Mixed Chloride/Amine Complexes of Dimolybdenum(II,II). 6. Stepwise Substitution of Amines by Tertiary Phosphines and Vice Versa: Stereochemical Hysteresis

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The substitution reactions of primary amines by tertiary phosphines in quadruply bonded dimolybdenum(II,II) complexes $Mo_2Cl_4(NH_2R)_4$ have been studied. The exchange reaction has been shown to result at room temperature in disubstituted species $Mo_2Cl_4(NH_2R)_2(PR_3)_2$ ($PR_3 = PMe_3$, $NH_2R = NH_2Pr^n$ (**1a**), NH_2Bu^t (**2a**), NH_2Cy (**3a**); $PR_3 = PMe_2Ph$, $NH_2R = NH_2Cy$ (**4a**)), while heating is needed to obtain fully substituted complexes $Mo_2Cl_4(PR_3)_4$. The crystal structure of disubstituted products has been investigated by X-ray crystallography and revealed that they all belong to the α-isomer, having both phosphine groups at the same Mo atom. Crystal data are as follows: for **1a**, tetragonal space group $I4_1/a$ with $a = 17.737(2)$ Å, $c = 15.6915(6)$ Å, and $Z = 8$; for **3a**, monoclinic space group $P2_1$ with $a = 10.963(3)$ Å, $b = 10.117(2)$ Å, $c = 13.323(4)$ Å, $\beta = 90.05(2)°$, and $Z = 2$; for **4a**, triclinic space group $P\bar{1}$ with $a = 9.329(3)$ Å, $b = 10.206(2)$ Å, $c = 18.975(3)$ Å, $\alpha = 85.45(2)°$, $\beta = 87.10(1)°$, $\gamma = 80.88(1)°$, and $Z = 2$. The substitution processes for the direct and reverse reactions have been monitored by ^{31}P NMR. They both proceed in a stepwise manner; however, a stereochemical hysteresis is taking place, i.e., the back reaction, the substitution of phosphines by amines, goes through another isomer of $Mo_2Cl_4(NH_2R)_2(PR_3)_2$, having phosphine ligands on different Mo atoms. This β-isomer is more thermodynamically stable and can be obtained by thermal conversion of the α-form. All chemical equilibria studied in the paper have been explained as governed by a higher trans effect of PR_3 groups compared to NH_2R groups.

Introduction

The ligand substitution reactions at the quadruply bonded Mo_2^{4+} core were the subject of several studies.[1−9] Among them there are two which examined the reaction of phosphine interchange in $Mo_2X_4(PR_3)_4$ (X = Me[5] or Cl[9]) species. In both cases it has been shown that substitution proceeds in stepwise manner (Scheme 1); however, different conclusions were drawn about the reaction mechanism. In the work published by Andersen et al.[5] the dissociative mechanism was proposed on a base of invariance of the reaction rates on the nature of the incoming group for phosphine interchange in $Mo_2Me_4(PEt_3)_4$. In a recently reported study by Chisholm and McInnes,[9] a rate dependence on the entering ligand in phosphine exchange at $Mo_2Cl_4(PR_3)_4$ was found and an interchange dissociative process was suggested.

The substitution reactions proceed without ligand rearrangement; therefore, the mixed-phosphine species **I** and **III** (Scheme 1) exist in one form, whereas the disubstituted product **II** can adopt two isomeric forms (Scheme 2), which differ by the location of substituent atoms on one (**IIa**) or both ends (**IIb**) of the molecule.

One detail in the above-mentioned studies[5,9] was of particular interest for us: in most of the cases the phosphine exchange led to the **IIb** structure, while in two reactions substitution by trimethylphosphine[9] resulted in the **IIa** isomer. The explanation given was based on the higher trans effect of the PMe_3 group compared to other phosphines used. Thus we decided to check how important this feature is by investigating the systems where the difference in trans effects between outgoing and incoming groups is pronounced.

We have recently reported a new class of quadruply bonded dimolybdenum complexes $Mo_2Cl_4N_4$ with secondary (N = $NHEt_2$)[10] and primary (N = NH_2Et, NH_2Pr^n, NH_2Bu^t, and NH_2Cy)[11] amines. The compound $Mo_2Cl_4(NHEt_2)_4$ has been shown[12] to undergo facile substitution reactions of the amine ligands by phosphines at room temperature to give species with the same core structure $Mo_2Cl_4(phosphine)_4$ (phosphine = PMe_3, PMe_2Ph, $PHEt_2$, dmpm, dmpe). However, similar substitution of primary amines does not occur in such an easy manner, terminating midway at room temperature, and heating is necessary to accomplish it. Moreover, back reaction (substitution of phosphines by amines) also takes place.

We report here the results of our study of stepwise substitution of amine ligands by tertiary phosphines, and vice versa, and the structure of intermediate products.

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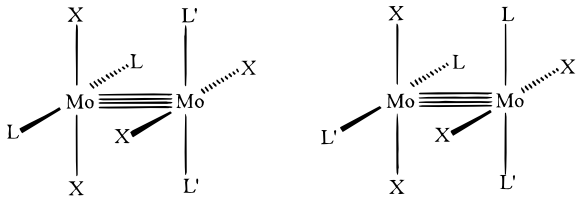
Scheme 1

$$Mo_2X_4(PR_3)_4 \xrightarrow{PR'_3} Mo_2X_4(PR_3)_3(PR'_3) \xrightarrow{PR'_3} Mo_2X_4(PR_3)_2(PR'_3)_2 \xrightarrow{PR'_3} Mo_2X_4(PR_3)(PR'_3)_3 \xrightarrow{PR'_3} Mo_2X_4(PR'_3)_4$$

I **II** **III**

Scheme 2



IIa or **IIc** **IIb** or **IId**

IIa, **IIb**: L = PR_3, L' = PR'_3 or **IIc**, **IId**: L = NH_2R, L' = PR_3

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. Amines were purchased from Aldrich, Inc., phosphines were provided by Strem Chemicals Inc., and benzene-d_6 was obtained from Cambridge Isotope Laboratories, Inc. Compounds $Mo_2Cl_4(NH_2R)_4$ (R = Pr^n, Bu^t, Cy),[11] $Mo_2Cl_4(NHEt_2)_4$,[10] and $Mo_2Cl_4(PHEt_2)_4$[12] were synthesized according to published procedures.

(1) Reactions of $Mo_2Cl_4(NH_2R)_4$ with PR_3 at Room Temperature. (i) Synthesis of $Mo_2Cl_4(NH_2Pr^n)_2(PMe_3)_2$ (1a). Trimethylphosphine (0.6 mL, 5.90 mmol) was added to a red solution of 0.08 g (0.14 mmol) of $Mo_2Cl_4(NH_2Pr^n)_4$ in 5 mL of toluene. After stirring overnight at room temperature, the color of the solution had changed to blue-violet. The solution was then filtered, and all volatile components were removed under vacuum. Yield: 0.08 g (94%).

Brown, plate-shaped crystals of $Mo_2Cl_4(NH_2Pr^n)_2(PMe_3)_2$ (**1a**) suitable for X-ray study were obtained by cooling a saturated solution of the compound in diethyl ether to −30 °C.

Anal. Calcd for $Mo_2Cl_4N_2P_2C_{12}H_{36}$: C, 23.87; H, 6.01; N, 4.64. Found: C, 24.57; H, 6.10; N, 4.16. ^{1}H NMR data (benzene-d_6, 22 °C) δ: 4.17 (br, t,4H, NH_2), 2.80 (m,4H, CH_2), 1.13 (m, 4H, CH'_2), 0.66 (t, 6H, CH_3) [$J(NH_2-CH_2) = J(CH_2-CH'_2) = J(CH'_2-CH_3) = 7$ Hz]; 1.39 (t, 18H, PCH_3) [$J(P-CH_3) = 4$ Hz]. ^{31}P NMR data (benzene-d_6, 22 °C) δ: −14.07 (s, PMe_3).

(ii) Synthesis of $Mo_2Cl_4(NH_2Bu^t)_2(PMe_3)_2$ (2a). Complex $Mo_2Cl_4(NH_2Bu^t)_4$ (0.08 g, 0.13 mmol) was dissolved in 50 mL of hexanes, and 0.6 mL of PMe_3 (5.90 mmol) was added to the purple solution. The color of the solution started to change immediately after the addition. After 30 min of stirring at room temperature the blue-violet solution was filtered and evaporated to dryness. Yield: 0.075 g (91%).

Violet block-shaped crystals of $Mo_2Cl_4(NH_2Bu^t)_2(PMe_3)_2$ (**2a**) were obtained in different ways: by slow evaporation of a concentrated benzene solution, or by cooling saturated solutions of the complex in hexanes or diethyl ether to −30 °C.

Anal. Calcd for $Mo_2Cl_4N_2P_2C_{14}H_{40}$: C, 26.60; H, 6.38; N, 4.43. Found: C, 26.94; H, 6.32; N, 4.20. ^{1}H NMR data (benzene-d_6, 22 °C) δ: 4.76 (s, br, 4H, NH_2), 1.33 (t, 18H, PMe_3) [$J(P-CH_3) = 4$ Hz], 1.19 (s, 18H, CH_3). ^{31}P NMR data (benzene-d_6, 22 °C) δ: −14.27 (s, PMe_3).

(iii) Synthesis of $Mo_2Cl_4(NH_2Cy)_2(PMe_3)_2$ (3a). A procedure similar to that described for the synthesis of $Mo_2Cl_4(NH_2Pr^n)_2(PMe_3)_2$ was followed to prepare $Mo_2Cl_4(NH_2Cy)_2(PMe_3)_2$ using $Mo_2Cl_4(NH_2Cy)_4$ as starting material. The blue-violet solid was isolated in a yield of 96%.

The violet plates of $Mo_2Cl_4(NH_2Cy)_2(PMe_3)_2$ (**3a**) used for the X-ray experiment were obtained by keeping a saturated solution of the compound in diethyl ether at −30 °C for a week.

Anal. Calcd for $Mo_2Cl_4N_2P_2C_{18}H_{44}$: C, 31.60; H, 6.48; N, 4.09. Found: C, 31.96; H, 6.54; N, 4.03. ^{1}H NMR data (benzene-d_6, 22 °C) δ: 4.56 (d, 4H, NH_2), 3.25 (m, 2H, CH), 1.8−0.7 (20H, CH_2) [$J(NH_2-CH)$ = 7 Hz]; 1.43 (t, 18H, PMe_3) [$J(P-CH_3) = 4$ Hz]. ^{31}P NMR data (benzene-d_6, 22 °C) δ: −13.70 (s, PMe_3).

(iv) Synthesis of $Mo_2Cl_4(NH_2Cy)_2(PMe_2Ph)_2$ (4a). The same procedure as described for $Mo_2Cl_4(NH_2Cy)_2(PMe_3)_2$ was used for the preparation of $Mo_2Cl_4(NH_2Cy)_2(PMe_2Ph)_2$, although 1 day was needed to complete the reaction with a quantitative (about 95%) yield.

Red-violet blocks of $Mo_2Cl_4(NH_2Cy)_2(PMe_2Ph)_2$ (**4a**) were formed by cooling a saturated solution of the complex in hexanes to −30 °C.

Anal. Calcd for $Mo_2Cl_4N_2P_2C_{28}H_{48}$: C, 41.61; H, 5.99; N, 3.47. Found: C, 41.56; H, 6.08; N, 3.16. ^{31}P NMR data (benzene-d_6, 22 °C) δ: −3.24 (s, PMe_2Ph).

(2) Reactions of $Mo_2Cl_4(NH_2R)_4$ with PR_3 under Reflux Conditions. (i) Synthesis of $Mo_2Cl_4(PMe_3)_4$. A toluene solution which contained 0.3 g (0.41 mmol) of $Mo_2Cl_4(NH_2Cy)_4$ and 10 mmol of PMe_3 was heated to its boiling point and kept under reflux for 1 h. The color of the solution changed from pink-purple to royal blue. The solution was cooled to room temperature, filtered, and evaporated under vacuum to dryness. Yield: 0.24 g (92%). The purity of the compound was checked by ^{1}H and ^{31}P NMR.[12]

(ii) Synthesis of $Mo_2Cl_4(PMe_2Ph)_4$. This compound was prepared similarly to $Mo_2Cl_4(PMe_3)_4$ and isolated as a royal blue powder in 90% yield. The purity of the compound was checked by ^{31}P NMR.[9]

(3) Solution ^{31}P NMR Study of the Reaction between $Mo_2Cl_4(NH_2R)_4$ and PR_3. (i) Reaction of $Mo_2Cl_4(NH_2Cy)_4$ with PMe_3. An excess of PMe_3 (7.0 mL of 1 M solution in toluene) was added to a solution of 0.20 g (0.27 mmol) of $Mo_2Cl_4(NH_2Cy)_4$ in 6 mL of deuterated benzene. The mixture was stirred at room temperature for 12 h and then was heated at 75 °C for 6 h. The course of the reaction was monitored by ^{31}P{^{1}H} NMR at 3 h intervals.

(ii) Reaction of $Mo_2Cl_4(NH_2Cy)_4$ with PMe_2Ph. A similar procedure was performed using 40 equiv of PMe_2Ph per 1 equiv of $Mo_2Cl_4(NH_2Cy)_4$.

(4) Solution ^{31}P NMR Study of the Reaction between $Mo_2Cl_4(PR_3)_4$ and NH_2R. (i) Reaction of $Mo_2Cl_4(PMe_3)_4$ with NH_2Cy. A solution of 0.10 g (0.16 mmol) of $Mo_2Cl_4(PMe_3)_4$ and 0.72 mL (6.29 mmol) of NH_2Cy in 5 mL of toluene was refluxed for 15 h. A combination of ^{1}H and ^{31}P{^{1}H} NMR spectra was used to estimate the ratio of the species in solution. In addition, the reaction mixture immediately after mixing of the reactants was monitored in situ by ^{31}P{^{1}H} NMR spectroscopy at 75 °C and 3 h intervals.

(ii) Reaction of $Mo_2Cl_4(PMe_2Ph)_4$ and $Mo_2Cl_4(PEt_2H)_4$ with NH_2Cy. Similar monitoring procedures were used to follow the reactions of $Mo_2Cl_4(PR_3)_4$ (PR_3 = PMe_2Ph and PEt_2H) with ca. 40 equiv of NH_2Cy.

(5) Solution ^{31}P NMR Study of the Isomerization of $Mo_2Cl_4(NH_2R)_2(PR_3)_2$. (i) Transformation of $Mo_2Cl_4(NH_2Cy)_2(PMe_3)_2$ (3a). A solution of 0.20 g of $Mo_2Cl_4(NH_2Cy)_2(PMe_3)_2$ (**3a**) (prepared as described in (1)) in 5 mL of toluene was refluxed for 3 days. The course of the transformation was monitored by ^{31}P{^{1}H} NMR at 6 h intervals.

(ii) Transformation of $Mo_2Cl_4(NH_2Bu^t)_2(PMe_3)_2$ (2a). A similar procedure was employed for a toluene solution of $Mo_2Cl_4(NH_2Bu^t)_2(PMe_3)_2$ (**2a**).

(6) Solution ^{31}P NMR Study of the Reaction between $Mo_2Cl_4(NH_2R)_2(PR_3)_2$ and PR_3'. (i) Reaction of $Mo_2Cl_4(NH_2Cy)_2(PMe_3)_2$ (3a) with PMe_2Ph. A solution which contained 0.20 g (0.29 mmol) of $Mo_2Cl_4(NH_2Cy)_2(PMe_3)_2$ (**3a**) (prepared as described in (1)) and 1.60 mL (11.20 mmol) of PMe_2Ph in 10 mL of toluene was stirred at room temperature for 2 days. The equilibrium was monitored by ^{31}P{^{1}H} NMR spectroscopy at 6 h intervals.

Table 1. Crystallographic Data for α-$Mo_2Cl_4(NH_2Pr^n)_2(PMe_3)_2$ (**1a**), α-$Mo_2Cl_4(NH_2Cy)_2(PMe_3)_2$ (**3a**), and α-$Mo_2Cl_4(NH_2Cy)_2(PMe_2Ph)_2$ (**4a**)

	1a	**3a**	**4a**
formula	$Mo_2Cl_4P_2N_2C_{12}H_{36}$	$Mo_2Cl_4P_2N_2C_{18}H_{44}$	$Mo_2Cl_4P_2N_2C_{28}H_{48}$
fw	604.05	684.17	808.30
space group	$I4_1/a$ (No. 88)	$P2_1$ (No. 4)	$P\bar{1}$ (No. 2)
a, Å	17.737(2)	10.963(3)	9.329(3)
b, Å		10.117(2)	10.206(2)
c, Å	15.6915(6)	13.323(4)	18.975(3)
α, deg			85.45(2)
β, deg		90.05(2)	87.10(1)
γ, deg			80.88(1)
V, Å^3	4936.6(8)	1477.7(7)	1776.9(7)
Z	8	2	2
$\rho_{calc.}$, g cm^{-3}	1.625	1.538	1.511
μ, mm^{-1}	1.577	1.327	1.117
radiation (λ, Å)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
temp, °C	−60	−60	−60
R1,[a] wR2[b] [$I > 2\sigma(I)$]	0.0276, 0.0625	0.0358, 0.0909	0.0547, 0.1222
R1,[a] wR2[b] (all data)	0.0326, 0.0670	0.0381, 0.0940	0.0739, 0.1391

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

Table 2. Selected Bond Distances (Å) and Angles (deg) for α-$Mo_2Cl_4(NH_2Pr^n)_2(PMe_3)_2$ (**1a**), α-$Mo_2Cl_4(NH_2Cy)_2(PMe_3)_2$ (**3a**), and α-$Mo_2Cl_4(NH_2Cy)_2(PMe_2Ph)_2$ (**4a**)

	1a	**3a**	**4a**
Mo(1)−Mo(2)	2.1250(6)	2.1289(9)	2.128(1)
Mo(1)−N(1)	2.240(3)	2.240(7)	2.229(6)
Mo(1)−N(2)		2.239(6)	2.250(7)
Mo(1)−Cl(1)	2.4292(9)	2.413(2)	2.415(2)
Mo(1)−Cl(2)		2.414(2)	2.417(2)
Mo(2)−P(1)	2.539(1)	2.529(2)	2.527(2)
Mo(2)−P(2)		2.535(2)	2.539(2)
Mo(2)−Cl(3)	2.4135(9)	2.432(2)	2.424(2)
Mo(2)−Cl(4)		2.422(2)	2.425(2)
N−Mo(1)−N	161.0(2)	160.9(2)	162.5(3)
Cl−Mo(1)−Cl	138.36(5)	140.82(7)	139.15(8)
P−Mo(2)−P	155.30(5)	155.43(7)	153.17(8)
Cl−Mo(2)−Cl	144.42(5)	146.00(7)	148.04(8)
Mo(2)−Mo(1)−N	99.51(9)	99.4(2)	98.8(2)
Mo(2)−Mo(1)−Cl	110.82(2)	109.59(6)	110.43(7)
Mo(1)−Mo(2)−P	102.35(2)	102.28(6)	103.41(6)
Mo(1)−Mo(2)−Cl	107.79(3)	107.00(6)	105.98(6)

(ii) Reaction of $Mo_2Cl_4(NH_2Bu^t)_2(PMe_3)_2$ (2a) with $PHEt_2$. A similar procedure was carried out employing $Mo_2Cl_4(NH_2Bu^t)_2(PMe_3)_2$ and PEt_2H as starting materials in diethyl ether.

(7) Solution ^{31}P NMR Study of the Reaction between $Mo_2Cl_4(NHEt_2)_4$ and PMe_3. A mixture of $Mo_2Cl_4(NHEt_2)_4$ and PMe_3 (1:40) in toluene was monitored by $^{31}P\{^1H\}$ NMR over the temperature range −70 to 20 °C until the spectrum showed $Mo_2Cl_4(PMe_3)_4$ as the only complex in solution.

Physical Measurements. ^{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. $^{31}P\{^1H\}$ NMR data were recorded at 22 °C on a UNITY-plus 300 multinuclear spectrometer at 121.4 MHz. Resonances in the $^{31}P\{^1H\}$ NMR data were referenced to an external standard 85% H_3PO_4 (0.00 ppm). Elemental analyses were done by Canadian Microanalytical Services, Ltd.

X-ray Crystallographic Procedures. Single crystals of compounds **1a**, **3a**, and **4a** were obtained as described above. X-ray diffraction experiments were carried out on a Nonius FAST diffractometer with an area detector using Mo Kα radiation. Details concerning data collection have been fully described elsewhere.[13] Each crystal was mounted on the tip of a quartz fiber with silicone grease, and the setup was quickly placed in the cold N_2 stream (−60 °C) of a low-temperature controller. Fifty reflections were used in cell indexing and about 250 reflections ($16° < 2\theta < 42°$) in cell refinement. Axial images were used to confirm the Laue group and all dimensions. The data were corrected for Lorentz and polarization effects by the MADNES program.[14] Reflection profiles were fitted and values of F^2 and $\sigma(F^2)$ for each reflection were obtained by the program PROCOR.[15]

All calculations were done on a DEC Alpha running VMS using programs SHELXTL[16] (structure solution) and SHELXL-93[17] (least-squares refinement). Neither metal nor ligand disorder has been detected. Anisotropic displacement parameters were assigned to all non-hydrogen atoms. Hydrogen atoms bonded to nitrogen were refined independently. The rest of the H atoms were included in the structure factor calculations at idealized positions. Relevant crystallographic data for complexes **1a**, **3a**, and **4a** are summarized in Table 1, and selected bond distances and angles are given in Table 2.

Results

$Mo_2Cl_4(NH_2R)_4 + PR_3$. The reaction between primary amine complexes $Mo_2Cl_4(NH_2R)_4$ and an excess of tertiary phosphines proceeds at room temperature as evidenced by the change of color from red to blue violet. Time of completion, which is dependent on both entering and leaving groups, increases in the order $PMe_3 < PMe_2Ph$ and $NH_2Bu^t < NH_2Cy < NH_2Pr^n$. The elemental analyses of the products were consistent with the formula $Mo_2Cl_4(NH_2R)_2(PR_3)_2$. The ^{31}P NMR spectra in benzene solution showed only a singlet which was slightly downfield (Table 3) from that for the corresponding $Mo_2Cl_4(PR_3)_4$ species. The ^{1}H NMR spectra displayed signals for the NH_2R group (close to those in $Mo_2Cl_4(NH_2R)_4$ starting materials) and the phosphine. The integrals showed that the amine/phosphine ratios were 1:1. Thus we found that the title reactions stop at the doubly substituted stage at room temperature in contrast to reactions with the analogous dimolybdenum complexes with secondary amines,[10] which exhibit instantly full substitution under similar conditions.

The X-ray diffraction study has been performed in order to determine which isomer, **IIc** or **IId**, is the reaction product. The crystal structure investigation revealed that complexes of the type $Mo_2Cl_4(NH_2R)_2(PR_3)_2$ ($PR_3 = PMe_3$; $NH_2R = NH_2Pr^n$ (**1a**), NH_2Cy (**3a**) and $PR_3 = PMe_2Ph$; $NH_2R = NH_2Cy$ (**4a**))

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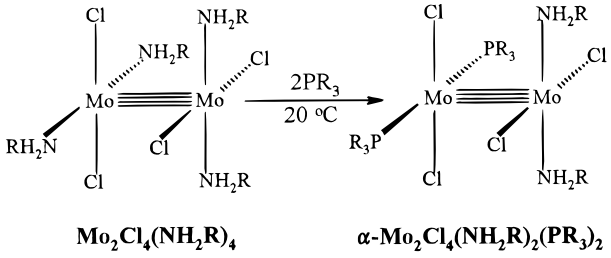
Table 3. Summary of $^{31}P\{^1H\}$ NMR Data in Benzene-d_6 for the Compounds under Discussion

compound	δ (ppm), J (Hz)
$Mo_2Cl_4(NH_2Pr^n)_3(PMe_3)$	−6.05(s)
α-$Mo_2Cl_4(NH_2Pr^n)_2(PMe_3)_2$	−14.07 (s)
$Mo_2Cl_4(NH_2Bu^t)_3(PMe_3)$	−6.32(s)
α-$Mo_2Cl_4(NH_2Bu^t)_2(PMe_3)_2$	−14.27 (s)
β-$Mo_2Cl_4(NH_2Bu^t)_2(PMe_3)_2$	−2.33 (s)
$Mo_2Cl_4(NH_2Bu^t)(PMe_3)_3$	0.07 (t, 1PMe_3), −10.85 (d, 2PMe_3), ^3J(PP) = 22
$Mo_2Cl_4(NH_2Cy)_3(PMe_3)$	−5.88(s)
α-$Mo_2Cl_4(NH_2Cy)_2(PMe_3)_2$	−13.70 (s)
β-$Mo_2Cl_4(NH_2Cy)_2(PMe_3)_2$	−2.34 (s)
$Mo_2Cl_4(NH_2Cy)(PMe_3)_3$	−0.45 (t, 1PMe_3), −10.51 (d, 2PMe_3), ^3J(PP) = 22
$Mo_2Cl_4(PMe_3)_4$	−8.68 (s)
$Mo_2Cl_4(NH_2Cy)_3(PMe_2Ph)$	3.72(s)
α-$Mo_2Cl_4(NH_2Cy)_2(PMe_2Ph)_2$	−3.24 (s)
β-$Mo_2Cl_4(NH_2Cy)_2(PMe_2Ph)_2$	5.92 (s)
$Mo_2Cl_4(NH_2Cy)(PMe_2Ph)_3$	6.86 (t, 1PMe_2Ph), −0.92 (d, 2PMe_2Ph), ^3J(PP) = 21
$Mo_2Cl_4(PMe_2Ph)_4$	0.29(s)
$Mo_2Cl_4(NH_2Cy)_3(PHEt_2)$	9.36(s)
β-$Mo_2Cl_4(NH_2Cy)_2(PHEt_2)_2$	12.19 (s)
$Mo_2Cl_4(NH_2Cy)(PHEt_2)_3$	13.49 (t, 1$PHEt_2$), 2.95 (dd, 2$PHEt_2$), ^3J(PP) = 21
$Mo_2Cl_4(PHEt_2)_4$	3.97(*d*)
α-$Mo_2Cl_4(NH_2Bu^t)_2(PHEt_2)(PMe_3)$	1.20 (d, 1$PHEt_2$), −13.77 (d, 1PMe_3), ^2J(PP) = 165
α-$Mo_2Cl_4(NH_2Cy)_2(PMe_3)(PMe_2Ph)$	−5.09 (d, 1PMe_2Ph), −11.77 (d, 1PMe_3), ^2J(PP) = 163
$Mo_2Cl_4(NHEt_2)_3(PMe_3)$	−6.84(s)
α-$Mo_2Cl_4(NHEt_2)_2(PMe_3)_2$	−14.61 (s)
β-$Mo_2Cl_4(NHEt_2)_2(PMe_3)_2$	−1.94 (s)
$Mo_2Cl_4(NHEt_2)(PMe_3)_3$	1.10 (t, 1PMe_3), −10.97 (d, 2PMe_3), ^3J(PP) = 22

Scheme 3



$Mo_2Cl_4(NH_2R)_4$ **α-$Mo_2Cl_4(NH_2R)_2(PR_3)_2$**

are all obtained (Scheme 3) with a structure of type **IIc**, that is, with both phosphine groups located on the same molybdenum atom (Figures 1−3). We designate this isomer as α, by analogy with chelating diphosphine complexes.[18]

High temperature is required to complete the substitution of primary amine ligands by phosphines. While refluxing in toluene, the color of the solution gradually changes to royal blue, and complexes $Mo_2Cl_4(PR_3)_4$ can be identified in the resulting mixture in nearly quantitative yield (Scheme 4).

The progress of the reactions was monitored by $^{31}P\{^1H\}$ NMR to follow the sequential substitution of primary amine ligands by phosphines. At 20 °C within 1 h after the addition of PR_3 to a deuterated benzene solution of $Mo_2Cl_4(NH_2R)_4$, a strong ^{31}P signal due to the monosubstituted product is observed as well as a small signal due to the disubstituted compound. As can be seen in Figure 4, after 12 h at 20 °C reaction to give the $Mo_2Cl_4(NH_2R)_2(PR_3)_2$ product is essentially complete, and there is no indication of any other product, nor is there any further change in the spectrum, even though excess PR_3 is present. The liberation of NH_2R can also be observed by ^1H NMR.

When the reaction mixture is heated to 75 °C, signals due to $Mo_2Cl_4(NH_2R)(PR_3)_3$, a doublet and a triplet as expected, promptly appear as well as a singlet due to the completely substituted molecule, $Mo_2Cl_4(PR_3)_4$. The fourth substitution step is much more rapid than the third, and therefore the signals for $Mo_2Cl_4(NH_2R)(PR_3)_3$ never become very strong. All of this can be seen in the upper three spectra of Figure 4.

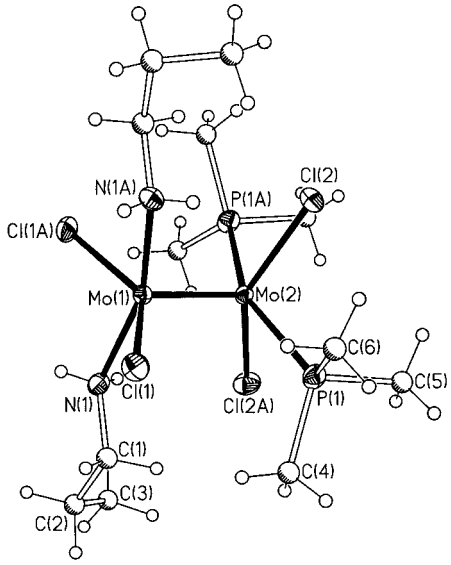


Figure 1. Perspective drawing of the α-isomer of $Mo_2Cl_4(NH_2Pr^n)_2(PMe_3)_2$ (**1a**). Atoms are represented by thermal ellipsoids at the 40% probability level. Carbon and hydrogen atoms are shown as spheres of arbitrary radii.

Since we have isolated and crystallographically characterized three of the $Mo_2Cl_4(NH_2R)_2(PR_3)_2$ molecules prepared by the reaction of $Mo_2Cl_4(NH_2R)_4$ with PR_3 and shown that they all have the α structure, **IIc**, it is clear that the overall pathway from $Mo_2Cl_4(NH_2R)_4$ to $Mo_2Cl_4(PR_3)_4$ traverses this intermediate, as shown in Scheme 5.

$Mo_2Cl_4(PR_3)_4$ + NH_2R. The reverse reaction, i.e., substitution of phosphine ligands in $Mo_2Cl_4(PR_3)_4$ by an excess of primary amine, also proceeds in a stepwise manner. Immediately after heating (to 75 °C) a toluene solution of $Mo_2Cl_4(PMe_3)_4$

(18) Best, S. A.; Smith, T. J.; Walton, R. A. *Inorg. Chem.* **1978**, *17*, 99.

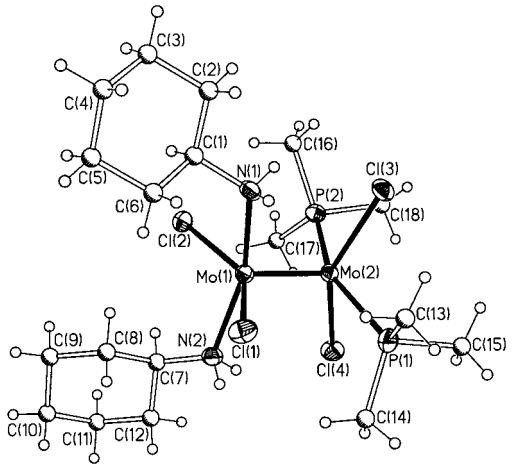


Figure 2. Perspective drawing of the α-isomer of $Mo_2Cl_4(NH_2Cy)_2(PMe_3)_2$ (**3a**). Atoms are represented by thermal ellipsoids at the 40% probability level. Carbon and hydrogen atoms are shown as spheres of arbitrary radii.

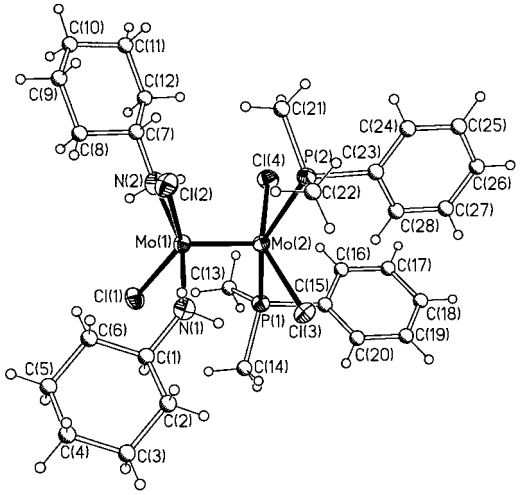
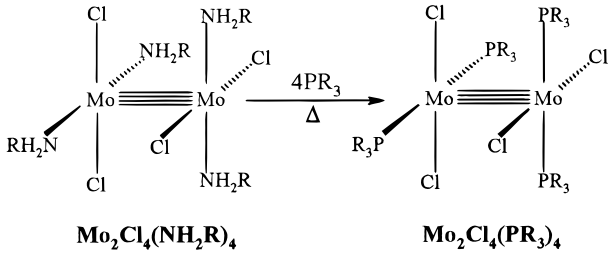


Figure 3. Perspective drawing of the α-isomer of $Mo_2Cl_4(NH_2Cy)_2(PMe_2Ph)_2$ (**4a**). Atoms are represented by thermal ellipsoids at the 40% probability level. Carbon and hydrogen atoms are shown as spheres of arbitrary radii.

Scheme 4



and NH_2Cy, the doublet and triplet signals of the complex $Mo_2Cl_4(NH_2Cy)(PMe_3)_3$ (Figure 5) as well as that of the free phosphine start to appear. Almost at the same time a new singlet begins to grow. Its position ($\delta = -2.34$) (Table 3) is quite different from the one for the α-isomer of $Mo_2Cl_4(NH_2Cy)_2(PMe_3)_2$ ($\delta = -13.70$). It is located between those for the PMe_3 groups in the $MoCl_2(NH_2Cy)(PMe_3)$ parts of the $Mo_2Cl_4(NH_2Cy)_3(PMe_3)$ ($\delta = -5.88$) and $Mo_2Cl_4(NH_2Cy)(PMe_3)_3$ ($\delta = -0.45$) species. We assign this signal to the β-isomer of $Mo_2Cl_4(NH_2Cy)_2(PMe_3)_2$ (type **IId**) in which the phosphine groups are on different molybdenum atoms.

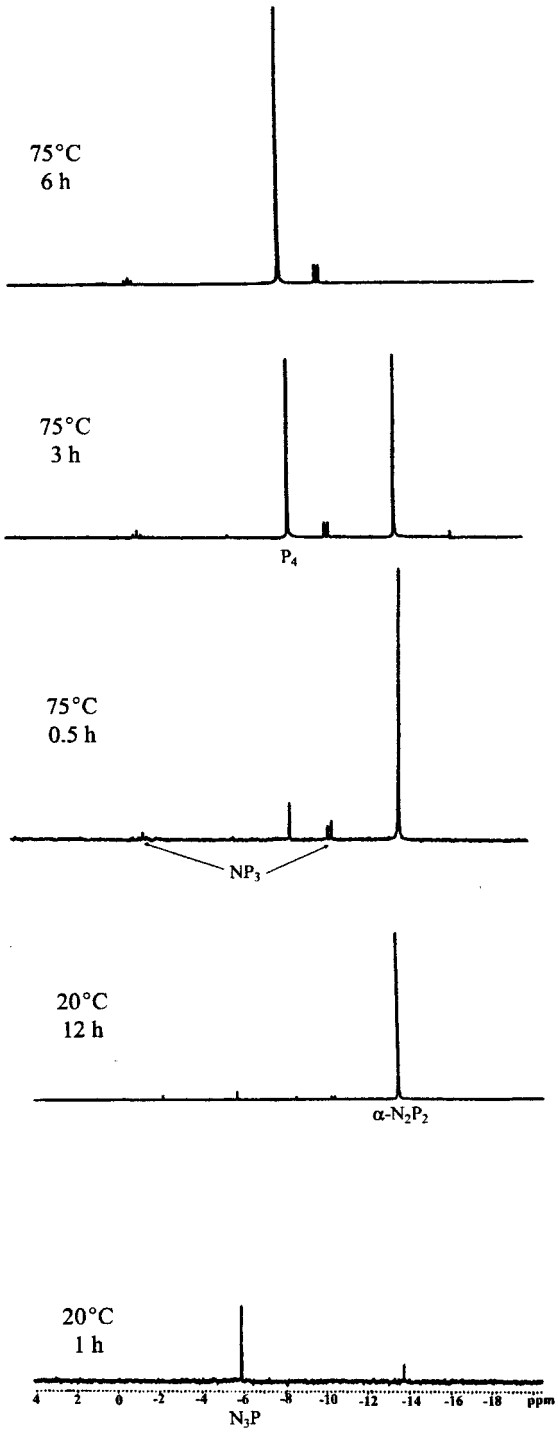


Figure 4. $^{31}P\{^1H\}$ monitoring of the reaction between $Mo_2Cl_4(NH_2Cy)_4$ and PMe_3 at various time intervals and temperatures in C_6D_6.

After 3 h of heating, the complex $Mo_2Cl_4(NH_2Cy)_3(PMe_3)$ was detected in solution (Figure 5), but the reaction is very slow at this point. Even after 15 h of reflux it was not completed, and the ^{31}P and ^1H NMR results taken together show the presence of three compounds in solution: β-$Mo_2Cl_4(NH_2Cy)_2(PMe_3)_2$, $Mo_2Cl_4(NH_2Cy)_3(PMe_3)$, and $Mo_2Cl_4(NH_2Cy)_4$[11] in an estimated ratio of 13:37:50.

All the results in Figures 4 and 5 are for PMe_3. When the phosphine is not as basic as PMe_3, its substitution by amine occurs without heating. After 1 day the reaction of $Mo_2Cl_4(PEt_2H)_4$ with NH_2Cy at room temperature shows a 1:1 mixture of starting material and β-$Mo_2Cl_4(NH_2Cy)_2(PEt_2H)_2$, and residual amounts of other species.

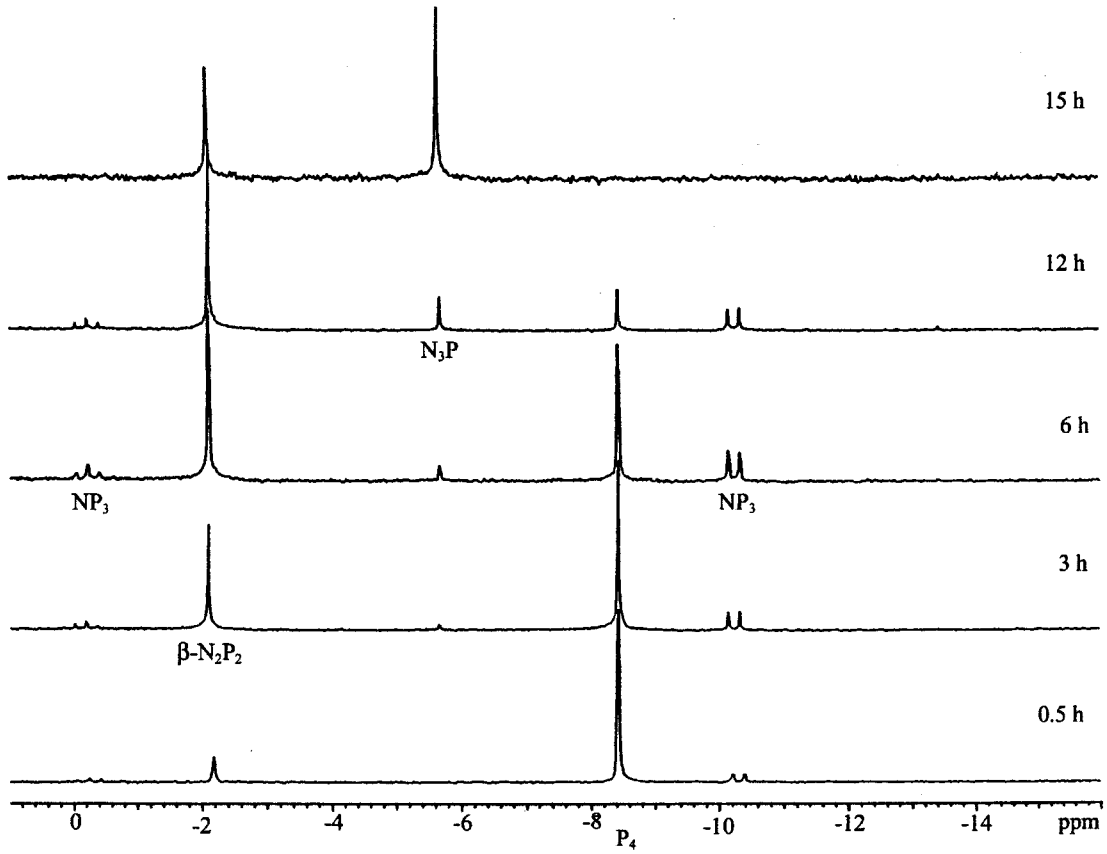
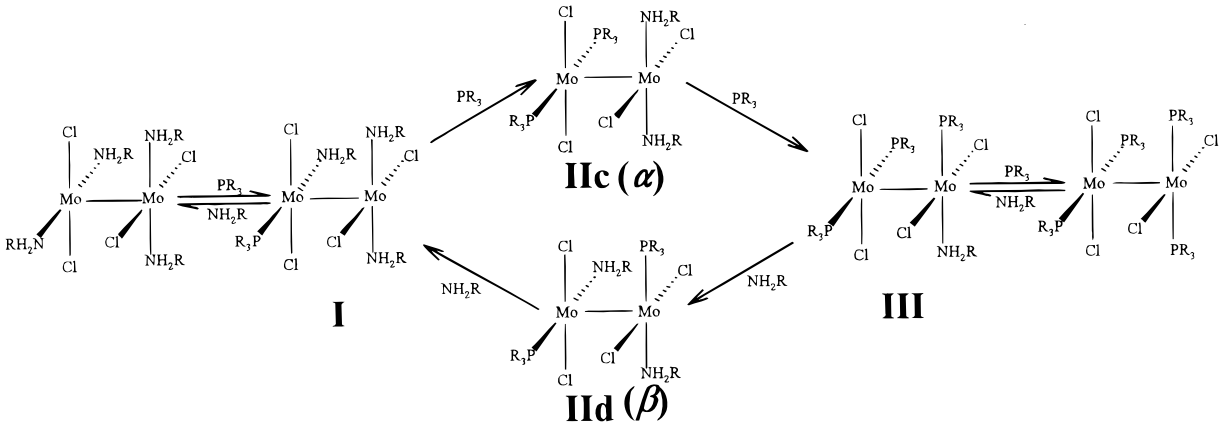


Figure 5. ^{31}P $\{^1H\}$ monitoring of the reaction between $Mo_2Cl_4(PMe_3)_4$ and NH_2Cy at 75 °C in toluene at 3 h time intervals.

Scheme 5



The results displayed in Figures 4 and 5 clearly show that the overall interconversion of $Mo_2Cl_4(NH_2R)_4$ and $Mo_2Cl_4(PR_3)_4$ compounds proceeds through isomeric intermediates of composition $Mo_2Cl_4(NH_2R)_2(PR_3)_2$, depending on the direction, as shown in Scheme 5. This phenomenon can be designated as a "stereochemical hysteresis".

$\alpha \rightarrow \beta$ Isomerization of $Mo_2Cl_4(NH_2R)_2(PR_3)_2$. The α-isomers of $Mo_2Cl_4(NH_2R)_2(PR_3)_2$ are relatively stable in solution at room temperature, even in the presence of free phosphine or amine. However, soon after heating a solution of the pure compound in toluene, signals corresponding to $Mo_2Cl_4(NH_2R)_3(PR_3)$, $Mo_2Cl_4(NH_2R)(PR_3)_3$, $Mo_2Cl_4(PR_3)_4$, and $Mo_2Cl_4(NH_2R)_4$[11] (the latter was detected by ^1H NMR) appear (Figure 6). The β-isomer of $Mo_2Cl_4(NH_2R)_2(PR_3)_2$ soon becomes the major component of the mixture, but even after 3 days of reflux the concentrations of other species (except the α-isomer) are still significant (Figure 6). The main source of the β-isomer is, evidently, the complex $Mo_2Cl_4(NH_2R)(PR_3)_3$ which, we know, can undergo a substitution reaction (Scheme 5) with free amine. Another possible mechanism for isomerization, an intermolecular "internal flip" of a dimolybdenum unit within the cubic cage of ligands (Scheme 6), which comes to mind by analogy with $\alpha \rightarrow \beta$ isomerization of diphosphine complexes $Mo_2Cl_4(P\text{-}P)_2$,[19] is not a likely route in this case. Attempts to see if this might occur in the solid state were unsuccessful because of the low thermal stability of the α-$Mo_2Cl_4(NH_2R)_2(PR_3)_2$ species.

α-$Mo_2Cl_4(NH_2R)_2(PR_3)_2$ + PR'_3. After 3 h of stirring a mixture of α-$Mo_2Cl_4(NH_2Cy)_2(PMe_3)_2$ and an excess of PMe_2Ph in toluene at room temperature, two doublets (Table 3) of equal intensity appeared. Shortly after that the signal corre-

(19) (a) Agaskar, P. A.; Cotton, F. A. *Inorg. Chem.* **1986**, *25*, 15. (b) Cotton, F. A.; Kitagawa, S. *Polyhedron* **1988**, *7*, 463. (c) Cayton, R. H.; Chisholm, M. H. *Inorg. Chem.* **1991**, *30*, 1422. (d) McVitie, A.; Peacock, R. D. *Polyhedron* **1992**, *11*, 2531.

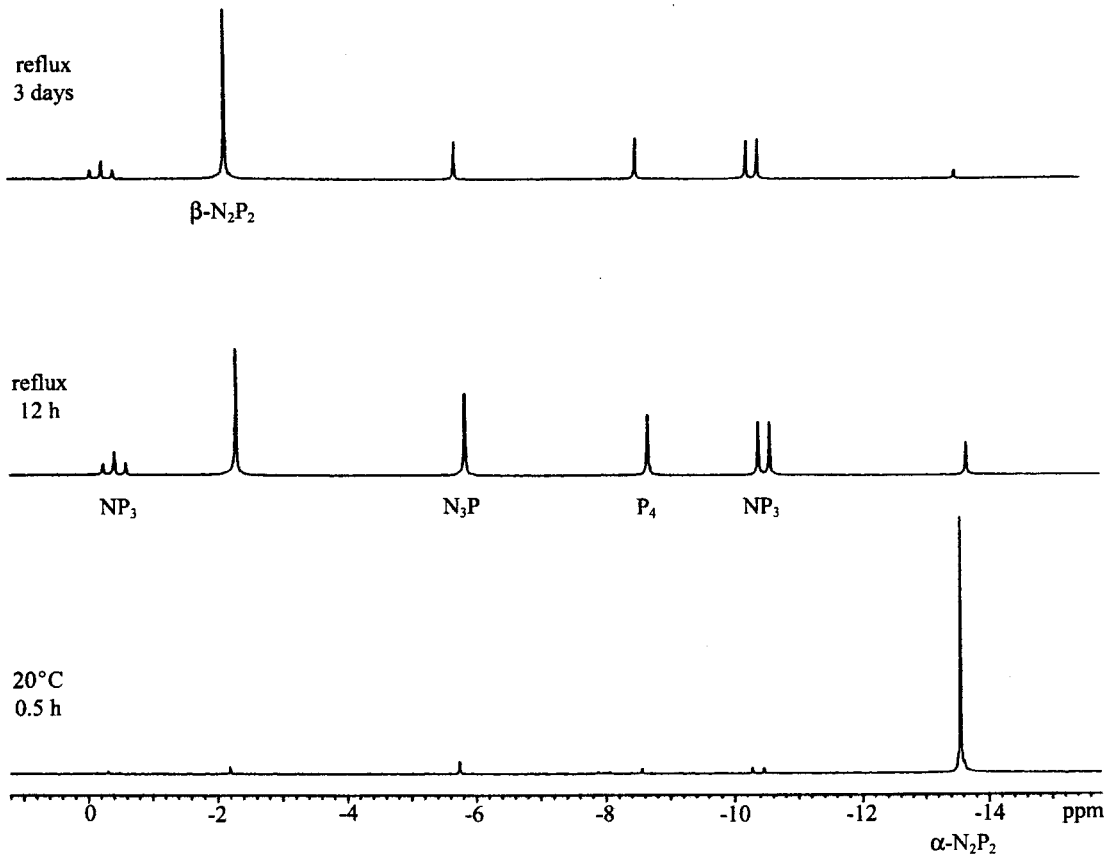
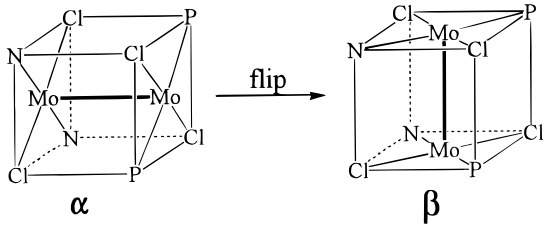


Figure 6. $^{31}P\{^1H\}$ spectra of α-$Mo_2Cl_4(NH_2Cy)_2(PMe_3)_2$ at different time intervals after reflux in toluene.

Scheme 6



sponding to the α-$Mo_2Cl_4(NH_2Cy)_2(PMe_2Ph)_2$ complex started to grow. We, therefore, identified the first complex as α-$Mo_2Cl_4(NH_2Cy)_2(PMe_3)(PMe_2Ph)$ because the large P−P coupling constant shows that both phosphine groups are on the same molybdenum atom. After 55 h the starting material was almost consumed and the ratio of two PMe_2Ph containing complexes was 1:4 (Figure 7). Thus, at room temperature, only the exchange of phosphine groups has been observed (Scheme 7), but on heating, further substitution of the amine ligands proceeds.

$Mo_2Cl_4(NHEt_2)_4$ + PMe_3. Reactions of the secondary amine complex $Mo_2Cl_4(NHEt_2)_4$ with phosphines have already been shown[12] to proceed at room temperature instantly giving $Mo_2Cl_4(PR_3)_4$ complexes. The $^{31}P\{^1H\}$ NMR monitoring of the reaction between $Mo_2Cl_4(NHEt_2)_4$ and an excess of PMe_3 at low temperatures showed that the substitution process is similar to that in the case of primary amine complexes (Scheme 5). The monosubstituted product and α-$Mo_2Cl_4(NHEt_2)_2(PMe_3)_2$, which we identified by analogy with the corresponding NH_2R species (Table 3), appear at about −40 °C. The replacement of the third group is not important until about 10 °C, and after that the substitution was quickly completed.

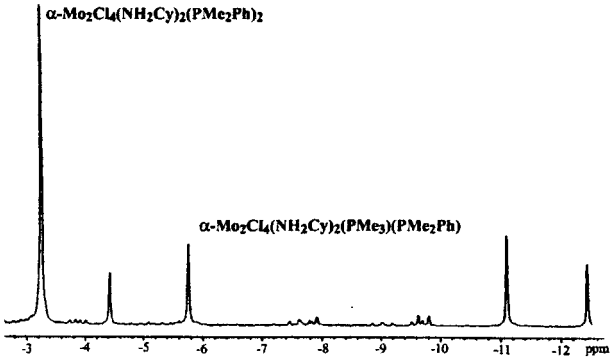


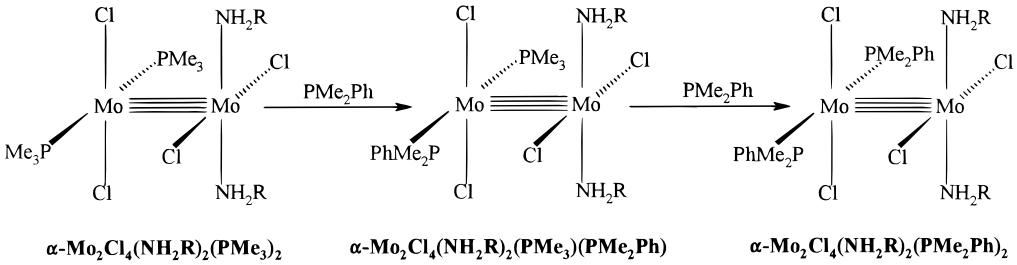
Figure 7. $^{31}P\{^1H\}$ spectrum of reaction mixture α-$Mo_2Cl_4(NH_2Cy)_2(PMe_3)_2$ and PMe_2Ph after 55 h at room temperature in toluene.

In an attempt to isolate α-$Mo_2Cl_4(NHEt_2)_2(PMe_3)_2$ we tried a reaction with only 2 equiv of phosphine. However, we observed in the reaction mixture all species (Table 3), including the *β*-isomer of $Mo_2Cl_4(NHEt_2)_2(PMe_3)_2$ which, most likely, results from the substitution of one PMe_3 group in $Mo_2Cl_4(NHEt_2)(PMe_3)_3$ by amine.

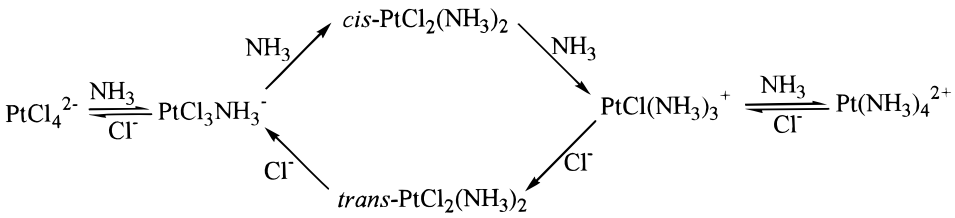
Discussion

All equilibria reported in this paper can be explained by the pronounced difference in the trans effects of NH_2R and PR_3 groups. Reaction of a dimolybdenum complex with primary amine ligands, $Mo_2Cl_4(NH_2R)_4$, with tertiary phosphines at room temperature stops at the disubstituted stage. After the first amine has been replaced by a PR_3 ligand, the next NH_2R group to be exchanged is that opposite to phosphine, thus giving the disubstituted product as the α-isomer (two phosphine groups at the same Mo atom). At low temperature (20 °C) the reaction

Scheme 7



Scheme 8



does not proceed further although the two PR_3 groups continue to exchange with free phosphine in solution. That has been proven by the reaction of α-$Mo_2Cl_4(NH_2R)_2(PR_3)_2$ with PR'_3 in which it is phosphines, but not amines, that are replaced. First and second substitutions at room temperature give α-$Mo_2Cl_4(NH_2R)_2(PR_3)(PR'_3)$ and α-$Mo_2Cl_4(NH_2R)_2(PR'_3)_2$, respectively, even if the less basic phosphines (PR'_3 = PMe_2Ph, PEt_2H) are used against PMe_3. The third substitution in $Mo_2Cl_4(NH_2R)_4$ must involve an NH_2R group trans to another amine ligand and requires heating to proceed. The compound $Mo_2Cl_4(NH_2R)(PR_3)_3$ is never present in the reaction mixture in high concentration. Once it appears, the replacement of the last NH_2R group, which is now activated by being located trans to a PR_3 ligand, proceeds rapidly.

The reverse reaction, the substitution of phosphines by amines, also proceeds in a stepwise manner, but takes a slightly different route. It requires both heating and a long time to be accomplished. The second substitution in this process occurs at the other molybdenum atom, because it is much easier to replace the ligand which is opposite to the PR_3 group. That gives the other isomer of $Mo_2Cl_4(NH_2R)_2(PR_3)_2$, which we call the β isomer. The latter is, apparently, more thermodynamically stable and can be obtained by thermal conversion of the pure α-form. We have demonstrated that the main route to the β-form is by substitution of phosphine by amine in $Mo_2Cl_4(NH_2R)(PR_3)_3$ which, in turn, resulted from the replacement of NH_2R by PR_3 in the α-form:

$$2Mo_2Cl_4(NH_2R)_2(PR_3)_2 \rightleftarrows Mo_2Cl_4(NH_2R)_3(PR_3) + Mo_2Cl_4(NH_2R)(PR_3)_3$$

Further substitution of phosphine ligands by amines in the β-isomer of $Mo_2Cl_4(NH_2R)_2(PR_3)_2$ encounters difficulties and goes very slowly as both remaining PR_3 groups are now trans to the NH_2R groups. The complex $Mo_2Cl_4(NH_2R)_3(PR_3)$ is relatively stable in these conditions and could be clearly seen in the reaction mixture.

The substitution of secondary amine ligands in $Mo_2Cl_4(NHEt_2)_4$ by phosphines goes much faster than corresponding reactions with primary amine compounds, and monitoring at low temperature is required to observe the process. We have noted earlier[12] the partial dissociation of $NHEt_2$ groups in solution of starting material. That could make a difference in the reaction mechanism, although the substitution sequence seems to be the same as in the case of primary amines.

The "stereochemical hysteresis" observed here, as shown in Scheme 5, has an interesting formal relationship (and has its origin in the same fundamental concept of the trans effect) as the classic chemistry of obtaining *cis*- or *trans*-$PtCl_2(NH_3)_2$ that is presented in most textbooks of inorganic chemistry (Scheme 8). In this classic case the controlling factor is that the trans effect order is Cl > NH_3, whereas in the present case we depend on the trans effect order PR_3 > NH_2R.

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: Three 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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