mixture was stirred for 24 h at room temperature to give a clear yellow solution. All volatiles of the reaction mixture were removed under vacuum. The residue was washed with *n*-hexane (15 mL × 2), then purified by column chromatography on SiO_2 using dichloromethane as the eluent, the yellow band was collected, and the solvents were removed under reduced pressure to provide complex **12** as a green solid. Yield, 30% (57.8 mg, 0.084 mmol). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 9.27 (d, $J_{H\text{-}H}$ = 15.6 Hz, 1H, CH=C*H*Ph), 7.80–7.82 (m, 2H), 7.70–7.75 (m, 6H), 7.60–7.62 (m, 1H), 7.45–7.58 (m, 11H), 7.26 (dd, $J_{H\text{-}H}$ = 15.6 Hz, $J_{P\text{-}H}$ = 7.7 Hz, 1H, -C*H*=CHPh), 5.80 (q, J = 7.2 Hz, 2H, C*H*$_2$), 1.74 (t, J = 7.1 Hz, 3H, C*H*$_3$). ^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2): δ 12.5 (s, J_{PtP} = 2122.7 Hz). ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2): δ 271.0 (d, J = 148.6 Hz, Pt = *C*), 166.5 (HC=*C*HPh), 134.2 (d, J = 10.2 Hz, *o*- or *m*-PPh$_3$), 133.8 (*ipso*-Ph), 133.7 (d, J = 10.5 Hz, -H*C*=CPh$_2$), 132.3 (*p*-Ph), 129.8 (s, *p*-PPh$_3$), 129.3, 128.8 (d, J = 49.5 Hz, *ipso*-PPh$_3$), 128.6, 127.4 (d, J = 10.2 Hz, *o*- or *m*-PPh$_3$), 78.3 (d, J = 2.7 Hz, *C*H$_2$), 13.7 (*C*H$_3$). Anal. Calcd. for $C_{35}H_{31}Cl_2OPPt$: C, 54.98, H, 4.09. Found: C, 50.81, H, 4.02.

Synthesis of 13. To a solution of $[PtCl_2(PPh_3)]_2$ (300 mg, 0.283 mmol) in $CHCl_3$ (25 mL) was added 2-methylbut-3-yn-2-ol (487 mg, 5.80 mmol) and ethanol (4 mL). The reaction mixture was stirred for 10 h at room temperature to give a clear yellow solution. All volatiles of the reaction mixture were removed under vacuum. The residue was washed with *n*-hexane (10 mL × 2), then recrystallized from DCM/n-hexane to provide complex **13** as a yellow solid. Yield, 50% (185 mg, 0.283 mmol). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.66–7.71 (m, 6H), 7.51–7.54 (m, 3H), 7.42–7.47 (m, 6H), 6.37 (s, 1H, C*H*=CMe$_2$), 5.60 (m, 1H, OC*H*$_2$), 4.92 (m, 1H, OC*H*$_2$), 2.31 (s, 3H, CH$_3$), 1.70 (s, 3H, CH$_3$), 1.34 (t, J = 7.1 Hz, 3H, OCH$_2$C*H*$_3$). ^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2): δ 8.0 (s, J_{PtP} = 4105.0 Hz). ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2): δ 247.6 (d, J = 4.2 Hz, Pt = *C*), 167.9 (HC=*C*Ph$_2$), 134.6 (H*C*=CPh$_2$), 133.5 (d, J = 10.4 Hz, *o*- or *m*-PPh$_3$), 130.9 (d, J = 2.3 Hz, *p*-PPh$_3$), 128.3 (d, J = 64.1 Hz, *ipso*-PPh$_3$), 127.8 (d, J = 11.3 Hz, *o*- or *m*-PPh$_3$), 79.4 (*C*H$_2$), 28.7 (*C*H$_3$), 23.7 (*C*H$_3$),13.2 (*C*H$_3$). Anal. Calcd. for $C_{25}H_{27}Cl_2OPPt$: C, 46.89, H, 4.25. Found: C, 46.91, H, 4.21.

Synthesis of 14A. A mixture of the platinum vinylcarbene **8** (200 mg, 0.261 mmol) and NaI (391 mg, 2.61 mmol) in THF (15 mL) was stirred for 5 min at room temperature. All volatiles of the reaction mixture were removed under vacuum. The residue was extracted with DCM (5 mL × 2) and dried under reduced pressure to provide complex **14A** as a yellow solid. Yield: 95% (235 mg, 0.247 mmol). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.84 (d, J = 1.8 Hz, 1H, C*H*=CPh$_2$) 7.63–7.68 (m, 6H), 7.38–7.49 (m, 19H), 5.04 (q, J = 7.1 Hz, 2H, C*H*$_2$), 1.09 (t, J = 7.1 Hz, 3H, C*H*$_3$). ^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2): δ 8.6 (s, J_{PtP} = 2118.8 Hz). ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2): δ 269.9 (d, J = 141.3 Hz, Pt = *C*), 154.9 (d, J = 2.5 Hz, HC=*C*Ph$_2$), 139.6 (*ipso*-CPh$_2$), 138.3 (*ipso*-CPh$_2$), 134.6 (d, J = 10.8 Hz, *o*- or *m*-PPh$_3$), 133.5 (d, J = 8.0 Hz, HC=CPh$_2$), 130.9 (d, J = 50.0 Hz, *ipso*-PPh$_3$), 130.3, 129.6 (d, J = 1.9 Hz, *p*-PPh$_3$), 129.2, 129.0, 128.0, 127.8, 127.2, 127.0 (d, J = 9.8 Hz, *o*- or *m*-PPh$_3$), 79.2 (d, J = 3.5 Hz, *C*H$_2$), 12.1 (*C*H$_3$). Anal. Calcd. for $C_{35}H_{31}I_2OPPt$: C, 44.37, H, 3.30. Found: C, 44.44, H, 3.49.

Synthesis of 14B. A solution of **14A** (200 mg, 0.211 mmol) in THF (15 mL) was stirred for 2 days at 90 °C, all volatiles of the reaction mixture were removed under vacuum to provide complex **14B** as a yellow solid. Yield, 95% (190 mg, 0.200 mmol). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.71–7.77 (m, 6H), 7.51–7.54 (m, 3H), 7.42–7.48 (m, 8H), 7.30–7.39 (m, 5H), 7.06–7.10 (m, 4H), 4.93–5.01 (m, 1H, C*H*$_2$), 4.31–4.39 (m, 1H, C*H*$_2$), 0.73 (t, J = 7.1 Hz, 3H, C*H*$_3$). ^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2): δ 7.7 (s, J_{PtP} = 3924.2 Hz). ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2): δ 249.1 (s, Pt = *C*), 155.5 (HC=*C*Ph$_2$), 139.2 (*ipso*-CPh$_2$), 138.2 (*ipso*-CPh$_2$), 132.8 (d, J = 10.9 Hz, *o*- or *m*-PPh$_3$), 131.3, 130.8(*p*-PPh$_3$), 130.7, 129.6(d, J = 62.3 Hz, *ipso*-PPh$_3$), 128.8, 128.0, 127.9, 127.7 (d, J = 10.0 Hz, *o*- or *m*-PPh$_3$), 127.6, 127.1, 78.7 (*C*H$_2$), 11.4 (*C*H$_3$). Anal. Calcd. for $C_{35}H_{31}I_2OPPt$: C, 44.37, H, 3.30. Found: C, 44.19, H, 3.52.

Synthesis of 15. A mixture of the platinum vinylcarbene **8** (300 mg, 0.392 mmol) and PPh_3 (411 mg, 1.56 mmol) in DCM (20 mL) was stirred for 15 min at room temperature. All volatiles of the reaction mixture were then removed under vacuum. The residue was washed with ether (10 mL × 3) and dried under reduced pressure to provide complex **15** as a yellow solid. Yield, 90% (339 mg, 0.352 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76–7.79 (m, 12H), 7.33–7.40 (m, 18H), 7.24–7.26 (m, 1H), 7.14–7.18 (m, 3H), 6.99–7.03 (m, 2H), 6.72–6.74 (m, 2H), 6.68 (s, 1H, C*H*=CPh$_2$), 6.22–6.24 (m, 2H). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 19.8 (t, J = 3532.1 Hz). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 205.7 (t, J = 5.3 Hz, Pt-*C*O), 143.4 (HC=*C*Ph$_2$), 142.4 (*ipso*-CPh$_2$), 138.3 (*ipso*-CPh$_2$), 136.3 (t, J = 6.4 Hz, HC=CPh$_2$), 134.3 (t, J = 6.4 Hz, *o*- or *m*-PPh$_3$), 129.8 (t, J = 27.8 Hz, *ipso*-PPh$_3$), 129.7 (*p*-PPh$_3$), 129.3, 127.6, 127.4 (t, J = 5.3 Hz, *o*- or *m*-PPh$_3$), 127.2, 127.2, 126.7, 125.8.

Decarbonylation of 15. **Condition A.** A solution of **15** (100 mg, 0.104 mmol) in DCM (15 mL) was refluxed for 20 h. All volatiles of the reaction mixture were then removed under vacuum. The residue was extracted with Et_2O (5 mL × 3) to leave a colorless residue. The solvent of the extract was removed under reduced pressure and dried under reduced pressure to provide complex **16A** as a pale yellow solid. Yield, 10% (9.7 mg, 0.010 mmol). The colorless residue was dried under reduced pressure to provide complex **16B.** Yield, 70% (68.0 mg, 0.073 mmol).

Condition B. A solution of **15** (50.0 mg, 0.052 mmol) in $CHCl_3$ (1 mL) was refluxed for one hour. All volatiles of the reaction mixture were removed under vacuum. The residue was dried under reduced pressure to provide complex **16B** as a pale yellow solid. Yield, 99% (48.1 mg, 0.051 mmol). Complex **16B** could also be obtained from **16A** as follows. A solution of **16A** (20.0 mg, 0.021 mmol) in $CHCl_3$ (0.4 mL) was refluxed for one hour. All volatiles of the reaction mixture were removed under vacuum to provide complex **16B** as pale yellow solid. Yield, 99% (19.8 mg, 0.021 mmol). Characterization data of **16A**: ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.56–6.98 (m, 39H), 6.66–6.68 (m, 2H). ^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2): δ 21.1 (d, J_{PP} = 15.5 Hz, J_{PtP} = 1641.8 Hz), 16.2 (d, J_{PP} = 14.6 Hz, J_{PtP} = 4450.0 Hz). ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2): δ 149.7 (dd, J_{PC} = 114.1 Hz, 9.9 Hz, HC=*C*Ph$_2$), 146.5 (d, J = 4.1 Hz, *ipso*-CPh$_2$), 145.4 (d, J = 11.0 Hz, H*C*=CPh$_2$), 140.4 (*ipso*-CPh$_2$), 134.2 (d, J = 10.3 Hz, *o*- or *m*-PPh$_3$), 133.5 (d, J = 11.3 Hz, *o*- or *m*-PPh$_3$), 131.0

(d, $J = 44.4$ Hz, *ipso*-PPh_3), 130.9, 130.0 (d, $J = 62.0$ Hz, *ipso*-PPh_3), 129.5 (d, $J = 2.0$ Hz, *p*-PPh_3), 129.0 (*p*-PPh_3), 127.1 (d, $J = 11.0$ Hz, *o*- or *m*-PPh_3), 127.0 (d, $J = 9.5$ Hz, *o*- or *m*-PPh_3), 126.4, 126.3, 126.2, 125.1, 124.2. Anal. Calcd. for $C_{50}H_{41}ClP_2Pt$: C, 64.27, H, 4.42. Found: C, 63.95, H, 4.63. Characterization data of **16B**: ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.48–7.54 (m, 12H), 7.36–7.39 (m, 6H), 7.28–7.33 (m, 12H), 7.22–7.24 (m, 1H), 7.09–7.11 (m, 4H), 6.95–6.99 (m, 3H), 6.78–6.80 (m, 1H), 6.50–6.52 (m, 2H). $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2): δ 24.4 (s, $J_{PtP} = 3122.5$ Hz). $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2): δ 145.9 (*ipso*-CPh_2), 145.1 (*ipso*-CPh_2), 139.5 (t, $J = 3.9$ Hz, HC=CPh_2), 136.1 (t, $J = 9.6$ Hz, HC=CPh_2), 134.3 (t, $J = 6.0$ Hz, *o*- or *m*-PPh_3), 129.6 (*p*-PPh_3), 129.5 (t, $J = 27.9$ Hz, *ipso*-PPh_3), 129.0, 127.1 (t, $J = 5.3$ Hz, *o*- or *m*-PPh_3), 126.2, 126.1, 126.0, 125.0, 123.8. Anal. Calcd. for $C_{50}H_{41}ClP_2Pt$: C, 64.27, H, 4.42. Found: C, 64.22, H, 4.31.

Crystallographic analysis. Single crystals of **8, 9, 13, 16B** suitable for X-ray diffraction were grown from toluene solutions layered with hexane. Intensity data were collected on a Rigaku-Oxford Diffraction SuperNova diffractometer at 100 K. Diffraction data were processed using the CrysAlisPro software (version 1.171.35.19). Empirical absorption corrections were performed using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm in the CrysAlisPro software suite. Structure solution and refinement for all compounds were performed using the Olex2 software package (which embedded SHELXL) [31,32]. All the structures were solved by direct methods, expanded by difference Fourier syntheses and refined by full matrix least-squares on F^2. All non-hydrogen atoms were refined anisotropically with a riding model for the hydrogen atoms except noted separately. Further crystallographic details are summarized in Tables S1–S12. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 1870324, 1870323, 1870322, 1870321. Copies of these data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Computational detail. All structures were optimized at the B3LYP level of density functional theory [33]. Frequency calculations were also performed to confirm the characteristics of the calculated structures as minima. In the B3LYP calculations, the effective core potentials (ECPs) of Hay and Wadt with a double-ζ valence basis set (LanL2DZ) were used to describe Pt, P, and Cl atom, while the standard 6-31G(d) basis set was used for C, O, and H [34]. Polarization functions were added for Pt ($\zeta(f) = 0.993$), P ($\zeta(d) = 0.387$), and Cl ($\zeta(d) = 0.640$) [35]. All the calculations were performed with the Gaussian 03 software package [36].

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jorganchem.2018.10.016.

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