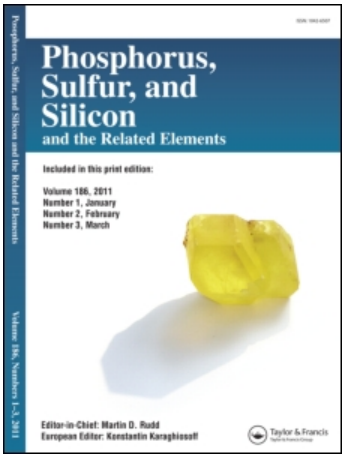

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Coordination Chemistry of a Bulky 1,3-Diphosphapropene with Carbonyltungsten(0) Moieties

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COORDINATION CHEMISTRY OF A BULKY 1,3-DIPHOSPHAPROPENE WITH CARBONYLTUNGSTEN(0) MOIETIES

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(Z)-2-Chloro-3,3-diphenyl-1-(2,4,6-tri-t-butylphenyl)-1,3-diphosphapropene was derived from chlorodiphenylphosphine and 1-chloro-2-(2,4,6-tri-t-butylphenyl)-2-phosphaethenyllithium and utilized for complex formations as a ligand of the corresponding carbonyltungsten(0) complexes.

Keywords: Coordination; 1,3-diphosphapropene; kinetic stabilization; phosphorus; tungsten

1,3-Diphosphapropene is an attractive candidate for ligands of transition metal complexes, because it has a low-coordinated $\lambda^3\sigma^2$-phosphorus and a normal $\lambda^3\sigma^3$-phosphorus within a system. Until now, several compounds including 1,3-diphosphapropene system have been derived.[1,2] But research on coordination of the 1,3-diphosphapropene derivatives toward transition metals has been limited.[3–5] On the other hand, several metal complexes of η^3-1,3-diphosphaallyl ligand have been reported so far.[6,7] We report the preparation of 2-chloro-3,3-diphenyl-1-(2,4,6-tri-*t*-butylphenyl)-1,3-diphosphapropene (**1**) and its coordinating properties toward carbonyltungsten(0) moieties.

RESULTS AND DISCUSSION

A kinetically stabilized phosphaethenyllithium *Z*-**1** was prepared from 2,2-dichloro-1-(2,4,6-tri-*t*-butylphenyl)-1-phosphaethene and butyllithium, and was allowed to react with chlorodiphenylphosphine

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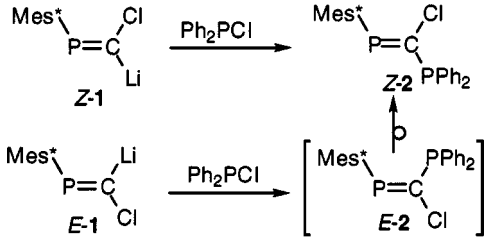

FIGURE 1

to afford the corresponding 2-chloro-1,3-diphosphapropene (*Z*-**2**) in good yield (78%).[8] In the ^{31}P-NMR spectrum, a peak due to the P=C phosphorus atom appeared in a lower field with a large $^{2}J_{PP}$ value [δ_P 302.4 (P=C), 13.4 (PPh_2), $^{2}J_{PP}$ 277 Hz], suggesting the *E*-configuration. Similarly, starting from *E*-**1** and chlorodiphenylphosphine, an attempt was made to prepare *E*-**2**. Although NMR signals due to *E*-**2** were observed (δ_P 325.1, 3.0, $^{2}J_{PP}$ 15 Hz) in the reaction mixture, *E*-**2** were observed (δ_P 325.1, 3.0, $^{2}J_{PP}$ 15 Hz) in the reaction mixture, *E*-**2** was isomerized to *Z*-**2** after the usual workup procedure, probably due to large repulsion between the Mes* group and the Ph_2P group (Figure 1).[8]

Next we investigated the coordination properties of *Z*-**2** on carbonyltungsten(0) moieties. At first, *Z*-**2** was allowed to react with an equivalent amount of $W(CO)_5$(thf) to afford the corresponding pentacarbonyltungsten(0) complex **3** in 39% yield as yellow prisms (Figure 2).[8] The coordination on tungsten seemed to occur at the Ph_2P phosphorus atom, assumed by a satellite signal due to the tungsten atom in the ^{31}P-NMR spectrum of **3** [δ_P 328.0, 34.2 ($^{1}J_{PW}$ 187 Hz), $^{2}J_{PP}$ 187 Hz].

As *Z*-**2** was expected to be a good chelating ligand, we tried to prepare a chelate complex of *Z*-**2** by use of $W(CO)_4$(cod) (cod = 1,5-cyclooctadiene), and obtained **4** in 19% yield as red crystals together with 63% recovery of *Z*-**2** (Figure 2).[8] In the ^{31}P-NMR spectrum of **4**,

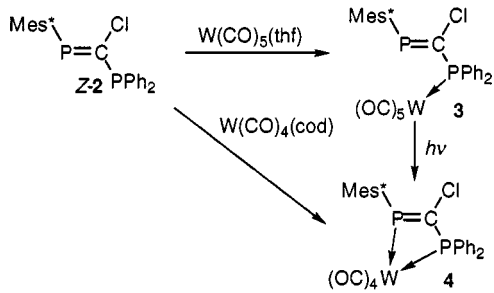

FIGURE 2

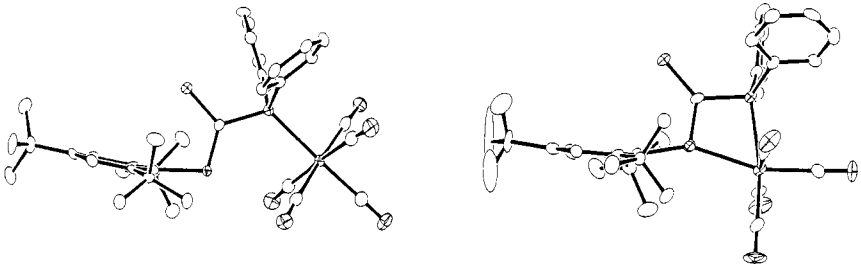

FIGURE 3 Molecular structures of **3** (left) and **4** (right).[8]

a peak due to the P=C phosphorus atom is observed in a higher field than that for *Z*-**2**, and both of the phosphorus atoms are accompanied by satellite peaks due to the tungsten atom [δ_P 263.7 ($^1J_{PW}$ 213 Hz, P=C), 19.1 ($^1J_{PW}$ 202 Hz, Ph_2P), $^2J_{PP}$ 116 Hz].

The structures of **3** and **4** were confirmed by x-ray crystallography (Figure 3).[8] For **3**, the P2–W distance is 2.540(1) Å, and the P1–C1 distance is 1.675(4) Å, which is a normal value for the P=C bond.[1] The P1, P2, C1, C1, and W atoms are almost coplanar, and the tungsten atom locates in the same side of lone pairs of the P1 atom with the P1 · · · W distance of 3.97 Å. Complex **3** did not react with excess amount of $W(CO)_5$(thf) to afford the bistungsten complex, probably due to steric congestion around the P=C phosphorus atom. For **4**, the P=C phosphorus atom coordinates in an end-on mode that corresponds to a large $^1J_{PW}$ 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–C1 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)°.

Chelate complex **4** was also derived by photoirradiation of **3**. Thus, a tetrahydrofuran (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 (Figure 2). No *E*/*Z* isomerization of **3** was observed, probably due to the steric hindrance between the Mes* and Ph_2P moieties.[8]

CONCLUSION

We studied the coordination chemistry of diphosphapropene *Z*-**2** with carbonyltungsten(0) moieties. We obtained a monodentate and chelate complex of a 1,3-diphosphapropene (**3** and **4**). We are now trying to prepare various types of 1,3-diphosphapropenes from **2**, and their metal complexes of the type **3** and **4**, as well.

REFERENCES

[1] M. Regitz and O. J. Scherer, *Multiple Bonds and Low Coordination in Phosphorus Chemistry* (Georg Thieme Verlag, Stuttgart, 1990).
[2] K. B. Dillon, F. Mathey, and J. F. Nixon, *Phosphorus: The Carbon Copy* (John Wiley & Sons, Chichester, 1998).
[3] R. Appel and W. Schuhn, *J. Organomet. Chem*., **329,** 179 (1987).
[4] D. Bourissou, Y. Canac, H. Gornitzka, C. J. Marsden, A. Baceiredo, and G. Bertrand, *Eur. J. Inorg. Chem.*, **1999,** 1479 (1995).
[5] C. A. Akpan, P. B. Hitchcock, J. F. Nixon, M. Yoshifuji, T. Niitsu, and N. Inamoto, *J. Organomet. Chem*., **338,** C35 (1988).
[6] W. Keim, R. Appel, S. Gruppe, and F. Knoch, *Angew. Chem., Int. Ed. Engl*., **26,** 1012 (1987).
[7] H. H. Karsch, H.-U. Reisacher, B. Huber, G. Müller, W. Malisch, and K. Jörg, *Angew. Chem., Int. Ed. Engl*., **25,** 455 (1986).
[8] S. Ito and M. Yoshifuji, *Chem. Commun*., 1208 (2001).