*Journal of Organometallic Chemistry*, 414 (1991) 165–176
Elsevier Sequoia S.A., Lausanne
JOM 21880

# Organotransition-metal complexes of multidentate ligands

## XV *. Chelate-assisted synthesis of molybdenum(II) carbonyl complexes; crystal structure of [Mo($\eta^2$-dppm)($\eta^1$-dppm)$(CO)_2Br_2$] (dppm = bis(diphenylphosphino)methane)

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(Received February 8th, 1991)

**Abstract**

The bis(3,5-dimethylpyrazol-1-yl)methane ($H_2CPz'_2$) of the air-stable compounds, $[Mo(H_2CPz'_2)(CO)_2Br_2]$ and $[Mo(H_2CPz'_2)(CO)_2(\eta^3\text{-allyl})Br]$, is easily removed in the course of reaction with phosphorus donors whose cone angles are less than or equal to 125° to give, respectively, $[MoL_n(CO)_2Br_2]$ (L = $PMe_3$ or $P(OMe)_3$, $n = 3$: L = dppm or dppe, $n = 2$) and $[MoL_n(CO)_2(\eta^3\text{-allyl})Br]$ (L = $PMe_3$ or $P(OMe)_3$, $n = 2$: L = dppm or dppe, $n = 1$). This demonstrates that a variety of molybdenum(II) carbonyl complexes can be obtained readily from $[Mo(CO)_6]$ through the chelate assistance of the nitrogen bidentate ligand, $H_2CPz'_2$, where dppm is bis(diphenylphosphino)methane and dppe is 1,2-bis(diphenylphosphino)ethane. The structure of $[Mo(dppm)_2(CO)_2Br_2]$ has been determined by X-ray crystallography supporting the conclusion that both $[Mo(dppm)_2(CO)_2Br_2]$ and $[Mo(dppe)_2(CO)_2Br_2]$ include one bidentate and one unidentate dppm or dppe ligands respectively, space group $P\bar{1}$, $a = 12.999(4)$, $b = 13.917(4)$, $c = 14.592(5)$ Å, $\alpha = 78.85(3)$, $\beta = 71.63(3)$, $\gamma = 73.02(3)°$, $V = 2381.1(13)$ Å, $Z = 2$, $D_{calc} = 1.507$ g/cm$^3$, $R = 0.032$ and $R_w = 0.031$ on 5542 reflections with $I > 3.0\sigma(I)$.

## Introduction

It is a well established fact of basic organic chemistry that a chair conformation is more stable than either a boat or twist form for the six-membered carbon skeleton of cyclohexane, due to the strain energy present in the latter two forms [2]. Thus, when a boat form was observed for the six-membered metallacyclic skeleton. $\overline{\mathrm{Mo{-}N{-}N{-}C{-}N{-}N}}$, formed by chelation of $H_2CPz'_2$ ($Pz'$ = 3,5-dimethylpyrazol-1-yl) with a metal atom in the solid-state structure of $[Mo(H_2CPz'_2)(CO)_4]$ (**1**) [3] in

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* For Part XIV see ref. 1.

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our laboratory, we soon recognized that this strained metallacycle has a fragile nature [1]. In this report, we wish to demonstrate that this nature can enable us to obtain various molybdenum(II) carbonyl complexes [4–8]. The stability in air, apparently induced sterically by the metallacycle, of the two precursor complexes, $[Mo(H_2CPz'_2)(CO)_2Br_2]$ (**2**) [9] and $[Mo(H_2CPz'_2)(CO)_2(\eta^3\text{-allyl})Br]$ (3) [10] used in this study, is another reason why our approach to the molybdenum complexes is a good one compared with the approach common in the literature, which starts from the air-sensitive complexes, $[MO(MeCN)_2(CO)_3Br_2]$ [11] and $[Mo(MeCN)_2(CO)_2(\pi\text{-allyl})Br]$ [12].

## Results and discussion

### *Synthesis*

Following the discovery in our laboratory [13] that prolonged thermal reaction between $[Mo(CO)_6]$ and $H_2CPz'_2$ in 1,2-dimethoxyethane can convert the intermediate compound, $[Mo(H_2CPz'_2)(CO)_4]$ (**1**), into an insoluble dimeric product $[Mo(H_2CPz'_2)(CO)_3]_2$, it was realized that some dimer must still be present in the solution after two hours of the thermal reaction in the solvent for preparation of **1** as reported earlier [3], which reduces the net yield of **1** to 79%. Since compounds **2** and **3**, obtained from **1** [9,10], are the starting material for other molybdenum compounds mentioned below, a search for an alternative way to improve the synthesis of **1** is desirable. A literature survey suggested we could use trimethylamine *N*-oxide (TMNO) [14] to reach our goal. Indeed, this approach proved to be successful and a yield as high as 95% of **1** is obtained. Hence, we have now developed easy methods to prepare **2** and **3** from $[Mo(CO)_6]$, whereby a variety of

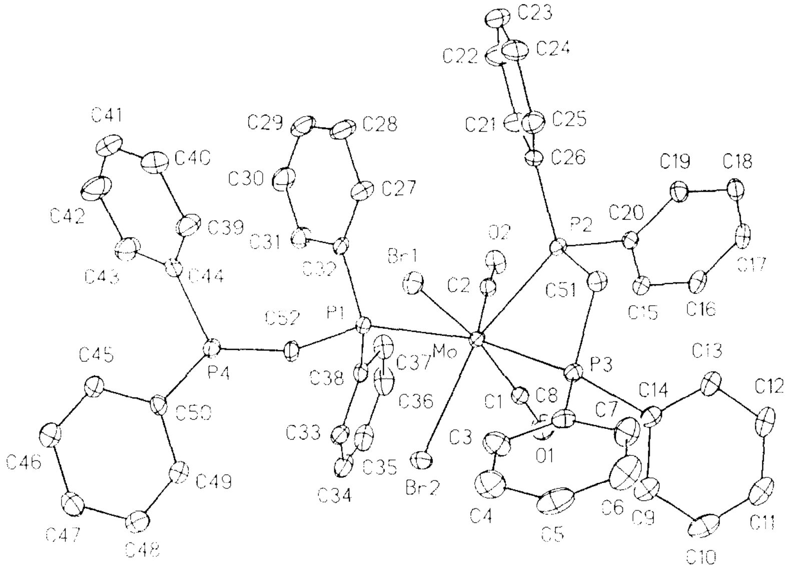
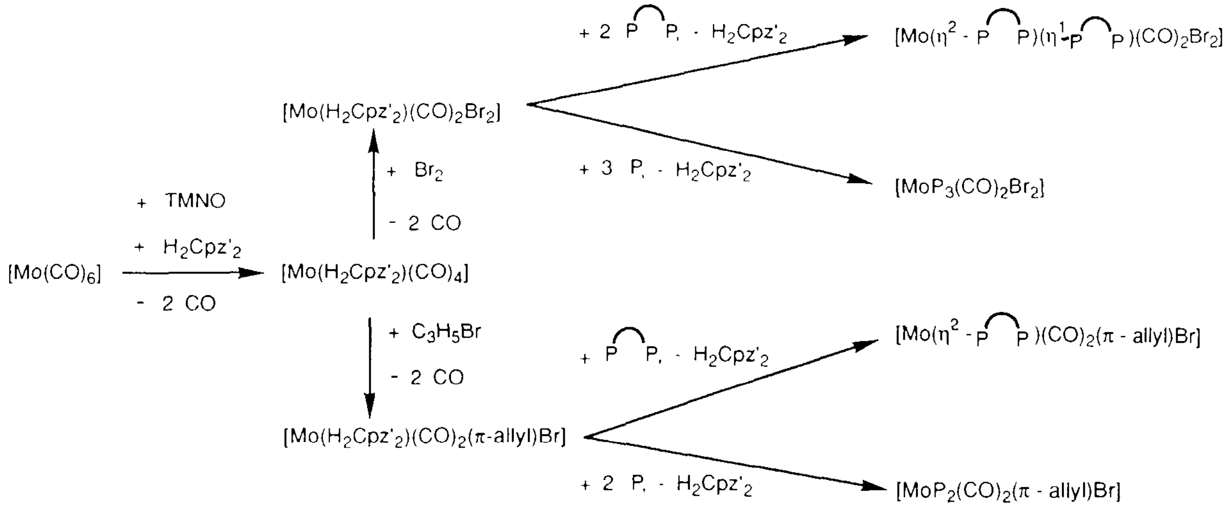


Fig. 1. Structure of $[Mo(\eta^2\text{-dppm})(\eta^1\text{-dppm})(CO)_2Br_2]$, (**5**) with atomic numbering scheme. The probability ellipsoids are at the 50% level.


[Mo(CO)6]
+ TMNO
+ H2Cpz'2
- 2 CO
[Mo(H2Cpz'2)(CO)4]
+ Br2
- 2 CO
[Mo(H2Cpz'2)(CO)2Br2]
+ C3H5Br
- 2 CO
[Mo(H2Cpz'2)(CO)2(π-allyl)Br]
+ 2 P P, - H2Cpz'2
[Mo(η2 - P P)(η1-P P)(CO)2Br2]
+ 3 P, - H2Cpz'2
[MoP3(CO)2Br2]
+ P P, - H2Cpz'2
[Mo(η2 - P P)(CO)2(π - allyl)Br]
+ 2 P, - H2Cpz'2
[MoP2(CO)2(π - allyl)Br]

Scheme 1

molybdenum(II) complexes, except for some bulky phosphine ligands such as $PPh_3$ (cf. discussion below), can be obtained quite readily (Scheme 1).

*Substitution*

The relative rate of the replacement reaction between the phosphorus ligand and compound **2** or **3** can be monitored by measuring solution IR spectra every 10 minutes. We found that the substitution of $H_2CPz'_2$ in **2** or **3** with $PMe_3$ (cone angle 118° [15]), $P(OMe)_3$ (107°), dppm (121°) or dppe (125°) is quite rapid (the conversion is completed within 10 minutes) and gives only the 18-electron substituted product, $[MoL_n(CO)_2Br_2]$ (L = $PMe_3$ or $P(OMe)_3$, $n = 3$; L = dppm or dppe, $n = 2$) and $[MoL_n(CO)_2(\eta^3\text{-allyl})Br]$ (L = $PMe_3$ or $P(OMe)_3$, $n = 2$; L = dppm or dppe, $n = 1$) (Scheme 1). In contrast no signal of any reaction between $PPh_3$ (cone angle 145° [15]) and **2** or **3** is observed when the same conditions are applied for 14 hours, where dppm is bis(diphenylphosphino)methane and dppe is 1,2-bis(diphenylphosphino)ethane. Apparently, these reactions and those reported from other laboratories [7,8,16–18] indicate that the steric effect is more important than the electronic effect. The steric bulk of $PPh_3$ [15] and that of $H_2CPz'_2$ [9b] work together to impede the substitution of $H_2CPz'_2$ in **2** to form either a 16-electron compound, $[Mo(PPh_3)_2(CO)_2Br_2]$, or an 18-electron species, $[Mo(PPh_3)_3(CO)_2Br_2]$ [19], and to inhibit the replacement of $H_2CPz'_2$ in **3** to afford the unknown $[Mo(PPh_3)_2(CO)_2(\eta^3\text{-allyl})Br]$. Once the phosphorus ligands are admitted, with small or nonexistent steric interactions with $H_2CPz'_2$, to the coordination sphere of

Table 1

Crystal data for $[Mo(\eta^2\text{-dppm})(\eta^1\text{-dppm})(CO)_2Br_2]$ (**5**)

| | |
|---|---|
| Formula | $C_{52}H_{44}Br_2MoO_2P_4$ |
| Color | Orange red |
| $D_{calc}$ (g/cm$^3$) | 1.507 |
| Crystal size (mm) | 0.64 × 0.40 × 0.40 |
| Crystal system | triclinic |
| Space group | $P\bar{1}$ (No. 2) |
| Cell dimensions: | |
| $a$ (Å) | 12.999(4) |
| $b$ (Å) | 13.917(4) |
| $c$ (Å) | 14.592(5) |
| $\alpha$ (°) | 78.85(3) |
| $\beta$ (°) | 71.63(3) |
| $\gamma$ (°) | 73.02(3) |
| $V$ (Å$^3$) | 2381.1(13) |
| $Z$ (molecules/unit cell) | 2 |
| Data collection mode | $2\theta:\theta$ |
| $2\theta$ range (°) | 2.5 to 50.0 |
| $h,k,l$ (quadrant collected) | ±14, ±16, 17 |
| Radiation | Mo-$K_\alpha$ ($\lambda$ = 0.71073 Å) |
| $\mu$ (mm$^{-1}$) | 2.102 |
| Absorption correction | empirical |
| NO [a]/NV [a] | 5542/726 |
| $R$ [a], $R_w$ [a], GOF [a] | 0.032, 0.031, 1.05 |

[a] For the meaning of each term, see text.

Table 2

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($A^2 \times 10^3$) of the non-hydrogen atoms in **5**

| | *x* | *y* | *z* | $U_{eq}$ [a] |
|---|---|---|---|---|
| Mo | 2760(1) | 2456(1) | 7739(1) | 27(1) |
| Br(1) | 2609(1) | 4119(1) | 6461(1) | 41(1) |
| Br(2) | 782(1) | 3272(1) | 8905(1) | 50(1) |
| P(1) | 1438(1) | 2058(1) | 6971(1) | 30(1) |
| P(2) | 4792(1) | 2400(1) | 6972(1) | 28(1) |
| P(3) | 3603(1) | 3439(1) | 8540(1) | 32(1) |
| P(4) | −777(1) | 2841(1) | 6324(1) | 36(1) |
| O(1) | 2619(3) | 898(3) | 9571(3) | 69(2) |
| O(2) | 3902(3) | 329(2) | 7046(2) | 49(1) |
| C(1) | 2672(3) | 1487(4) | 8897(3) | 40(2) |
| C(2) | 3489(3) | 1137(3) | 7262(3) | 34(2) |
| C(3) | 2002(5) | 5325(4) | 8682(4) | 54(2) |
| C(4) | 1589(5) | 6294(4) | 8931(4) | 64(3) |
| C(5) | 2180(6) | 6701(4) | 9320(4) | 66(3) |
| C(6) | 3200(6) | 6146(4) | 9441(4) | 68(3) |
| C(7) | 3611(5) | 5173(4) | 9195(4) | 54(2) |
| C(8) | 3011(4) | 4743(3) | 8822(3) | 37(2) |
| C(9) | 3297(5) | 2913(4) | 10505(4) | 52(2) |
| C(10) | 3603(6) | 2525(4) | 11355(4) | 66(3) |
| C(11) | 4695(6) | 2046(4) | 11315(4) | 63(3) |
| C(12) | 5481(5) | 1954(4) | 10447(4) | 57(3) |
| C(13) | 5185(5) | 2368(4) | 9588(4) | 46(2) |
| C(14) | 4096(4) | 2853(3) | 9608(3) | 36(2) |
| C(15) | 5535(4) | 661(3) | 8193(3) | 35(2) |
| C(16) | 6346(4) | −24(3) | 8568(3) | 42(2) |
| C(17) | 7439(4) | −13(3) | 8187(4) | 46(2) |
| C(18) | 7756(4) | 693(4) | 7426(3) | 44(2) |
| C(19) | 6957(4) | 1388(3) | 7049(3) | 38(2) |
| C(20) | 5834(3) | 1383(3) | 7419(3) | 29(2) |
| C(21) | 5671(5) | 1726(4) | 5157(4) | 53(2) |
| C(22) | 6164(5) | 1787(5) | 4170(4) | 65(3) |
| C(23) | 6429(5) | 2668(5) | 3687(4) | 64(3) |
| C(24) | 6223(5) | 3470(5) | 4175(4) | 59(3) |
| C(25) | 5719(4) | 3411(4) | 5163(3) | 46(2) |
| C(26) | 5432(3) | 2537(3) | 5668(3) | 31(2) |
| C(27) | 2938(4) | 1906(4) | 5137(3) | 47(2) |
| C(28) | 3371(5) | 1621(5) | 4202(4) | 63(3) |
| C(29) | 2873(5) | 1029(4) | 3907(4) | 64(3) |
| C(30) | 1978(5) | 731(4) | 4524(4) | 61(3) |
| C(31) | 1546(5) | 1012(4) | 5455(4) | 50(2) |
| C(32) | 2031(3) | 1597(3) | 5775(3) | 35(2) |
| C(33) | −207(4) | 1283(4) | 8454(3) | 43(2) |
| C(34) | −635(5) | 505(5) | 9053(4) | 58(3) |
| C(35) | −96(5) | −480(5) | 8938(4) | 63(3) |
| C(36) | 861(6) | −699(5) | 8237(5) | 66(3) |
| C(37) | 1339(5) | 58(4) | 7631(4) | 52(2) |
| C(38) | 794(3) | 1065(3) | 7731(3) | 36(2) |
| C(39) | 413(5) | 3696(4) | 4486(4) | 55(2) |
| C(40) | 694(5) | 3849(5) | 3485(4) | 68(3) |
| C(41) | 243(6) | 3435(6) | 2988(5) | 81(3) |
| C(42) | −484(6) | 2863(7) | 3465(5) | 97(4) |
| C(43) | −768(5) | 2691(5) | 4477(4) | 73(3) |

Table 2 (Continued)

| | $x$ | $y$ | $z$ | $U_{eq}$ [a] |
|---|---|---|---|---|
| C(44) | −319(3) | 3120(3) | 4994(3) | 38(2) |
| C(45) | −2450(4) | 4621(3) | 6009(4) | 44(2) |
| C(46) | −3363(4) | 5409(4) | 6314(4) | 51(2) |
| C(47) | −3778(4) | 5564(4) | 7277(4) | 54(2) |
| C(48) | −3282(4) | 4907(4) | 7940(4) | 54(2) |
| C(49) | −2382(4) | 4107(4) | 7643(3) | 49(2) |
| C(50) | −1935(3) | 3949(3) | 6671(3) | 37(2) |
| C(51) | 4837(4) | 3476(3) | 7492(3) | 34(2) |
| C(52) | 277(4) | 3131(3) | 6776(3) | 35(2) |

[a] Equivalent isotropic $U$ defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

the central metal atom, probably involving an $\eta^3$–$\eta^1$ conversion of the allyl group to avoid the formation of a 20-electron intermediate or transition state, the rupture of the strained metallacycle takes place and gives the substituted products. Although Dieck and Friedel reported in 1969 that either $PPh_3$ or $P^nBu_3$ can eliminate the allyl group of $[Mo(MeCN)_2(CO)_2(\eta^3\text{-allyl})X]$ (X = halide) to form $[Mo(MeCN)_2(PR'_3)_2(CO)_2]$ (R′ = Ph or $^n$Bu) [18a], we did not observe such reactions in our experiments. A detailed analysis based on our results and those of others [7,8,16–18] as well as the molecular orbital analysis [20] appears to show that the allyl-eliminated route has a higher energy barrier than the simple substitution route for the reactions between $[Mo(N\text{–}N)(CO)_2(\eta^3\text{-allyl})Br]$ (N–N = one nitrogen bidentate ligand or two nitrogen unidentate ligands) and phosphorus ligands. Accordingly, when the phosphorus ligands cannot tolerate the large nonbonded interactions by following the substitution route, they then follow the elimination route. From the structure of $[Mo(PhHCPz'_2(CO)_2(\eta^3\text{-allyl})Br]$ [1], we believe that the steric effect of the boat metallacycle can somewhat inhibit the initial attack of the phosphorus ligands such as $PPh_3$ or $P^nBu_3$ on one terminal carbon atom of the allyl group [16] even though this nucleophilic attack often takes place on the face of the allyl group away from the metal. Hence, when the bidentate ligand, $H_2CPz'_2$, in **3** is replaced with two unidentate ligands, MeCN, the allyl compound resulting from this replacement, $[Mo(MeCN)_2(CO)_2(\eta^3\text{-allyl})Br]$, removes the boat metallacycle and can react with either $PPh_3$ or $P^nBu_3$ to give $[Mo(MeCN)_2(PR'_3)_2(CO)_2]$ as observed [18].

It is quite interesting to note that among the products from the above substitution reactions only the new compound $[Mo(PMe_3)_2(CO)_2(\eta^3\text{-allyl})Br]$ displays a doublet signal for $PMe_3$ protons and a triplet of doublet for either *anti-* or *syn*-protons of allyl, which indicates that two $PMe_3$ together with two CO form a horizontal plane while the trihapto allyl and the Br atom lie trans to one another in apical positions above and below the plane. Thus, this structure is similar to that for $[Mo(bpy)_2(CO)_2(\eta^3\text{-allyl})NCS]$ (bpy = 2,2′-bipyridine) [21] and different from that for $[Mo(P(OMe)_3)_2(CO)_2(\eta^3\text{-allyl})Cl]$ [8], in which two $P(OMe)_3$ molecules are *trans* to each other. Apparently, it is now the electronic effect rather than the steric influence that is determining the observed structures as $PMe_3$ is larger than $P(OMe)_3$ (the cone angle of $PMe_3$ is 118° while that of $P(OMe)_3$ is 107° [15]). The effective $\pi$-acid, CO, may prefer to take the positions *trans* to two more $\sigma$-donating $PMe_3$ ligands, stabilizing the complex by effectively removing the excessive

Table 3

Selected bond lengths (Å) and angles ( ° ) for **5**

| | | | |
|---|---|---|---|
| *Bond lengths* | | | |
| Mo–Br(1) | 2.677(1) | Mo–Br(2) | 2.660(1) |
| Mo–P(1) | 2.555(2) | Mo–P(2) | 2.508(1) |
| Mo–P(3) | 2.595(2) | Mo–C(1) | 1.942(4) |
| Mo–C(2) | 1.954(4) | P(1)–C(32) | 1.829(4) |
| P(1)–C(38) | 1.828(5) | P(1)–C(52) | 1.837(4) |
| P(2)–C(20) | 1.829(4) | P(2)–C(26) | 1.817(4) |
| P(2)–C(51) | 1.828(6) | P(3)–C(8) | 1.826(4) |
| P(3)–C(14) | 1.827(5) | P(3)–C(51) | 1.840(4) |
| P(4)–C(44) | 1.841(4) | P(4)–C(50) | 1.835(4) |
| P(4)–C(52) | 1.864(6) | O(1)–C(1) | 1.150(5) |
| O(2)–C(2) | 1.152(5) | C(3)–C(4) | 1.372(8) |
| C(3)–C(8) | 1.379(7) | C(4)–C(5) | 1.374(11) |
| C(5)–C(6) | 1.732(10) | C(6)–C(7) | 1.375(8) |
| C(7)–C(8) | 1.388(9) | C(9)–C(10) | 1.384(9) |
| C(9)–C(14) | 1.391(6) | C(10)–C(11) | 1.368(10) |
| C(11)–C(12) | 1.355(8) | C(12)–C(13) | 1.395(8) |
| C(13)–C(14) | 1.373(7) | C(15)–C(16) | 1.376(7) |
| C(15)–C(20) | 1.396(5) | C(16)–C(17) | 1.357(7) |
| C(17)–C(18) | 1.376(7) | C(18)–C(19) | 1.373(7) |
| C(19)–C(20) | 1.388(6) | C(21)–C(22) | 1.377(7) |
| C(21)–C(26) | 1.379(8) | C(22)–C(23) | 1.371(9) |
| C(23)–C(24) | 1.354(10) | C(24)–C(25) | 1.381(7) |
| C(25)–C(26) | 1.381(7) | C(27)–C(28) | 1.391(7) |
| C(27)–C(32) | 1.375(6) | C(28)–C(29) | 1.378(11) |
| C(29)–C(30) | 1.348(9) | C(30)–C(31) | 1.382(8) |
| C(31)–C(32) | 1.383(9) | C(33)–C(34) | 1.388(8) |
| C(33)–C(38) | 1.388(6) | C(34)–C(35) | 1.361(9) |
| C(35)–C(36) | 1.352(8) | C(36)–C(37) | 1.386(8) |
| C(37)–C(38) | 1.386(6) | C(39)–C(40) | 1.380(8) |
| C(39)–C(44) | 1.368(7) | C(40)–C(41) | 1.353(12) |
| C(41)–C(42) | 1.349(12) | C(42)–C(43) | 1.395(9) |
| C(43)–C(44) | 1.384(10) | C(45)–C(46) | 1.380(6) |
| C(45)–C(50) | 1.396(7) | C(46)–C(47) | 1.372(8) |
| C(47)–C(48) | 1.377(8) | C(48)–C(49) | 1.378(7) |
| C(49)–C(50) | 1.388(6) | | |
| *Bond angles* | | | |
| Br(1)–Mo–Br(2) | 90.7(1) | Br(1)–Mo–P91) | 83.3(1) |
| Br(2)–Mo–P91) | 79.1(1) | Br(1)–Mo–P(2) | 79.5(1) |
| Br(2)–Mo–P(2) | 150.4(1) | P(1)–Mo–P(2) | 126.6(1) |
| Br(1)–Mo–P(3) | 83.8(1) | Br(2)–Mo–P(3) | 86.6(1) |
| P(1)–Mo–P(3) | 160.6(1) | P(2)–Mo–P(3) | 64.7(1) |
| Br(1)–Mo–C(1) | 165.9(1) | Br(2)–Mo–C(1) | 77.7(1) |
| P(1)–Mo–C(1) | 101.8(2) | P(2)–Mo–C(1) | 106.8(1) |
| P(3)–Mo–C(1) | 87.6(2) | Br(1)–Mo–C(2) | 119.2(1) |
| Br(2)–Mo–C(2) | 135.3(1) | P(1)–Mo–C(2) | 73.1(1) |
| P(2)–Mo–C(2) | 72.4(1) | P(3)–Mo–C(2) | 126.1(1) |
| C(1)–Mo–C(2) | 74.8(2) | Mo–P(1)–C(32) | 117.8(2) |
| Mo–P(1)–C(38) | 110.9(2) | C(32)–P(1)–C(38) | 103.7(2) |
| Mo–P(1)–C(52) | 114.8(2) | C(32)–P(1)–C(52) | 102.3(2) |
| C(38)–P(1)–C(52) | 106.1(2) | Mo–P(2)–C(20) | 118.6(1) |
| Mo–P(2)–C(26) | 124.1(2) | C(20)–P(2)–C(26) | 103.0(2) |
| Mo–P(2)–C(51) | 97.7(2) | C(20)–P(2)–C(51) | 101.4(2) |
| C(26)–P(2)–C(51) | 109.3(2) | Mo–P(3)–C(8) | 125.8(2) |

Table 3 (Continued)

| | | | |
|---|---|---|---|
| Mo–P(3)–C(14) | 120.5(2) | C(8)–P(3)–C(14) | 100.7(2) |
| Mo–P(3)–C(51) | 94.4(2) | C(8)–P(3)–C(51) | 105.3(2) |
| C(14)–P(3)–C(51) | 107.9(2) | C(44)–P(4)–C(50) | 102.1(2) |
| C(44)–P(4)–C(52) | 105.2(2) | C(50)–P(4)–C(52) | 98.8(2) |
| Mo–C(1)–O(1) | 178.6(5) | Mo–C(2)–O(2) | 175.3(3) |
| C(4)–C(3)–C(8) | 120.7(6) | C(3)–C(4)–C(5) | 120.3(6) |
| C(4)–C(5)–C(6) | 120.0(5) | C(5)–C(6)–C(7) | 119.7(7) |
| C(6)–C(7)–C(8) | 121.0(6) | P(3)–C(8)–C(3) | 123.5(4) |
| P(3)–C(8)–C(7) | 118.2(3) | C(3)–C(8)–C(7) | 118.3(4) |
| C(10)–C(9)–C(14) | 120.6(5) | C(9)–C(10)–C(11) | 119.9(5) |
| C(10)–C(11)–C(12) | 120.4(6) | C(11)–C(12)–C(13) | 120.0(6) |
| C(12)–C(13)–C(14) | 120.7(4) | P(3)–C(14)–C(9) | 116.7(4) |
| P(3)–C(14)–C(13) | 125.0(3) | C(9)–C(14)–C(13) | 118.2(5) |
| C(16)–C(15)–C(20) | 119.9(4) | C(15)–C(16)–C(17) | 120.7(4) |
| C(16)–C(17)–C(18) | 120.5(5) | C(17)–C(18)–C(19) | 119.5(5) |
| C(18)–C(19)–C(20) | 120.9(4) | P(2)–C(20)–C(15) | 122.2(3) |
| P(2)–C(20)–C(19) | 119.0(3) | C(15)–C(20)–C(19) | 118.4(4) |
| C(22)–C(21)–C(26) | 121.2(5) | C(21)–C(22)–C(23) | 119.4(6) |
| C(22)–C(23)–C(24) | 120.6(5) | C(23)–C(24)–C(25) | 120.0(6) |
| C(24)–C(25)–C(26) | 120.8(5) | P(2)–C(26)–C(21) | 118.8(3) |
| P(2)–C(26)–C(25) | 123.1(4) | C(21)–C(26)–C(25) | 118.0(4) |
| C(28)–C(27)–C(32) | 120.9(6) | C(27)–C(28)–C(29) | 119.4(5) |
| C(28)–C(29)–C(30) | 120.1(5) | C(29)–C(30)–C(31) | 120.7(7) |
| C(30)–C(31)–C(32) | 120.6(5) | P(1)–C(32)–C(27) | 119.3(4) |
| P(1)–C(32)–C(31) | 122.3(3) | C(27)–C(32)–C(31) | 118.2(4) |
| C(34)–C(33)–C(38) | 120.1(5) | C(33)–C(34)–C(35) | 121.1(5) |
| C(34)–C(35)–C(36) | 119.1(6) | C(35)–C(36)–C(37) | 121.4(5) |
| C(36)–C(37)–C(38) | 120.2(5) | P(1)–C(38)–C(33) | 121.9(4) |
| P(1)–C(38)–C(37) | 119.9(3) | C(33)–C(38)–C(37) | 118.1(4) |
| C(40)–C(39)–C(44) | 120.8(6) | C(39)–C(40)–C(41) | 120.4(6) |
| C(40)–C(41)–C(42) | 120.4(6) | C(41)–C(42)–C(43) | 119.9(9) |
| C(42)–C(43)–C(44) | 120.2(7) | P(4)–C(44)–C(39) | 126.1(4) |
| P(4)–C(44)–C(43) | 115.5(4) | C(39)–C(44)–C(43) | 118.4(5) |
| C(46)–C(45)–C(50) | 121.1(5) | C(45)–C(46)–C(47) | 120.8(5) |
| C(46)–C(47)–C(48) | 118.9(4) | C(47)–C(48)–C(49) | 120.7(5) |
| C(48)–C(49)–C(50) | 121.4(5) | P(4)–C(50)–C(45) | 123.2(3) |
| P(4)–C(50)–C(49) | 119.4(3) | C(45)–C(50)–C(49) | 117.2(4) |
| P(2)–C(51)–P(3) | 96.3(3) | P(1)–C(52)–P(4) | 116.0(3) |

electron-density accumulated on the central metal atom resulted from the PMe$_3$ donation. Hence, this preference favours co-planarity for two CO and two PMe$_3$ groups as observed.

### *The solid-state structure of [Mo(dppm)$_2$(CO)$_2$Br$_2$] (5)*

Crystals of **5** have two equivalent mononuclear units in a triclinic unit cell. The molecular geometry, with numbering scheme, is depicted in the ORTEP drawing (Fig. 1). For further crystallographic details see Experimental and Table 1.

The fractional coordinates and equivalent isotropic displacement coefficients of all the non-hydrogen atoms and the selected bond lengths and angles are given in Tables 2 and 3, respectively. The anisotropic displacement coefficients of these atoms (Table 4), the fractional atomic coordinates and isotropic displacement coefficients of all the hydrogen atoms (Table 5) and $F_o$ vs $F_c$ (Table 6) are available from the authors.

The structure consists of discrete units of [Mo(dppm)$_2$(CO)$_2$Br$_2$] (**5**) as shown in Fig. 1, containing one bidentate and one unidentate dppm ligand. Since the spectral data of **5** are similar to those of [Mo(dppe)$_2$(CO)$_2$Br$_2$], this complex should also have one bidentate and one unidentate dppe ligand. In this figure, the geometry of **5** is almost equally distorted from a capped trigonal prism and from a capped octahedron; the capped trigonal prism consists of a bromine atom, Br(2), in the unique capping position [Mo–Br(2) 1.942(4) Å], a carbonyl group, C(1)O(1), a bromine atom, Br(1), and two phosphorus atoms, P(1) and P(3), in the capped quadrilateral face [Mo–C(1) 1.942(4); Mo–Br(1) 2.677(1); Mo–P(1) 2.555(2); Mo–P(3) 2.595(2) Å] and a carbonyl group, C(2)O(2), and a phosphorus atom, P(2), in the unique edge [Mo–C(2) 1.954(4); Mo–P(2) 2.508 (1) Å]. In contrast the capped octahedron is made up of C(2) in the capping position, P(1), P(2), and Br(1) in the capped face, and C(1), P(3), and Br(2) in the uncapped face. Thus, the geometry of **5** is more similar to that of [Mo(dppm)$_2$(CO)$_2$Cl$_2$] (**6**) [22] than to those of [Mo(dpam)$_2$(CO)$_2$Cl$_2$] [22] or of [W(dpam)$_2$(CO)$_2$Br$_2$] (dpam = bis(diphenylarsino)methane) [23]. However, although Br$^-$ is usually considered to be a softer ligand and a better σ-donor than Cl$^-$ for the soft divalent transition-metal atom such as Mo$^{II}$ in **5** or **6** [24], the Mo–CO bond lengths of 1.91(2) and 1.82(3) Å in **6** are not larger as expected but slightly shorter on average than those of 1.942(4) and 1.954(4) Å in **5**. We think that this feature can be attributed to the greater distortion of bond angles, X–Mo–CO (X = Cl or Br), away from 180 ° in **5** than those in **6**: 77.7(1), 119.2(1), 135.3(1), 165.9(1)° in **5**, and 83.9(8), 115.5(7), 141.5(7), 170.4(7)° in **6**. The resulting accumulation of electron density on the central metal atom by the σ-donation of bromide cannot effectively be dissipated through metal–CO back-bonding so the Mo–CO bond order in **5** is less than that in **6**.

On final question is why the reaction between the 16-electron compound, [Mo[H$_2$CPz$'_2$)(CO)$_2$Br$_2$] (**2**), and the phosphorus ligand gives the 18-electron product, [Mo($\eta^2$-L$_2$)($\eta^1$-L$_2$)(CO)$_2$br$_2$] (L$_2$-dppm or dppe) or [Mo(L$'$)$_3$(CO)$_2$Br$_2$] (L$'$ = PMe$_3$ or P(OMe)$_3$), rather than the unknown 16-electron product, [Mo($\eta^2$-L$_2$)(CO)$_2$Br$_2$] or [Mo(L$'$)$_2$(CO)$_2$Br$_2$], respectively. A careful comparison of the structures of **2** [9], **5**, and [Mo(PMe$_2$Ph)$_3$(CO)$_2$Cl$_2$] (**7**) [25] leads us to believe that the steric bulk of PMe$_3$, P(OMe$_3$), dppm or dppe is small by comparison with that of H$_2$CPz$'_2$ in **2**, so that the seven-coordinate 18-electron product is obtained.

In summary, the facile synthesis of **1**, **2** and **3** from [Mo(CO)$_6$] and the facile replacement of H$_2$CPz$'_2$ of **2** and **3** with phosphorus ligands with cone angles less than or equal to 125 °, leading to substituted molybdenum(II) carbonyl complexes, are presented (Scheme 1). This approach using the air-stable compounds, **2** and **3**, to prepare metal carbonyl derivatives containing phosphorus ligands represents a useful new reaction from the viewpoint of inorganic synthesis.

## Experimental

The general operations and the spectral measurements were carried out as previously described [26]. Compounds, [Mo(H$_2$CPz$'_2$)(CO)$_2$Br$_2$] and [Mo(H$_2$CPz$'_2$)(CO)$_2$($\eta^3$-allyl)Br], were prepared from [Mo(H$_2$CPz$'_2$)(CO)$_4$] according to published procedures [9,10]. The phosphorus ligands of PMe$_3$ (1.0 *M* solution in tetrahydrofuran), $P(OMe)_3$, $PPh_3$, dppm and dppe are commercially available and were used directly without further purification. In order to compare the relative progress of the substitution reactions between $[Mo(H_2CPz'_2)(CO)_2Br_2]$ and $[Mo(H_2CPz'_2)(CO)_2(\eta^3\text{-allyl})Br]$ and phosphorus ligands, a solution IR spectrum was measured once every 10 minutes. The reactions for $PMe_3$ were performed in tetrahydrofuran (THF) while those for other ligands were conducted in $CH_2Cl_2$.

### *Preparation of $[Mo(H_2CPz'_2)(CO)_4]$*

The original procedure for this compound [3] was modified as follows: A solution of TMNO (2.50 g, 22 mmol) in MeOH (20 ml) was added to a vigorously stirred solution of $[Mo(CO)_6]$ (2.64 g, 10 mmol) and $H_2CPz'_2$ (2.06 g, 10 mmol) in benzene (40 ml). After stirring for 5 h at room temperature, the solvents were removed under vacuum. The yellow product was then recrystallized from $CH_2Cl_2$/MeOH to give 3.89 g (95%). This product was confirmed to be $[Mo(H_2CPz'_2)(CO)_4]$ by comparison with IR and NMR spectra.

### *Substitution between $[Mo(H_2CPz'_2)(CO)_2Br_2]$ or $[Mo(H_2CPz'_2)(CO)_2(\eta^3\text{-allyl})Br]$ and the phosphorus ligands of $PMe_3$, $P(OMe)_3$, $PPh_3$, dppm or dppe*

A solution of the phosphorus ligands (2 mmol of dppm or dppe, 3 mmol of $PMe_3$, $P(OMe)_3$ or $PPh_3$) dissolved in $CH_2Cl_2$ or THF was added to a stirred solution of $[Mo(H_2CPz'_2)(CO)_2Br_2]$ or $[Mo(H_2CPz'_2)(CO)_2(\eta^3\text{-allyl})Br]$ (1 mmol) in $CH_2Cl_2$ or THF. An solution IR spectrum after 10 min indicated that no signal of any reaction was observed for $PPh_3$ while the substitution for dppm, dppe, $PMe_3$ or $P(OMe)_3$ was completed so that the solvent was removed under vacuum from the solution. Recrystallization gave pure compounds of $[Mo(dppm)_2(CO)_2Br_2]$ (from MeOH, yield 78%), $[Mo(dppe)_2(CO)_2Br_2]$ (from MeOH, yield 75%), $[Mo(PMe_3)_3(CO)_2Br_2]$ (from $CH_2Cl_2$/MeOH, yield 82%), $[Mo(P(OMe)_3)_3(CO)_2Br_2]$ (from $Et_2O$/hexane, yield 70%), $[Mo(dppm)(CO)_2(\eta^3\text{-allyl})Br]$ (from $CH_2Cl_2$/MeOH, yield 80%), $[Mo(dppe)(CO)_2(\eta^3\text{-allyl})Br]$ (from $CH_2Cl_2$/MeOH, yield 85%), $[Mo(P(OMe)_3)_2(CO)_2(\eta^3\text{-allyl})Br]$ (from $CH_2Cl_2$/ hexane, yield 80%), and $[Mo(PMe_3)_2(CO)_2(\eta^3\text{-allyl})Br]$ (from $CH_2Cl_2$/MeOH, yield 77%). These products, except for $[Mo(PMe_3)_2(CO)_2(\eta^3\text{-allyl})Br]$ which is a new compound, are further confirmed by comparing both IR and NMR spectral data with those from the literature reports [4–8]. After 14 h, another IR spectrum showed no signal of reaction between $PPh_3$ and $[Mo(H_2CPz'_2)(CO)_2Br_2]$ or $[Mo(H_2CPz'_2)(CO)_2(\eta^3\text{-allyl})Br]$. The reactions were then discontinued.

$[Mo(PMe_3)_2(CO)_2(\eta^3\text{-allyl})Br]$ was characterized as follows: IR (THF) *: $\nu(CO)$ 1932s, 1830s $cm^{-1}$. Anal. Found: C, 30.89; H, 5.41. $C_{11}H_{23}BrMoO_2P_2$ calcd.: C, 31.08, H, 5.46%. $^1H$ NMR ** ($CDCl_3$, 100 MHz, 23°C): $\delta$ 1.60 (d, 18H, $PMe_3$, $J(P,H) = 8.5$); 2.72 (dt, 2H, *anti*-hydrogen atoms of allyl, $J(P,H) = 2.7$, $J(H,H) = 12.5$); 3.66 (dt, 2H, *syn*-hydrogen atoms of allyl, $J(P,H) = 5.2$, $J(H,H) = 7.6$); 5.00 (m, 1H, central hydrogen atom of allyl).

### *X-Ray diffraction study of $[Mo(dppm)_2(CO)_2Br_2]$ (5)*

Methods of data collection, data analysis and structure solution and refinement have been presented elsewhere [27]. Crystals of **5** were grown from $CH_2Cl_2$/hexane

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* Abbreviations: s, strong.

** Abbreviations: d, doublet; dt, triplet of doublet; m, multiplet, $J$ in Hz, $\delta$ in ppm.

at room temperature. Sixteen independent reflections with $13.07 \leqslant 2\theta \leqslant 26.92°$ were used for least-squares determination of the cell constants. No sign was observed of crystal deterioration during data collection. However, the compound shows a large $\mu$ of 2.102 $mm^{-1}$ and absorption correction was performed (transmission factor: min 0.621 and max 0.968). Hydrogen atoms were located from difference maps and refined isotropically while all non-hydrogen atoms were refined anisotropically. The refinements converged with $R = 0.032$ and $R_w = 0.031$ based on 5542 observed reflections with $I > 3.0\sigma(I)$ ($R = \Sigma || F_o | - | F_c || / \Sigma(F_o |$, $R_w = [\Sigma w(| F_o | - | F_c |)^2 / \Sigma w | F_o |^2]^{1/2}$. $w = (\sigma^2(F) + 0.0005F^2)^{-1}$. Goodness-of-fit (GOF) = 1.05 (GOF = $[\Sigma w(| F_o | - | F_c |)^2/(\text{NO} - \text{NV})]^{1/2}$, NO = number of observed reflections, NV = number of variables). $(\Delta/\sigma)_{max}$ in the final refinement cycle was 0.001. The maximum height in the final difference map was 0.66 e/Å$^3$. Other pertinent crystal data are listed in Table 1.

## Acknowledgement

The authors wish to thank the National Science Council, ROC, for financial support.

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