Mixed Chloride/Amine Complexes of Dimolybdenum(II,II). 2. Reactions of $Mo_2Cl_4(NHEt_2)_4$ with Monodentate and Bidentate Phosphines. New Type of Compounds Mo_2Cl_4(diphosphine)$_4$

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Received August 13, 1998

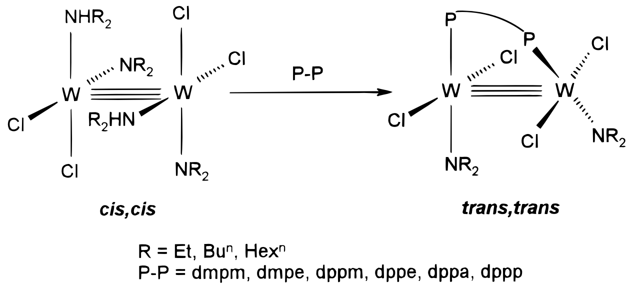
The complex $Mo_2Cl_4(NHEt_2)_4$ (**1**) undergoes facile substitution reactions of the amine ligands by phosphines to give compounds with the same core structure, Mo_2Cl_4(phosphine)$_4$, where the phosphine is PMe_3 (**2**), PMe_2Ph (**3**), $PHEt_2$ (**4**), dmpm (bis(dimethylphosphino)methane) (**5**), or dmpe (1,2-bis(dimethylphosphino)ethane) (**6**). Complexes of the type $M_2X_4L_4$ are well-known with monodentate ligands, but there is no previous crystallographically verified example of the $M_2X_4L_4$ type of compound in which L is a potentially bidentate ligand acting as a unidentate ligand. $Mo_2Cl_4(\eta^1\text{-dmpm})_4$ (**5**) can be isolated in good yield as the kinetic product of the substitution reaction at room temperature. When a solution of **5** in THF is heated, transformation into the more stable compound $Mo_2Cl_4(\mu\text{-dmpm})_2$ (**7**) takes place. $Mo_2Cl_4(\eta^1\text{-dmpe})_4$ (**6**) is stable in solution in the presence of free phosphine and can be detected by NMR. Over time it converts to a polymeric material which precipitates from the solution. For dppm (bis(diphenylphosphino)methane) (**8**) and dppa (bis(diphenylphosphino)amine) (**9**), only products of the stoichiometry Mo_2Cl_4(diphosphine)$_2$ were obtained. The crystal structures of the complexes **4** and **5** have been investigated by X-ray diffraction. The crystallographic parameters for them are as follows: for **4**, orthorhombic space group *Pbcn* with $a = 7.6015(8)$ Å, $b = 20.120(8)$ Å, $c = 19.070(6)$ Å, and $Z = 4$; for **5**, hexagonal space group $P6_422$ with $a = 12.396(1)$ Å, $c = 21.960(2)$ Å, and $Z = 3$. Both structures have a $Mo_2Cl_4P_4$ core where the phosphorus atoms are *trans* one to another on each metal center. The Mo−Mo distances of 2.137(1) Å (**4**) and 2.137(1) Å (**5**) are consistent with quadruple bonding.

Introduction

In part 1 of this series we reported[1] the synthesis and the detailed molecular structure of $Mo_2Cl_4(NHEt_2)_4$ (**1**), a quadruply-bonded dimolybdenum compound with diethylamine ligands. The properties of **1** make it an advantageous starting material to explore new fields in dinuclear molybdenum(II) chemistry. Although the Mo−$NHEt_2$ bonds in the complex are strong enough to stabilize the compound, they are very labile. Therefore, substitution reactions of the amines by other ligands were expected to be very fast. In this work we present the first examples of ligand substitution in reactions of **1** with phosphines.

The substitution of amine groups by monodentate and bidentate phosphines has been studied for some ditungsten(III) compounds.[2] In particular, it has been shown by us[2e,f,i] that the reactions between $W_2Cl_4(NR_2)_2(NHR_2)_2$ (R = Et, Bu^n, Hex^n) and diphosphines (dmpm, dmpe, dppm, dppe, dppa, dppp) occur even at −40° C to produce directly $W_2Cl_4(NR_2)_2$(P-P) products.

Scheme 1



One interesting question that arose from this study was why the cis,cis isomer of the starting material gives the trans,trans isomer as the kinetic product (Scheme 1) since that requires a reaction mechanism involving ligand rearrangement.

It has been suggested that the key initial step in these reactions involves the coordination of one PR_2 group of the diphosphine to one W atom, leaving the other PR_2 moiety free.

Recently, it has been found by Chisholm and McInnes[3] that the substitution of monophosphines ($PR_3 = PEt_3$, PMe_2Ph) in a complex $Mo_2Cl_4(PR_3)_4$ by dmpe gave a compound that they formulated as $Mo_2Cl_4(\eta^1\text{-dmpe})_4$ on the basis of ^{31}P NMR data. We can now offer further evidence that compounds of that type really exist, and we report here the crystal structure of $Mo_2Cl_4(\eta^1\text{-dmpm})_4$ where all four potentially bidentate dmpm ligands are coordinated as monodentate groups.

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(1) Cotton, F. A.; Dikarev, E. V.; Herrero, S. *Inorg. Chem.* **1998**, *37*, 5862.

(2) (a) Bradley, D. C.; Hursthouse, M. B.; Powell, H. R. *J. Chem. Soc., Dalton Trans.* **1989**, 1537. (b) Cotton, F. A.; Yao, Z. *J. Cluster Sci.* **1994**, *5*, 11. (c) Cotton, F. A.; Dikarev, E. V.; Wong, W.-Y. *Inorg. Chem.* **1997**, *36*, 80. (d) Cotton, F. A.; Dikarev, E. V.; Nawar, N.; Wong, W.-Y. *Inorg. Chem.* **1997**, *36*, 559. (e) Cotton, F. A.; Dikarev, E. V.; Wong, W.-Y. *Inorg. Chem.* **1997**, *36*, 902. (f) Cotton, F. A.; Dikarev, E. V.; Nawar, N.; Wong, W.-Y. *Inorg. Chim. Acta* **1997**, *262*, 21. (g) Cotton, F. A.; Dikarev, E. V.; Wong, W.-Y. *Inorg. Chem.* **1997**, *36*, 3268. (h) Cotton, F. A.; Dikarev, E. V.; Wong, W.-Y. *Inorg. Chem.* **1997**, *36*, 2670. (i) Cotton, F. A.; Dikarev, E. V.; Wong, W.-Y. *Polyhedron* **1997**, *16*, 3893.

(3) Chisholm, M. H.; McInnes, J. M. *J. Chem. Soc., Dalton Trans.* **1997**, 2735.

10.1021/ic980972w CCC: $18.00

Experimental Section

General Procedures. All manipulations were carried out under an atmosphere of dry oxygen-free argon or nitrogen with standard Schlenk techniques. Solvents were dried and deoxygenated by refluxing over suitable reagents before use. $NHEt_2$ was purchased from Aldrich, Inc. PMe_3, PMe_2Ph, $PHEt_2$, dmpm, dmpe, and dppa were obtained from Strem Chemicals. Lancaster provided dppm. Benzene-d_6, toluene-d_8, and chloroform-d_1 were obtained from Cambridge Isotope Laboratories, Inc., and used as received. $Mo_2Cl_6(THF)_3$ was synthesized according to the published procedure.[4] Sodium amalgam was prepared inside a drybox by dissolving a weighed amount of metallic sodium in an approximately measured quantity of mercury that was pumped under vacuum for at least 1 h in a Schlenk flask.

(A) Synthesis of $Mo_2Cl_4(NHEt_2)_4$ (1). We used a convenient modification of the published[1] synthetic procedure for **1**. A flask which contained a suspension of 0.15 g (0.242 mmol) of $Mo_2Cl_6(THF)_3$ in 10 mL of THF was kept sunk in a dry ice/ethanol bath. $NHEt_2$ 1 mL, (9.67 mmol) and 2 equiv of Na/Hg amalgam (0.4%) were added to the flask, and the mixture was allowed to reach room temperature. The suspension was stirred vigorously for 24 h before 50 mL of benzene was added to assist the precipitation of NaCl. After 30 min the suspension was filtered to give a purple solution of $Mo_2Cl_4(NHEt_2)_4$ stabilized by the presence of a small amount of free amine.

(B) Synthesis of $Mo_2Cl_4(PHEt_2)_4$ (4). A 0.98 M solution of $PHEt_2$ in hexanes (2 mL) was added to a stirred solution of $Mo_2Cl_4(NHEt_2)_4$ (**1**) (prepared following procedure A) at room temperature. The color of the solution immediately changed to turquoise blue. The solvents and the excess of amine and phosphine were removed under vacuum right after the addition of the phosphine. The compound $Mo_2Cl_4(PHEt_2)_4$ (**4**) was extracted with 50 mL of hot hexanes. Yield: 0.11 g (66%). Single crystals of **4** were obtained by layering hexanes over a saturated solution of the compound in toluene.

Anal. Calcd for **4**: C, 27.69; H, 6.39. Found: C, 28.47; H, 6.38. IR data [KBr pellet, ν (cm^{-1})]: 2965 (s), 2933 (m), 2873 (m), 2359 (m), 1449 (m), 1414 (m), 1380 (w), 1247 (w), 1099 (m), 1055 (w), 1045 (s), 1035 (s), 992 (m),856 (m), 815 (vs), 757 (m), 700 (m), 682 (vw), 636 (w). ^1H NMR data ($CDCl_3$, 22 °C): δ 1.09 (m, CH_3, $^3J(CH_2CH_3)$ = 7.8 Hz, $^3J(PCH_2CH_3)$ = 7.8 Hz); 2.06 (m, CH_2, $^2J(PCH_2)$ = 101.1 Hz, $^3J(P(H)CH_2)$ = 2.4 Hz); 4.78 (center of a broad multiplet, P*H*). $^{31}P\{^1H\}$ NMR data ($CDCl_3$, 22 °C): δ 2.45 (s). CV (CH_2Cl_2, 22° C, V vs Ag/AgCl): $E_{1/2}(ox) = +0.64$, $E_{p,a} = +1.60$. UV−vis [$CHCl_3$; λ_{max}, nm]: 615 ($\delta-\delta^*$ transition).

Synthesis of $Mo_2Cl_4(PMe_3)_4$ (2). The procedure followed a course similar to that for **4**, except that in this case 0.2 mL (1.947 mmol) of PMe_3 was added. Yield: 0.12 g (75%). Single crystals of **2** were obtained upon cooling a solution in hexanes to −30° C. The compound was identified by $^{31}P\{^1H\}$ NMR[3] and X-ray crystallography.[5]

^1H NMR data (benzene-d_6, 22 °C): δ 1.43 (m, CH_3). $^{31}P\{^1H\}$ NMR data (benzene-d_6, 22 °C): δ −8.68 (s).

Synthesis of $Mo_2Cl_4(PMe_2Ph)_4$ (3). The same procedure as in the preparation of **4** was followed except in this case 0.3 mL (2.079 mmol) of PMe_2Ph was added. Yield: 0.15 g (70%). A solution of **3** in hot hexanes was slowly cooled to −30° C to obtain single crystals. The compound was identified by $^{31}P\{^1H\}$ NMR[3] and X-ray crystallography.[6]

(C) Synthesis of $Mo_2Cl_4(dmpm)_4$ (5). To a stirred solution of **1** (prepared with the procedure described in section A) was added 0.33 mL (2.043 mmol) of dmpm at room temperature. The color of the solution changed to royal blue. Right after the addition of dmpm, the solution was evaporated to dryness. Compound **5** was extracted with 50 mL of hexanes, and the solvent was removed under vacuum. Yield: 0.15 g (71%). Single crystals of **5** were obtained by keeping a hexanes solution at −30 °C.

Anal. Calcd for **5**: C, 27.35; H, 6.43. Found: C, 27.77; H, 6.45. IR data [KBr pellet, ν (cm^{-1})]: 2964 (w), 2954 (w), 2901 (w), 1431 (m), 1412 (w), 1287 (w), 1274 (w), 1261 (m), 1156 (w), 1099 (m), 1023 (m), 950 (s), 908 (vs), 882 (w), 838 (vw), 803 (m), 783 (m), 742 (m), 708 (m), 690 (w), 674 (vw), 624 (vw). ^1H NMR data (toluene-d_8, 22 °C): δ 0.89 (d, CH_3, $^2J(MoPCH_2PCH_3)$ = 3.6 Hz), 1.76 (t, CH_3, $^2J(MoPCH_3)$ = 3.6 Hz), 2.14 (m, CH_2, $^2J(PCH_2P)$ = $^2J(PCH_2P)$ = 1.5 Hz). $^{31}P\{^1H\}$ NMR data (toluene-d_8, 22 °C): δ 1.15 (m, MoP_a), −60.05 (m, P_b).

Synthesis of $Mo_2Cl_4(dmpe)_4$ (6). To a stirred solution of **1** at room temperature was added 0.33 mL (1.933 mmol) of dmpe, and the color instantaneously changed to dark blue. The solvents, the amine, and the excess of phosphine were immediately evaporated under vacuum to give a royal blue solid. Yield: 0.17 g (75%). All attempts to grow crystals of **6** have failed. Some blue insoluble polymeric solid was always precipitated from solutions.

$^{31}P\{^1H\}$ NMR data (toluene-d_8, 22 °C): δ −0.39 (m, MoP_a), −48.07 (m, P_b).

(D) Synthesis of $Mo_2Cl_4(dppm)_2$ (8). A purple solution of **1** was added to a flask which contained 0.74 g (1.933 mmol) of dppm. At the beginning a sky-blue color was seen for an instant. The mixture was stirred for 90 min at room temperature. The solution was concentrated to approximately 15 mL and then filtered. The turquoise blue solid was washed with 10 mL of benzene and dried in a vacuum. Yield: 0.15 g (55%). Hexanes were layered over a green solution of **8** in dichloromethane to obtain single crystals. The compound was identified by NMR[7] and X-ray crystallography.[8]

$^{31}P\{^1H\}$ NMR data ($CDCl_3$, 22 °C): δ 15.56 (s).

Synthesis of $Mo_2Cl_4(dppa)_2$ (9). The same procedure as for the isolation of **8** was followed in this case. The green solution obtained was evaporated to dryness, and the residue was washed with THF. Yield: 0.13 g (50%). Single crystals of **9** were obtained by layering hexanes over a dichloromethane solution. The compound was identified by NMR and X-ray crystallography.[9]

(E) Reaction between $Mo_2Cl_4(dmpm)_4$ (5) and $Mo_2Cl_4(NHEt_2)_4$ (1). A solution of 0.07 g (0.080 mmol) of **5** in 45 mL of hexanes was layered over a solution of 0.05 g (0.08 mmol) of **1** in 45 mL of toluene at room temperature. When the diffusion was completed, blue crystals of $Mo_2Cl_4(dmpm)_2$ (**7**) were obtained in nearly quantitative yield. The compound was identified by NMR[10] and X-ray crystallography.[11]

IR data [KBr pellet, ν (cm^{-1})]: 2964 (w), 2908 (vw), 1428 (w), 1409 (w), 1357 (vw), 1296 (w), 1284 (w), 1261 (m), 1096 (br,s), 1026 (br,m), ∼950 (sh,vs), 936 (vs), 896 (vw), 803 (s), 764 (vw), 749 (w), 734 (vw),719 (vw), 686 (vw), 654 (vw). ^1H NMR data ($CDCl_3$, 22 °C): δ 1.53 (t, CH_3), 3.09 (m, CH_2). $^{31}P\{^1H\}$ NMR data ($CDCl_3$, 22 °C): δ −0.13 (s).

Transformation of $Mo_2Cl_4(dmpm)_4$ (5) into $Mo_2Cl_4(dmpm)_2$ (7). A royal blue solution of 0.07 g (0.08 mmol) of **5** in 15 mL of THF was refluxed for 15 min to form a colorless solution and a blue precipitate. The solvent was removed, and the residue was dissolved in 10 mL of CH_2Cl_2. Hexanes (10 mL) were layered over the turquoise solution. In a few days the blue crystals of **7** were obtained in nearly quantitative yield.

Physical Measurements. Electrochemical measurements were carried out on dichloromethane solutions that contained 0.1 M tetra-*n*-butylammonium hexafluorophosphate (TBAH) as the supporting electrolyte. A stream of nitrogen was bubbled through the solution during

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(4) Boyd, I. W.; Wedd, A. G. *Aust. J. Chem.* **1976**, *29*, 1829.

(5) Cotton, F. A.; Extine, M. W.; Felthouse, T. R.; Kolthammer, B. W. S.; Lay, D. G. *J. Am. Chem. Soc.* **1981**, *103*, 4040.

(6) Cotton, F. A.; Daniels, L. M.; Powell, G. L.; Kahaian, A. J.; Smith, T. J.; Vogel, E. F. *Inorg. Chim. Acta* **1988**, *144*, 109.

(7) Harwood: W. S.; Qi, J.-S.; Walton, R. A. *Polyhedron* **1986**, *5*, 15.

(8) Crystal data for $Mo_2Cl_4(\mu\text{-dppm})_2{\cdot}2CH_2Cl_2$ ($\mathbf{8}{\cdot}2CH_2Cl_2$): monoclinic, $P2_1/n$ (No. 14), a = 18.030(1) Å, b = 14.5108(7) Å, c = 23.221(1) Å, β = 112.778(4)°, V = 5601.5(5) $Å^3$, Z = 4, ρ_{calcd} = 1.509 g/cm^3, T = 213 K, full-matrix refinement on F^2 (Nonius FAST area detector, SHELXL-93), R1 (on F_o) = 0.058, wR2 (on F_o^2) = 0.159, GOF = 1.102 for 593 parameters, 7270 unique data (6690 with $I > 2\sigma(I)$). See Supporting Information for other structure details.

(9) Arnold, D. I.; Cotton, F. A.; Kühn, F. E. *Inorg. Chem.* **1996**, *35*, 5764.

(10) Cotton, F. A.; Falvello, L. R.; Harwood: W. S., Powell, G. L.; Walton, R. A. *Inorg. Chem.* **1986**, *25*, 3949.

(11) Crystal data for $Mo_2Cl_4(\mu\text{-dmpm})_2{\cdot}0.5C_6H_{14}$ ($\mathbf{7}{\cdot}0.5C_6H_{14}$): tetragonal, $I\bar{4}$ (No. 82), a = 12.699(2) Å, c = 16.015(4) Å, V = 2582.7(9) $Å^3$, Z = 4, ρ_{calcd} = 1.669 g/cm^3, T = 173 K, full-matrix refinement on F^2 (Enraf-Nonius CAD4 diffractometer, SHELXL-93), R1 (on F_o) = 0.031, wR2 (on F_o^2) = 0.079, GOF = 1.053 for 112 parameters, 2278 unique data (1732 with $I > 2\sigma(I)$). See Supporting Information for other structure details.

measurements. $E_{1/2}$ values, determined as $(E_{p,a} + E_{p,c})/2$, were referenced to the Ag/AgCl electrode at room temperature. Under our experimental conditions, $E_{1/2} = +0.47$ V vs Ag/AgCl for the ferrocenium/ferrocene couple. Voltammetric experiments were done with the use of a Bioanalytical Systems Inc. electrochemical analyzer model 100. The scan rate was 100 mV/s at a Pt disk electrode. Infrared spectra were recorded on a Perkin-Elmer 16PC FTIR spectrometer using KBr pellets. ^{1}H NMR spectra were obtained on a UNITY-plus 300 multinuclear spectrometer. Resonances were referenced internally to the residual proton impurity in the deuterated solvent. ^{31}P{^{1}H} NMR data were recorder at 22° C on a UNITY-plus 300 multinuclear spectrometer at 121.4 MHz. Resonances in ^{31}P{^{1}H} NMR data were referenced to an external standard 85% H_3PO_4 (0.00 ppm). Electronic spectral data were obtained in $CHCl_3$ using a Cary-17D UV−vis spectrophotometer. Elemental analyses were done by Canadian Microanalytical Services, Ltd.

X-ray Crystallographic Procedures. Single crystals of compounds **4** and **5** were obtained as described above. The X-ray diffraction study of **4** was carried out on a Nonius FAST diffractometer with an area detector using Mo Kα radiation. Details for data collection have been fully described elsewhere.[12] The crystal was mounted on the tip of a quartz fiber with silicone grease, and the setup was quickly placed in the cold nitrogen stream (−60° C) of the model FR 558-S low-temperature controller. Fifty reflections were used in cell indexing and 250 reflections in cell refinement ($18° < 2\theta < 42°$). Axial images were used to confirm the Laue group and all dimensions. Data were corrected for Lorentz and polarization effects by the MADNES program.[13] Reflection profiles were fitted and values of F^2 and $\sigma(F^2)$ for each reflection were obtained by the program PROCOR.[14] Systematic absences in the data uniquely determined the space group to be *Pbcn*. After the heavy atoms had been refined anisotropically, it became apparent that three of the four methyl groups of the diethylphosphine ligands were disordered. Also, a second pair of Mo atoms, i.e., the second orientation of the Mo−Mo unit, was located. It was included in the refinement, and its site occupancy factor (sof) converged to a final value of 0.039. Hydrogen atoms were placed in idealized positions and were not refined except for those bonded to P atoms.

The X-ray diffraction study of **5** was performed at 20° C with a Rigaku AFC5R diffractometer using Cu Kα radiation. The crystal was glued onto the tip of a glass fiber with epoxy cement. A least-squares analysis of the setting angles of 25 reflections with $58° < 2\theta < 78°$ provided accurate unit cell parameters. Three standard reflections were measured during data collection and displayed no decay in intensity. A total of 3354 reflections in the range $8° < 2\theta < 120°$ were collected using the $\omega-2\theta$ scan technique. Empirical absorptions based on ψ scans of 6 reflections were applied to the data using the TEXAN software package.[15] Examination of the axial photographs and the systematic absences narrowed the choice of space groups to $P6_222$ and $P6_422$. The refinement was successful in the space group $P6_422$. All non-hydrogen atoms were included in the structure factor calculations at idealized positions and were allowed to ride on the neighboring carbon atoms.

All calculations were done on a DEC Alpha running VMS using programs SHELXTL[16] (structure solution) and SHELXL-93[17] (least-squares refinement). Relevant crystallographic data for complexes **4** and **5** are summarized in Table 1.

Table 1. Crystallographic Data for $Mo_2Cl_4(PHEt_2)_4$ (**4**) and $Mo_2Cl_4(\eta^1\text{-dmpm})_4$ (**5**)

	4	**5**
formula	$Mo_2Cl_4P_4C_{16}H_{44}$	$Mo_2Cl_4P_8C_{20}H_{56}$
fw	694.07	878.09
space group	*Pbcn* (No. 60)	$P6_422$ (No. 181)
a, Å	7.6015(8)	12.396(1)
b, Å	20.120(8)	
c, Å	19.070(6)	21.960(2)
γ, deg.		120
V, Å^3	2917(2)	2922.3(4)
Z	4	3
ρ_{calcd}, g cm^{-3}	1.581	1.497
μ, mm^{-1}	1.449	10.988
radiation (λ, Å)	Mo Kα (0.710 73)	Cu Kα (1.541 84)
temp, °C	−60	20
R1,[a] wR2[b] [$I > 2\sigma(I)$]	0.035, 0.078	0.034, 0.089
R1,[a] wR2[b] (all data)	0.041, 0.083	0.037, 0.092

[a] $R1 = \Sigma ||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$.

Results and Discussion

Synthetic Aspects. As stated[1] in part I, the diethylamine groups in the complex $Mo_2Cl_4(NHEt_2)_4$ (**1**) are very labile and undergo easy substitution by other ligands. We have started to study reactions of **1** where the amine ligands are replaced by phosphines. The replacement of secondary amines by monodentate and bidentate phosphines was previously shown[2e,f,i] to start at low temperatures and to proceed smoothly for the ditungsten(III) complexes of the type $W_2Cl_4(NR_2)_2(NHR_2)_2$ (R = Et, Bu^n, Hex^n). Some molybdenum halide/amine compounds were also used before for ligand exchange reactions with phosphines. Thus, $Mo_2Br_4(py)_4$ was known[18] to produce the $Mo_2Br_4(PBu^n_3)_4$ species when treated with tri-*n*-butylphosphine. The complex $Mo_2Cl_4(py)_4$ was employed[19] in the formation of α- and β-isomers of Mo_2Cl_4(P-P)$_2$ when reacted with dppe or dppp. All these reactions were done in refluxing alcohols. In the present work the replacement of $NHEt_2$ ligands in **1** by monodentate (PMe_3, PMe_2Ph, $PHEt_2$) or bidentate (dmpm, dmpe) phosphines was shown to be instantaneous at room temperature as indicated by the immediate change in color from purple to blue. All isolated compounds had the stoichiometry of Mo_2Cl_4(phosphine)$_4$, although this was just an intermediate product in the case of diphosphines.

Generally speaking, the above-described processes are examples of one of the common methods for the synthesis of dimolybdenum(II) species,[20a] namely, ligand exchange in the preformed $Mo_2X_4L_4$ (L = neutral donor). For monodentate phosphines the present technique gives a good alternative to known methods. The successful isolation of $Mo_2Cl_4(PHEt_2)_4$ was of particular interest since we have recently faced the problem of the deprotonation of the $PHEt_2$ ligand and formation of phosphido bridges[21] when the substituted group is not a labile neutral donor but rather an anionic ligand such as Cl^-.

The most remarkable result is the synthesis of $Mo_2Cl_4(\eta^1\text{-dmpm})_4$ (**5**), which is one of a new class of compounds. Compound **5** is stable in hexanes, benzene, or toluene, but a turquoise blue precipitate appeared in a short period of time

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(12) Cotton, F. A.; Dikarev, E. V.; Feng, X. *Inorg. Chim. Acta* **1995**, *237*, 19.

(13) Pflugrath, J.; Messerschmitt, A. MADNES, Munich Area Detector (New EEC) System, version EEC 11/9/89, with enhancements by Enraf-Nonius Corp., Delft, The Netherlands. A description of MADNES appears in the following: Messerschmitt, A.; Pflugrath, J. *J. Appl. Crystallogr.* **1987**, *20*, 306.

(14) (a) Kabsch, W. *J. Appl. Crystallogr.* **1988**, *21*, 67; (b) **1988**, *21*, 916.

(15) TEXSAN-TEXRAY, Crystal Structure Analysis Package; Molecular Structure Corp.: Houston, TX, 1985.

(16) *SHELXTL V.5*; Siemens Industrial Automation Inc.: Madison, WI, 1994.

(17) Sheldrick, G. M. In *Crystallographic Computing 6*; Flack, H. D., Parkanyi, L., Simon, K., Eds.; Oxford University Press: Oxford, U.K., 1993; p 111.

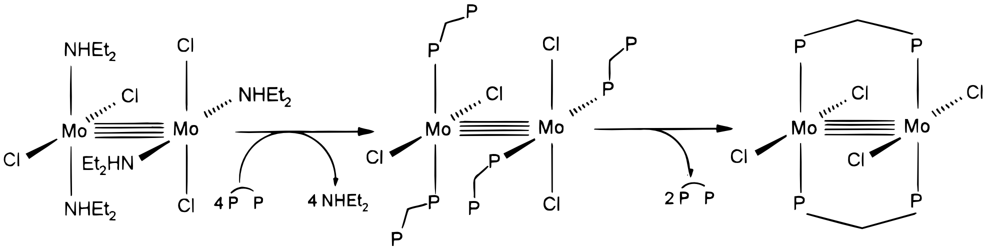
(18) San Filippo, J., Jr.; Sniadoch, H. J.; Grayson, R. L. *Inorg. Chem.* **1974**, *13*, 2121.

(19) Cole, N. F.; Derringer, D. R.; Fiore, E. A.; Knoechel, D. J.; Schmitt, R. K.; Smith, T. J. *Inorg. Chem.* **1985**, *24*, 1978.

(20) (a) Cotton, F. A.; Walton, R. A. *Multiple Bonds Between Metal Atoms*, 2nd ed.; Oxford University Press: New York, 1993; Table 3.1.2, p 181; (b) Table 3.1.3, p 196.

(21) Cotton, F. A.; Dikarev, E. V.; Petrukina, M. A. *Inorg. Chem.* **1998**, *37*, 6035.

Scheme 2



when it was dissolved in THF or immediately if the solution was heated. In dichloromethane the color of the solution changes from royal blue to turquoise blue. The product of transformation was identified as $Mo_2Cl_4(\mu\text{-dmpm})_2$[10,11] (**7**). The interaction between $Mo_2Cl_4(NHEt_2)_4$ (**1**) and dmpm is thus a two-step process (Scheme 2). Complex **5** with four dmpm dangling ligands is the kinetic product on the way to the more thermodynamically stable compound **7** having two bridging diphosphines.

The same sequence also takes place in the case of dmpe, with the major difference that $Mo_2Cl_4(\eta^1\text{-dmpe})_4$ (**6**) is not stable in solution for very long and converts to some insoluble polymeric product when one is trying to grow crystals at low or room temperatures. Complex **6** was first mentioned by Chisholm and McInnes[3] based on ^{31}P NMR studies of the substitution of the monodentate phosphines in $Mo_2Cl_4(PR_3)_4$ ($PR_3 = PEt_3$, PMe_2Ph) with dmpe. In that work, too, the transformation of **6** to an unidentified material prevented its isolation and complete characterization.

With other bidentate phosphines (dppm, dppa) we have readily obtained the bridged complexes of the type $Mo_2Cl_4(\mu\text{-diphosphine})_2$ at room temperature. Nevertheless, the initial change of colors for the reaction mixtures indicates that the dangling compounds are formed as the kinetic products and the reaction sequence is as described by Scheme 2. This assumption needs additional investigation by the NMR monitoring of corresponding processes at low temperature. The stability of the dangling complexes may depend on several factors, including the bulkiness of P-bonded groups and the number of bridgehead atoms in the diphosphine.

We have previously suggested monodentate coordination of bidentate phosphines as an initial step when the amine ligands are replaced in ditungsten(III) compounds. It has been shown that the reactions of $W_2Cl_4(NR_2)_2(NHR_2)_2$ (R = Et, Bu^n, Hex^n) having cis,cis geometry[2d] with diphosphines (dmpm, dmpe, dppm, dppe, dppa, dppp) give the *trans*,*trans*-$W_2Cl_4(NR_2)_2$(P-P) species[2e,f,i] (Scheme 1). Also, from the trans,trans starting material[22] with primary amine and amido ligands $W_2Cl_4(NHBu^t)_2(NH_2Bu^t)_2$, the cis,cis isomers of $W_2Cl_4(NHBu^t)_2$(P-P)[2c] (P-P = dmpm, dmpe, dppm, dppe) are obtained. Both those processes require ligand rearrangements that can presumably be achieved through initial unidentate coordination of phosphine. However, we have failed to obtain unambiguous NMR evidence for the proposed intermediate complexes.

We have recognized that the newly synthesized complex **5** might be a good starting material containing four phosphorus atoms capable of being coordinated to other metal centers, thereby building up oligomers or polymers. Our first attempt to react **5** with the parent amine compound **1** gave only the dinuclear complex $Mo_2Cl_4(\mu\text{-dmpm})_2$ (**7**) as the only isolated product (eq 1), but we still think more interesting results may be obtained under suitable conditions.

$$Mo_2Cl_4(NHEt_2)_4 + Mo_2Cl_4(\eta^1\text{-dmpm})_4 \rightarrow 2Mo_2Cl_4(\mu\text{-dmpm})_2 + 4NHEt_2 \quad (1)$$

NMR Data. In the ^1H NMR spectrum of **4** there are three groups of signals centered at 1.09, 2.06, and 4.78 ppm, which integrate as 6:4:1 as expected for CH_3 and CH_2 groups, and the hydrogen atom bonded directly to the phosphorus atom. The $^{31}P\{^1H\}$ NMR spectrum of **4** shows a singlet at 2.45 ppm, very close to the shift found for the signal of the phosphorus nuclei in the complex $Re_2Cl_4(PHEt_2)_4$.[21] In the ^1H NMR spectrum of **5** the signals of the methyl groups appear at 0.89 and 1.76 ppm, which we tentatively assign to those on the free and coordinated phosphorus atoms, respectively. The methylene group signal appears at 2.14 ppm, very close to those observed for the dangling dmpm groups in the spectra of *trans*-$[RuH(dmpm)_2(\eta^1\text{-dmpm})]PF_6$ (2.01 ppm) and $[FeH(dmpm)_2(\eta^1\text{-dmpm})]BF_4$ (2.13 ppm).[23] The resonances of the methylene group of the chelate dmpm ligands in those complexes appear at 3.42 and 3.28 ppm. For the bridging dmpm in **7** the corresponding multiplet is observed at 3.09 ppm.

Compound **5** displays a $^{31}P\{^1H\}$ NMR spectrum with two multiplets at 1.15 and −60.05 ppm. The first one is very close to the singlet that appears in the spectrum of **7** (−0.13 ppm) while the other resembles the signal of free dmpm (−54.9 ppm). Therefore, the former is assigned to the phosphorus atom coordinated to molybdenum and the latter to the dangling phosphorus atom. In the spectrum of the above-mentioned *trans*-$[RuH(dmpm)_2(\eta^1\text{-dmpm})]PF_6$, the signal at 2.12 ppm was assigned to the coordinated phosphorus of the η^1-dmpm group and the signal at −54.6 ppm to the noncoordinated one. A similar pattern for the dangling dmpe ligands was observed in the $^{31}P\{^1H\}$ NMR spectrum of **6** (−0.39 and −48.07 ppm). This result is in accord with the data reported before,[3] although the signals do not have exactly the same chemical shifts because the spectra were recorded at different temperatures.

Electrochemistry. Complex **4** exhibits electrochemical behavior typical of the dimolybdenum(II) compounds of the type $Mo_2X_4(PR_3)_4$ (X = halide).[20b] In dichloromethane solution it undergoes a reversible one-electron oxidation at +0.64 V corresponding to the $Mo_2Cl_4(PHEt_2)_4^{0/+1}$ couple. The second oxidation takes place at a quite positive potential with $E_{p,a}$ = +1.60 V and is irreversible. The one-electron reduction of **4** occurs at a potential value lower than −1.50 V and has not been registered in dichloromethane. No redox activity other than irreversible oxidation at $E_{p,a}$ = +0.60 V has been observed for solutions of **5**, probably due to decomposition processes.

Structural Details. $Mo_2Cl_4(PHEt_2)_4$ (4). The compound adopts the orthorhombic space group *Pbcn* with four molecules

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(22) Bradley, D. C.; Errington, R. J.; Hursthose, M. B.; Short, R. L. *J. Chem. Soc., Dalton Trans.* **1986**, 1305.

(23) Wong, W. K.; Chiu, K. W.; Wilkinson, G.; Howes, A. J.; Motevalli, M.; Hursthouse, M.B. *Polyhedron* **1985**, *4*, 603.

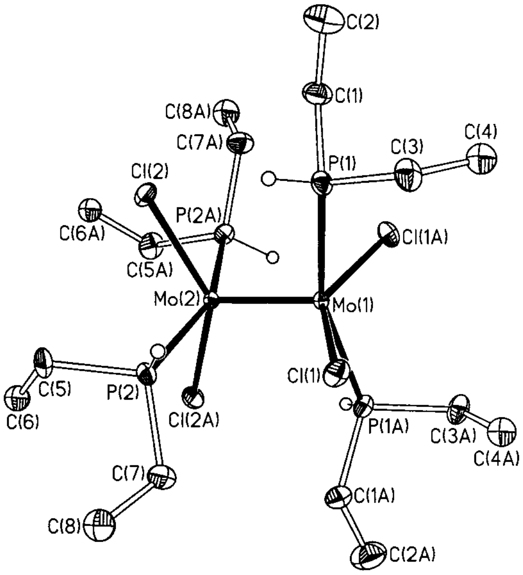

Figure 1. Perspective drawing of $Mo_2Cl_4(PHEt_2)_4$ (**4**). Atoms are represented by thermal ellipsoids at the 40% probability level. Hydrogen atoms of ethyl groups are omitted for clarity.

Table 2. Selected Bond Distances (Å) and Angles (deg) for $Mo_2Cl_4(PHEt_2)_4$ (**4**)

Mo(1)−Mo(2)	2.1368(9)		
Mo(1)−P(1)	2.534(1)	Mo(2)−P(2)	2.534(1)
Mo(1)−Cl(1)	2.415(1)	Mo(2)−Cl(2)	2.425(1)
P(1)−Mo(1)−P(1A)	160.79(6)	P(2)−Mo(2)−P(2A)	158.60(6)
P(1)−Mo(1)−Cl(1)	84.40(5)	P(2)−Mo(2)−Cl(2)	84.32(4)
P(1)−Mo(1)−Cl(1A)	89.19(4)	P(2)−Mo(2)−Cl(2A)	88.45(4)
Cl(1)−Mo(1)−Cl(1A)	140.89(6)	Cl(2)−Mo(2)−Cl(2A)	140.38(6)
Mo(2)−Mo(1)−P(1)	99.61(3)	Mo(1)−Mo(2)−P(2)	100.70(3)
Mo(2)−Mo(1)−Cl(1)	109.56(3)	Mo(1)−Mo(2)−Cl(2)	109.81(3)

per unit cell. The geometry of the molecule of **4** resembles that of the parent complex $Mo_2Cl_4(NHEt_2)_4$ (**1**)[1] with two *trans*-$MoCl_2(PHEt_2)_2$ units joined by a quadruple Mo−Mo bond with a length of 2.1368(9) Å (Figure 1). The average P−Mo−P angle for diethylphosphine groups on each metal center is 159.70(6)° (Table 2). $Mo_2Cl_4(PHEt_2)_4$ belongs to the well-known type of 1,3,6,8-isomers for the molybdenum halide/phosphine complexes of the $Mo_2X_4(PR_3)_4$ stoichiometry (X = F,[24a] Cl,[5] Br,[24b,c] I,[24c,d] $PR_3 = PMe_3$; X = Cl, $PR_3 = PEt_3$,[24e] PMe_2Ph,[6] $PHPh_2$,[6] $PMePh_2$[24f]), all of which are characterized by an $Mo_2X_4P_4$ core with virtual symmetry D_{2d}. It should be noted that we have recently reported[21] the analogous triply-bonded rhenium complex, $Re_2Cl_4(PHEt_2)_4$, but this was found to be the 1,2,7,8-isomer with diethylphosphine ligands cis on each metal atom.

The key dimensions of complex **4** (Table 2) are about as anticipated. There is even less influence of P−H···Cl hydrogen bonding on the structural parameters than we observed[1] in the crystal structure of **1**, and the molecule of **4** has an eclipsed geometry with P−Mo−Mo−Cl torsion angles of 1.9° and 2.2°. The rotational orientations of the $PHEt_2$ ligands are all similar to those observed[6] for $PHPh_2$ analogue; they direct the alkyl groups outward and place the H atoms more or less above the metal−metal bond (Mo−Mo−P−H torsion angle is 50.3°). A two-way disorder was detected for the Mo_2 unit with the second orientation having a very low occupancy, namely, 3.9%.

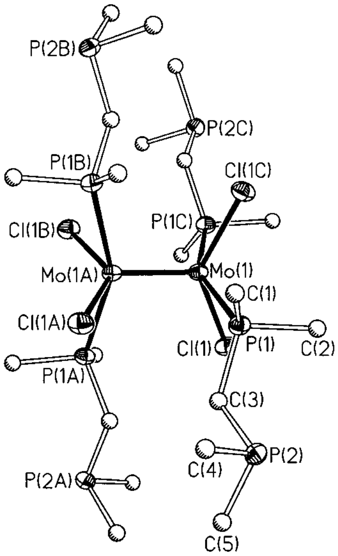

Figure 2. Perspective drawing of $Mo_2Cl_4(\eta^1\text{-dmpm})_4$ (**5**). Atoms are represented by thermal ellipsoids at the 40% probability level. Carbon atoms are shown as spheres of an arbitrary radius. Hydrogen atoms are omitted for clarity.

Table 3. Selected Bond Distances (Å) and Angles (deg) for $Mo_2Cl_4(\eta^1\text{-dmpm})_4$ (**5**)

Mo(1)−Mo(1A)	2.137(1)
Mo(1)−P(1)	2.551(1)
Mo(1)−Cl(1)	2.413(1)
P(1)−Mo(1)-P(1C)	153.63(7)
P(1)−Mo(1)-Cl(1)	84.98(4)
P(1)−Mo(1)-Cl(1C)	85.15(4)
Cl(1)−Mo(1)-Cl(1C)	135.65(8)
Mo(1A)-Mo(1)−P(1)	103.18(3)
Mo(1A)-Mo(1)−Cl(1)	112.17(4)

$Mo_2Cl_4(\eta^1\text{-dmpm})_4$ (5). Compound **5** crystallizes in the hexagonal space group $P6_422$ with three molecules per unit cell. Each molecule is built around a Mo−Mo quadruple bond (2.137(1) Å) with four chlorides and four bis(dimethylphosphino)methane groups, each acting as a monodentate ligand through one of its phosphorus atoms (Figure 2). The eclipsed $Mo_2Cl_4P_4$ core structure has D_{2d} symmetry as for above-mentioned complexes of $Mo_2Cl_4(PR_3)_4$ stoichiometry. In fact, all principal bond lengths, angles, and torsion angles for **5** (Table 3) are very close to those in the corresponding structures of monodentate phosphine compounds.

The crystal symmetry and rather rare space group for **5** are related to the packing of the molecules in the unit cell (Figure 3), which must create room for the long $PCH_2P(CH_3)_2$ chains. The separation between dangling phosphorus atoms and metal atoms is very large: the closest molybdenum center is located 5.50 Å from P(2). It is interesting to speculate on whether the same packing would occur for an analogous complex with the monodentate dimethyl-*sec*-butylphosphine ligand, which, unfortunately, is not commercially available.

Complex **5** represents the first structurally characterized dimetal compound of the type $M_2X_4(P\text{-}P)_4$ (X = halide, P-P = bidentate phosphine). In fact, it is the first example of a complex with more than two dangling diphosphines. Actually, monodentate coordination of the bidentate ligands is not especially rare. For bidentate phosphines such species mostly occur for dppm, but they are also known for dmpm, dmpa, dppe, dppee,

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[24] (a) Cotton, F. A.; Wiesinger, K. J. *Inorg. Chem.* **1992**, *31*, 920.(b) Ahmed, K. J.; Chisholm, M. H.; Huffman, J. C. *Organometallics* **1985**, *4*, 1168. (c) Hopkins, M. D.; Schaefer, W. P.; Bronikowski, M. J.; Woodruff, W. H.; Miskowski, V. M.; Dallinger, R. F.; Gray, H. B. *J. Am. Chem. Soc.* **1987**, *109*, 408. (d) Cotton, F. A.; Poli, R. *J. Am. Chem. Soc.* **1986**, *108*, 5628. (e) Cotton, F. A.; Daniels, L. M.; Shang, M.; Yao, Z. *Inorg. Chim. Acta* **1994**, *215*, 103. (f) Cotton, F. A.; Czuchajowska, J.; Luck, L. R. *J. Chem. Soc., Dalton Trans.* **1991**, 579.

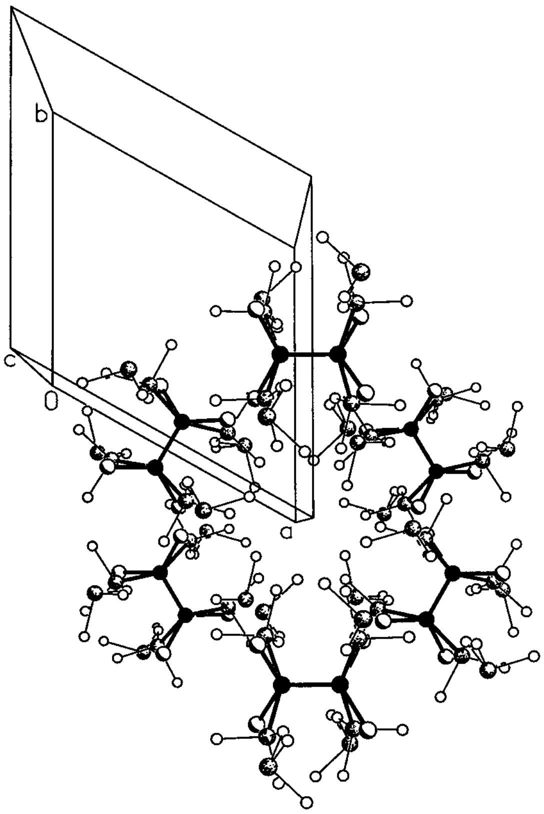
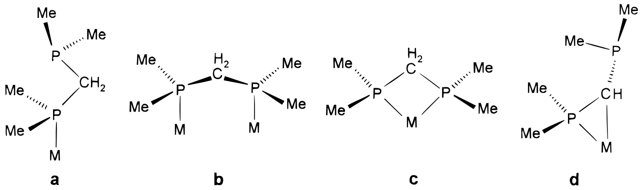


Figure 3. Fragment of the packing diagram of $Mo_2Cl_4(\eta^1\text{-dmpm})_4$ (**5**). The view is almost down the *c*-axis of the unit cell. All atoms are shown as spheres of arbitrary radii. Hydrogen atoms are omitted for clarity.

bis(di-*tert*-butylphosphino)methane, bis(diphenylphosphino)selenide, bis(diphenylphosphino)methylene-triphenyl-phosphorane, and 1,2-bis(diphenylphosphino)hexafluorocyclopentene. For molybdenum a total of six crystal structures of complexes with unidentate diphosphine coordination (all with the dppm ligand) have been reported: five of them are mononuclear, $MoX_2(CO)_2(\eta^2\text{-dppm})(\eta^1\text{-dppm})$[25] (X = Cl, Br, I, NCS) and $Mo(CO)_3(\eta^2\text{-phen})(\eta^1\text{-dppm})$;[26] the other is the single metal−metal bonded molecule $Mo_2(Cp)_2(CO)_3(\mu\text{-}\sigma,\pi\text{-CNBu}^t)(\eta^1\text{-dppm})$.[27]

As for the dmpm ligand, monodentate coordination was found prior to this work in three mononuclear complexes: $Fe(dmpm)_2(\eta^1\text{-dmpm})$, $RuH(dmpm)_2(\eta^1\text{-dmpm})$,[23] and $Cr(Cp)Cl_2(\eta^1\text{-dmpm})$.[28] The unidentate bonding mode (Chart 1a) is one of several known for bis(diphenylphosphino)methane. The most common coordination for this ligand is apparently the bridging bidentate coordination (Chart 1b) which was, in particular, reported for numerous dimolybdenum species[29] that are related to the complex **7**, $Mo_2Cl_4(\mu\text{-dmpm})_2$.[10] Despite the steric constraints on four-membered rings, dmpm is also well-known for its ability to act as a bidentate chelating ligand (Chart 1c). A number of such structures have been previously described; among them there are three mononuclear molybdenum complexes.[30] The P−Mo−P angle in this type of molecule is typically about 66°, while the P−C−P angle is around 95°. Finally, it is worth mentioning that there is a bidentate *C,P* bonding mode (Chart 1d) of the deprotonated form of dmpm which occurs[31] in a mononuclear Zr(IV) complex.

Chart 1



Concluding Remarks

This report describes our first effort to explore the chemistry of the newly-synthesized dimolybdenum complex $Mo_2Cl_4(NHEt_2)_4$ (**1**) in substitution reactions with monodentate and bidentate phosphines. Compound **1** has proved to be an interesting starting material offering further access to the chemistry of Mo_2^{4+}. The most important result of the present study is the first isolation of a member of a new class of quadruply-bonded dimolybdenum complexes, $Mo_2Cl_4(P\text{-}P)_4$, in which all four diphosphine groups act as unidentate ligands, namely, $Mo_2Cl_4(\eta^1\text{-dmpm})_4$ (**5**). Compounds of this type are shown to be kinetic products on the way to the well-known $Mo_2Cl_4(P\text{-}P)_2$ molecules. Preliminary data on the mechanism of the substitution reactions between **1** and other bidentate phosphines indicate that the successive stages are formation of the dangling complex, then chelate complex, and finally, bridged species. This appears not to depend strongly on the size and number of atoms connecting the two ends of the diphosphine. This investigation is continuing.

The lability of the $NHEt_2$ ligands in $Mo_2Cl_4(NHEt_2)_4$ (**1**) will be the subject of further study. Our success in synthesizing and characterizing the product **5** encourages us to believe that the use of **1** as a starting material will allow the preparation of still other compounds that have not been obtained by other methods.

Acknowledgment. We are grateful to the National Science Foundation for support of this work. S.H. thanks the Spanish Dirección General de Enseñanza Superior for financial support.

Supporting Information Available: Four X-ray crystallographic files, in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(25) (a) Drew, M. G. B.; Wolters, A. P.; Tomkins, I. B. *J. Chem. Soc., Dalton Trans.* **1977**, 974. (b) Shiu, K.-B.; Yih, K.-H.; Wang, S.-L.; Liao, F.-L. *J. Organomet. Chem.* **1991**, *414*, 165. (c) Cotton, F. A.; Matusz, M. *Polyhedron* **1987**, *6*, 261. (d) Blagg, A.; Hutton, A. T.; Shaw, B. L. *Polyhedron* **1987**, *6*, 95.

(26) Cano, M.; Campo, J. A.; Perez-Garcia, V.; Gutierrez-Puebla, E.; Alvarez-Ibarra, C. *J. Organomet. Chem.* **1990**, *382*, 397.

(27) Riera, V.; Ruiz, M. A.; Villafane, F.; Bois, C.; Jeannin, Y. *J. Organomet. Chem.* **1990**, *382*, 407.

(28) Fettinger, J. C.; Mattamana, S. P.; Poli, R.; Rogers, R. D. *Organometallics* **1996**, *15*, 4211.

(29) (a) Canich, J. A. M.; Cotton, F. A.; Daniels, L. M.; Lewis, D. B. *Inorg. Chem.* **1987**, *26*, 4046. (b) Chisholm, M. H.; Folting, K.; Huffman, J. C.; Kramer, K. S.; Tatz, R. J. *Organometallics* **1992**, *11*, 4029. (c) John, K. D.; Geib, S. J.; Hopkins, M. D. *Organometallics* **1996**, *15*, 4357. (d) Cotton, F. A.; Dunbar, K. R.; Hong, B.; James, C. A.; Matonic, J. H.; Thomas, J. L. C. *Inorg. Chem.* **1993**, *32*, 5183.

(30) (a) Cotton, F. A.; Poli, R. *Inorg. Chem.* **1986**, *25*, 3703. (b) George, T. A.; Ma, L.; Shailh, S. N.; Tisdale, R. C.; Zubieta, J. *Inorg. Chem.* **1990**, *29*, 4789. (c) Tilset, M.; Vollhardt, K. P. C.; Boese, R. *Organometallics* **1994**, *13*, 3146.

(31) Karsch, H. H.; Grauvogl, G.; Deubelly, B.; Muller, G. *Organometallics* **1992**, *11*, 4238.