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Preliminary Communication

Molybdenum carbonyl derivatives containing eight- and nine-membered diphosphine chelating rings: the synthesis of [Mo(CO)$_4$(dppp$_e$)] (dppp$_e$ = Ph$_2$P(CH$_2$)$_5$PPh$_2$) and [Mo(CO)$_4$(dpph)] (dpph = Ph$_2$P(CH$_2$)$_6$PPh$_2$) and the crystal structure of the latter

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Abstract

Treatment of [Mo(CO)$_4$(NBD)] (NBD = bicyclo[2.2.1]hepta-2,5-diene) with dppp$_e$ and with dpph in refluxed CH$_2$Cl$_2$ under N$_2$ atmosphere yields [Mo(CO)$_4$(dppp$_e$)] and [Mo(CO)$_4$(dpph)] which have distorted octahedral structures containing eight- and nine-membered rings formed by the central metal and the corresponding chelating long-backbone diphosphine ligands.

Key words: Crystal structures; Molybdenum complexes; Carbonyl complexes; Bidentate phosphine ligand complexes; Chelate complexes

There are some reports concerning the reaction between Ph$_2$P(CH$_2$)$_n$PPh$_2$ (dppp$_e$ for n = 5; dpph for n = 6) and Group 6B metal carbonyls. The dibridged bimetallic complex, *trans*-Mo$_2$(CO)$_8$(μ-dpph)$_2$ was prepared from [Mo(CO)$_6$] and dpph in refluxed toluene by the thermolytic method [1]. The monobridged dinuclear complexes, [(CO)$_5$M{Ph$_2$P(CH$_2$)$_n$PPh$_2$}M(CO)$_5$] were prepared from [M(CO)$_6$] and 0.5 molar equiv. Ph$_2$P(CH$_2$)$_n$PPh$_2$ in refluxed EtOCH$_2$CH$_2$OCH$_2$CH$_2$OH (M = Mo, n = 5, 6) [2] and from the same starting materials with Me$_3$NO as initiator in CH$_3$CN (M = Cr, Mo and W; n = 5, 6) [3]. In the present work, the unusual eight- and nine-membered ring mononuclear complexes, [Mo(CO)$_4$(dppp$_e$)] (**1**) and [Mo(CO)$_4$(dpph)] (**2**), were also synthesized from the same materials, but with [Mo(CO)$_4$(NBD)] (NBD = bicyclo[2.2.1]hepta-2,5-diene) as intermediate which contains NBD as labile ligand. To compare the structure with its analogues, [Mo(CO)$_4${Ph$_2$P(CH$_2$)$_n$PPh$_2$}] (n = 1–4) [4–6], the crystal structure of the latter was investigated by X-ray diffraction method.

Tetracarbonylbis(diphenylphosphino)pentanemolybdenum (**1**) and tetracarbonylbis(diphenylphosphino)hexanemolybdenum (**2**) were prepared as follows. [Mo(CO)$_4$(NBD)] was prepared by refluxing stoichiometric amounts of [Mo(CO)$_6$] and NBD in purified toluene under nitrogen for 1 h. The reaction medium was toluene instead of petroleum either which was used in a previous report [7, 8]. A mixture of [Mo(CO)$_4$(NBD)] (0.150 g, 0.5 mmol) and Ph$_2$P(CH$_2$)$_n$PPh$_2$ (0.220 g, 0.5 mmol for dppp$_e$; 0.227 g, 0.5 mmol for dpph) in dichloromethane (15 cm^3) was stirred at room temperature under nitrogen atmosphere over a period of 3 h. After the mixture was filtered, the filtrate was evaporated to dryness under diminished pressure and the crude product was recrystallized from CH$_2$Cl$_2$/n-hexane. **1**: yield 0.303 g, 82%. *Anal.* Found: C, 61.16; H, 4.69. Calc. for C$_{32}$H$_{28}$MoO$_4$P$_2$: C, 60.92; H, 4.65%. ν_{max} 2016s, 1916sh, 1883s,br cm^{-1} (CO). δ_P (CDCl$_3$) 26.18 ppm. δ_H (CDCl$_3$) 1.29–2.38 (10H, m, 5-CH$_2$) and 7.20–7.73 (20H, m, 4-C$_6$H$_5$). **2**: yield 0.332 g, 84%. *Anal.* Found: C, 61.19; H, 4.71. Calc. for C$_{34}$H$_{32}$MoO$_4$P$_2$: C, 61.64; H, 4.87%. ν_{max} 2014s, 1916sh, 1879s,br cm^{-1} (CO). δ_P (CDCl$_3$) 30.26 ppm. δ_H (CDCl$_3$) 0.91–2.31 (12H, m, 6-CH$_2$) and 7.22–7.74 (20H, m, 4-C$_6$H$_5$).

The method for preparation of the title compounds with [Mo(CO)$_4$(NBD)] as intermediate followed by substitution of the NBD ligand with diphosphine may be the most suitable method so far. The singly bridging compound and the *trans* dibridged complex will contaminate the product if the thermolytic route or chemical oxidation method is followed. The IR spectra of **1** and **2** are similar and have the typical pattern of [M(CO)$_4$L$_2$] [9]. Solutions in CDCl$_3$ show a singlet resonance in the ^{31}P NMR spectra at 26.18 and 30.26 for **1** and **2**, respectively, which are comparable with those for singly bridging complexes [3].

The crystal data for **2** are as follows: C$_{34}$H$_{32}$MoO$_4$P$_2$, M_r = 662.5, light greenish yellow crystals (0.20 × 0.25 × 0.35 mm) prepared from dichloromethane–n-hexane by solute diffusion method, triclinic, space group $P\bar{1}$, a = 9.7578(9), b = 10.4313(9), c = 17.874(2) Å, α = 75.217(8), β = 78.493(8), γ = 64.537(7)°, V = 1579.8(3) Å^3, Z = 2, D_c = 1.393 g cm^{-3}, $F(000)$ = 1360, Enraf-Nonius CAD4 diffractometer, graphite-monochromated

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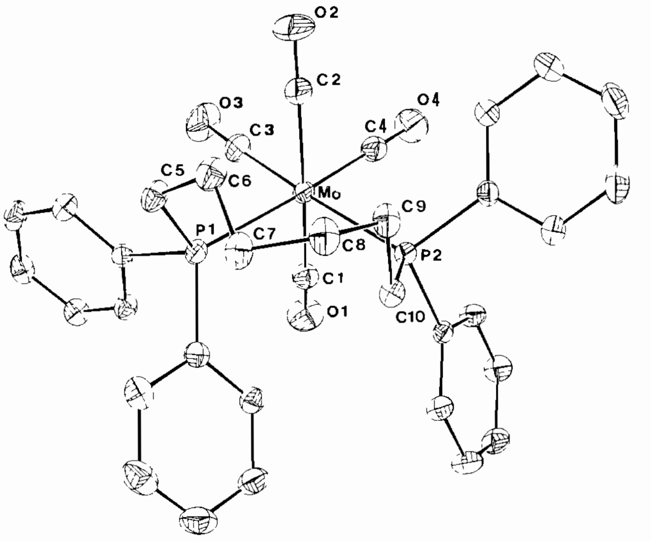

Fig. 1. Molecular structure of $[Mo(CO)_4\{Ph_2P(CH_2)_6PPh_2\}]$ with hydrogen atoms omitted. Selected bond lengths (Å) and angles (°): Mo–P(1) 2 5767(8), Mo–P(2) 2.5821(7), Mo–C(1) 2.023(3), Mo–C(2) 2.036(3), Mo–C(3) 1.968(3), Mo–C(4) 1.979(3), P(1)–Mo–P(2) 97.81(2), P(1)–Mo–C(1) 91.55(8), P(1)–Mo–C(2) 93.39(9), P(1)–Mo–C(3) 86.61(9), P(1)–Mo–C(4) 174.56(9), P(2)–Mo–C(1) 91.35(8), P(2)–Mo–C(2) 96.92(9), P(2)–Mo–C(3) 175.40(9), P(2)–Mo–C(4) 87.31(8), C(1)–Mo–C(2) 169.7(1), C(1)–Mo–C(3) 87 3(1), C(1)–Mo–C(4) 86.5(1), C(2)–Mo–C(3) 84.0(1), C(2)–Mo–C(4) 87.8(1), C(3)–Mo–C(4) 88.2(1).

Mo Kα radiation ($\lambda = 0.7107$ Å), μ(Mo Kα) = 10.8 cm^{-1}, $T = 298$ K, unit cell: 25 reflections, 2θ range 22.94–29.40°. The $\theta/2\theta$ mode was employed with scan width = $0.70 + 0.35 \tan \theta$. Three standard reflections monitored every 2 h: variation on I was $< 4\%$. Of 5737 reflections measured ($1.0 < 2\theta < 49.8°$, h, k, l: -10 to 11, 0 to 12, -20 to 21, respectively), 5544 were unique, giving 4753 observed ($I > 2.5\ \sigma(I)$). An absorption correction was made according to experimental ψ scans (maximum, minimum transmission factors = 0.999, 0.961). The structure was solved by the heavy atom method. All isotropic H atoms were calculated after isotropic refinement and included in the structure factor calculation but not refined. Non-hydrogen atoms were refined with anisotropic thermoparameters. The weighting scheme, $w = 1/\sigma^2(F_o)$, was employed with $\sigma(F_o)$ from counting statistics. The last least-squares cycle was calculated with 73 atoms, 370 parameters and 4753 reflections with maximum shift/e.s.d. = 0.001. The quantity minimized was $\Sigma w(KF_o - F_c)^2$, final R, R_w and S being 0.027, 0.025 and 2.37. Peaks in the final ΔF map were 0.230 to -0.260 e Å^{-3}. No correction for extinction was made. Atomic scattering factors were taken from ref. 10. The computing programs used were the NRC VAX package [11] and ORTEP [12].

The structure of **2** is shown in Fig. 1. The coordination around the metal is a distorted octahedron with the equatorial plane being formed by two P atoms and the two mutually *cis* CO groups which are *trans* to the bidentate diphosphine ligand; the deviation of the Mo atom from this plane is 0.029(1) Å. Distortions are due to the formation of the nine-membered chelating ring and also the difference between the Mo–P and Mo–CO bond lengths. The Mo–C bond lengths of the two mutually *cis* CO groups are shorter than those of the other two mutually *trans* carbonyls, since phosphorus is known to be a poorer acceptor than CO. The bite angle of P–Mo–P is 97.81(2)° which is larger than those of other analogues, $[Mo(CO)_4\{Ph_2P(CH_2)_nPPh_2\}]$ (67.3(1) for $n = 1$ [5], 80.2(1) for $n = 2$ [6], 89.74(4) for $n = 3$ [4], 91.65(4)° for $n = 4$ [4]). The increase in the P–Mo–P bond angle with the additional member of the chelating ring is attributed to the ring effect, the nine-membered ring being more bulky than the others.

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References

1 C.-H. Ueng and G.-Y Hwang, *J Chem Soc , Dalton Trans.,* (1991) 1643.
2 W.H. Dietsche, *Tetrahedron Lett ,* (1966) 6187.
3 T.S.A Hor, *Inorg. Chim Acta, 158* (1989) 5.
4 C -H Ueng and G.-Y. Hwang, *Acta Crystallogr., Sect C, 47* (1990) 522
5 K.K. Cheung, T.F Lai and K.S Mok, *J Chem Soc A,* (1971) 1644.
6 I Bernal, G.M. Reisner, G.R Dobson and C.B. Dobson, *Inorg Chim Acta, 121* (1986) 199.
7 M A Bennett, L Pratt and G Wilkinson, *J. Chem Soc ,* (1961) 2037
8 T.J. Chow, M.-Y. Wu and L.-K. Liu, *J Organomet Chem , 281* (1985) C33
9 J. Chatt and H R. Watson, *J Chem Soc.,* (1961) 4980.
10 *International Tables for X-ray Crystallography,* Vol. 4, Kynoch, Birmingham, UK, 1974
11 A C. Larson, F.L. Lee, Y Le Page, M. Webster, J.-P. Charland and E J. Gabe, *NRCVAX Crystal Structure System,* Chemistry Division, NRC, Ottawa, Canada, 1990.
12 C K. Johnson, *ORTEP, Rep ORNL-3794,* Oak Ridge National Laboratory, TN, USA, 1965.