2930 *Inorg. Chem.* **1996,** *35,* 2930−2936

# Quadruply Bonded Complexes Containing Bridging Acetate and $\eta^3$-Phosphine Ligands. Synthesis and Structural Characterization of $Mo_2(OAc)Cl_3(\eta^3\text{-tetraphos-2})$ and $Mo_2(OAc)Cl_3(\eta^3\text{-etp})$ (tetraphos-2 = $P(CH_2CH_2PPh_2)_3$; etp = $Ph_2PCH_2CH_2P(Ph)CH_2CH_2PPh_2$)

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*Received September 8, 1995*[⊗]

The complexes $Mo_2(OAc)Cl_3(\eta^3\text{-tetraphos-2})$ (tetraphos-2 = $P(CH_2CH_2PPh_2)_3$, **1**, and $Mo_2(OAc)Cl_3(\eta^3\text{-etp})$(etp = $Ph_2PCH_2CH_2P(Ph)CH_2CH_2PPh_2$), **2**, were prepared by reactions of $Mo_2(OAc)_2Cl_2(PPh_3)_2$ with tetraphos-2 and etp, respectively, in $CH_2Cl_2$. Their UV−vis and $^{31}P$-NMR spectra have been recorded and their structures have been determined. Crystal data for **1**: space group *Pbca*, $a = 24.450$ (2) Å, $b = 27.486$ (3) Å, $c = 15.017$ (3) Å, $V = 10091$ (2) Å$^3$, and $Z = 8$, with final residuals $R = 0.0683$ and $R_w = 0.0724$. Both the tetraphos-2 and etp ligands coordinate to the Mo centers in tridentate fashions with chelating/bridging bonding modes. The complexes that are also bridged by the acetate ligands are twisted about the metal−metal bonds with average twist angles of 13.2° for **1** and 11.4° for **2,** respectively. The lowest energy bands at 643 nm (14 389 cm$^{-1}$, $\epsilon = 909$ M$^{-1}$ cm$^{-1}$) for **1** and 644 nm (14388 cm$^{-1}$, $\epsilon = 1536$ M$^{-1}$ cm$^{-1}$) for **2** can be assigned to $\delta \rightarrow \delta^*$ transitions. The study on $^{31}P\{^1H\}$ NMR spectra of **1** and **2** concluded that the through metal−metal quadruple bonding coupling $|^3J_{P-Mo-Mo-P}|$ is about 20 ± 1 Hz.

## Introduction

The dimolybdenum (II) tetraacetate $Mo_2(O_2CR)_4$ and its derivatives such as $Mo_2Cl_8^{4-}$ have traditionally been the starting materials for the synthesis of complexes containing the quadruply bonded $Mo_2^{4+}$ core.[1] The most extensively studied reactions of dimolybdenum(II) carboxylates involve the preparation of complexes of the type $Mo_2(OAc)_2X_2P_2$, $Mo_2(OAc)_2X_2(PP)$, and $Mo_2(OAc)Cl_3P_3$, where P and PP represent monodentate and bidentate phosphine ligand, respectively and X represents an alkyl, amido, siloxide, or halide ligand. These complexes can be envisaged as the intermediates of the stepwise deacetylation of $Mo_2(OAc)_4$ to form $Mo_2X_4(PP)_2$ or $Mo_2X_4P_4$.

Complexes of the type $Mo_2(OAc)_2X_2P_2$ that have been reported include $Mo_2(O_2CC_6H_5)_2Br_2(PBu_3)_2$,[2,3] $Mo_2(O_2CMe)_2Cl_2(PBu_3)_2$,[4] $Mo_2(O_2CCMe_3)_2Cl_2(PEt_3)_2$,[5] and $Mo_2(O_2CMe)_2Cl_2(PPh_3)_2$.[6] These complexes were structurally characterized and shown to have a torsional angle close to zero. Molecules of the type $Mo_2(OAc)_2X_2(PP)$ that have been reported include the cases PP = $Ph_2PCH_2CH_2PPh_2$, *cis*-$Ph_2PCH{=}CHPPh_2$, and 1,2-$C_6H_4(PPh_2)_2$, and on the basis of the spectroscopic data, they have all been assigned as a cis arrangement of the acetate groups and a bridging bonding mode for the PP ligand.[7] These complexes were considered to be the most stable when the overall rotation geometry remains eclipsed.[7] For complexes of the type $Mo_2(OAc)Cl_3P_3$, only $Mo_2(OAc)Cl_3(PMe_3)_3$ has been reported[8] and the twist angle is evidently close to zero. The X-ray structure of $[Mo_2(O_2CCH_3)_2(dmpe)_2](BF_4)_2$ shows that the dmpe ligands bridge the Mo atoms so as to maintain a rigorously eclipsed rotational geometry.[9] Quadruply bonded complexes with a bridging $RCO_2^-$ ligand and stereoelectronically similar ones usually have the eclipsed conformation. For complexes of the type $MoX_4(PP)_2$, the molecules adopt a staggered or partially staggered geometry around the metal−metal bond due to ligand constraints. The minimization of nonbonded repulsions from the sets of ligands usually favors a rotation away from the eclipsed conformation.[1]

We report here complexes of the types $Mo_2(OAc)Cl_3(\eta^3\text{-tetraphos-2})$ and $Mo_2(OAc)Cl_3(\eta^3\text{-etp})$, where tetraphos-2 = $P(CH_2CH_2PPh_2)_3$ and etp = $Ph_2PCH_2CH_2P(Ph)CH_2CH_2PPh_2$. The complexes are bridged by both the acetate ligand and the $\eta^3$-phosphine ligand and are twisted about the Mo−Mo quadruple bonds.

## Experimental Section

**General Procedures.** All manipulations were carried out under an atmosphere of dry, oxygen-free nitrogen by using Schlenk techniques or a nitrogen box, unless otherwise noted. Solvents were dried and deoxygenated by refluxing over the appropriate reagents before use. Methanol was purified by distillation from magnesium, *n*-hexane from sodium/benzophenone, and dichloromethane from $P_2O_5$. The visible absorption spectra in dichloromethane were recorded on a Hitachi U-2000 spectrophotometer. The $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker 200 NMR spectrometer or on a Bruker AM 300 WB spectrometer.

**Starting Materials.** The complex $Mo_2(OAc)_2Cl_2(PPh_3)_2$ was prepared according to a previously published procedure.[7] The reagents

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[⊗] Abstract published in *Advance ACS Abstracts,* May 1, 1996.

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S0020-1669(95)01187-6 CCC: $12.00

**Table 1.** Crystal Data for $Mo_2Cl_3(OAc)(tetraphos\text{-}2)\cdot THF$

| | |
|---|---|
| formula | $Mo_2Cl_3P_4O_3C_{48}H_{53}$ |
| fw | 1100.08 |
| space group | *Pbca* |
| *a*, Å | 24.449(3) |
| *b*, Å | 27.485(5) |
| *c*, Å | 15.017(1) |
| *V*, Å$^3$ | 10090(2) |
| *Z* | 8 |
| $d_{calc}$,g/cm$^3$ | 1.45 |
| cryst size, mm | 0.10 × 0.15 × 0.25 |
| $\mu$(Mo Kα),mm$^{-1}$ | 89.12 |
| data collcn instrum | Rigaku AFC5R |
| radiation monochromated in incident beam($\lambda$(Cu Kα),Å) | 1.5418 |
| orientation reflcns: no.; range (2$\theta$),deg | 20; $19.3 < 2\theta < 28.4$ |
| temp, °C | 23 |
| scan method | $2\theta-\omega$ |
| data collcn range (2$\theta$), deg | $5 \leq 2\theta \leq 115$ |
| no. of unique data | 7637 |
| no. o obsed data | 2083 |
| criterion for obsd | $I > 2\sigma(I)$ |
| no. of params refined | 236 |
| transm factors (max; min) | 1; 0.872 |
| $R^a$ | 0.0683 |
| $R_w{}^b$ | 0.0724 |
| quality-of-fit indicator$^c$ | 1.98 |
| largest shift/esd,final cycle | 0.32 |
| largest peak,e/Å$^3$ | 0.534 |

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$. $w = 1/[\sigma^2(F_o) + gF_o{}^2]$. [c] Quality-of-fit $= [\sum w(|F_o| - |F_c|)^2/N_{observed} - N_{parameters})]^{1/2}$

tris(2-(diphenylphosphino)ethyl)phosphine (tetraphos-2) and bis(2-(diphenylphosphino)ethyl)phenylphosphine (etp) were purchased from Strem Chemical Co..

**Preparation of $Mo_2(OAc)Cl_3$(tetraphos-2).** $Mo_2(OAc)_2Cl_2(PPh_3)_2$ (0.20 g, 0.22 mmol) and tetraphos-2 (0.148 g, 0.22 mmol) were placed in a flask containing 20 mL of $CH_2Cl_2$. The mixture was then stirred at room temperature for 6 h to yield a green solution. The solvent of the green solution was evaporated and the solid redissolved in a minimum amount of $CH_2Cl_2$, followed by addition of *n*-hexane to precipitate the green solid. The product was then dried under reduced pressure. Yield: 0.158 g (69%). UV−vis spectrum in $CH_2Cl_2$: 643 nm. Anal. Calcd for $C_{44}H_{45}Cl_3O_2P_4Mo_2$ (MW = 1027.91): C, 51.41; H, 4.41. Found: C, 51.27; H, 4.43.

**Preparation of $Mo_2(OAc)Cl_3$(etp).** $Mo_2(OAc)_2Cl_2(PPh_3)_2$ (0.10 g, 0.11 mmol) and etp (0.064 g, 0.12 mmol) were placed in a flask containing 10 mL of $CH_2Cl_2$. The mixture was then stirred at room temperature for 2 h to yield a green solution. The solvent of the green solution was evaporated and the solid washed with ether and then dried under reduced pressure to give a green product. Yield: 0.076 g (75%). UV−vis spectrum in $CH_2Cl_2$: 644 nm. Anal. Calcd for $C_{36}H_{36}Cl_3O_2P_3Mo_2$ (MW = 891.84): C, 48.48; H, 4.07. Found: C, 48.04; H, 4.29.

**X-ray Crystallography.** The diffraction data of the complex $Mo_2(OAc)Cl_3$(tetraphos-2) were collected on a Rigaku AFC5R diffractometer driven by MSC/AFC Diffractometer Control Software[10] at 20 ± 1 °C, which was equipped with graphite-monochromated Cu Kα ($\lambda_\alpha$ = 1.5418 Å) radiation. Data reduction was carried by standard methods in the program "TEXSAN".[11] Basic information pertaining to crystal parameters and structure refinement is summarized in Table 1. Tables 2 and 3 list positional parameters and selected bond distances and angles, respectively.

**Table 2.** Atomic Coordinates and Equivalent Isotropic Displacement Coefficients (Å$^2$) for $Mo_2Cl_3(OAc)(tetraphos\text{-}2)\cdot THF$

| atom | *x* | *y* | *z* | *B*(eq) |
|---|---|---|---|---|
| Mo(1) | 0.19870(9) | 0.20475(6) | 0.1888(1) | 3.6(1) |
| Mo(2) | 0.23914(8) | 0.14930(6) | 0.1152(1) | 3.5(1) |
| Cl(1) | 0.2451(3) | 0.2816(2) | 0.1818(3) | 3.9(3) |
| Cl(2) | 0.1184(3) | 0.1721(2) | 0.2559(4) | 4.5(4) |
| Cl(3) | 0.1781(3) | 0.0806(2) | 0.1061(4) | 4.5(4) |
| P(1) | 0.1373(3) | 0.2441(2) | 0.0740(4) | 2.8(4) |
| P(2) | 0.2330(3) | 0.1756(2) | −0.0481(3) | 2.9(4) |
| P(3) | 0.3294(3) | 0.1885(2) | 0.0891(4) | 3.1(4) |
| P(4) | 0.1957(3) | 0.0426(2) | −0.2104(4) | 4.3(4) |
| O(1) | 0.2418(8) | 0.1851(5) | 0.3065(9) | 4(1) |
| O(2) | 0.2770(6) | 0.1216(5) | 0.230(1) | 4(1) |
| C(1) | 0.270(1) | 0.147(1) | 0.300(2) | 4(2) |
| C(2) | 0.301(1) | 0.1304(8) | 0.383(2) | 6(2) |
| C(3) | 0.170(1) | 0.2607(8) | −0.032(1) | 4(1) |
| C(4) | 0.179(1) | 0.2150(7) | −0.090(1) | 4(1) |
| C(5) | 0.2928(9) | 0.2108(8) | −0.079(1) | 4(1) |
| C(6) | 0.3246(9) | 0.2348(7) | 0.003(1) | 3(1) |
| C(7) | 0.235(1) | 0.1269(7) | −0.132(1) | 4(1) |
| C(8) | 0.186(1) | 0.0948(8) | −0.135(2) | 6(2) |
| C(9) | 0.110(1) | 0.2998(8) | 0.121(1) | 4.0(5) |
| C(10) | 0.076(1) | 0.2969(9) | 0.190(2) | 5.5(6) |
| C(11) | 0.054(1) | 0.340(1) | 0.231(2) | 5.7(7) |
| C(12) | 0.071(1) | 0.3833(9) | 0.203(2) | 5.5(6) |
| C(13) | 0.106(1) | 0.386(1) | 0.133(2) | 5.9(7) |
| C(14) | 0.125(1) | 0.344(1) | 0.092(1) | 5.0(6) |
| C(15) | 0.0757(9) | 0.2127(7) | 0.034(1) | 2.6(5) |
| C(16) | 0.039(1) | 0.2400(9) | −0.019(2) | 5.7(7) |
| C(17) | −0.008(1) | 0.217(1) | −0.056(2) | 7.0(7) |
| C(18) | −0.013(1) | 0.169(1) | −0.043(2) | 5.9(6) |
| C(19) | 0.023(1) | 0.1415(8) | 0.005(2) | 5.4(6) |
| C(20) | 0.069(1) | 0.1645(8) | 0.045(1) | 4.5(6) |
| C(21) | 0.3728(9) | 0.2123(8) | 0.180(1) | 3.2(5) |
| C(22) | 0.398(1) | 0.1767(8) | 0.232(2) | 5.7(7) |
| C(23) | 0.430(1) | 0.195(1) | 0.303(2) | 5.9(6) |
| C(24) | 0.437(1) | 0.242(1) | 0.316(2) | 6.3(7) |
| C(25) | 0.412(1) | 0.2774(8) | 0.268(2) | 5.1(6) |
| C(26) | 0.378(1) | 0.2616(9) | 0.196(2) | 5.5(6) |
| C(27) | 0.376(1) | 0.1440(8) | 0.039(1) | 3.3(5) |
| C(28) | 0.359(1) | 0.098(1) | 0.024(1) | 5.3(6) |
| C(29) | 0.394(1) | 0.063(1) | −0.018(2) | 8.0(8) |
| C(30) | 0.444(1) | 0.079(1) | −0.041(2) | 7.4(8) |
| C(31) | 0.463(1) | 0.124(1) | −0.028(2) | 10(1) |
| C(32) | 0.428(1) | 0.158(1) | 0.014(2) | 6.6(7) |
| C(33) | 0.134(1) | 0.0086(8) | −0.197(2) | 5.3(6) |
| C(34) | 0.102(1) | 0.008(1) | −0.123(2) | 8.0(8) |
| C(35) | 0.052(1) | −0.019(1) | −0.118(2) | 9.3(9) |
| C(36) | 0.036(1) | −0.044(1) | −0.194(2) | 10(1) |
| C(37) | 0.067(1) | −0.043(1) | −0.265(2) | 7.5(8) |
| C(38) | 0.114(1) | −0.018(1) | −0.270(2) | 6.1(7) |
| C(39) | 0.243(1) | 0.0070(8) | −0.146(1) | 4.0(5) |
| C(40) | 0.279(1) | −0.0216(9) | −0.195(2) | 5.4(6) |
| C(41) | 0.319(1) | −0.051(1) | −0.158(2) | 6.5(7) |
| C(42) | 0.321(1) | −0.055(1) | −0.067(2) | 7.0(7) |
| C(43) | 0.285(1) | −0.029(1) | −0.015(2) | 6.5(7) |
| C(44) | 0.246(1) | 0.0015(8) | −0.055(1) | 5.3(6) |
| O(3) | 0.341(2) | 0.098(2) | 0.653(4) | 27(2) |
| C(45) | 0.361(2) | 0.066(2) | 0.590(3) | 17(1) |
| C(46) | 0.410(2) | 0.044(2) | 0.631(4) | 17(2) |
| C(47) | 0.413(2) | 0.063(2) | 0.713(3) | 16(1) |
| C(48) | 0.380(3) | 0.103(2) | 0.718(3) | 17(2) |

A green crystal of $Mo_2(OAc)Cl_3$(tetraphos-2) was mounted in a capillary tube with epoxy cement. The unit cell constants were determined from 20 reflections with 2$\theta$ in the range from 19 to 29°. These were consistent with the orthorhombic crystal system, and the space group was subsequently determined to be *Pbca* from the systematic absences.

Routine $2\theta-\omega$ data collection was used to scan a possible 7637 data points in the range $5 < 2\theta < 115°$. Three check reflections monitored throughout the data collection displayed no significant gain or loss in intensity. Empirical absorptions based on azimuthal ($\Psi$) scans of reflections of Eulerian angle $\chi$ near 90° were applied to the data.

The programs in "TEXSAN" were used to solve the structure, which led to the locations of the positions of several heavier atoms. The remaining atoms were found in a series of alternating difference Fourier maps and least-square refinements. The positions of the hydrogen

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(10) MSC/AFC Diffractometer Control Software. Molecular Structure Corporation, 3200 Research Forest Drive, The Woodlands, TX, 1988.

(11) TEXSAN, TEXRAY Structure Analysis Package. Molecular Structure Corporation, 3200 Research Forest Drive, The Woodlands, TX, 1993.

**Table 3.** Selected Bond Distances (Å) and Angles (deg) for $Mo_2Cl_3(OAc)$(tetraphos-2)·THF

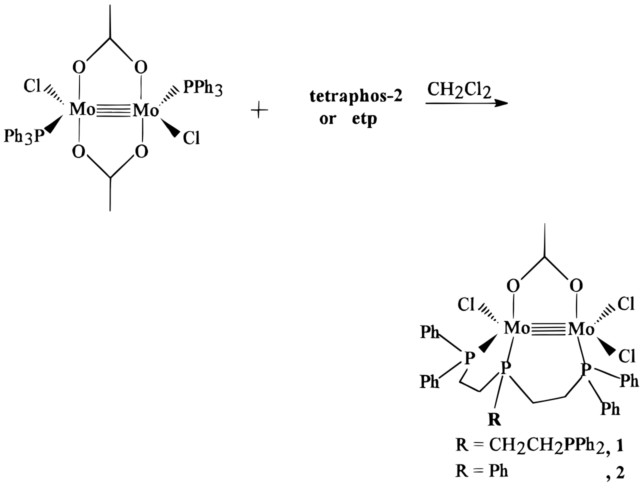
| | | | |
|---|---|---|---|
| Mo(1)−Mo(2) | 2.126(3) | P(2)−C(7) | 1.84(2) |
| Mo(1)−Cl(1) | 2.399(6) | P(3)−C(6) | 1.82(2) |
| Mo(1)−Cl(2) | 2.382(7) | P(3)−C(21) | 1.84(2) |
| Mo(1)−P(1) | 2.529(6) | P(3)−C(27) | 1.84(2) |
| Mo(1)−O(1) | 2.13(1) | P(4)−C(8) | 1.84(2) |
| Mo(2)−Cl(3) | 2.412(6) | P(4)−C(33) | 1.85(3) |
| Mo(2)−P(2) | 2.562(5) | P(4)−C(39) | 1.78(2) |
| Mo(2)−P(3) | 2.487(7) | O(1)−C(1) | 1.27(3) |
| Mo(2)−O(2) | 2.10(1) | O(2)−C(1) | 1.27(3) |
| P(1)−C(3) | 1.84(2) | C(1)−C(2) | 1.52(3) |
| P(1)−C(9) | 1.82(2) | C(3)−C(4) | 1.54(2) |
| P(1)−C(15) | 1.83(2) | C(5)−C(6) | 1.60(3) |
| P(2)−C(4) | 1.82(2) | C(7)−C(8) | 1.49(3) |
| P(2)−C(5) | 1.81(2) | | |
| Mo(2)−Mo(1)−Cl(1) | 112.9(2) | P(1)−C(15)−C(16) | 117(2) |
| Mo(2)−Mo(1)−Cl(2) | 109.4(2) | P(1)−C(15)−C(20) | 122(2) |
| Mo(2)−Mo(1)−P(1) | 103.2(1) | Mo(2)−P(2)−C(4) | 122.8(7) |
| Mo(2)−Mo(1)−O(1) | 91.1(4) | Mo(2)−P(2)−C(5) | 110.3(6) |
| Cl(1)−Mo(1)−Cl(2) | 137.7(2) | Mo(2)−P(2)−C(7) | 116.5(6) |
| Cl(1)−Mo(1)−P(1) | 82.8(2) | C(4)−P(2)−C(5) | 100.4(9) |
| Cl(1)−Mo(1)−O(1) | 91.4(5) | C(4)−P(2)−C(7) | 102(1) |
| Cl(2)−Mo(1)−P(1) | 87.7(2) | C(5)−P(2)−C(7) | 101(1) |
| Cl(2)−Mo(1)−O(1) | 87.8(5) | Mo(2)−P(3)−C(6) | 111.0(7) |
| P(1)−Mo(1)−O(1) | 165.7(4) | Mo(2)−P(3)−C(21) | 123.2(7) |
| Mo(1)−Mo(2)−Cl(3) | 107.6(2) | Mo(2)−P(3)−C(27) | 109.3(8) |
| Mo(1)−Mo(2)−P(2) | 105.5(2) | C(6)−P(3)−C(21) | 108.2(9) |
| Mo(1)−Mo(2)−P(3) | 100.6(2) | C(6)−P(3)−C(27) | 102.5(9) |
| Mo(1)−Mo(2)−O(2) | 92.2(4) | C(21)−P(3)−C(27) | 100(1) |
| Cl(3)−Mo(2)−P(2) | 97.5(2) | C(8)−P(4)−C(33) | 103(1) |
| Cl(3)−Mo(2)−P(3) | 151.6(2) | C(8)−P(4)−C(39) | 100(1) |
| Cl(3)−Mo(2)−O(2) | 92.0(4) | C(33)−P(4)−C(39) | 102(1) |
| P(2)−Mo(2)−P(3) | 77.2(2) | Mo(1)−O(1)−C(1) | 115(1) |
| P(2)−Mo(2)−O(2) | 156.2(4) | Mo(2)−O(2)−C(1) | 115(1) |
| P(3)−Mo(2)−O(2) | 84.0(4) | O(1)−C(1)−O(2) | 126(2) |
| Mo(1)−P(1)−C(3) | 116.2(8) | O(1)−C(1)−C(2) | 117(2) |
| Mo(1)−P(1)−C(9) | 108.1(7) | O(2)−C(1)−C(2) | 117(2) |
| Mo(1)−P(1)−C(15) | 120.6(7) | P(1)−C(3)−C(4) | 110(1) |
| C(3)−P(1)−P(2) | 107(1) | P(2)−C(4)−C(3) | 113(1) |
| C(3)−P(1)−C(15) | 100.7(9) | P(2)−C(5)−C(6) | 115(1) |
| C(9)−P(1)−C(15) | 103(1) | P(3)−C(6)−C(5) | 107(1) |
| P(4)−C(8)−C(7) | 112(1) | P(2)−C(7)−C(8) | 116(2) |

atoms were fixed as riding models during the least-square refinements. The final residuals of the refinement were $R = 0.0682$ and $R_w = 0.0723$, respectively.

## Results and Discussions

**Syntheses and Structures.**[12] The green title complexes $Mo_2(OAc)Cl_3$(tetraphos-2), **1**, and $Mo_2(OAc)Cl_3$(etp), **2,** were synthesized by reactions of $Mo_2(OAc)_2Cl_2(PPh_3)_2$ with 1 equiv of tetraphos-2 or etp in $CH_2Cl_2$. The yields were 69% and 75%, respectively. Clearly, the products received their third chloride atom from the $CH_2Cl_2$ solvent. The reactions are shown in Scheme 1.

**Scheme 1.** Formation Scheme for **1** and **2**



Green crystals of $Mo_2(OAc)Cl_3$(tetraphos-2) conform to the space group Pbca with eight molecules in a unit cell. Figure 1 shows the ORTEP diagram for $Mo_2(OAc)Cl_3$(tetraphos-2). It is seen from Figure 1 that one of the molybdenum atoms is coordinated by one chlorine atom and two phosphorus atoms while the other molybdenum atom is coordinated by two chloride atoms and one phosphorus atom. The two molybdenum atoms are also bridged by the $OAc^-$ ligand. The two phosphorus atoms coordinated to the same molybdenum atom are cis to each other due to ligand constraints. In the complex $Mo_2(OAc)Cl_3(PMe_3)_3$, these two phosphorus atoms are trans to each other. The tetraphos-2 ligand forms one chelating ring and one bridging ring with the Mo atoms, which are five- and six-membered, respectively. The six-membered ring formed by the molybdenum atoms and the tetraphos-2 ligand adopts the less sterically demanding boat configuration. The tetraphos-2 ligand is coordinated to the molybdenum atoms in a tridentate fashion. This type of bonding mode has been found in the complex *rac*-$Mo_2Cl_4(PEt_3)(\eta^3$-tetraphos-2).[13] As in the case of *rac*-$Mo_2Cl_4(PEt_3)(\eta^3$-tetraphos-2),[13] the central phosphorus atoms of the achiral ligand tetraphos-2 become chiral upon coordination to the molybdenum atoms. Racemic (*R* and *S*) mixtures of ligands have been obtained. Green crystals of **2** conform to the space group $P2_1/c$ with eight molecules in a unit cell.[12] The crystallographic asymmetric unit comprises two independent molecules (**2a** and **2b**). Figure 2 shows a representative ORTEP diagram for **2b**. The structures of **2** are similar to that of **1** and the difference is that the central phosphorus atom of **1** is coordinated with a phenyl group while that of **2** with a dangling $-CH_2CH_2PPh_2$ unit.

Figure 3 shows the views of the inner part of **1** looking down the Mo−Mo bond. The Δ configuration formed by the four smallest torsional angles (average 13.2°) is found for $Mo_2(OAc)Cl_3$(tetraphos-2). Since the complex crystallized in the centrosymmetric space group *Pbca*, it should have four molecules with Δ/*R* configuration and the other four with Λ/*S* configuration in a unit cell. Complex **2a** has a Δ configuration with an average twist angle of 11.4° while **2b** has a Λ configuration with an average twist angle of 11.7°. The internal rotation angles of complexes **1**, **2**, and *rac*-$Mo_2Cl_4(PEt_3)(\eta^3$-tetraphos-2) are listed in Table 4 for comparison. It is interesting that these molecules have a similar trend of internal rotation angles,

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[12] The data collection for **2** has been tried several times and the procedures were similar to those for **1**. However, the crystal decayed more than 16% during data collection. The best results of refinement and crystal data are as follows: space group $P2_1/c$, $a = 13.245$ (2) Å, $b = 29.784$ (3) Å, $c = 23.989$ (2) Å, $\beta = 94.501$ (3)°, $V = 9433.8$ (2) Å$^3$, and $Z = 8$, with final residuals $R = 0.0986$ and $R_w = 0.1280$. Each asymmetric unit contains two independent molecules. Selected bond distances (Å) and bond angles (deg): Mo(1)−Mo(2) = 2.121(3), Mo(3)−Mo(4) = 2.134(3), Mo(3)−Cl(4) = 2.410(9), Mo(3)−P(5) = 2.583(8), Mo(3)−P(7) = 2.501(9), Mo(3)−O(3) = 2.11(2), Mo(4)−Cl(5) = 2.363(9), Mo(4)−Cl(6) = 2.403(7), Mo(4)−P(6) = 2.521(8), Mo(4)−O(4) = 2.12(2); Mo(4)−Mo(3)−Cl(4) = 108.9(2), Mo(4)−Mo(3)−P(5) = 104.5(2), Mo(4)−Mo(3)−P(7) = 99.8(2), Mo(4)−Mo(3)−O(3) = 91.7(4), Cl(4)−Mo(3)−P(5) = 96.9(3), Cl(4)−Mo(3)−P(7) = 151.1(3), Cl(4)−Mo(3)−O(3) = 89.2(5), P(5)−Mo(3)−P(7) = 78.0(3), P(5)−Mo(3)−O(3) = 159.6(5), P(7)−Mo(3)−O(3) = 87.3(5), Mo(3)−Mo(4)−Cl(5) = 106.8(2), Mo(3)−Mo(4)−Cl(6) = 110.7(2), Mo(3)−Mo(4)−P(6) = 105.6(2), Mo(3)−Mo(4)−O(4) = 92.0(4), Cl(5)−Mo(4)−Cl(6) = 142.4(3), Cl(5)−Mo(4)−P(6) = 85.6(3), Cl(5)−Mo(4)−O(4) = 87.0(6), Cl(6)−Mo(4)−P(6) = 83.6(3), Cl(6)−Mo(4)−O(4) = 92.6(6), P(6)−Mo(4)−O(4) = 162.3(5). Complete tables of crystal data, anisotropic thermal parameters, bond distances, and bond angles are provided as Supporting Information.

[13] Cotton, F. A.; Hong, B. *Inorg. Chem.* **1993**, *32*, 2354.

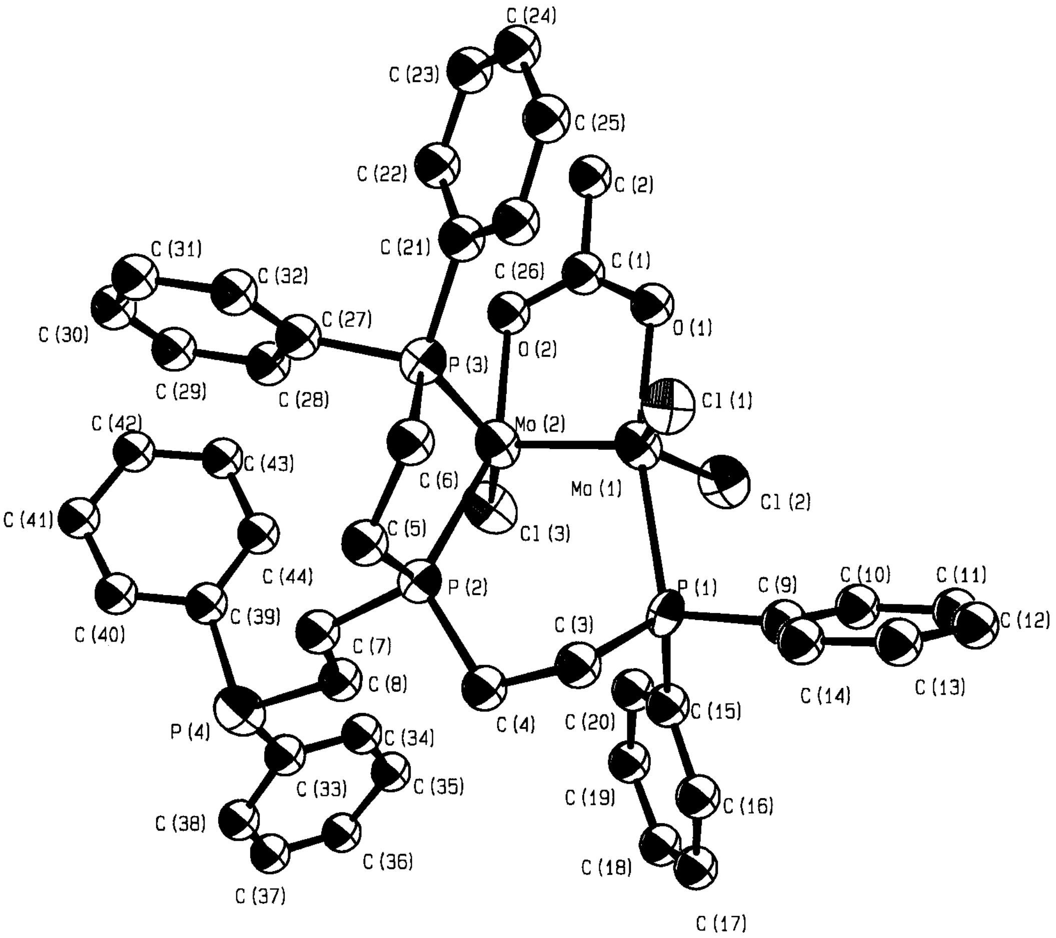

**Figure 1.** ORTEP drawing of **1** in its entirety.

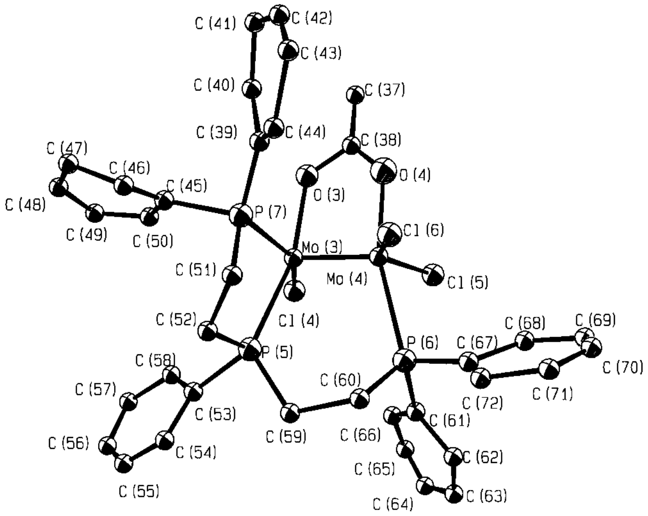

**Figure 2.** ORTEP drawing of **2** in its entirety.

starting from the largest P—Mo—Mo—P angles to the smallest P—Mo—Mo—Cl or O—Mo—Mo—O angles. It is also noted that although **1** and **2** have bridging acetate ligands while $Mo_2Cl_4(PEt_3)(\eta^3$-tetraphos-2) has only monodentate chloride and phosphorus atoms, their average twist angles are similar. All the quadruple-bonded complexes containing a bridging acetate ligand and a diphosphine ligand reported so far have twist angles equal to or close to zero.[7,9] The title complexes provide unique opportunities to compare the effect of a bridging acetate ligand and a bridging polydentate phosphine ligand on the twist angle, and it is clearly shown that the nonbonded steric repulsions resulting form the chelating/bridging bonding mode play a major role in determining the twist angle. In addition, although the ligands in the two complexes **1** and **2**, one involving a dangling $-CH_2CH_2PPh_2$ and the other a Ph group, are sufficiently different that both inter- and intramolecular nonbonded forces may be very different in the two cases, their twist angles are similar.

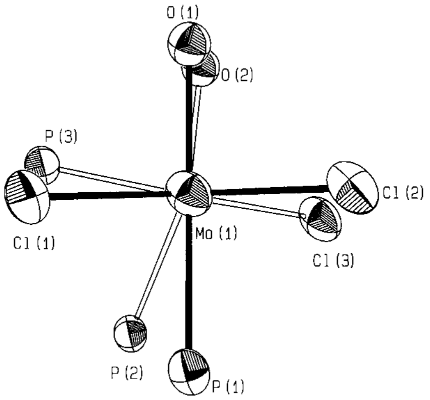

**Figure 3.** View looking down the Mo—Mo bond for **1**. The benzene carbon atoms are not shown for clarity.

As shown in Table 3, there are three distinctly different Mo—P bond lengths in the compound. The two Mo—P bonds that are trans to the acetate ligand have longer bond distances, 2.529(6) and 2.562(5) Å, than the one that is trans to the chloride atom, which is 2.487(7) Å. This indicates that the acetate ligand has a larger trans effect than the chloride ligand. In the complex $Mo_2(OAc)Cl_3(PMe_3)_3$, it was found that the Mo—P bond length in which the phosphorus atom is trans to the acetate oxygen is 2.517(9) Å and is shorter than the other

**Table 4.** Comparison of the Internal Rotation Angles (deg) for Compounds with $\eta^3$-Phoshpine Ligands

| complex | P−Mo−Mo−P | Cl−Mo−Mo−Cl | Cl−Mo−Mo−P | P(O)−Mo−Mo−Cl(O) | av |
|---|---|---|---|---|---|
| **1** | 22.1 | 11 | 13.9 | 6.2 | 13.2 |
| **2a** | 18.7 | 8.8 | 11.2 | 7.0 | 11.4 |
| **2b** | −19.0 | −9.8 | −10.1 | −6.7 | −11.4 |
| **3**[a] | 19.4 | 12.5 | 10.0 | 4.7 | 11.7 |

[a] Complex **3** = $Mo_2Cl_4(PEt_3)(\eta^3$-tetraphos-2).

**Table 5.** Comparison of the Mo−Mo Bond Distances and Torsional Angles for Several Complexes with Bridging $OAc^-$ Ligands

| complexes | Mo−Mo, Å | $\chi$, deg |
|---|---|---|
| $Mo_2Cl_3(OAc)(\eta^3$-tetraphos-2)[a] | 2.126(3) | 13.2 |
| $Mo_2(OAc)Cl_3(\eta^3$-etp) (**2a**)[a] | 2.13 | 11.4 |
| $Mo_2(OAc)Cl_3(\eta^3$-etp) (**2b**)[a] | 2.13 | 11.8 |
| $Mo_2Cl_4(PEt_3)(\eta^3$-tetraphos-2)[b] | 2.132(3) | 11.7 |
| $Mo_2Cl_3(OAc)(PMe_3)_3$[c] | 2.121(2) | 0 |
| $Mo_2(OAc)[(PhN)_2CCH_3]_3$[d] | 2.107(1) | 0 |
| $Mo_2(OAc)(ambt)_3$[e] | 2.093(3) | 1.9 |
| $(C_3N_2H_5)[Mo_2(OAc)[CH_3Ga(C_3N_2H_3)O]_4]$[f] | 2.127(1) | 0 |

[a] This work. [b] Reference 13. [c] Reference 8. [d] Reference 15. [e] Reference 16. [f] Reference 17.

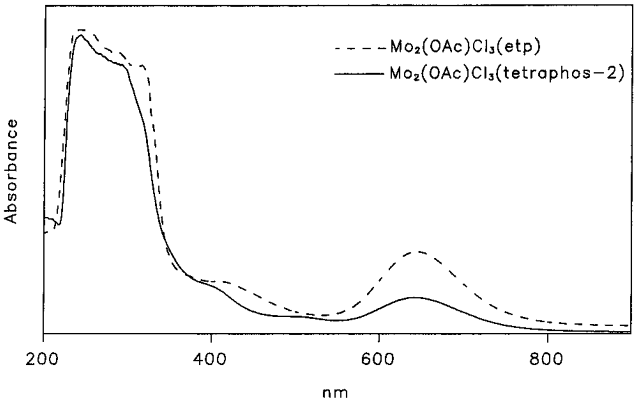

**Figure 4.** UV−vis spectra of **1** and **2** in $CH_2Cl_2$.

two equivalent Mo−P bonds (2.550(6) Å), where the trans group is another phosphine ligand. Combining these two results, it can be concluded that the trans effect series for complexes of the type $Mo_2(OAc)Cl_3P_3$ is $Me_3P > CH_3CO_2^- > Cl^-$. The order of this series is similar to that found for the complex $Mo_2(O_2CCMe_3)_2Cl_2(PEt_3)_2$, i.e., $PEt_3P > Me_3CCO_2^- > Cl^-$.[14] The Mo−O bond distances of complex **1**, 2.10(1) and 2.13(1) Å are typical for complexes which are bridged by a single acetate ligand, i.e., $Mo_2(OAc)[(PhN)_2CCH_3]_3$, 2.162(5) Å,[15] $Mo_2(OAc)(ambt)_3$(ambt = anion of 2-amino-4-methylbenzothizole), 2.16(1) Å,[16] $Mo_2(OAc)Cl_3(PMe_3)_3$,[8] 2.10(4) Å, and $(C_3N_2H_5)[Mo_2(OAc)[CH_3Ga(C_3N_2H_3)O]_4]$, 2.102(8) Å.[17] Table 5 lists the Mo−Mo bond distances and twist angles for some complexes bridged by a single acetate ligand and those for $Mo_2Cl_4(PEt_3)(\eta^3$-tetraphos-2). The correlation between the Mo−Mo bond distance and twist angle fit quite well for the first four molecules since they have the same chelating/bridging bonding modes.

**Spectroscopic Studies. (1) Absorption Spectrum.** The absorption spectra for **1** and **2**, which were measured in $CH_2Cl_2$, are shown in Figure 4. The lowest energy bands at 643 nm (14 389 $cm^{-1}$, $\epsilon = 909\ M^{-1}\ cm^{-1}$) for **1** and 644 nm (14 388 $cm^{-1}$, $\epsilon = 1536\ M^{-1}\ cm^{-1}$) for **2** can be assigned to $\delta \rightarrow \delta^*$ transitions. Clearly, the two complexes have similar $\delta \rightarrow \delta^*$ transition energy in solution, which is similar to that of *rac*-$Mo_2Cl_4(PEt_3)(\eta^3$-tetraphos-2) (660 nm). It is noted that although these three complexes have similar $\delta \rightarrow \delta^*$ transition energies in solution, the absorption coefficients of the $\delta \rightarrow \delta^*$ transition for **1** and **2**, which are 1536, and 909 $M^{-1}\ cm^{-1}$, respectively, are significantly smaller than that of *rac*-Mo-$MoCl_4(PEt_3)(\eta^3$-tetraphos-2) (660 nm, 3590 $M^{-1}\ cm^{-1}$). The proposed "intensity-borrowing"[18] from the nearby LMCT transition in *rac*-$Mo_2Cl_4(PEt_3)(\eta^3$-tetraphos-2) should be more important. This is consistent with the prediction that complexes with oxygen donor ligands, such as **1** and **2**, should have higher energy LMCT states than $Cl^-$, $Br^-$ or $I^-$-containing compounds, and thus a smaller probability for mixing between the LMCT character and the $\delta \rightarrow \delta^*$ transition. Also the Mo−Mo−O angles of 91.1 and 92.2° in **1** will result in an ineffective intensity-stealing mechanism for the mixing of CT with $\delta \rightarrow \delta^*$ transition and thus a small intensity. The second lowest energy bands appear at 412 nm (20 284 $cm^{-1}$) for **1** and 501 nm (19 608 $cm^{-1}$) for **2**, respectively.

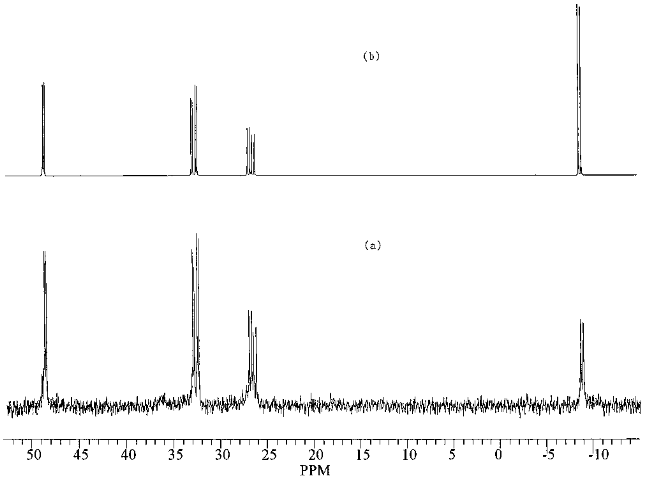

**Figure 5.** $^{31}P\{^1H\}$-NMR spectrum of **1** in $CD_2Cl_2$ (a) along with its simulation (b).

**(2) NMR Spectroscopy.** The $^{31}P\{^1H\}$-NMR spectrum of complex **1** consists of four sets of peaks centered at −8.71, 26.37, 32.40, and 48.38 ppm, respectively, as shown in Figure 5a. The assignment of the peak at −8.71 ppm to atom P(4) is clear since atom P(4) is the only one that does not coordinate to the metal centers and should have chemical shifts similar to that of the free phosphine ligand. This assignment can be verified by the fact that P(4) can only couple with P(2) to show as a doublet. It follows that the peak at 26.37 ppm can be assigned to the central phosphorus atom P(2) since it is the only atom that atom P(4) couples. This coupling is seen in Figure 6, which shows a homonuclear shift-correlated 2-D NMR spectrum for $^{31}P$ nuclei with $^1H$ decoupling and delay period to emphasize the small coupling (∼20 Hz) for **1**. The distinction between P(1) and P(3) is based on the following difference.

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(14) Arenivar, J. D.; Mainz, V. V.; Ruben, H.; Anderson, R. A. *Inorg. Chem.* **1982**, *21*, 2649.

(15) Cotton, F. A.; Ilsley, W. H.; Kaim, W. *Inorg. Chem.* **1981**, *20*, 930.

(16) Cotton, F. A.; Ilsley, W. H. *Inorg. Chem.* **1981**, *20*, 572.

(17) Breakell, K. R.; Rettig, S. J.; Storr, A.; Trotter, J. *Can. J. Chem.* **1983**, *61*, 1659.

(18) Hopkins, M. D.; Gray, H. B.; Miskowski, V. M. *Polyhedron* **1987**, *6*, 705.

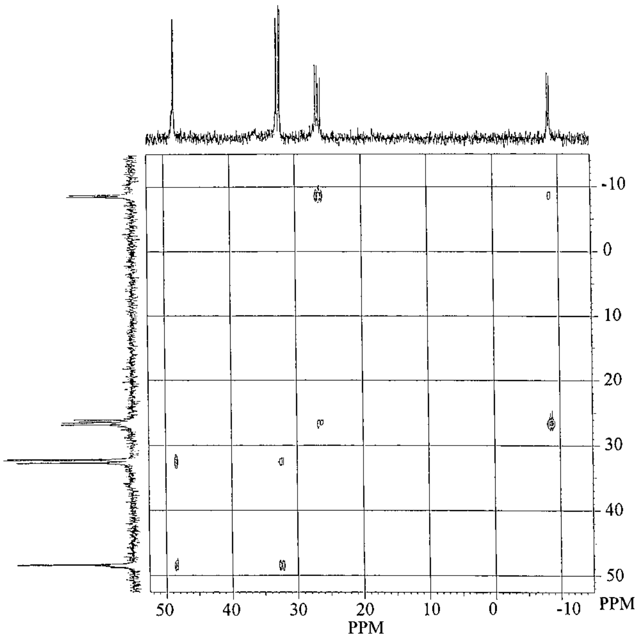

**Figure 6.** Homonuclear shift-correlated 2-D NMR spectrum for $^{31}$P nuclei with $^{1}$H decoupling for **1**.

**Table 6.** $^{31}$P{$^{1}$H} NMR Data for $Mo_2(OAc)Cl_3(\eta^3$-tetraphos-2)

| nuclei | $\delta$, ppm | coupling | $J_{\mathrm{P-P}}$, Hz |
|---|---|---|---|
| P(1) | 48.38 | P(1)−P(2) | 4.1 |
| P(2) | 26.37 | P(1)−P(3) | 20.1 |
| P(3) | 32.40 | P(2)−P(3) | 57.7 |
| P(4) | −8.71 | P(2)−P(4) | 33.7 |

Both P(1) and P(3) can couple with P(2) through the connecting chain ($^{3}J_{\mathrm{P-C-C-P}}$) and through the Mo atom, i.e., $^{2}J_{\mathrm{P-Mo-P}}$ for P(3) and $^{3}J_{\mathrm{P-Mo-Mo-P}}$ for P(1). It is a general trend that $^{2}J_{\mathrm{P-Mo-P}}$ is often much larger than $^{3}J_{\mathrm{P-Mo-Mo-P}}$.[19] The peak at 32.40 ppm is thus assigned to P(3) since the coupling constant of P(2)−P(3) is 57.7 Hz. The peak at 48.38 ppm is then assigned to P(1). It is noted that P(2) and P(3) are coordinated to the same Mo atoms and should have similar coordination shifts. The P(1) atom that coordinated to the Mo center with two chlorine atoms has the largest downfield chemical shift. The coupling constants of the two phosphorus atoms that form the bridge, i.e. P(1) and P(2), is only 4.1 Hz. Spectrum simulation was done for an ABCD spin system by employing the coupling constants listed in Table 6, and produced the result shown in Figure 5b.

Figure 7a shows the $^{31}$P{$^{1}$H}-NMR spectrum of complex **2**. The spectrum consists of three sets of peaks centered at 21.80, 30.46, and 48.61 ppm, respectively. On the basis of the assignments for **1**, the peak at 48.61 ppm can be first assigned to P(6) since it is the only P atom that coordinated to the Mo center with two chlorine atoms. It follows that P(5) can be assigned to the peak at 21.80 ppm since it does not couple with P(6), as seen in Figure 8. These are the two phosphorus atoms that form the bridging bonding. The peak at 30.46 ppm is then assigned to P(7). This assignment is consistent with the fact for **2** that among the three phosphorus atoms bonding to molybdenum atoms, the central one has the most upfield chemical shifts. Spectrum simulation was done for an ABC spin system by employing the coupling constants listed in Table 7, and produced the result shown in Figure 7b.

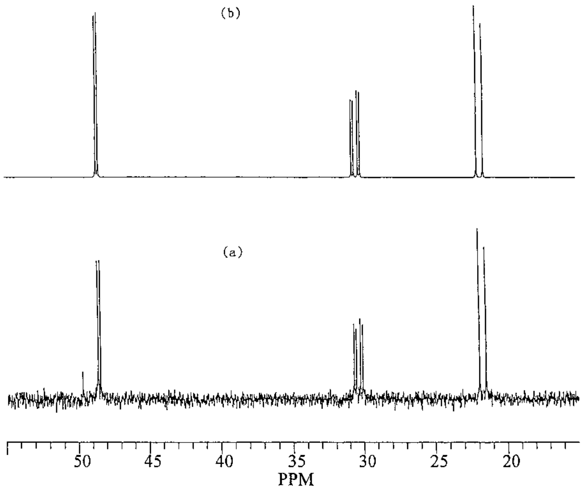

**Figure 7.** $^{31}$P{$^{1}$H}-NMR spectrum of **2** in $CD_2Cl_2$ (a) along with its simulation (b).

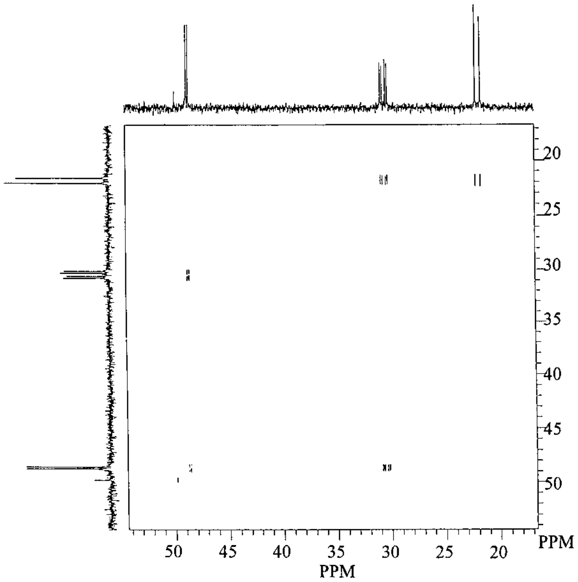

**Figure 8.** Homonuclear shift-correlated 2-D NMR spectrum for $^{31}$P nuclei with $^{1}$H decoupling for **2**.

**Table 7.** $^{31}$P{$^{1}$H} NMR Data for $Mo_2(OAc)Cl_3(\eta^3$-etp)

| nuclei | $\delta$, ppm | coupling | $J_{\mathrm{P-P}}$, Hz |
|---|---|---|---|
| P(5) | 21.80 | P(5)−P(6) | 0 |
| P(6) | 48.61 | P(6)−P(7) | 20.5 |
| P(7) | 30.46 | P(5)−P(7) | 55.6 |

An interesting aspect about the observed coupling constant is the relative weighting of the contributions via the metal and via the ligand "backbone" in complexes **1** and **2**. As seen in Tables 6 and 7, the coupling constant between P(1) and P(2) in **1** is 4.1 Hz and that between P(5) and P(6) in **2** is 0 Hz (due to the limit of the instrument resolution). The $^{2}J_{\mathrm{P-Mo-P}}$ values are 57.7 and 55.6 Hz in **1** and **2**, respectively. If the observed couplings can be divided into metal, $^{2}J_{\mathrm{P-Mo-P}}$ or $^{3}J_{\mathrm{P-Mo-Mo-P}}$, and backbone, $^{3}J_{\mathrm{P-C-C-P}}$, contributions, where the latter is assumed to be similar to the coupling in the free ligand,[20] the magnitudes of the observed coupling constants would require the contributions from $^{2}J_{\mathrm{P-Mo-P}}$ and backbone coupling $^{3}J_{\mathrm{P-C-C-P}}$ to be of the same sign, while the contributions from $^{3}J_{\mathrm{P-Mo-Mo-P}}$,

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[19] (a) Verkade, J. G. *Coord. Chem. Rev.* **1972**, *9*, 1. (b) McFarlane, W.; Rycroft, D. S. *J. Chem. Soc., Faraday Trans.* **1974**, *70*, 377. (c) Pregosin, P. S.; Kunz, R. W. *$^{31}$P and $^{13}$C NMR of Transition Metal Phosphorus Complexes*; Diehl, P., Fluck, E., Kosfeld, R., Eds.; NMR Basic Principle and Progress 16; Springer-Verlag: New York, 1979. (d) Finer, E. G.; Harris, R. K. *Prog. NMR Spectrosc.* **1971**, *6*, 61.

[20] Grim, S. O.; Barth, R. C.; Mitchell, J. D.; Gaudio, J. D. *Inorg. Chem.* **1977**, *16*, 1776.

and ${}^3J_{P-C-C-P}$ in the same six-membered ring to be of opposite sign, assuming the Karplus-type angular dependence of the coupling constants in the ring system to be minimal. Comparison of the ${}^3J_{P-C-C-P}$ values of the free tetraphos-2 and etp ligands, 20.1 and 19.7 Hz, respectively, with the observed coupling constants of **1** and **2** clarify this aspect. It is also noted that the coupling constants of P(1)−P(3) in **1** and P(6)−P(7) in **2**, which couple only through metal−metal bonds, are similar and are 20.1 and 20.5 Hz respectively. Thus, we could probably conclude that the through metal-metal quadruple bond coupling $|{}^3J_{P-Mo-Mo-P}|$ is about 20 ± 1 Hz. The $|{}^2J_{P-Mo-P}|$ value is about 37 ± 1 Hz. The $|{}^2J_{P-Mo-P}|$ value for the $[Ph_2P(CH_2)_nPR'R'']$-$Mo(CO)_4$ system were found to be 28 Hz.[20]

**Acknowledgment.** We thank the National Science Council of the Republic of China for support.

**Supporting Information Available:** Tables of anisotropic thermal parameters, bond distances, and bond angles for **1** and tables of crystal data, atomic coordinates, anisotropic thermal parameters, bond distances and bond angles, and twist angles for **2** (16 pages). Ordering information is given on any current masthead page.

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