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Reaction of η^2-enone and enal-platinum(0) complexes with Lewis acidic compounds ☆

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Abstract

Reaction of η^2-enone and enal-platinum(0) complexes $Pt(CH_2{=}CHCOR)(PPh_3)_2$ (R = H, Me) with Lewis acidic compounds BX_3 (X = F, C_6F_5) afforded adducts formed by coordination of boron to oxygen of the carbonyl group. The X-ray structure determination of the adduct formed from $B(C_6F_5)_3$ and η^2-methylvinylketone complex showed no strong interaction between Pt and carbonyl carbon. In contrast to the inability of the palladium(0) η^2-enone complexes to form any Me_3Al adduct, η^2-cyclohexenoneplatinum(0) complex formed an isolable adduct with Me_3Al, the structure of which was also confirmed by X-ray analysis. The NMR spectral parameters (Pt–C, Pt–P and P–P coupling constants) of these adducts were compared with those of the original η^2-enone or enal-platinum(0) complexes as well as the ordinary η^3-allylplatinum cation $[Pt(PPh_3)_2(MeCHCHCH_2)]^+$.

Keywords: Platinum complex; η^2-Enone complex; η^2-Enal complex; Lewis acid

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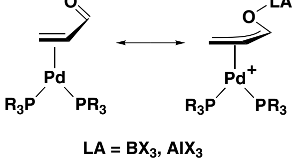
1. Introduction

The transition metal-catalyzed conjugate addition of various organometallic reagents, e.g., AlR_3, ZnR_2, Cp_2ZrRCl, InR_3, and BR_3, to α,β-unsaturated carbonyl compounds is one of the most useful reactions in organic synthesis and yet one of the least understood reactions [1,2]. Recently, we reported [3] that the coordination of Lewis acid, such as BR_3 and AlR_3, to η^2-enone and enal complexes of palladium led to continuous structure variation from acid-coordinated η^2-olefin type to zwitterionic η^3-allyl type (Scheme 1). These Lewis acid adducts could be model complexes as intermediates in transition metal-catalyzed conjugate addition of alkylmetals to α,β-unsaturated carbonyl compounds. Analogous platinum complexes can be expected to have a higher stability compared to their palladium analogs and to provide additional spectroscopic information due to the presence of the NMR-active ^{195}Pt nucleus. Here, we report on the preparation and spectroscopic properties of the platinum complexes by the reaction of η^2-enone and enal complexes with Lewis acids.

2. Results and discussion

The reaction of the enone complex $Pt(CH_2{=}CHCOCH_3)(PPh_3)_2$ with $BF_3 \cdot OEt_2$ or $B(C_6F_5)_3$ gave platinum complexes (**1a**, **1b**) quantitatively, having the expected composition in the elemental analysis (Eq. 1).



Scheme 1. Resonance forms of Lewis acid adducts.

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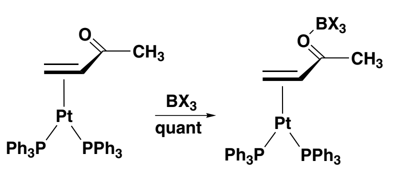
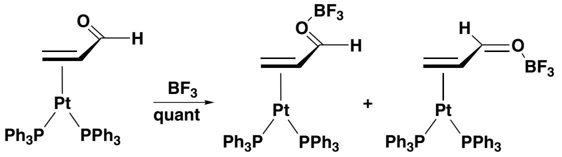
The X-ray structure analysis of **1b** shows $B(C_6F_5)_3$-coordinated η^2-enoneplatinum structure (Fig. 1), in which the Pt–C(carbonyl) distance (2.97(1) Å) is very close to the corresponding distance (2.91(2) Å) in the acid-free η^2-enone complex $Pt(PhCH{=}CHCOCH_3)(PPh_3)_2$ [4]. The overall structural features of **1b** are similar to those of the palladium analog $Pd(PhCH{=}CHCCH_3(OB(C_6F_5)_3))(PPh_3)_2$ already reported [3]. The reaction of the enal complex $Pt(CH_2{=}CHCHO)(PPh_3)_2$ with $BF_3 \cdot OEt_2$ led to isolation of the complex **2**, which existed as a mixture of two isomers (anti and syn; see Eq. 2) in solution. The anti form is the major isomer in solution, as confirmed by NOE measurements.

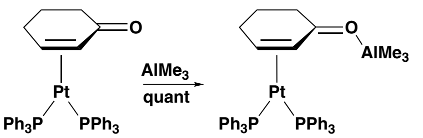


(1)

1a X = F, **1b** X = C_6F_5



anti **2** syn **2'** (2)



3 (3)

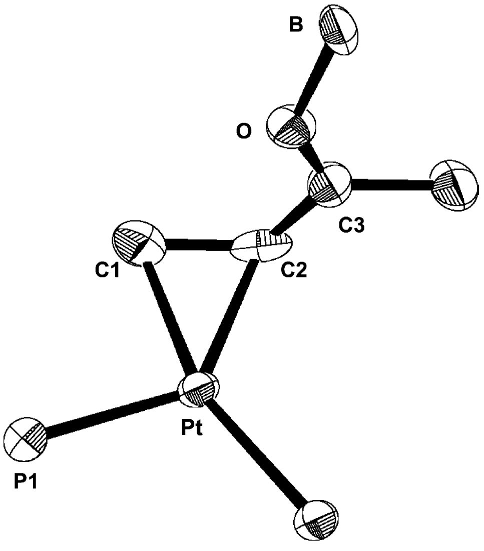


Fig. 1. ORTEP drawing of **1b**. Thermal ellipsoids are drawn at the 50% probability level. All H atoms, phenyl groups and C_6F_5 groups are omitted for clarity. Selected bond lengths (Å) and angles (deg): Pt–P1 = 2.262(4), Pt–P2 = 2.302(4), Pt–C1 = 2.16(2), Pt–C2 = 2.20(1), Pt–C3 = 2.97(1), C1–C2 = 1.47(2), C2–C3 = 1.37(2), C3–O = 1.29(2), O–B = 1.51(2), P1–Pt–P2 = 106.4(1).

In the previous study on a series of palladium(0)-Lewis acid adducts, any adduct was not isolated by using Me_3Al, the acidity of which is considerably weaker than other acids employed [3]. Reaction of platinum(0) η^2-cyclohexenone complex with Me_3Al afforded an isolable adduct **3** (Eq. 3). The isolation of **3** would have been attained by the higher Lewis basicity of the carbonyl oxygen of the coordinated enone ligand in the platinum than in the palladium complexes. The platinum(0)-olefin bond is expected to contain the greater π back bond component than the palladium(0)-olefin bond [5], suggesting the higher electron density accumulated on the olefinic part as well as on the carbonyl substituent in platinum than in palladium complexes [6]. The X-ray structure analysis of **3**, though not accurate enough for detailed discussion of bond length, showed occurrence of expected Al–O interaction (Fig. 2). The Pt–C(carbonyl) distance (3.04(5) Å) is too long to suggest the η^3-allyl electronic structure. There is a significant deviation of the aluminum atom from the least squares plane determined by C1–C2–C3–O, where aluminum is positioned away from platinum. The Al–O–C3–C2 torsion angle is −136°. The X-ray structure reports on adducts between trialkyl or triarylaluminum and carbonyl compounds have been rare, because it is difficult to isolate these in the pure state due to the oc-

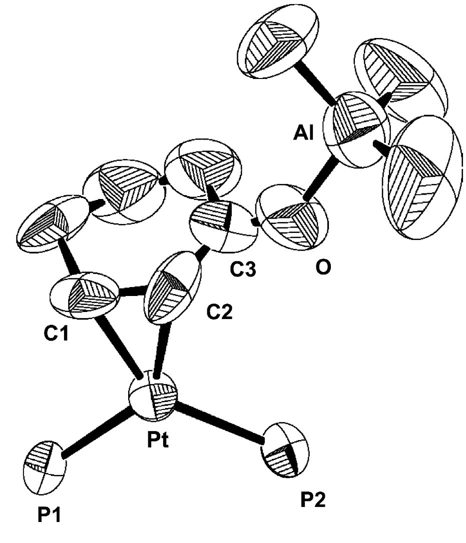


Fig. 2. ORTEP drawing of **3**. Thermal ellipsoids are drawn at the 50% probability level. All H atoms and phenyl groups are omitted for clarity. Selected bond lengths (Å) and angles (deg): Pt–P1 = 2.251(9), Pt–P2 = 2.321(9), Pt–C1 = 2.11(3), Pt–C2 = 2.23(4), Pt–C3 = 3.04(5), C1–C2 = 1.45(5), C2–C3 = 1.30(6), C3–O = 1.19(5), O–Al = 1.80(3), P1–Pt–P2 = 110.3(3).

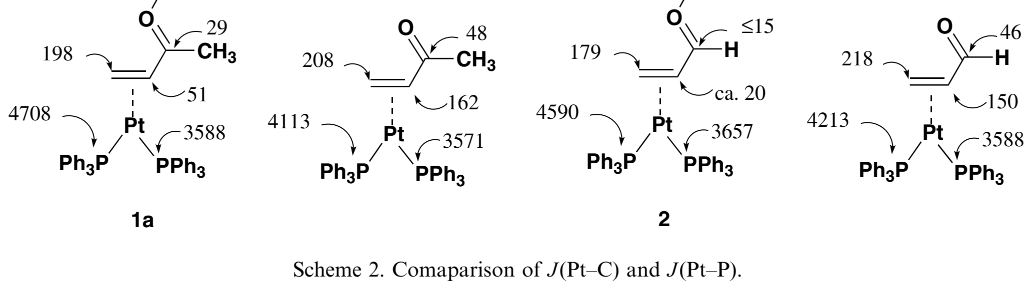
currence of the fast transfer of the organic group from aluminum to the coordinated carbonyl substrate [7].

The degree of the contribution of the η^3-coordination mode to the structure of the Lewis acid adducts with enone or enal complexes in solution could be evaluated from ^{13}C and ^{31}P NMR data. In the previous study on the palladium analogs, the chemical shift of the carbonyl carbon was used as a criterion for estimating the degree of contribution of the η^3-allyl structure to the overall structure of the Lewis acid adducts [3]. The higher chemical shift of the carbonyl carbon resonance was correlated with the greater η^3-allyl contribution. The chemical shift of the carbonyl carbon in **1** (192.3 in **1a**; 204.3 in **1b**) is much the same as that (202.2) in the original acid-free enone complex $Pt(CH_2{=}CHCOCH_3)(PPh_3)_2$, while the corresponding resonance in **2** (162.2) is considerably upfield shifted from the original platinum(0)-enal complex $Pt(CH_2{=}CHCHO)(PPh_3)_2$ (193.1). Also, in the palladium series, there is another empirical rule; the P–P coupling increased from the smallest values for acid-free Pd(0) enone complexes, e.g. $Pd(CH_2{=}CHCOCH_3)(PPh_3)_2$ (12.2 Hz) [8] through Lewis acid adducts (13.5–37.4 Hz) [3] to the largest values for ordinary η^3-allylpalladium(II) complexes, e.g. $[Pd(\eta^3\text{-}PhCHCHCH_2)(PPh_3)_2]^+$ (46.5 Hz) [3]. A variation of the P–P coupling according to the type of the complex was also observed in the platinum series, although the order of the amount of P–P coupling constant is completely reversed compared to the palladium series. Thus, the P–P couplings of **1** (17.1 Hz in **1a**; 18.9 Hz in **1b**) are smaller than that (37.8 Hz) of $Pt(CH_2{=}CHCOCH_3)(PPh_3)_2$, but larger than that (9.0 Hz) of the η^3-allylplatinum cation $[Pt(\eta^3\text{-}MeCHCHCH_2)(PPh_3)_2]^+$ [9]. The P–P coupling constant of **2** (5.8 Hz), which is far from that of the acid-free enal complex (37.8 Hz), is closer to that of the η^3-allylplatinum cation than those of **1** are. These trends in the carbonyl carbon shifts and P–P coupling constants appear to suggest the greater contribution of the η^3-allyl structure in **2** than in **1**. That the enal-acid adduct contains the greater η^3-allyl character than the enone-acid adduct was also noted in the analogous palladium series [3].

It should be pointed out, however, that the P–P coupling constant may be affected by some unspecified factors. For instance, it would be affected by the P–M–P angle, which in turn is influenced by the steric bulk of the other ligand groups. Note that the P–P coupling constant of **2** is 5.8 Hz, while that of **2′** is 15.6 Hz (see Section 3). Before the factors responsible for the variation of the P–P coupling are elucidated, there remains ambiguity in relying on this parameter for assessing the degree of contribution, perhaps very small in nature, of the η^3-allyl structure to Lewis acid adducts of M(0)-enone or enal complexes.

Comparison of the Pt–C and Pt–P coupling constants between **1a** or **2** and their parent complexes $Pt(CH_2{=}CHCOR)(PPh_3)_2$ shown in Scheme 2 seems also interesting. Upon complexation of BF_3 to the carbonyl oxygen, the Pt–C couplings for the olefinic carbons become smaller, with the particular attention being paid to the Pt–C coupling for the inner olefin-carbon that is remarkably smaller than that of the acid-free complex. Moreover, the Pt–P coupling for the phosphorus nucleus located trans to the inner olefin-carbon becomes considerably larger upon BF_3 complexation. Apparently the interaction between Pt and the inner olefin-carbon becomes much weaker upon the Lewis acid adduct formation [10].

There is another puzzling aspect in Pt–C coupling. Any spin–spin coupling larger than 15 Hz (the full width at half maximum) could not be observed between Pt and the carbonyl carbon of **2**, where the corresponding Pt–C coupling in the acid-free enal complex is larger (46 Hz). These observations are somewhat in contradiction to an idea suggested by the trend in the carbonyl carbon chemical shift that the carbonyl carbon interacts with Pt to some extent in the Lewis acid adduct **2** (see above). The decrease of Pt–C(carbonyl) coupling, though smaller in difference, is also observed upon formation of **1a** from $Pt(CH_2{=}CHCOCH_3)(PPh_3)_2$. The Pt–C couplings of the type shown in the Scheme 2 would be functions of several factors, and more extensive work is clearly necessary for a better understanding of the correlation between electronic structure and spectroscopic features of adducts from M(0)-enone or enal complex and Lewis acids.



1a **2**

Scheme 2. Comaparison of J(Pt–C) and J(Pt–P).

3. Experimental

General. All manipulations were conducted under a nitrogen atmosphere using standard Schlenck or drybox techniques. ^{1}H, ^{31}P and ^{13}C nuclear magnetic resonance spectra were recorded on JEOL GSX-270S and JEOL AL-400 spectrometers. The chemical shifts in the ^{1}H nuclear magnetic resonance spectra were recorded relative to Me$_4$Si, or C_6D_6 (δ 7.16). The chemical shifts in the ^{13}C spectra were recorded relative to Me$_4$Si, C_6D_6 (δ 128) or CD_2Cl_2 (δ 53.8). The chemical shifts in the ^{31}P spectra were recorded using 85% H_3PO_4 as an external standard. Elemental analyses were performed at the Instrumental Analysis Center, Faculty of Engineering, Osaka University. X-ray crystal data were collected by a Rigaku RAXIS-RAPID Imaging Plate diffractometer.

Materials. Unless indicated otherwise, all solvents used in this work were distilled prior to use. THF, hexane and C_6D_6 were distilled from sodium benzophenone ketyl, CD_2Cl_2 from CaH_2. All commercially available reagents were distilled and degassed prior to use. $B(C_6F_5)_3$ (3.9 wt% PF-3/Isoper E solution) was donated by Asahi Glass Co.

3.1. Synthesis of $(CH_2CHCCH_3(OBF_3))Pt(PPh_3)_2$ (1a)

To a solution of $Pt(CH_2{=}CH_2)(PPh_3)_2$ (201.4 mg, 0.269 mmol) in 10 ml of THF was added 44.5 μl of $CH_2{=}CHCOCH_3$ (37.5 mg, 0.535 mmol) and 33.7 μl of $BF_3 \cdot OEt_2$ (37.7 mg, 0.266 mmol) at room temperature. The reaction mixture was concentrated in vacuo to give yellow solids quantitatively. The solids were washed with hexane to give 218.8 mg of **1a** in 95% isolated yield and recrystallized from THF/hexane solution to give yellow solids (111.6 mg, 48%). ^{1}H NMR (C_6D_6): δ 1.68 (d, $J_{HP} = 7.3$ Hz, 3H), 1.94 (ddd, $J_{HH} = 6.9, 10.5$ Hz, $J_{HP} = 6.5$ Hz, 1H), 2.89 (ddd, $J_{HH} = 8.6, 10.5$ Hz, $J_{HP} = 4.5$ Hz, 1H), 3.60 (dd, $J_{HH} = 6.9, 8.6$ Hz, 1H), 6.83–7.04 (m, 24H), 7.33–7.43 (m, 6H). ^{31}P NMR (C_6D_6): δ 26.36 (d, $J_{PP} = 17.1$ Hz, $J_{PPt} = 3588$ Hz), 28.51 (d, $J_{PP} = 17.1$ Hz, $J_{PPt} = 4708$ Hz). ^{13}C NMR (CD_2Cl_2): δ 22.5 (s), 38.8 (d, $J_{CP} = 37.9$ Hz, $J_{CPt} = 198.3$ Hz), 68.4 (t, $J_{CP} = 6.4$, $J_{CPt} = 50.7$ Hz), 128.7–134.6 (m), 192.3 (br, $J_{CPt} = 29.3$ Hz). Anal. Calc. for $C_{40}H_{36}BF_3OP_2Pt$: C; 56.02, H; 4.23. Found: C, 55.72; H, 4.39.

3.2. Synthesis of $(CH_2CHCCH_3(OB(C_6F_5)_3))Pt(PPh_3)_2$ (1b)

To a solution of $Pt(CH_2{=}CH_2)(PPh_3)_2$ (206.5 mg, 0.276 mmol) in 8 ml of THF was added 46.1 μl of $CH_2{=}CHCOCH_3$ (38.8 mg, 0.554 mmol) and 5.0 ml of $B(C_6F_5)_3$ (142.0 mg, 0.277 mmol) at room temperature. The reaction mixture was concentrated in vacuo to give yellow solids quantitatively. The solids were washed with hexane and recrystallized from TFH/hexane solution to give 195.1 mg of **1b** in 54% isolated yield. ^{1}H NMR (C_6D_6): δ 1.07 (d, $J_{HP} = 7.2$ Hz, 3H), 1.99 (ddd, $J_{HH} = 1.7, 16.0$ Hz, $J_{HP} = 6.9$ Hz, 1H), 2.85 (dddd, $J_{HH} = 1.7, 7.8$ Hz, $J_{HP} = 4.0, 11.7$ Hz, 1H), 3.79 (ddd, $J_{HH} = 7.8, 16.0$ Hz, $J_{HP} = 7.9$ Hz, 1H), 6.74–6.91 (m, 24H), 7.19–7.23 (m, 6H). ^{31}P NMR (C_6D_6): δ 27.22 (d, $J_{PP} = 18.9$ Hz, $J_{PPt} = 4762$ Hz), 28.65 (d, $J_{PP} = 18.9$ Hz, $J_{PPt} = 3566$ Hz). ^{13}C NMR (C_6D_6): δ 24.1 (s), 38.7 (d, $J_{CP} = 37.5$ Hz, $J_{CPt} = 192.1$ Hz), 64.3 (dd, $J_{CP} = 8.7, 5.1$ Hz, $J_{CPt} = 67.0$ Hz), 127.6–150.2 (m), 204.3 (br, $J_{CPt} = 30.2$ Hz). Anal. Calc. for $C_{58}H_{36}BF_{15}OP_2Pt$: C, 53.52; H, 2.79. Found: C, 53.20; H, 3.15.

3.3. Synthesis of $(CH_2CHCH(OBF_3))Pt(PPh_3)_2$ (2/2′ = 88/12)

To a solution of $Pt(CH_2{=}CH_2)(PPh_3)_2$ (144.1 mg, 0.193 mmol) in 4 ml of THF was added 15.0 μl of $CH_2{=}CHCHO$ (12.6 mg, 0.225 mmol) and 26.0 μl of $BF_3 \cdot OEt_2$ (29.2 mg, 0.205 mmol) at room temperature. The reaction mixture was concentrated in vacuo to give yellow solids quantitatively. The solids were washed with hexane to give 140.0 mg of **2/2′** in 88% isolated yield. An analytical sample was prepared by recrystallization from THF/hexane solution. **2**. ^{1}H NMR (C_6D_6): δ 2.19 (ddd, $J_{HH} = 3.6, 12.8$ Hz, $J_{HP} = 7.3$ Hz, 1H), 2.72 (ddd, $J_{HH} = 4.3, 8.1, 12.8$ Hz, 1H), 3.73 (dd, $J_{HH} = 3.6, 8.1$ Hz, 1H), 6.83–7.12 (m, 18H), 7.30–7.48 (m, 12H). ^{31}P NMR (C_6D_6): δ 20.86 (d, $J_{PP} = 5.8$ Hz, $J_{PPt} = 3657$ Hz), 26.94 (d, $J_{PP} = 5.8$ Hz, $J_{PPt} = 4590$ Hz). ^{13}C NMR (C_6D_6): δ 40.0 (d, $J_{CP} = 36.5$ Hz, $J_{CPt} = 179.2$ Hz), 71.4 (br, $J_{CPt} =$ ca. 20 Hz), 127.6–135.0 (m), 162.2 (br). **2′**. ^{1}H NMR (C_6D_6): δ 1.70(m, 1H), 2.46 (m, 1H), 3.32 (m, 1H). The other resonances are hidden by those of the major isomer. ^{31}P NMR (C_6D_6): δ 27.11 (d, $J_{PP} = 15.6$ Hz, $J_{PPt} = 4884$ Hz), 30.25 (d, $J_{PP} = 15.6$ Hz, $J_{PPt} = 3497$ Hz). Anal. Calc. for $C_{39}H_{34}BF_3OP_2Pt$: C, 55.53; H, 4.06. Found; C, 55.24; H, 3.89.

3.4. Synthesis of $(CHCHC(OAlMe_3)CH_2CH_2CH_2)Pt(PPh_3)_2$ (3)

To a solution of $Pt(CH_2{=}CH_2)(PPh_3)_2$ (105.3 mg, 0.141 mmol) in 5 ml of THF was added 13.7 μl of cyclohexenone (13.6 mg, 0.141 mmol) and 0.14 ml (1.00 M) of a solution of $AlMe_3$ in hexane at room temperature. The reaction mixture was concentrated in vacuo to give yellow solids quantitatively. The solids were washed with hexane and recrystallized from THF/hexane solution to give yellow crystals (71.6 mg, 57%). ^{1}H NMR (C_6D_6): δ −0.30 (s, 9H), 0.86 (m 1H), 1.23 (m, 1H), 1.75 (m, 1H), 1.89 (m, 1H), 2.32 (m, 1H), 2.42 (m, 1H), 3.05 (m, 1H), 4.30 (t, $J_{HP} = 6.8$ Hz, $J = 29.4$ Hz, 1H), 6.82–7.03 (m, 18H), 7.31–7.33(m, 12H). ^{31}P NMR (C_6D_6): δ 22.44 (d, $J_{PP} = 33.0$ Hz, $J_{PPt} = 4741$ Hz), 31.34 (d, $J_{PP} = 33.0$ Hz, $J_{PPt} = 3289$ Hz). For this compound, accurate elemental analyses were precluded by extremely air sensitivity and/or systematic problems with elemental analysis of organometallic compounds [11].

3.5. *X-ray structure determination*

Summary of crystal data, data collection, and structure refinement parameters for complex **1b** and **3** is listed in Table 1 and Table 2, respectively.

Table 1
X-ray data for complex **1b**

Empirical formula	$C_{58}H_{36}F_{15}OBP_2Pt$
Formula weight	1301.75
Crystal dimensions	0.25 × 0.25 × 0.25 mm
Crystal system	triclinic
2θ range	2.6–54.9°
Lattice parameters	$a = 11.1845(2)$ Å
	$b = 14.7241(2)$ Å
	$c = 17.4782(6)$ Å
	$\alpha = 65.804(1)°$
	$\beta = 84.084(1)°$
	$\gamma = 82.8979(9)°$
	$V = 2601.0(1)$ Å^3
Space group	*P*-1 (No. 2)
Z value	2
D_{calcd}	1.662 g/cm^3,
F_{000}	1280.00
Radiation	Mo Kα ($\lambda = 0.71069$ Å)
Temperature	0.0 °C
No. of reflections measured	Total: 24868
	Unique: 11767
Residuals: R; R_w	0.076; 0.088
Goodness-of-fit indicator	1.99

Table 2
X-ray data for complex **3**

Empirical formula	$C_{45}H_{47}AlOP_2Pt$
Formula weight	887.88
Crystal dimensions	0.50 × 0.25 × 0.25 mm
Crystal system	monoclinic
2θ range	3.9–55.0°
Lattice parameters	$a = 17.210(3)$ Å
	$b = 14.000(3)$ Å
	$c = 18.476(4)$ Å
	$\beta = 116.768(9)°$
	$V = 3974(1)$ Å^3
Space group	$P2_1/a$ (No. 14)
Z value	4
D_{calcd}	1.484 g/cm^3,
F_{000}	1784.00
Radiation	Mo Kα ($\lambda = 0.71069$ Å)
Temperature	23.0 °C
No. of reflections Measured	Total: 26417
	Unique: 8890
Residuals: R; R_w	0.070; 0.089
Goodness-of-fit indicator	3.91

Acknowledgements

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[10] The Pt–C coupling for the allyl center carbon in $[Pt(\eta^3\text{-}MeCH\text{-}CHCH_2)(PPh_3)_2]^+$ is small (24 Hz) compared to those for the allyl terminal carbon (108 Hz) [8].

[11] See the Supporting Information in the following: M.J. Carney, P.J. Walsh, R.G. Bergman, J. Am. Chem. Soc. 112 (1990) 6426.