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Preliminary communication

Synthesis and crystal structure of the complex *cis*-1,3-bis(diphenylphosphino)dicyclopentadiene tetracarbonylmolybdenum

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Abstract

The interaction of *cis*-$Mo(CO)_4(Ph_2PCl)_2$ with 2 equivalents of $(C_5H_5)Tl$ in refluxing toluene gives the complex *cis*-1,3-bis(diphenylphosphino)(dicyclopentadiene(tetracarbonyl)molybdenum in high yield. The compound has been fully characterized by analytical, spectroscopic, and X-ray diffraction methods. A mechanism for the formation of the complex is proposed.

The (diphenylphosphino)cyclopentadienyl anion $Ph_2P(C_5H_4)^-$, has been shown to be a very versatile reagent in organometallic synthesis. Its use as heterodifunctional reagent to bring two hetero metal centers in close proximity has received considerable attention recently [1]. Although the anion is rather stable, its parent compound, (diphenylphosphino)cyclopentadiene, $Ph_2P(C_5H_5)$, is rather unstable and decomposes slowly at room temperature [2]. Little work has been done on the reactivity of coordinated $Ph_2P(C_5H_5)$. In this communication, we report the synthesis of (*cis*-1,3-bis(diphenylphosphino)dicyclopentadiene)(tetracarbonyl)molybdenum, the 1,3-bis(diphenylphosphino)dicyclopentadiene ligand in which is formed via intramolecular Diels–Alder dimerization of two $Ph_2P(C_5H_5)$ ligands.

When *cis*-$Mo(CO)_4(Ph_2PCl)_2$ was treated with 2 equivalents of $(C_5H_5)Tl$ in refluxing toluene, work up gave light yellow crystals of stoichiometry $(C_{34}H_{30}P_2)Mo(CO)_4$ [3] in high yield (80%), recrystallization from a toluene/n-hexane mixture.

The infrared spectrum of the complex in KBr exhibited three absorptions, at 2017s, 1916s, and 1880vs(br) cm^{-1}. The absorption pattern is indicative of a *cis*-configuration for the four terminal carbonyl groups. The mass spectrum of the

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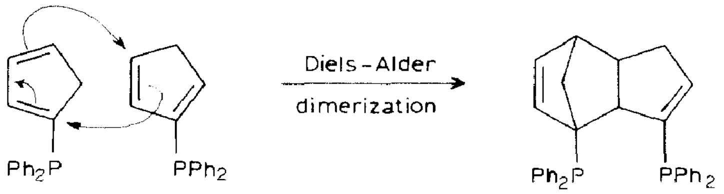

(1)

(I)

complex had the highest peak at m/z 596, corresponding to the $(M-4CO)^+$ fragment $(C_{34}H_{30}P_2)Mo$. The ^{31}P $\{^1H\}$ NMR spectrum of the complex exhibited two singlets, of relative intensity 1/1, at δ 22.6 and 36.3 ppm. The ^1H NMR spectrum of the complex was very complicated. In addition to the phenyl resonances, it exhibited three multiplets of intensity 1/1/1 at δ 6.67, 6.19, and 5.19 ppm, respectively, in the olefinic proton region, and four multiplets of intensity 2/1/3/1 at δ 2.94, 2.74, 2.02 and 0.74 ppm, respectively, in the aliphatic proton region. The spectroscopic data suggested that the phosphine ligands was 1,3-bis(diphenylphosphino)dicyclopentadiene (I) formed via intramolecular Diels–Alder dimerization of (diphenylphosphino)cyclopentadiene as shown in eq. 1.

An X-ray diffraction study [4*] was carried out to establish the structure of the complex. An ORTEP drawing and selected bond lengths and bond angles of the complex are shown in Fig. 1 and its caption. All bond distances and bond angles are normal. The carbon–carbon distances for C(12)–C(13) and C(18)–C(19) are 1.322(5) and 1.317(5) Å, respectively, indicative of C=C bonds.

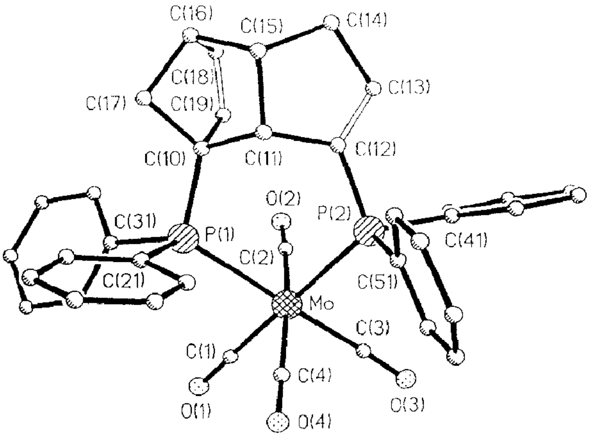

Fig. 1. An ORTEP drawing of *cis*-$(C_{34}H_{30}P_2)Mo(CO)_4$ with thermal ellipsoids at 30% probability. Selected bond distances (Å) and angles (deg): Mo–P(1), 2.550(1); Mo–P(2), 2.540(1); Mo–C(1), 1.992(4); Mo–C(2), 2.035(3); Mo–C(3), 1.979(3); Mo–C(4), 2.019(3); C(11)–C(12), 1.505(4); C(12)–C(13), 1.322(5); C(13)–C(14), 1.510(5); C(10)–C(19), 1.530(4); C(18)–C(19), 1.317(5); C(16)–C(18), 1.512(5); P(1)–Mo–P(2), 89.4(1); P(2)–C(12)–C(11), 120.5(2); P(2)–C(12)–C(13), 128.1(2); P(1)–C(10)–C(11), 112.2(2); P(1)–C(10)–C(17), 121.2(2); P(1)–C(10)–C(19), 116.6(2); C(11)–C(12)–C(13), 111.4(3); C(12)–C(13)–C(14), 114.0(3); C(10)–C(19)–C(18), 107.9(3); C(16)–C(18)–C(19), 108.1(3). The carbon–carbon double bonds are shown as open bonds.

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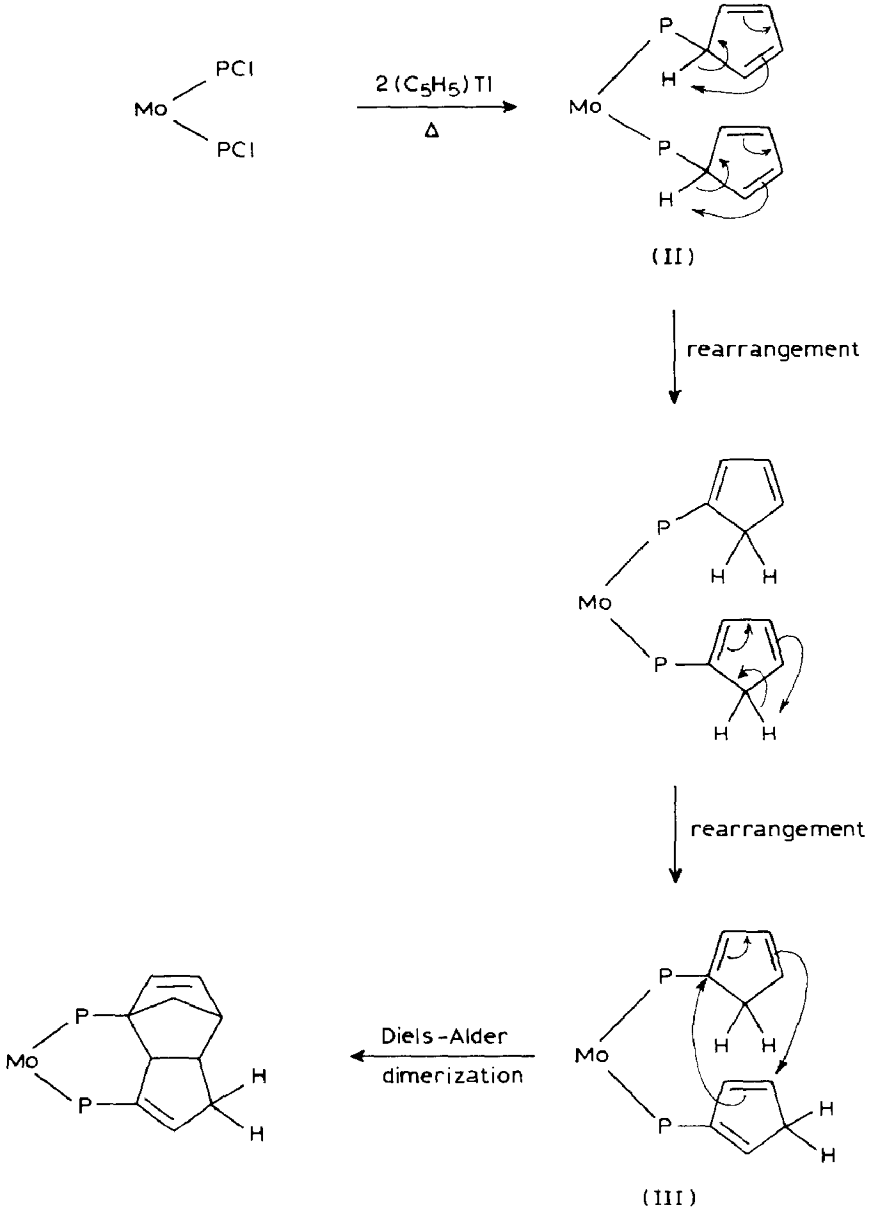
* Reference number with asterisk indicates a note in the list of references.



Scheme 1. Mo = *cis*-Mo(CO)$_4$; P = Ph$_2$P.

The ORTEP drawing reveals a *cis*-configuration for the four terminal carbonyl groups and shows that the two $Ph_2P(C_5H_5)$ ligands had indeed undergone dimerization to produce the 1,3-bis(diphenylphosphino)dicyclopentadiene ligand. The formation of the complex probably involves the mechanism shown in Scheme 1. *cis*-Mo(CO)$_4$(Ph$_2$PCl)$_2$ reacts with $(C_5H_5)Tl$ to produce intermediate II, which rearranged to give III. III then underwent intramolecular Diels-Alder dimerization to produce the final product.

Acknowledgements. Financial support from the Hong Kong Polytechnic is gratefully acknowledged.

References

1 G.K. Anderson and M. Lin, Organometallic, 7 (1988) 2285, and ref. therein.

2 C.P. Casey, R.M. Bullock, W.C. Fultz and A.L. Rheingold, Organometallics, 1 (1982) 1591.

3 $(C_{34}H_{30}P_2)Mo(CO)_4$: light yellow, M.p. 198 °C dec. Analysis: found: C, 64.6; H, 4.4; P, 8.6. $C_{38}H_{30}O_4P_2Mo$ calcd.: C, 64.4; H, 4.3; P, 8.7%. IR (cm^{-1}, in KBr): $\nu_{max}(CO)$, 2017s, 1916s, 1880vs(br). MS: m/z 596 $(M-4CO)^+$. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 22.6(s), 36.3(s) ppm. ^1H NMR ($CDCl_3$): phenyl protons, δ 6.19 (2OH, m) ppm; olefinic protons, δ 6.67 (1H, m), 6.19(1H, m), 5.19(1H, m) ppm; aliphatic protons: 2.94(2H, m), 2.74(1H, m), 2.02(3H, m), 0.74(1H, m) ppm.

4 Crystal data for $C_{38}H_{30}O_4P_2Mo$: $MW = 708.56$, monoclinic, a 17.305(4), b 10.396(2), c 19.833(2) Å, β 115.52(1)°, V 3220(1) Å^3, space group $P2_1/c$, $Z = 4$, D_c 1.46 g cm^{-3}. Diffraction measurements were recorded on a Nicolet R3m four-circle diffractometer (graphite-monochromatized Mo-K_α radiation, λ 0.71069 Å. The structure was solved by heavy atom method and refined by least-squares. 9425 reflections were recorded over a range of $2\theta_{max}$ 60°, 6100 unique reflections with $|F_0| > 6\sigma(|F_0|)$ were used in the refinement. All non-hydrogen atoms were set anisotropic and hydrogen atoms were fixed at calculated position (C–H fixed at 0.96 Å). A weighting scheme of $w = [\sigma^2(F_0) + 0.0005|F_0|^2]^{-1}$ was applied for the least squares analysis. Final residuals were $R = 0.036$ and $R_w = 0.045$. Full lists of atomic parameters, final thermal parameters and observed and calculated structure factors are available from the authors.