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Mo and W Dihalide Complexes with Uncommon Trigonal-Prismatic Geometry Imposed by the Linear Tetraphosphine Ancillary Ligand and Their Reactivities toward Diazoalkanes

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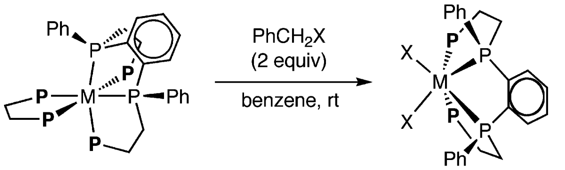
New Mo and W tetraphosphine–dihalide complexes [$MX_2(\kappa^4$-**P4**)] (**2**, MX = MoCl, MoBr, WBr; **P4** = *meso*-*o*-$C_6H_4(PPhCH_2CH_2PPh_2)_2$) with uncommon trigonal-prismatic geometries have been prepared. Treatment of ethyl diazoacetate with **2** (MX = MoCl) resulted in catalytic carbenoid-group coupling to give diethyl maleate and fumarate, whereas reactions of **2** with trimethylsilyldiazoalkane formed the diazoalkane complexes *trans*-[MX(NN═CHSiMe$_3$)(κ^4-**P4**)]$^+$ (**3**$^+$) and *cis,mer*-[MoCl$_2$(NN═CHSiMe$_3$)(κ^3-**P4**)]. The molecular structures of **2** (MX = MoCl) and **3**[PF$_6$] (MX = WBr) were crystallographically determined.

Low-valent, early transition metal complexes are known to display unique reactivities due to their strong electron-donating abilities. The extensively studied Group 6 metal complexes, bearing tertiary phosphine ligands, have been shown to facilitate various bond-breaking and -making reactions, as well as reducion of unsaturated molecules, such as alkenes, alkynes, nitriles, and dinitrogen.[1,2] However, the systems investigated previously are limited mostly to mono- and bidentate phosphine complexes, while studies involving polydentate phosphines are still quite rare.[3]

Recently, we reported the preparation of the Mo and W complexes [M(dppe)(κ^4-**P4**)] (M = Mo (**1a**), W (**1b**); dppe = $Ph_2PCH_2CH_2PPh_2$) having the linear tetraphosphine ligand **P4**, i.e., *meso*-*o*-$C_6H_4(PPhCH_2CH_2PPh_2)_2$.[4] One of the attractive features of **P4** is that it forms two types of chelate rings with different stabilities upon complexation. Thus, our recent study has revealed that **P4** can readily change the coordination mode from κ^4 to κ^3, as well as κ^2, by dissociating one or both of the outer phosphorus atoms.[5] This hapticity change may occur due to the steric strain arising from the formation of three consecutive five-membered chelate rings with P−M−P angles that are much smaller than 90°. The chelate rings consisting of conformationally loose ethylene groups are more likely to open than the relatively tightly bound phenylene-containing chelate ring. In this paper, we wish to describe further the influence of this ring strain in a κ^4-coordinating **P4** ligand on the geometry and reactivities of its Mo and W complexes.

We have discovered that reactions of the Mo complex **1a** with excess amounts (2.5−3 equiv) of $PhCH_2Cl$ or $PhCH_2Br$ take place at room temperature to form the dihalide complexes [$MoX_2(\kappa^4$-**P4**)] (X = Cl (**2a**), Br (**2a′**)) as green crystals in moderate yields (eq 1).[6] Dissociation of the dppe ligand and the presence of $PhCH_2CH_2Ph$ in the reaction mixture were confirmed. The W congener **1b** reacted with $PhCH_2Br$ more slowly than **1a** to give the dibromide complex [$WBr_2(\kappa^4$-**P4**)] (**2b**) in 42% yield, but the reaction of **1b** with $PhCH_2Cl$ did not proceed.



1a (M = Mo)
1b (M = W)

P = PPh_2

2a (M = Mo, X = Cl)
2a' (M = Mo, X = Br)
2b (M = W, X = Br)

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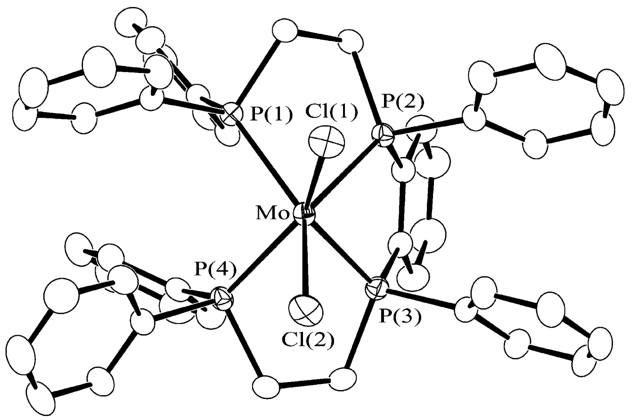
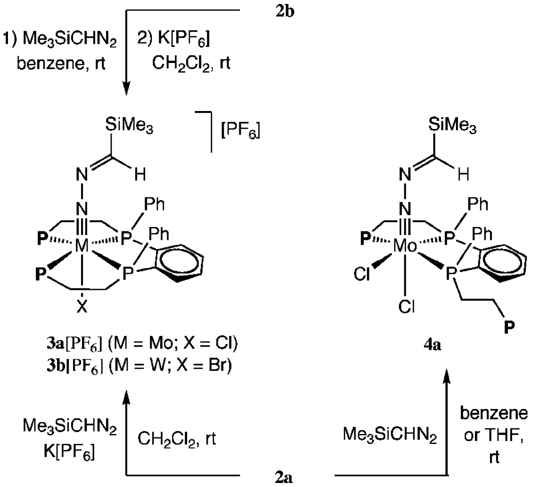


Figure 1. Molecular structure of **2a**. Hydrogen atoms are omitted for clarity. Bond distances (Å) and angles (deg): Mo−Cl(1), 2.4452(6); Mo−Cl(2), 2.447(1); Mo−P(1), 2.4335(8); Mo−P(2), 2.4128(7); Mo−P(3), 2.3792(7); Mo−P(4), 2.4499(5); Cl(1)−Mo−Cl(2), 81.14(2); Cl(1)−Mo−P(1), 86.02(2); Cl(1)−Mo−P(2), 88.46(2); Cl(2)−Mo−P(3), 88.00(2); Cl(2)−Mo−P(4), 80.54(2); P(1)−Mo−P(2), 73.16(2); P(2)−Mo−P(3), 73.30(2); P(3)−Mo−P(4), 74.32(2); P(1)−Mo−P(4), 90.20(2).

Scheme 1



By X-ray crystallography, the structure of **2a** has been determined unequivocally as shown in Figure 1. The Mo center in **2a** has a trigonal-prismatic geometry, in which one of the rectangular faces is capped by the tetradentate **P4** ligand. The three edges of the prism are defined by the pairs of the outer P atoms (P(1) and P(4)), the inner P atoms (P(2) and P(3)), and the chloride ligands. The twist angles ϕ are only 2°, 4°, and 4° with respect to these edges, respectively, where the values of ϕ have been defined previously by Stiefel and co-worker with the limiting values being 0° and 60° for trigonal-prismatic and octahedral structures.[7] The dihedral angle between two basal triangles is 12°. Well-resolved NMR signals indicate that all complexes of **2** are diamagnetic, and the $^{31}P\{^1H\}$ NMR spectra of these complexes, which exhibit two signals each assignable to the outer and the inner P nuclei, confirm the C_s symmetry.

It is noteworthy that trigonal-prismatic structure is uncommon for six-coordinate Mo(II) and W(II) complexes.[8] All the other structurally determined complexes of the type $[MX_2(tP)_4]$ (M = Mo, W; X = halogens; tP = tertiary phosphine ligand) adopt a trans octahedral geometry.[9] It is also to be noted that these trans complexes are paramagnetic due to the high-spin d^4 electron configuration of such high-symmetry structures. The presence of three consecutive strained chelate rings is the likely reason why complexes of structure type **2** disfavor an octahedral geometry of trans or even cis configuration. In the solid-state structure of **2a**, the P−Mo−P angles in the three five-membered chelate rings fall in the range 73−75°, and the sum of these values at ~221° is much smaller than 270° required to locate all four P atoms at the equatorial sites in the idealized octahedron. Even the meridional arrangement of two adjacent chelate rings results in a distortion between the mutually trans P atoms, as observed in the octahedral complex **1** (see the artwork in eq 1), in which the trans P−M−P angles within **P4** are at 152.63(9)° and 152.55(7)° for M = Mo and W, respectively.[4] Therefore, it is likely that the tetradentate **P4** ligand determines the geometry of **2** not electronically but by its intrinsic steric constraints.

Most reactions of *trans*-$[MX_2(tP)_4]$ are proposed to be initiated by dissociation of phosphine or, less commonly, the X^- ligands,[2] and therefore, the complexes with bidentate phosphine ligands such as *trans*-$[MX_2(dppe)_2]$ are less reactive than monophosphine complexes. In the case of **2**, the 16-electron metal center is not as sterically protected and directly accessible, since the **P4** ligand covers only one hemisphere of the metal. Thus, reactions of **2** with ethyl diazoacetate rapidly occurred at room temperature to form unstable complexes, which spontaneously decomposed to give a mixture of diethyl maleate and diethyl fumarate. When a 10-fold molar amount of ethyl diazoacetate was treated with **2a**, a total of ~2.8 mol (per mol of **2a**) of these carbenoid-coupling products was detected in a molar ratio of ca. 2:3. To our knowledge, Mo complexes that can catalyze the carbenoid coupling of diazo compounds are quite rare.[10] Indeed, *trans*-$[MoCl_2(dppe)_2]$ did not react with ethyl diazoacetate. Since neither the detection of any intermediary

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(6) The following method was used to synthesize **2a**. To a red suspension of **1a** (2.51 g, 1.94 mmol) in benzene (230 mL) was added $PhCH_2Cl$ (0.70 mL, 6.1 mmol). After the mixture had been stirred in the dark at room temperature for 48 h, deposited green microcrystals of **2a** were filterd off, washed with benzene and diethyl ether, and dried in vacuo to give 1.25 g (73% yield). ^1H NMR (CD_2Cl_2): δ 2.2−2.5 (m, 4H, PCH_2), 2.8−3.0, 3.45−3.65 (m, 2H each, PCH_2), 6.15−7.75 (m, 34H, aromatic). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 101.8, 141.9 (AA′XX′ pattern: $J_{AX} + J_{AX'} = 56$ Hz). Complexes **2a′** and **2b** are prepared from the cooresponding **1** and $PhCH_2Br$ in an analogous manner. **2a′**: 82% yield. ^1H NMR (CD_2Cl_2): δ 2.2−2.4, 2.55−2.75, 3.0−3.2, 4.05−4.25 (m, 2H each, PCH_2), 6.0−7.75 (m, 34H, aromatic). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 98.7, 142.0 (AA′XX′ pattern: $J_{AX} + J_{AX'} = 53$ Hz). **2b**: 42% yield. ^1H NMR (CD_2Cl_2): δ 1.9−2.1, 2.25−2.5, 2.55−2.8, 3.25−3.45 (m, 2H each, PCH_2), 6.3−7.8 (m, 34H, aromatic). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 55.6 (br with ^{183}W satellites, $J_{PW} = 246$ Hz), 105.1 (br with ^{183}W satellites, $J_{PW} = 258$ Hz).

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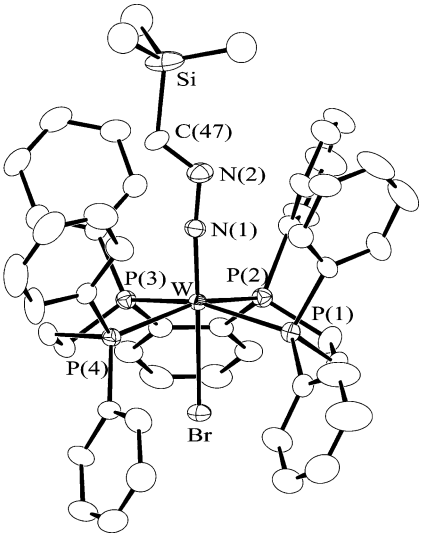

Figure 2. Structure of the cationic part of **3b**[PF_6]. The major conformer of the disordered $SiMe_3$ group is shown. Hydrogen atoms are omitted for clarity. Bond distances (Å) and angles (deg): W−Br, 2.6626(5); W−P(1), 2.494(1); W−P(2), 2.437(1); W−P(3), 2.426(1); W−P(4), 2.506(1); W−N(1), 1.757(4); N(1)−N(2), 1.324(6); N(2)−C(47), 1.255(8); Si−C(47), 1.854(6); Br−W−P, 78.80(3)−81.14(3); Br−W−N(1), 178.0(1); P(1)−W−P(2), 80.03(4); P(1)−W−P(3), 154.81(4); P(1)−W−P(4), 111.66(4); P(2)−W−P(3), 80.51(4); P(2)−W−P(4), 154.80(4); P(3)−W−P(4), 81.05(4); P−W−N(1), 98.3(1)−100.8(1); W−N(1)−N(2), 173.2(4); N(1)−N(2)−C(47), 122.2(5); Si−C(47)−N(2), 121.7(5).

metal−carbene species nor the carbene-group transfer to alkenes or aldehydes has been achieved,[11] the study has been extended to the reactions with different diazoalkanes.

Treatment of W complex **2b** with the mildly reactive diazoalkane Me_3SiCHN_2 at room temperature gave the cationic diazoalkane complex *trans*-[WBr(NN=$CHSiMe_3$)(κ^4-**P4**)]Br (**3b**Br), which was isolated as the PF_6^- salt **3b**[PF_6] in 55% yield (Scheme 1).[12] Crystallographic study of **3b**[PF_6] has revealed that the cation **3b**$^+$ has a highly distorted octahedral structure, where the terminal N-bound diazoalkane ligand and bromide are located mutually trans, as shown in Figure 2. The κ^4-**P4** ligand occupies the equatorial coordination sites in a fashion that the phenyl groups attached to the inner P atoms are oriented syn to the diazoalkane ligand. A short W−N distance at 1.757(4) Å indicates the presence of W−N multiple bonding, and the essentially linear W−N−N linkage, the bent N−N−C array (122.2(5)°), and the N=C double bond length (1.255(8) Å) suggest that this ligand is best interpreted by a hydrazone-like structure as a $2\sigma,4\pi$ electron donor to the W(IV) center. These characteristics are quite similar to those of the numerous diazoalkane complexes of the analogous ligand environment *trans*-$[MX(NN{=}CRR')(tP)_4]^+$ and the related complexes such as *cis,mer*-$[MX_2(NN{=}CRR')(tP)_3]$, which have been derived from the dinitrogen complexes $[M(N_2)_2(tP)_4]$.[13] For **3b**$^+$, strong trans influence of the diazoalkane ligand presumably results in the trans geometry in spite of the larger strain due to the planar coordination of κ^4-**P4**. In **3b**$^+$, to reduce this strain, the P−Mo−P angle in each chelate ring is slightly widened to 80−81° from those in **2**, and all the W−P bonds are bent toward the bromide ligand by ca. 10° to decrease the wide P(1)−W−P(4) angle to some extent (111.66(4)°).[14]

Reactions of the Mo complex **2a** with Me_3SiCHN_2 were also carried out which disclosed the formation of two types of diazoalkane complexes depending on the reaction conditions. When the reaction was conducted in benzene or THF at room temperature, rapid formation of the neutral diazoalkane complex *cis,mer*-[$MoCl_2$(NN=$CHSiMe_3$)(κ^3-**P4**)] (**4a**) was observed. Although the isolation of pure **4a** was hampered by its instability, spectroscopic data suggest that the diazoalkane ligand is analogous to that in **3b**[PF_6]. By contrast, stirring a CH_2Cl_2 solution of **2a** and Me_3SiCHN_2 afforded the quite stable cation **3a**$^+$, which was isolated as **3a**[PF_6] in good yield after anion metathesis with K[PF_6]. The formation of the neutral κ^3-**P4** complex in the case of Mo may be due to the less electron-rich nature of Mo, when compared to W, and this should stabilize the neutral species. Investigations to further explore the coordination chemistry of these complexes and their utility in molecular transformations are in progress.

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Supporting Information Available: Crystallographic data of **2a**·2(THF) and **3b**[PF_6] in CIF format and detailed experimental information. This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) Selected spectroscopic data are as follows. **3b**[PF_6]: ^1H NMR ($CDCl_3$): δ −0.28 (s, 9H, $SiMe_3$), 5.62 (s, 1H, N=CH). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 40.3 (AA′XX′ pattern with ^{183}W satellites, J_{PW} = 306 Hz), 81.5 (AA′XX′ pattern with ^{183}W satellites, J_{PW} = 268 Hz), $J_{AX} + J_{AX'}$ = 157 Hz. IR (KBr): ν(N=C) 1573 cm^{-1}. **3a**[PF_6]: ^1H NMR ($CDCl_3$): δ −0.25 (s, 9H, $SiMe_3$), 5.49 (s, 1H, N=CH). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 66.5, 101.9 (AA′XX′ pattern: $J_{AX} + J_{AX'}$ = 148 Hz). IR (KBr): ν(N=C) 1573 cm^{-1}. **4a**: ^1H NMR (C_6D_6): δ −0.35 (s, 9H, $SiMe_3$), 6.58 (s, 1H, N=CH). $^{31}P\{^1H\}$ NMR (C_6D_6): δ −10.4 (d, J = 40 Hz), 49.9 (d, J = 205 Hz), 53.8 (ddd, J = 205, 40, 5 Hz), 103.8 (d, J = 5 Hz). IR (KBr): ν(N=C) 1585 cm^{-1}.

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