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Preparation of carbonyltungsten(0) complexes of 2-chloro-3,3-diphenyl-1-(2,4,6-tri-*tert*-butylphenyl)-1,3-diphosphapropene

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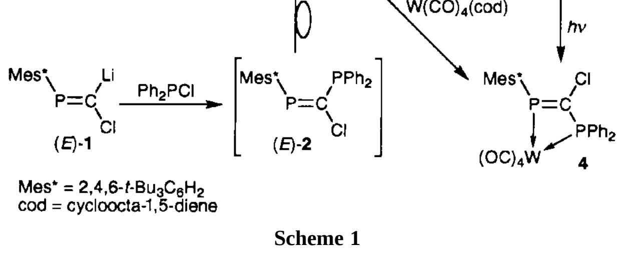
Received (in Cambridge, UK) 27th March 2001, Accepted 10th May 2001
First published as an Advance Article on the web 13th June 2001

(*Z*)-2-Chloro-3,3-diphenyl-1-(2,4,6-tri-*tert*-butylphenyl)-1,3-diphosphapropene was prepared from chlorodiphenylphosphine and 1-chloro-2-(2,4,6-tri-*tert*-butylphenyl)-2-phosphaethenyllithium and used for metal complex formation as a ligand to provide carbonyltungsten(0) complexes.

The 1,3-diphosphapropene system is an attractive ligand system for metal complex formation because two different types of phosphorus atoms are included within the system; *i.e.* a low-coordinated $\lambda^3\sigma^2$-phosphorus atom[1,2] and a common $\lambda^3\sigma^3$-phosphorus atom. However, research on coordination of the 1,3-diphosphapropene derivatives toward transition metals has been limited, whereas several metal complexes of η^3-1,3-diphosphaallyl ligands have been reported so far.[3,4] Indeed, the only reported example concerns the X-ray structural analysis of an iron(0) complex of 1,3-diphosphapropene prepared through an intramolecular cyclization of a bulky 1,3-diphosphaallene by ourselves.[5] There have been no reports on X-ray structural analysis of transition metal complexes of 1,3-diphosphapropene itself. Furthermore, the catalytic abilities of transition metal complexes of low-coordinated phosphorus compounds are of current interest,[6–10] and thus detailed study of the coordination chemistry of the 1,3-diphosphapropene system is crucial. Here we report the preparation and X-ray structural determination of carbonyltungsten complexes of a 1,3-diphosphapropene derivative kinetically stabilized by the 2,4,6-tri-*tert*-butylphenyl group (Mes*) including a selective coordination reaction of either the monodentate or chelate form.

A kinetically stabilized (*Z*)-1-chloro-2-(2,4,6-tri-*tert*-butylphenyl)-2-phosphaethenyllithium (*Z*-**1**) was prepared from 2,2-dichloro-1-(2,4,6-tri-*tert*-butylphenyl)-1-phosphaethene and butyllithium, and was allowed to react with chlorodiphenylphosphine (Scheme 1)[11] to afford the corresponding 2-chloro-1,3-diphosphapropene (*Z*-**2**) in good yield (78%) after silica-gel column chromatographic purification (hexane–toluene, v/v = 5/1). Compound *Z*-**2** was characterized spectroscopically.† In the ^{31}P NMR spectrum, a peak due to the P=C phosphorus atom appeared at low field (δ_P 302.4) with a large $^2J_{PP}$ value (277 Hz), suggesting an *E*-configuration. Similarly, starting from *E*-**1** and chlorodiphenylphosphine,[11a] an attempt was made to prepare *E*-**2**. Although NMR signals due to *E*-**2** were observed in the reaction mixture (δ_P 325.1, 3.0, $^2J_{PP}$ 15 Hz), *E*-**2** was isomerized to *Z*-**2** after the usual work-up procedure, probably due to large repulsion between the Mes* group and the Ph$_2$P group.



Scheme 1

Next we investigated the coordination property of *Z*-**2** towards tungsten(0). Initially, *Z*-**2** was allowed to react with an equivalent amount of W(CO)$_5$(thf) for 6 h at room temperature to afford the corresponding pentacarbonyltungsten(0) complex **3** in 39% yield as yellow prisms after recrystallisation from hexane (Scheme 1).‡ The coordination on tungsten seemed to occur at the Ph$_2$P phosphorus atom as suggested by a satellite signal due to the tungsten atom in the ^{31}P NMR spectrum of **3**. The reason for this type of coordination might be explicable taking the stronger basicity of the Ph$_2$P group into account,[12] while Bertrand and coworkers reported an NMR study to suggest the coordination at the low-coordinated $\lambda^3\sigma^2$-phosphorus atom in a 1,3-diphosphapropene system.[4] In the ^{13}C NMR spectrum, the chemical shift of the P=C carbon atom is similar to that for *Z*-**2**, but the two $^1J_{PC}$ values are quite different (79 and 4 Hz) indicating low electronic interaction between the PPh$_2$ group and the P=C carbon atom. The structure of **3** was unambiguously determined by X-ray crystallography and Fig. 1 displays an ORTEP drawing.§ The P2–W distance is 2.540(1) Å, which is similar to that for W(CO)$_5$(PPh$_3$) [2.545(1) Å].[13] The P1–C(1) distance is 1.675(4) Å, which is a normal value for the P=C bond.[1] The P1, P2, C1, Cl, W atoms are almost coplanar and the tungsten atom is located on the same side of lone pairs of the P1 atom with a P1···W distance of 3.97 Å. Complex **3** did not react with an excess amount of W(CO)$_5$(thf) to afford the bis-tungsten complex, probably due to steric congestion around the P=C phosphorus atom.[4]

The structure of **3** indicates that *Z*-**2** is a good chelating ligand, and therefore we tried to prepare a chelate complex of *Z*-**2** by use of W(CO)$_4$(cod) (cod = cycloocta-1,5-diene) at room

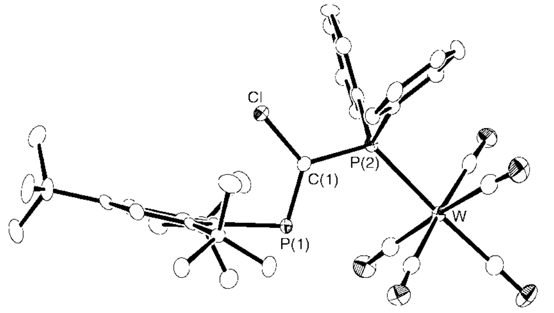


Fig. 1 An ORTEP drawing of **3** with 50% probability ellipsoids. Hydrogen atoms are omitted for clarity. Bond lengths (Å) and angles (°): W–P(2) 2.540(1), C(1)–Cl 1.740(4), P(1)–C(1) 1.675(4), P(1)–C_{ipso}(Mes*) 1.840(4), C(1)–P(2) 1.829(4), P(2)–C_{ipso}(Ph) 1.828(4), P(2)–C_{ipso}(Ph′) 1.835(4); C(1)–P(1)–C_{ipso}(Mes*) 103.1(2), W–P(2)–C(1) 119.3(1), W–P(2)–C_{ipso}(Ph) 110.6(1), W–P(2)–C_{ipso}(Ph′) 116.5(1), C(1)–P(2)–C_{ipso}(Ph) 104.6(2), C(1)–P(2)–C_{ipso}(Ph′) 99.8(2), C_{ipso}(Ph)–P(2)–C_{ipso}(Ph′) 104.3(2), Cl–C(1)–P(1) 124.9(2), Cl–C(1)–P(2) 115.4(2), P(1)–C(1)–P(2) 119.2(2).

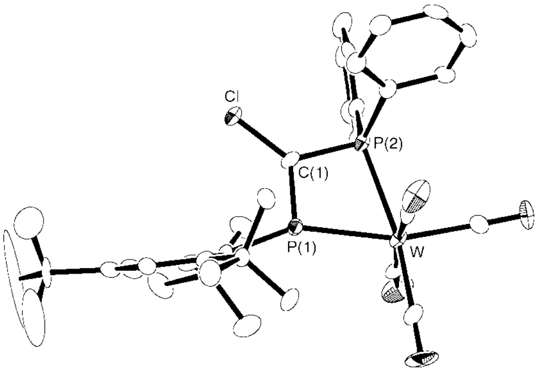


Fig. 2 An ORTEP drawing of **4** with 50% probability ellipsoids. Hydrogen atoms are omitted for clarity. Bond lengths (Å) and angles (°): W–P(1) 2.489(3), W–P(2) 2.526(3), C(1)–Cl 1.73(1), P(1)–C(1) 1.651(10), P(1)–C_{ipso}(Mes*) 1.82(1), C(1)–P(2) 1.82(1), P(2)–C_{ipso}(Ph) 1.83(1), P(2)–C_{ipso}(Ph′) 1.81(1), C(1)–P(1)–C_{ipso}(Mes*) 108.6(5), P(1)–W–P(2) 65.1(1), W–P(2)–C(1) 93.5(3), W–P(1)–C(1) 99.4(4), W–P(1)–C_{ipso}(Mes*) 152.0(3), W–P(2)–C_{ipso}(Ph) 115.6(4), W–P(2)–C_{ipso}(Ph′) 127.6(4), C(1)–P(2)–C_{ipso}(Ph) 109.7(5), C(1)–P(2)–C_{ipso}(Ph′) 104.5(5), C_{ipso}(Ph)–P(2)–C_{ipso}(Ph′) 103.9(5), Cl–C(1)–P(1) 131.2(6), Cl–C(1)–P2 126.8(6), P(1)–C(1)–P(2) 101.8(5).

temperature. After 12 h, **4** was obtained in 19% yield as red crystals together with 63% recovery of *Z*-**2**, after purification by gel permeation chromatographic separation (Scheme 1).‡ A trace amount of **4** was also obtained by the reaction of *Z*-**2** and W(CO)$_5$(thf). In the ^{31}P NMR spectrum of **4**, a peak due to the P=C phosphorus atom is observed at a higher field than that for *Z*-**2**, and both of the two phosphorus atoms show satellite peaks due to the presence of the tungsten atom. Moreover, the coupling constant between the P=C phosphorus and the tungsten (213 Hz) is reasonable for a complex with an end-on coordinating mode.[14] On the other hand, Appel and coworkers reported a side-on coordination with Fe(0) on the P=C moiety in the 1,3-diphosphapropene system.[3] In the ^{13}C NMR spectrum of **4**, a peak due to the P=C carbon atom has a higher chemical shift than that for *Z*-**2**, and the two $^{1}J_{PC}$ values are small (23 and 9 Hz). Two different chemical shifts were observed for CO_{eq} carbons together with two different $^{2}J_{PC}$ values, probably due to the coordination by two different types of phosphorus atoms. The structure of **4** was unambiguously determined by X-ray crystallography and Fig. 2 depicts an ORTEP drawing.§ The P=C phosphorus atom coordinates in the end-on mode which leads to a large $^{1}J_{PW}$ value in the NMR spectrum. The P1–W distance [2.489(3) Å] is shorter than the P2–W distance [2.526(3) Å], and the P1–C(1) distance [1.651(10)] is normal for the P=C bond. The P1–W–P2 angle is small with a value of 65.1(1)°. The P1–C(1)–P2 and C(1)–P2–W angles, 93.5(3) and 101.8(5)°, respectively, are smaller than the corresponding angles for **3**.

Chelate complex **4** was also derived by photo-irradiation of **3**. A THF solution of **3** was irradiated with a medium-pressure mercury lamp at 5 °C for 16 h in an NMR tube to afford **4** almost quantitatively. No *E*/*Z* isomerization of **3** was observed probably due to the steric hindrance between the Mes* and Ph$_2$P moieties.[15]

Compound **2** contains a chlorine atom at the sp^2-carbon atom which can potentially be substituted. We are now attempting to prepare various types of 1,3-diphosphapropenes from **2**, as well as metal complexes of the type **3** and **4**.

This work was supported in part by a Grant-in-Aid for Scientific Research (No. 12042208) from the Ministry of Education, Science, Sports and Culture, Japan.

Notes and references

† *NMR data* for **2**: ^{1}H NMR (200 MHz, CDCl$_3$) δ 7.4–7.5 (4H, arom.), 7.3–7.4 (8H, arom.) 1.41 (18H, *o*-Bu^t), 1.31 (9H, *p*-Bu^t); ^{13}C{^{1}H} NMR (50 MHz, CDCl$_3$) δ 169.0 (dd, $^{1}J_{PC}$ 72, $^{1}J_{PC}$ 54 Hz, P=C), 153.2 (d, $^{2}J_{PC}$ 2 Hz, *o*-Mes*), 150.8 (*p*-Mes*), 136.2 (dd, $^{1}J_{PC}$ 62, $^{3}J_{PC}$ 27 Hz, *ipso*-Mes*), 135.8 (dd, $^{1}J_{PC}$ 16, $^{3}J_{PC}$ 11 Hz, *ipso*-Ph), 133.6 (d, $^{2}J_{PC}$ 20 Hz, *o*-Ph), 128.8 (*p*-Ph), 122.0 (*m*-Mes*), 37.8 (d, $^{3}J_{PC}$ 1 Hz, *o*-*C*Me$_3$), 35.1 (*p*-*C*Me$_3$), 32.9 (d, $^{4}J_{PC}$ 7 Hz, *o*-C*Me*$_3$), 31.4 (*p*-C*Me*$_3$); ^{31}P{^{1}H} NMR (81 MHz, CDCl$_3$) δ 302.4 (P=C), 13.4 (PPh$_2$), $^{2}J_{PP}$ 277 Hz.

‡ *Spectroscopic data*: for **3**: yellow prisms (hexane), mp 196–198 °C (decomp.); ^{1}H NMR (200 MHz, CDCl$_3$) δ 7.6–7.7 (4H, arom.), 7.4–7.5 (6H, arom.), 7.36 (2H, d, $^{4}J_{PH}$ 2 Hz, *m*-Mes*), 1.35 (18H, *o*-Bu^t), 1.29 (9H, *p*-Bu^t); ^{13}C{^{1}H} NMR (50 MHz, CDCl$_3$) δ 199.3 (d, $^{2}J_{PC}$ 23 Hz, CO_{ax}), 197.0 (dd, $^{2}J_{PC}$ 7, $^{2}J_{PC}$ 7 Hz, CO_{eq}), 163.5 (dd, $^{1}J_{PC}$ 79, $^{1}J_{PC}$ 4 Hz, P=C), 153.3 (d, $^{2}J_{PC}$ 3 Hz, *o*-Mes*), 151.3 (*p*-Mes*), 135.1 (dd, $^{1}J_{PC}$ 61, $^{3}J_{PC}$ 18 Hz, *ipso*-Mes*), 134.5 (dd, $^{1}J_{PC}$ 44, $^{3}J_{PC}$ 10 Hz, *ipso*-Ph), 132.7 (d, $^{2}J_{PC}$ 12 Hz, *o*-Ph), 130.2 (d, $^{4}J_{PC}$ 2 Hz, *p*-Ph), 128.6 (d, $^{3}J_{PC}$ 10 Hz, *m*-Ph), 122.3 (*m*-Mes*), 37.5 (*o*-*C*Me$_3$), 35.0 (*p*-*C*Me$_3$), 32.6 (d, $^{4}J_{PC}$ 7 Hz, *o*-C*Me*$_3$), 31.2 (*p*-C*Me*$_3$); ^{31}P{^{1}H} NMR (81 MHz, CDCl$_3$) δ 328.0 (P=C), $^{1}J_{PW}$ 187 Hz, 34.2 (PPh$_2$), $^{2}J_{PP}$ 187 Hz; IR (KBr) ν 2071, 1988, 1936, 1919 cm^{-1}, FAB-MS *m*/*z* 804 (M$^+$ − CO; 53%), 692 (M$^+$ −5CO; 79%), 275 (Mes*P$^+$ − 1; 100%). Anal. Calc. for $C_{36}H_{39}ClO_5P_2W$: C, 51.91; H, 4.72; Cl, 4.26. Found: C, 51.92; H, 4.78; Cl, 4.30%. For **4**: red prisms (hexane), mp 220–222 °C (decomp.); ^{1}H NMR (200 MHz, CDCl$_3$) δ 7.6–7.7 (4H, arom.), 7.4–7.5 (8H, arom.), 1.61 (18H, *o*-Bu^t), 1.34 (9H, *p*-Bu^t); ^{13}C{^{1}H} NMR (50 MHz, CDCl$_3$) δ 208.4 (dd, $^{2}J_{PC}$ 36, $^{2}J_{PC}$ 6 Hz, CO_{eq}), 207.7 (dd, $^{2}J_{PC}$ 25, $^{2}J_{PC}$ 12 Hz, CO_{eq}), 203.2 (dd, $^{2}J_{PC}$ 10, $^{2}J_{PC}$ 7 Hz, CO_{ax}), 156.4 (dd, $^{1}J_{PC}$ 23, $^{1}J_{PC}$ 9 Hz, P=C), 155.6 (d, $^{2}J_{PC}$ 2 Hz, *o*-Mes*), 153.6 (d, $^{4}J_{PC}$ 2 Hz, *p*-Mes*), 132.5 (d, $^{2}J_{PC}$ 14 Hz, *o*-Ph), 131.5 (dd, $^{1}J_{PC}$ 38, $^{3}J_{PC}$ 16 Hz, *ipso*-Ph), 130.9 (d, $^{4}J_{PC}$ 2 Hz, *p*-Ph), 130.8 (d, $^{3}J_{PC}$ 11 Hz, *m*-Ph), 125.7 (dd, $^{1}J_{PC}$ 26, $^{3}J_{PC}$ 26 Hz, *ipso*-Mes*), 122.5 (d, $^{3}J_{PC}$ 6 Hz, *m*-Mes*), 38.3 (d, $^{3}J_{PC}$ 1 Hz, *o*-*C*Me$_3$), 35.3 (d, $^{5}J_{PC}$ 1 Hz, *p*-*C*Me$_3$), 33.2 (d, $^{4}J_{PC}$ 3 Hz, *o*-C*Me*$_3$), 31.0 (*p*-C*Me*$_3$); ^{31}P{^{1}H} NMR (81 MHz, CDCl$_3$) δ 263.7 (P=C), $^{1}J_{PW}$ 213 Hz, 19.1 (PPh$_2$), $^{1}J_{PW}$ 202 Hz, $^{2}J_{PP}$ 116 Hz; IR (KBr) ν 2019, 1923, 1903, 1890 cm^{-1}, FAB MS *m*/*z* 804 (M$^+$; 59%), 692 (M$^+$ − 4CO; 96%), 275 (Mes*P$^+$ − 1; 90%), 154 (PhPCCl$^+$ − 1; 100%). Anal. Calc. for $C_{35}H_{39}ClO_4P_2W$: C, 52.23; H, 4.88; Cl, 4.40. Found: C, 52.50; H, 4.95; Cl, 4.52%.

§ *Crystal data*: for **3**: $C_{36}H_{39}ClO_5P_2W$, M = 832.95, monoclinic, $P2_1/c$ (no. 14), a = 10.062(5), b = 25.244(3), c = 13.845(2) Å, β = 93.920(3)°, V = 3508(1) Å^3, Z = 4, D_c = 1.577 g cm^{-3}, μ = 3.504 mm^{-1}, T = 120(1) K, $2\theta_{max}$ = 50.1°, 5861 total reflections, 5487 observed reflections [$I > 1\sigma(I)$], $R1$ = 0.031, R_w = 0.073, S = 0.96 for 562 parameters, CCDC 159934.

For **4**: $C_{35}H_{39}ClO_4P_2W$, M = 804.94, orthorhombic, $P2_12_12_1$ (no. 19), a = 16.687(2), b = 21.984(3), c = 9.310(3) Å, V = 3415(1) Å^3, Z = 4, D_c = 1.565 g cm^{-1}, μ = 3.594 mm^{-1}, T = 125(1) K, $2\theta_{max}$ = 50.1°, 3318 total reflections, 3132 observed reflections [$I > 2\sigma(I)$], $R1$ = 0.049, R_w = 0.110, S = 1.27 for 389 parameters, CCDC 159933.

See http://www.rsc.org/suppdata/cc/b1/b102810n/ for crystallographic data in CIF or other electronic format.

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