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Preparation, properties, and catalytic activity of transition-metal complexes containing a ligated 2-methyl-3,3-diphenyl-1,3-diphosphapropene skeleton

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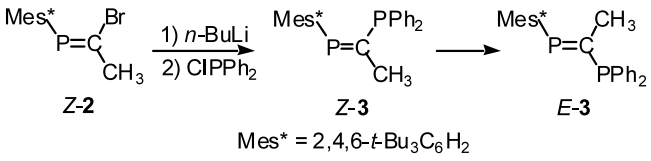
Abstract—2-Methyl-3,3-diphenyl-1-(2,4,6-tri-*t*-butylphenyl)-1,3-diphosphapropene behaved as an unsymmetrical chelating ligand for transition metal complexes and the 1,3-diphosphapropene moiety was hydrolyzed to afford the 1,3-diphosphapropan-1-ol derivative upon coordination. The palladium complex showed catalytic activity for the Sonogashira coupling reaction.

We have recently reported preparation of a bulky 2-chloro-1,3-diphosphapropene Mes*P=C(Cl)PPh_2 (**1**; Mes* = 2,4,6-*t*-$Bu_3C_6H_2$) as a primitive compound involving an unsaturated sp^2 phosphorus and a normal sp^3 phosphino group.[1] Basically, **1** takes the *Z* configuration to avoid the steric congestion between the Mes* group and the PPh_2 moiety, which is advantageous to act as a chelate ligand. The 1,3-diphosphapropene skeleton behaves like an unsymmetrical chelating ligand and displays a stepwise coordination nature on the tungsten(0) metal.[1] On the other hand, **1** did not afford any palladium or platinum complexes. Some phosphorus-carbon double-bondings were reported to be activated on coordination to the transition metals to cause saturation of the P=C bond[2] leading to an undesired reaction of **1** with a palladium or a platinum reagent. We[3] and others[4] have utilized several low-coordinated phosphorus compounds for ligands of synthetic catalysts containing palladium or platinum, and we were prompted to explore 1,3-diphosphapropene derivatives which afford the corresponding palladium or platinum complexes.[5] We here report that a 3-methyl-3,3-diphenyl-1,3-diphosphapropene derivative afforded the corresponding chelate palladium(II) complex which catalyzed the Sonogashira coupling reaction.[6] In the course of the research, we also found that the P=C moiety was activated by palladium or platinum leading to the corresponding adduct upon hydrolysis.

(*Z*)-2-Bromo-1-(2,4,6-tri-*t*-butylphenyl)-1-phosphapropene (*Z*-**2**)[7] was allowed to react successively with butyllithium and chlorodiphenylphosphine to give (*E*)-2-methyl-1,3-diphosphapropene *E*-**3** in 66% yield (Scheme 1).[8] In this reaction, *Z*-**3** seemed to be unstable and isomerized to *E*-**3** probably due to the steric repulsion between the Mes* and the Ph_2P groups as we observed for **1**.[1] The *E*/*Z* isomerization of *E*-**3** was observed upon heating (100°C in toluene) to afford a mixture of **3** in *E*/*Z* = 2:1 ratio,[8] whereas no isomerization of **1** was observed under similar conditions.[1] Attempts to isolate *Z*-**3** by means of chromatography failed due to its instability on silica gel.

First of all, the coordination ability of *E*-**3** was studied. Compound *E*-**3** was allowed to react with $W(CO)_5$(thf) to afford monocoordinated complex **4** in 70% yield together with a small amount of chelate complex **5** (3% yield).[9] Furthermore, **4** was irradiated to afford **5** in 29% yield from **4** by releasing one CO ligand (Scheme 2).[9] In contrast to *E*-**3**, *E*/*Z* isomerization of **4** was not observed upon heating. The molecular structure of **5** was nearly homologous to the corresponding tungsten(0) complex of **1** (Fig. 1).[10]



Scheme 1. Preparation of *E*-**3** from *Z*-**2**.

Keywords: phosphaalkenes; kinetic stabilization; chelate ligand; Sonogashira coupling.

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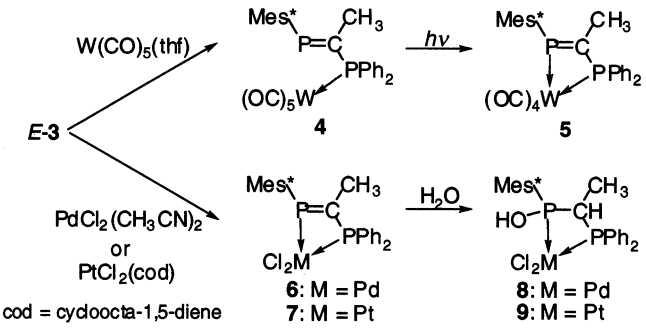


Scheme 2. Preparation of tungsten(0), palladium(II), and platinum(II) complexes from *E*-**3**.

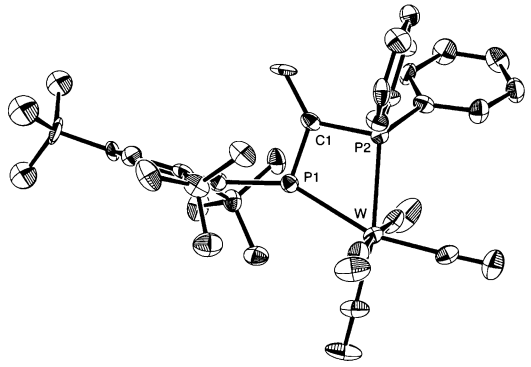


Figure 1. Molecular structure of **5**. The hydrogen atoms are omitted for clarity. The *p*-*t*-butyl group in the Mes* group is disordered and atoms with predominant occupancy factor (0.62) are shown.

In contrast to **1**, *E*-**3** formed palladium(II) and platinum(II) complexes: *E*-**3** was allowed to react with $PdCl_2(CH_3CN)_2$ to afford the corresponding palladium(II) complex **6**.[11] The result suggests that the coordination properties of the 1,3-diphosphapropene ligand strongly depend on the substituents. In the ^{31}P NMR spectrum, the sp^2 phosphorus in **6** shifted to a higher field than that of *E*-**3**, which still falls within the region of P=C resonance, indicating the end-on coordination (Scheme 2). Additionally, a platinum(II) complex **7** [δ_P 195.9 ($^1J_{PPt}=3898$ Hz), −22.4 ($^1J_{PPt}=2887$ Hz), $^2J_{PP}=50$ Hz] was also obtained by a similar reaction with $PtCl_2$(cycloocta-1,5-diene).

When **6** was allowed to react with an excess amount of water in THF/dichloromethane for 40 h, **8** was obtained almost quantitatively (Scheme 2).[12] Indeed, when we dissolved the powdered **8** in a 1:1 mixture of dichloromethane and 'wet' THF, pale-yellow prisms of **8** were formed at 0°C after a week. Figure 2a displays the molecular structure of **8** indicating that the addition of water occurred on the P=C bond in the *syn* fashion to give the *meso* isomers.[13] The solvent molecules, water and dichloromethane, were involved in the crystal, and indeed a transparent prism of **8** became an opaque solid in the air, probably due to loss of the involved solvents from the crystal lattice. Compound **8** is stable in the air and did not seem to be in an equilibrium of the Arbuzov type with the corresponding phosphine oxide.[14] The geometry around the palladium in **8** reveals a distorted square form while the Pd–P1–C1–P2 ring is almost planar. The Cl2–Pd bond, 2.3970(9) Å, is longer than that of Cl1–Pd, 2.3846(9) Å, indicating the greater *trans* effect of the P1 moiety compared with the PPh_2 group. The hydroxyl group in **8** displayed a hydrogen bond with water in the crystal showing the intermolecular H15…OH_2 distance of 1.57 Å. The P1–O1 bond, 1.567(3) Å, is similar to the 'P–O(H)' value in $[H(Ph_2PO)_2Au]_2$ (1.561(5) Å).[15] The P1 atom remarkably deviates from the Mes* plane, as indicated in the torsion angles of P1–C_{ipso}–C_{ortho}–$C_{t\text{-Bu}}$ [54.1(5) and 51.9(5)°], due to relief of the steric congestion. As for *E*-**3**, no hydrolyzed product was obtained suggesting that the palladium moiety enhances the reactivity of the P=C part. Although the detailed mechanism for the hydrolysis affording **8** is uncertain so far, the palladium atom might promote the *syn*-addition of water.[16] Complex **8** decomposed in chloroform in several hours to give 1,3,5-tri-*t*-butylbenzene, indicating the instability of **8** in the presence of a trace of acid.[17] Similarly, **7** afforded a hydrolyzed product **9** on silica gel (Fig. 2b).[18,19] The geometry around the platinum displays a planar square. The distance of the Cl1–Pt [2.368(4) Å] is longer than that of the Cl2–Pt [2.352(4) Å], which is similar to the geometries of **8**. The P1–O1 distance was observed by 1.60(2) Å.

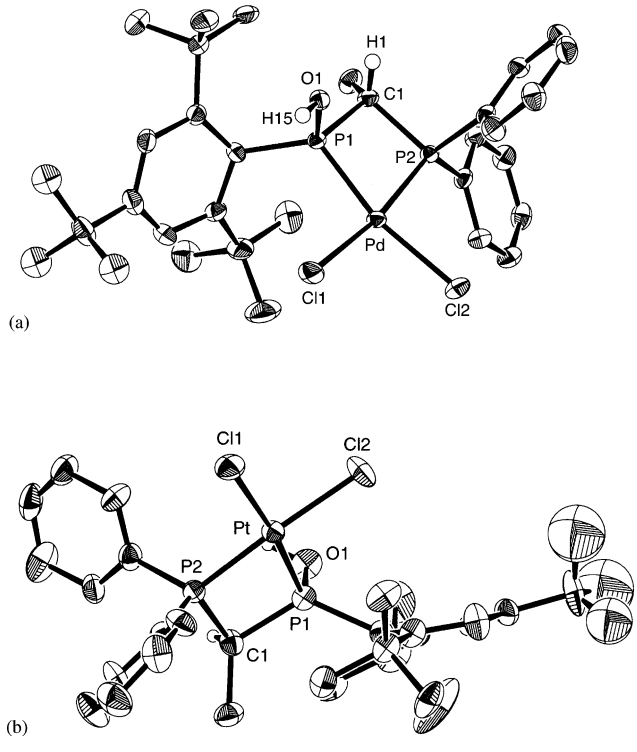


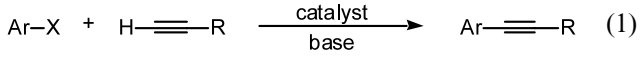
Figure 2. (a) Molecular structure of **8**. The hydrogen atoms except for H1 and H15 and the solvent molecules (CH_2Cl_2, H_2O) are omitted for clarity. The *p*-*t*-butyl group in the Mes* group is disordered and atoms with predominant occupancy factor (0.56) are shown. (b) Molecular structure of **9**. The hydrogen atoms except for OH and CH (C1) and the solvent molecules (C_2H_5OH, C_4H_8O) are omitted for clarity. The atoms in the *p*-*t*-butyl group are refined isotropically.

Table 1. Sonogashira coupling reaction (Eq. (1))[a]

Entry	Catalyst	ArX	R	Base	Temp.	Time (h)	Yield (%)
1	**6**/CuI	PhI	Ph	Et_3N	rt	4	99
2	**6**/CuI	PhI	Ph	Et_2NH	rt	4	49
3	**6**	PhI	Ph	Et_3N	rt	4	11
4	**6**/CuI	PhI	$SiMe_3$	Et_3N	rt	4	93
5	**6**/CuI	2-PyBr	Ph	Et_3N	rt	4	4
6	**6**/CuI	p-$O_2NC_6H_4Br$	Ph	Et_3N	rt	4	–[b]
7	**6**/CuI	PhBr	Ph	Et_3N	Reflux	17	4

[a] Reaction conditions: iodobenzene (2.0 mmol), phenylacetylene (2.0 mmol), **6** (0.050 mmol), copper(I) iodide (0.050 mmol), base (8 mL).
[b] PhC≡C–C≡CPh was obtained in 18% isolated yield.

Secondly, to estimate the catalytic property of **6**, we studied the Sonogashira coupling reaction under the original conditions, where a copper salt and a base[6] are employed (Eq. (1)).[20] As shown in Table 1, **6** catalyzed the coupling reaction of iodobenzene and acetylenes at room temperature to afford the corresponding acetylenes in moderate to excellent yields (Entry 1, 2 and 4). Copper(I) iodide was essential for the reaction to proceed, and triethylamine gave better results than diethylamine (Entry 2). As described in the literature,[6] these reaction conditions are mild and the experimental protocol is simple. We studied the Sonogashira coupling with other aryl halides, but, unfortunately, no satisfactory results were obtained. For example, 2-bromopyridine and bromobenzene and phenylacetylene afforded phenylacetylene in the presence of **6** under similar conditions; however, the yields were low (Entry 5 and 7). Although we previously reported that a palladium(II) complex containing ligated 3,4-diphosphinidenecyclobutene catalyzed the Sonogashira reaction of p-nitrobromobenzene with trimethylsilylacetylene under refluxing diethylamine,[3e] the present complex **6** did not catalyze this cross-coupling reaction. On the other hand, phenylacetylene was homocoupled to afford diphenylbutadiyne in the presence of p-nitrobromobenzene, **6**, copper(I) iodide and triethylamine (Entry 6). These results indicate that **6** forms an intermediate dialkynylpalladium(II) complex[21] during the reaction, and the mechanism of this coupling reaction might include a different path from the established one. We are now exploring reactions catalyzed by **6** in terms of observation or isolation of the reaction intermediates. Complex **8** can be considered to acted as a catalyst and thus we are studying the properties of **8** as well as **9**.[15]



(1)

Acknowledgements

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8. NMR data for *E*-**3**: $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ 294.4 (d, $^2J_{PP}$ 266 Hz), 9.2 (d, $^2J_{PP}$ 266 Hz); ^1H NMR (400 MHz, $CDCl_3$) δ 7.52–7.56 (4H, m, arom), 7.43 (2H, m, arom), 7.40–7.28 (6H, m, arom), 1.50 (18H, s, *o*-*t*-Bu), 1.43 (3H, dd, $^3J_{PH}$ 14 Hz, $^3J_{PH}$ 8 Hz, Me), 1.36 (9H, s, *p*-*t*-Bu); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 181.0 (dd, $^1J_{PC}$ 59 Hz, $^1J_{PC}$ 30 Hz, P=C), 153.8 (s, *o*-Mes*), 150.4 (s, *p*-Mes*), 139.6 (dd, $^1J_{PC}$ 69 Hz, $^3J_{PC}$ 26 Hz, *ipso*-Mes*), 137.4 (pt, ($^1J_{PC}$+$^3J_{PC}$)/2 15 Hz, *ipso*-Ph), 134.3 (d, $^2J_{PC}$ 19 Hz, *o*-Ph), 129.3 (s, *p*-Ph), 128.9 (d, $^3J_{PC}$ 7 Hz, *m*-Ph), 122.3 (s, *m*-Mes*), 38.6 (s, *o*-*C*Me$_3$), 35.6 (s, *p*-*C*Me$_3$), 33.5 (d, $^4J_{PC}$ 7 Hz, *o*-C*Me*$_3$), 32.1 (s, *p*-C*Me*$_3$), 22.6 (dd, $^2J_{PC}$ 15 Hz, $^2J_{PC}$ 9 Hz, Me). NMR data for *Z*-**3**: $^{31}P\{^1H\}$

NMR (162 MHz, $CDCl_3$) δ 323.4 (d, $^2J_{PP}$ 116 Hz), 34.4 (d, $^2J_{PP}$ 116 Hz).

9. **4**, **5**: A THF (10 mL) solution of *E*-**3** (100 mg, 0.205 mmol) was mixed with a THF solution of $W(CO)_5$(thf) (ca. 0.307 mmol, prepared from $W(CO)_6$ by irradiation with a medium-pressure Hg lamp (100 W) at 0°C in THF) at room temperature for 3 days. The solvent was removed in vacuo and the residue was purified by silica gel column chromatography (hexane/toluene 2:1) to afford **4**: 116 mg, 70%; $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ 331.6 (d, $^2J_{PP}$ 240 Hz), 26.5 (d, $^2J_{PP}$ 240 Hz, $^1J_{PW}$ (satellite) 246 Hz); ^1H NMR (400 MHz, $CDCl_3$) δ 7.61–7.38 (12H, m, arom), 1.40 (18H, s, *o*-*t*-Bu), 1.32 (9H, s, *p*-*t*-Bu), 1.27 (3H, dd, $^3J_{PH}$ 13 Hz, $^3J_{PH}$ 10 Hz, Me). Complex **4** (116 mg, 0.144 mmol) in THF was irradiated with a medium-pressure Hg lamp (100 W) at 0°C for 70 h to afford **5** after silica gel column chromatography (hexane/toluene 3:1), 33 mg, 29% yield. **5**: Orange crystals, mp 246°C (decomp); $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ 247.7 (d, $^2J_{PP}$ 115 Hz, $^1J_{PW}$ (satellite) 205 Hz), 3.1 (d, $^2J_{PP}$ 115 Hz, $^1J_{PW}$ (satellite) 200 Hz); ^1H NMR (400 MHz, $CDCl_3$) δ = 7.55–7.50 (4H, m, arom), 7.46–7.42 (8H, m, arom), 1.64 (18H, s, *o*-*t*-Bu), 1.43 (3H, dd, $^3J_{PH}$ 28 Hz, $^3J_{PH}$ 11 Hz, Me), 1.36 (9H, s, *p*-*t*-Bu); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 210.4 (dd, $^2J_{PC}$ 55 Hz, $^2J_{PC}$ 12 Hz, CO_{eq}), 209.8 (dd, $^2J_{PC}$ 38 Hz, $^2J_{PC}$ 14 Hz, CO_{eq}), 204.8 (dd, $^2J_{PC}$ 16 Hz, $^2J_{PC}$ 11 Hz, CO_{ax}), 186.5 (dd, $^1J_{PC}$ 45 Hz, $^1J_{PC}$ 31 Hz, P=C), 155.9 (s, *o*-Mes*), 153.3 (s, *p*-Mes*), 133.3 (dd, $^1J_{PC}$ 56 Hz, $^3J_{PC}$ 29 Hz, *ipso*-Mes*), 132.9 (d, $^2J_{PC}$ 21 Hz, *o*-Ph), 130.8 (d, $^4J_{PC}$ 3 Hz, *p*-Ph), 129.1 (d, $^3J_{PC}$ 16 Hz, *m*-Ph), 128.5 (pt, ($^1J_{PC}$+$^3J_{PC}$)/2 53 Hz, *ipso*-Ph), 122.6 (d, $^3J_{PC}$ 8 Hz, *m*-Mes*), 38.8 (s, *o*-CMe_3), 35.6 (s, *p*-CMe_3), 33.8 (d, $^4J_{PC}$ 4 Hz, *o*-CMe_3), 31.5 (s, *p*-CMe_3), 24.2 (dd, $^2J_{PC}$ 24 Hz, $^2J_{PC}$ 5 Hz, Me); IR (KBr) ν 2013, 1899, 1876 cm^{-1}. Anal. Found: C, 54.68; H, 5.21%. Calcd for $C_{36}H_{42}P_2O_4W$: C, 55.11; H, 5.39%. Complex **5** was obtained from the reaction of *E*-**3** and $W(CO)_5$(thf) in 3% yield.
10. X-ray crystallography for **5**: $C_{36}H_{42}O_4P_2W$, M = 784.52, crystal dimensions 0.15×0.10×0.10 mm^3, orthorhombic, space group $P2_12_12_1$ (no. 19), a = 16.791(1), b = 22.0884(9), c = 9.3064(4) Å, V = 3451.6(3) Å^3, Z = 4, T = 153 K, $2\theta_{max}$ = 55.0°, ρ = 1.510 g cm^{-1}, μ(MoKα) = 3.479 mm^{-1}, F_{000} = 1576.00, 24205 measured reflections, 4270 unique reflections (R_{int} = 0.068), $R1$ = 0.050 (I>2.0σ(I)), R_w = 0.057 (all data) (CCDC-208866).
11. **6**: A solution of a mixture of *E*-**3** (100 mg, 0.205 mmol) and $PdCl_2(MeCN)_2$ (0.205 mmol) in dichloromethane (5 mL) was stirred for 12 h. The reaction mixture was diluted with hexane (10 mL) to generate yellow precipitates of **6**. The precipitates were filtered and washed with hexane to afford **6**: 133 mg, 88% yield. Mp 220°C (decomp); $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ 224.3 (d, $^2J_{PP}$ 52 Hz), –9.2 (d, $^2J_{PP}$ 52 Hz); ^1H NMR (400 MHz, $CDCl_3$) δ 7.96–7.90 (4H, m, arom), 7.68–7.64 (2H, m, arom), 7.58–7.54 (6H, m, arom), 1.70 (18H, s, *o*-*t*-Bu), 1.69 (3H, dd, $^3J_{PH}$ 34 Hz, $^3J_{PH}$ 16 Hz, Me), 1.35 (9H, s, *p*-*t*-Bu); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 177.1 (dd, $^1J_{PC}$ 27 Hz, $^1J_{PC}$ 24 Hz, P=C), 157.6 (d, $^2J_{PC}$ 3 Hz, *o*-Mes*), 156.5 (d, $^4J_{PC}$ 2 Hz, *p*-Mes*), 134.0 (d, $^2J_{PC}$ 11 Hz, *o*-Ph), 133.4 (d, $^4J_{PC}$ 3 Hz, *p*-Ph), 129.1 (d, $^3J_{PC}$ 13 Hz, *m*-Ph), 125.8 (dd, $^1J_{PC}$ 54 Hz, $^3J_{PC}$ 7 Hz, *ipso*-Mes*), 123.9 (d, $^3J_{PC}$ 9 Hz, *m*-Mes*), 118.4 (dd, $^1J_{PC}$ 30 Hz, $^3J_{PC}$ 10 Hz, *ipso*-Ph), 38.7 (s, *o*-CMe_3), 35.9 (s, *p*-CMe_3), 34.1 (s, *o*-CMe_3), 31.4 (s, *p*-CMe_3), 21.5 (dd, $^2J_{PC}$ 17 Hz, $^2J_{PC}$ 3 Hz, Me). Anal. found: C, 53.63; H, 5.92%. Calcd for $C_{32}H_{42}Cl_2P_2Pd{\cdot}0.9CH_2Cl_2$: C, 53.22, H, 5.96%.
12. **8**: Mp 115°C (decomp, recrystalized from dichloromethane); $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ 35.8 (d, $^2J_{PP}$ 45 Hz), –32.9 (d, $^2J_{PP}$ 45 Hz); ^1H NMR (400 MHz, $CDCl_3$) δ 8.13 (2H, dd, $^2J_{PH}$ 13 Hz, $^3J_{HH}$ 7 Hz, *o*-Ph), 7.97 (2H, dd, $^2J_{PH}$ 13 Hz, $^3J_{HH}$ 7 Hz, *o*-Ph), 7.66–7.43 (8H, m, arom), 5.15 (1H, m, CH), 1.75 (9H, s, *o*-*t*-Bu), 1.65 (3H, dd, $^3J_{PH}$ 34 Hz, $^3J_{PH}$ 16 Hz, Me), 1.47 (9H, s, *o*-*t*-Bu), 1.33 (9H, s, *p*-*t*-Bu), (OH could not be assigned). Anal. Found: C, 54.48; H, 6.22%. Calcd for $C_{32}H_{44}Cl_2OP_2Pd{\cdot}0.5CH_2Cl_2$: C, 53.73; H, 6.26%.
13. X-ray crystallography for **8**·CH_2Cl_2·H_2O: $C_{33}H_{46}Cl_4O_2P_2Pd{\cdot}CH_2Cl_2{\cdot}H_2O$, M = 786.90, crystal dimensions 0.30×0.30×0.25 mm^3, monoclinic, space group $P2_1/c$ (no. 14), a = 16.609(1), b = 13.7163(8), c = 17.9531(9) Å, β = 114.692(2)°, V = 3716.1(4) Å^3, Z = 4, T = 120 K, $2\theta_{max}$ = 55.0°, ρ = 1.406 g cm^{-1}, μ(MoKα) = 0.900 mm^{-1}, F_{000} = 1624.00, 26852 measured reflections, 8192 unique reflections (R_{int} = 0.041), $R1$ = 0.057 (I>2.0σ(I)), R_w = 0.084 (all data) (CCDC-208864).
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16. Alternatively, the Wacker type oxidation process appeared to be included, although detailed study for it has not been performed so far.
17. The lifetime of **8** prolonged by using chloroform which was passed through basic alumina just before use.
18. **9**: Mp 150°C (decomp); $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ 16.7 (d, $^2J_{PP}$ 52 Hz, $^1J_{PPt}$ (satellite) 3407 Hz), –40.4 (d, $^2J_{PP}$ 52 Hz, $^1J_{PPt}$ (satellite) 3447 Hz); ^1H NMR (400 MHz, $CDCl_3$) δ 8.11 (2H, m, Ph), 7.97 (2H, m, Ph), 7.61–7.37 (8H, m, arom), 5.20 (1H, m, CH), 1.72 (9H, s, *o*-*t*-Bu), 1.64 (3H, dd, $^3J_{PH}$ 8 Hz, $^3J_{PH}$ 3 Hz, Me), 1.45 (9H, s, *o*-*t*-Bu), 1.32 (9H, s, *p*-*t*-Bu) (OH could not be assigned); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 160.1 (m, *o*-Mes*), 154.3 (d, $^4J_{PC}$ 4 Hz, *p*-Mes*), 152.8 (m, *o*-Mes*), 137.3 (d, $^2J_{PC}$ 11 Hz, *o*-Ph), 132.9 (d, $^1J_{PC}$ 41 Hz, *ipso*-Ph), 132.6 (s, *p*-Ph), 132.0 (s, *m*-Ph), 129.5 (dd, $^1J_{PC}$ 40 Hz, $^3J_{PC}$ 12 Hz, *ipso*-Mes*), 124.8 (d, $^3J_{PC}$ 3 Hz, *m*-Mes*), 124.7 (s, *m*-Mes*), 40.3 (dd, $^1J_{PC}$ 82 Hz, $^1J_{PC}$ 3 Hz, PCP), 35.5 (s, *o*-CMe_3), 35.1 (s, *p*-CMe_3), 33.2 (s, *o*-CMe_3), 31.2 (s, *p*-CMe_3), 26.0 (m, Me). Anal. Found: C, 47.59; H, 5.87%. Calcd for $C_{32}H_{44}Cl_2OP_2Pt{\cdot}2H_2O$: C, 47.53; H, 5.98%.
19. X-ray crystallography for **9**·C_2H_5OH·C_4H_8O, $C_{38}H_{58}Cl_2O_3P_2Pt$, M = 890.82, crystal dimensions 0.20×0.17×0.10 mm^3, orthorhombic, space group $P2_12_12_1$ (no. 19), a = 17.2751(6), b = 17.2986(7), c = 14.1019(8) Å, V = 4214.1(3) Å^3, Z = 4, T = 296 K, $2\theta_{max}$ = 55.0°, ρ = 1.404 g cm^{-1}, μ(MoKα) = 3.550 mm^{-1}, F_{000} = 1808.00, 32774 measured reflections, 5208 unique reflections (R_{int} = 0.099), $R1$ = 0.045 (I>3.0σ(I)), R_w = 0.062 (all data) (CCDC-208865).
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