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Synthesis, Characterization, and Reactivity of Molybdenum Organohydrazido(2−) Complexes with Phosphines as Ancillary Ligands. X-ray Structures of $[Mo(NNPh_2)_2Cl_2(PPh_3)]$ and $[Mo(NNMePh)_2Cl_2(PPh_3)_2]\cdot 0.5CH_2Cl_2$

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The complexes $[Mo(NNPh_2)_2Cl_2(PPh_3)]$ (**3**), $[Mo(NNMePh)_2Cl_2(PPh_3)_2]$ (**4**), $[Mo(NNRPh)_2Cl_2(PMePh_2)_2]$ (R = Ph, **5**; R = Me, **6**), $[Mo(NNRPh)_2Cl_2(PMe_2Ph)_2]$ (R = Ph, **7**; R = Me, **8**), and $[Mo(NNRPh)_2Cl_2(dppe)]$ (R = Ph, **9**; R = Me, **10**) have been obtained in good yields by reaction of $[Mo(NHNRPh)(NNRPh)(acac)Cl_2]$ (R = Me, **1**; R = Ph, **2**) with $PMe_{3-n}Ph_n$ ($n = 1-3$) or $Ph_2PCH_2CH_2PPh_2$ in acetonitrile. In refluxing toluene, **4** undergoes dissociation of a PPh_3 ligand to give $[Mo(NNMePh)_2Cl_2(PPh_3)]$ (**11**). Complexes **3**, **4**, and **11** react with an excess of acetylacetone in refluxing acetonitrile to give back **1** or **2**. Complexes **3**−**11** have been studied by ^1H, ^{31}P NMR, IR, and UV−visible spectroscopy and by electrochemistry. In addition, compounds **3** and **4**$\cdot 0.5CH_2Cl_2$ have been characterized by X-ray crystal analyses. Complex **3** is monoclinic, space group $P2_1/c$, with a = 21.787(5) Å, b = 17.638(1) Å, c = 20.066(14) Å, β = 95.32(1)°, and Z = 8. The structure was solved using 3965 unique observed reflections; the refinements of 735 variables gave final R and R_w values of 0.049 and 0.053, respectively. Compound **4**$\cdot 0.5CH_2Cl_2$ is triclinic, space group $P\bar{1}$, with a = 14.384(12) Å, b = 16.599(6) Å, c = 23.919(11) Å, α = 77.44(4)°, β = 77.51(1)°, γ = 64.39(2)°, and Z = 4. The structure was solved using 5456 unique observed reflections; the refinements of 901 variables converged to R and R_w values of 0.070 and 0.083, respectively. Complex **3** displays a distorted trigonal bipyramidal geometry with the *cis*-hydrazido ligands in the equatorial plane, while **4** displays a distorted octahedral geometry with *cis*-hydrazido and *trans*-phosphine ligands.

Introduction

Transition metal organohydrazido(2−) complexes are of current interest as potential models of intermediates in nitrogen fixation. Indeed, the protonation of dinitrogen complexes to yield ammonia and hydrazine involves the NNH_2 species as an intermediate.[2,3] The most commonly employed synthetic routes to organohydrazido(2−) complexes involve (i) protonation and alkylation of organodiazenido complexes, (ii) reaction of a metal halide with either unsymmetrically disubstituted hydrazines, *e.g.* $RR'NNH_2$, or their trimethylsilyl derivatives, *e.g.* $Me_3SiNHNRR'$, and (iii) condensation-type reactions of unsymmetrically disubstituted hydrazines with oxometal complexes, notably oxomolybdenum complexes.[3,4] A lot of complexes containing the *cis*-$[Mo(NNRR')_2]^{2+}$ and *cis*-$[MoO(NNRR')]^{2+}$ units have now been synthesized, and some of them have been authenticated by X-ray diffraction studies. The *cis*-$[Mo(NNRR')_2]^{2+}$ unit is present in a number of complexes with ancillary (N,S),[5] (O,S),[6] (S,S),[7−10] (N,N),[10] and (O,O)[11] chelated ligands, while the *cis*-$[MoO(NNRR')]^{2+}$ unit is found in a number of mononuclear complexes containing monodentate thiolate[12] or (O,O),[6,13,14] (O,S),[6] (S,S),[15] (N,O),[16] (N,S),[5] (S,O,S),[17] (S,S,S),[17] (S,N,S),[17,18] and (S,N,N,S)[19] chelated ligands. Symmetrical[13,14] and unsymmetrical[20] dinuclear molybdenum complexes and organohydrazido-derivatized polyoxomolybdates[21−23] have also been characterized. The $[Mo(NNRR')]^{4+}$ unit has also been described.[17,24] Although most of the structurally characterized complexes of NNH_2^{2-} contain phosphines, there have been comparatively few studies of [organohydrazido(2−)]molybde-

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num complexes containing phosphines as ancillary ligands.[8,10,25–28] This report deals with the synthesis and characterization of $[Mo(NNRPh)_2Cl_2(PPh_3)]$ (R = Ph, **3**; R = Me, **11**), $[Mo(NNMePh)_2Cl_2(PPh_3)_2]$ (**4**), $[Mo(NNRPh)_2Cl_2(PMePh_2)_2]$ (R = Ph, **5**; R = Me, **6**), $[Mo(NNRPh)_2Cl_2(PMe_2Ph)_2]$ (R = Ph, **7**; R = Me, **8**) and $[Mo(NNRPh)_2Cl_2(dppe)]$ (R = Ph, **9**; R = Me, **10**), which have been obtained by reaction of $[Mo(NHNRPh)(NNRPh)(acac)Cl_2]$ (R = Me, **1**; R = Ph, **2**) with the appropriate phosphine in acetonitrile.

Experimental Section

Chemicals. Acetylacetone, 1-methyl-1-phenylhydrazine, 1,1-diphenylhydrazine hydrochloride, triphenylphosphine, methyldiphenylphosphine, dimethylphenylphosphine, 1,2-bis(diphenylphosphino)ethane (dppe), tetrabutylammonium hexafluorophosphate, n-Bu_4NPF_6, and reagent grade solvents were obtained from commercial sources. The complexes $[Mo(NHNRPh)(NNRPh)(acac)Cl_2]$ (R = Me, **1**; R = Ph, **2**) were prepared as previously described.[29]

Dichlorobis{diphenylhydrazido(2−)}(triphenylphosphine)molybdenum(VI), $[Mo(NNPh_2)_2Cl_2(PPh_3)]$ (3). PPh_3 (0.17 g, 0.64 mmol) was added to a suspension of complex **2** (0.20 g, 0.32 mmol) in acetonitrile (6 mL). After gentle heating under stirring for 5 min and cooling to room temperature, a green microcrystalline solid was filtered off, washed with diethyl ether, and dried under *vacuo*. The complex was recrystallized from a mixture of n-hexane and dichloromethane to yield single crystals suitable for an X-ray structure determination. Yield: 89% (0.22 g). Mp: 184 °C. Anal. Calcd for $C_{42}H_{35}Cl_2MoN_4P$: C, 63.6; H, 4.45; N, 7.06. Found: C, 63.2; H, 4.45; N, 7.07. UV−vis [(CH_2Cl_2), λ_{max}, nm (log ϵ)]: 392 (4.11), 376 (sh, 4.10), 296 (sh, 4.26), 234 (4.64). IR (KBr, cm^{-1}): 3080 (w), ν(CH), 1595 (s) ν(NN), 1495 (s) ν(CC). ^1H NMR ($CDCl_3$): 6.91−7.50 (m, C_6H_5). $^{31}P\{^1H\}$ NMR ($CDCl_3$): 36.98 (s).

Dichlorobis{methylphenylhydrazido(2−)}bis(triphenylphosphine)molybdenum(VI), $[Mo(NNMePh)_2Cl_2(PPh_3)_2]$ (4). The yellow microcystalline solid formed upon gentle heating for 15 min of the mixture of complex **1** (0.20 g, 0.39 mmol) and PPh_3 (0.31 g, 1.18 mmol) in acetonitrile (10 mL) was collected and recrystallized as $[Mo(NNMePh)_2Cl_2(PPh_3)_2]\cdot 0.5CH_2Cl_2$ (**4**$\cdot 0.5CH_2Cl_2$) from dichloromethane−diethyl ether. Yield: 60% (0.22 g). Mp: 138 °C dec. Anal. Calcd for $C_{50.5}H_{47}Cl_3MoN_4P_2$: C, 64.5; H, 4.98; N, 6.01. Found: C, 65.10; H, 5.06; N, 6.00. UV−vis [(CH_2Cl_2), λ_{max}, nm (log ϵ)] 392 (sh, 4.08), 352 (4.19), 236 (4.67). IR (KBr, cm^{-1}): 3080 (w) ν(CH), 2940 (w) ν(CH), 1600 (s) ν(NN), 1490 (s) ν(CC). ^1H NMR ($CDCl_3$): 3.47 (s, 6H, NCH_3), 5.30 (s, 1H, CH_2Cl_2), 7.02−7.50 (m, 40H, C_6H_5). $^{31}P\{^1H\}$ NMR ($CDCl_3$): 38.02 (s, 1P); −6.19 (s, 1P). Actually, **4** is completely dissociated into **11** and PPh_3 in $CDCl_3$.

Dichlorobis{diphenylhydrazido(2−)}bis(methyldiphenylphosphine)molybdenum(VI), $[Mo(NNPh_2)_2Cl_2(PMePh_2)_2]$ (5). Complex **2** (1.00 g, 1.58 mmol) and an excess of $PMePh_2$ (0.96 g, 4.75 mmol) were mixed in acetonitrile (15 mL). After gentle heating for 10 min and cooling to −12 °C, an orange solid deposited within 1 h. This was filtered off, washed with diethyl ether, and recrystallized as **5**$\cdot CH_2Cl_2$ from dichloromethane layered with n-hexane at room temperature. Yield: 81% (1.20 g). Mp: 142 °C dec. Anal. Calcd for $C_{50}H_{46}Cl_2MoN_4P_2$ (**5**): C, 64.5; H, 4.98; N, 6.01. Found: C, 63.5; H, 5.24; N, 5.97. UV−vis [(CH_2Cl_2), λ_{max}, nm (log ϵ)]: 388 (4.09), 362 (4.09), 300 (sh, 4.19); 236 (4.61). IR (KBr, cm^{-1}): 3080 (w) ν(CH), 2930 (w) ν(CH), 1600 (s) ν(NN), 1495(s) ν(CC). ^1H NMR [**5**$\cdot CH_2Cl_2$ ($CDCl_3$)]: 2.38 (t, 6H, PCH_3), 5.30 (s, 2H, CH_2Cl_2), 6.96−7.60 (m, 40H, C_6H_5). $^{31}P\{^1H\}$ NMR ($CDCl_3$): 25.89 (s), 13.05 (s) and −27.60 (s). Actually, **5** undergoes partial dissociation in $CDCl_3$ to give $[Mo(NNPh_2)_2Cl_2(PMePh_2)]$ and $PMePh_2$.

Dichlorobis{methylphenylhydrazido(2−)}bis(methyldiphenylphosphine)molybdenum(VI), $[Mo(NNMePh)_2Cl_2(PMePh_2)_2]$ (6). Complex **1** (1.00 g, 1.97 mmol) and an excess of $PMePh_2$ (1.18 g, 5.91 mmol) were mixed in acetonitrile (20 mL). The mixture was stirred and gently heated for 10 min; then the solvent was evaporated under *vacuo*, diethyl ether was added to the residue,, and the mixture was vigorously stirred overnight. The solid was filtered off and washed with diethyl ether. A yellow microcrystalline solid was obtained from CH_2Cl_2 layered with n-hexane. This was recrystallized from n-hexane−diethyl ether as **6**$\cdot Et_2O$. Yield: 84% (1.33 g). Mp: 146 °C dec. Anal. Calcd for $C_{40}H_{42}Cl_2MoN_4P_2$ (**6**): C, 59.5; H, 5.24; N, 6.94. Found: C, 59.8; H, 5.76; N, 6.64. UV−vis [CH_2Cl_2, λ_{max}, nm (log ϵ)]: 392 (sh, 4.02), 346 (4.21), 320 (4.21), 238 (4.60). IR (KBr, cm^{-1}): 3070 (w) ν(CH)arom, 2980 (w) ν(CH), 2930 (w) ν(CH), 1600(s) ν(NN), 1495 (s) ν(CC). ^1H NMR [**6**$\cdot Et_2O$ ($CDCl_3$)]: 1.21 (t), 2.31 (t), 2.37 (t), 3.02 (s), 3.19 (s), 3.21 (s), 3.48 (q), 6.70−7.60 (m). $^{31}P\{^1H\}$ NMR ($CDCl_3$): 14.17 (s), 13.92 (s).

Dichlorobis{diphenylhydrazido(2−)}bis(dimethylphenylphosphine)molybdenum(VI), $[Mo(NNPh_2)_2Cl_2(PMe_2Ph)_2]$ (7). Complex **2** (0.20 g, 0.32 mmol) and PMe_2Ph (0.13 g, 0.95 mmol) were mixed in acetonitrile (10 mL). After gentle heating for 10 min, the solution was cooled to room temperature. A light green solid was obtained after addition of diethyl ether and standing at −12 °C for 2 h. This was filtered off, washed with diethyl ether, and recrystallized from acetonitrile−diethyl ether. Yield: 67% (0.85 g). Mp: 129 °C. Anal. Calcd for $C_{40}H_{42}Cl_2MoN_4P_2$: C, 59.5; H, 5.24; N, 6.94. Found: C, 59.5; H, 5.32; N, 7.00. UV−vis [(CH_2Cl_2), λ_{max}, nm (log ϵ)]: 392 (sh, 4.02), 344 (sh, 4.11), 302 (4.32), 238 (4.54). IR (KBr, cm^{-1}): 3080 (w) ν(CH), 2920 (w) ν(CH), 1600 (s) ν(NN), 1495 (s) ν(CC). ^1H NMR ($CDCl_3$): 1.92 (t, 12H, $P(CH_3)_2$), 6.60−7.59 (m, 30H, C_6H_5). $^{31}P\{^1H\}$ NMR ($CDCl_3$): 1.24 (s).

Dichlorobis{methylphenylhydrazido(2−)}bis(dimethylphenylphosphine)molybdenum(VI), $[Mo(NNMePh)_2Cl_2(PMe_2Ph)_2]$ (8). A mixture of complex **1** (0.20 g, 0.39 mmol) and PMe_2Ph (0.16 g, 1.18 mmol) in acetonitrile (15 mL) was gently heated for 15 min and then cooled to room temperature. The green precipitate was discarded, and the filtrate was concentrated up to 7 mL under *vacuo*. A yellow solid was obtained after addition of diethyl ether and standing at −12 °C for 3 h. This was recrystallized from diethyl ether−dichloromethane. Yield: 59% (0.24 g). Mp: 162 °C dec. Anal. Calcd for $C_{30}H_{38}Cl_2MoN_4P_2$: C, 52.7; H, 5.60; C, 8.19. Found: C, 52.8; H, 5.73; N, 8.32. UV−vis [(CH_2Cl_2), λ_{max}, nm (log ϵ)]: 378 (sh, 3.92), 310 (4.42), 238 (4.54). IR (KBr, cm^{-1}): 3080 (w) ν(CH), 2920 (w), ν(CH), 1600 (s) ν(NN), 1495 (s) ν(CC). ^1H NMR ($CDCl_3$): 1.83 [t, 12 H, $P(CH_3)_2$], 3.70 (s, 6 H, NCH_3), 5.03 (s, CH_2Cl_2), 6.92−7.50 (m, 20 H, 4 C_6H_5). $^{31}P\{^1H\}$ NMR ($CDCl_3$): 1.44 (s).

Dichlorobis{diphenylhydrazido(2−)}{bis(1,2-(diphenylphosphino)ethane)}-molybdenum(VI), $[Mo(NNPh_2)_2Cl_2(dppe)]$ (9). A mixture of complex **2** (1.00 g, 1.58 mmol) and dppe (0.69 g, 1.58 mmol) in acetonitrile (25 mL) was gently heated for 10 min. Then, the solvent was evaporated under *vacuo*, diethyl ether was added to the residue, and the mixture was stirred overnight. The yellow solid was filtered off and dissolved in a mixture of CH_2Cl_2 and n-hexane. Under these conditions an oil initially formed, which was separated. Then the solution was allowed to stand for 2 days at −12 °C, to yield large red crystals, which lost CH_2Cl_2 upon standing in air. Stable crystals of **9** were obtained from methanol. Yield: 84% (1.35 g). Mp: 150 °C dec. Anal. Calcd for $C_{50}H_{44}Cl_2MoN_4P_2$ (**9**): C, 64.6; H, 4.77; N, 6.02. Found: C, 63.5; H, 4.64; N, 5.84. UV−vis [(CH_2Cl_2), λ_{max}, nm (log ϵ)]: 478 (3.25), 370 (4.21), 292 (4.49), 236 (4.71). IR (KBr, cm^{-1}): 3080 (w), ν(CH), 2930 (w) ν(CH), 1598 (m) ν(NN), 1496 (s) ν(CC). ^1H NMR ($CDCl_3$): 2.20−3.50 (m, 4 H, PCH_2CH_2P), 7.11−7.94 (m, 40 H, C_6H_5). $^{31}P\{^1H\}$ NMR ($CDCl_3$): 38.35 (d, 1 P), 3.60 (d, 1P), $^2J_{P-P}$= 28.0 Hz.

Dichlorobis{methylphenylhydrazido(2−)}{bis(1,2-(diphenylphosphino)ethane)}molybdenum(VI), $[Mo(NNMePh)_2Cl_2(dppe)]$ (10). This complex was synthesized analogously to **9**, from 1.00 g (1.97 mmol) of complex **1** and 0.79 g (1.97 mmol) of dppe. The crude complex was recrystallized as **10**$\cdot CH_2Cl_2$ from a mixture of CH_2Cl_2 and n-hexane. Yield: 95% (1.67 g). Mp: 145 °C dec. Anal. Calcd for $C_{41}H_{42}Cl_4MoN_4P_2$: C, 55.3; H, 4.75. Found: C, 54.3; H, 4.73. UV−vis [(CH_2Cl_2), λ_{max}, nm (log ϵ)]: 468 (3.15), 368 (4.09), 292 (4.42), 234 (4.59). IR (KBr, cm^{-1}): 3080 (w), ν(CH), 2940 (w)

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Table 1. Summary of Crystallographic Data for Compounds **3** and **4**$\cdot$0.5CH_2Cl_2

	$[Mo(NNPh_2)_2Cl_2(PPh_3)]$	$[Mo(NNMePh)_2Cl_2(PPh_3)_2]\cdot$ 0.5CH_2Cl_2
fw	793.58	974.19
space group	$P2_1/c$	$P\bar{1}$
a, Å	21.787(5)	14.384(12)
b, Å	17.638(1)	16.599(6)
c, Å	20.066(14)	23.919(11)
α, deg	90.0	77.44(4)
β, deg	95.32(1)	77.51(1)
γ, deg	90.0	64.39(2)
V, Å^3	7678(7)	4978(12)
Z	8	4
T, °C	20	20
λ, Å	0.710 69	0.710 69
μ(Mo Kα), cm^{-1}	5.48	5.18
ϱ_{calc}, g cm^{-3}	1.37	1.30
R^a	0.049	0.070
$R_w{}^b$	0.053	0.083

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o{}^2]^{1/2}$ (w = 1.0).

ν(CH), 1600 (m) ν(NN), 1495 (sh) ν(CC). ^{1}H NMR ($CDCl_3$): 2.15−3.60 (m, 4 H, PCH_2CH_2P), 3.54 (s, NCH_3), 4.14 (s, NCH_3), 5.30 (s, CH_2Cl_2), 7.15−7.99 (m, 30 H, C_6H_5). $^{31}P\{^1H\}$ NMR ($CDCl_3$): 42.62 (d) and 9.35 (d), $^2J_{P-P}$ = 35.0 Hz; 37.78 (d) and 1.06 (d), $^2J_{P-P}$ = 19.8 Hz.

Dichlorobis{methylphenylhydrazido(2−)}(triphenylphosphine)-molybdenum(VI), $[Mo(NNMePh)_2Cl_2(PPh_3)]$ (11). Complex **4** (0.50 g) was refluxed in toluene (10 mL) for 1 h under N_2. The pale green solid was filtered off, washed with diethyl ether, and recrystallized from toluene. Yield: 92% (0.38 g). Mp: 182 °C. Anal. Calcd for $C_{32}H_{31}Cl_2MoN_4P$: C, 57.4; H, 4.67. Found: C, 56.8; H, 4.76. UV−vis [(CH_2Cl_2), λ_{max}, nm (log ϵ)]: 390 (sh, 3.81), 354 (3.89), 297 (3.83), 221 (4.38). IR (KBr, cm^{-1}): 3080 (w) ν(CH), 2940 (w) ν(CH), 1600 (m) ν(NN), 1490 (s) ν(CC). ^{1}H NMR ($CDCl_3$): 3.46 (s, 6 H, NCH_3), 7.02−7.47 (m, 25 H, C_6H_5). $^{31}P\{^1H\}$ NMR ($CDCl_3$): 38.05 (s).

Physical Measurements. Melting points were determined by using a Kofler apparatus. Microanalytical data were obtained on a Perkin-Elmer Model 2400 elemental analyzer. IR spectra were recorded on a Perkin-Elmer 599 spectrophotometer as KBr disks. Electronic spectra were recorded in CH_2Cl_2 solution on a Hewlett Packard 8452A spectrophotometer. ^{1}H NMR and ^{31}P NMR spectra were recorded in $CDCl_3$ (with TMS and H_3PO_4 as internal and external standards, respectively) on a Bruker AC-200P spectrometer. Cyclic voltammetry (CV) measurements were made with a homemade potentiostat of conventional design, using a standard three-electrode cell with platinum working and auxiliary electrodes and an aqueous saturated calomel electrode (SCE) as the reference. Solution concentrations were 2 mM for the complex under study and 0.1 M n-Bu_4NPF_6 for the supporting electrolyte. All measurements were carried out at room temperature (15 ± 2 °C) under nitrogen in CH_2Cl_2. Under these experimental conditions, the ferrocenium−ferrocene couple was located at +0.50 V.

X-ray Data Collection and Structure Determination of 3 and 4$\cdot$0.5CH_2Cl_2. X-ray data were recorded on a Philips PW1100 diffractometer using graphite-monochromated Mo Kα radiation. Crystals were sealed on glass fibers. Lattice parameters and the orientation matrix were obtained from a least-squares fit of the setting angles of 25 automatically centered reflections. Crystal data and data collection parameters are summarized in Table 1. The intensities of two standard reflections were monitored every 1 h; these showed no significant change during data collection. Intensities were corrected for Lorentz and polarization effects. An empirical absorption correction using DIFABS[30] was applied. All computations were performed on a Micro VAX II using the CRYSTALS system.[31] Both structures were solved by direct methods. Hydrogen atoms were not included in the refinements. Anisotropic thermal parameters were refined for all atoms. Corrections were made for extinction. Final refinements gave R = 0.049 and R_w = 0.053 for **3** and R = 0.070 and R_w = 0.083 for **4**$\cdot$0.5CH_2Cl_2. Scattering factors and corrections for anomalous dispersion were taken from ref 32. Atomic positional parameters are listed in Tables 2 and 3. Selected intramolecular bond distances and angles are given in Tables 4 and 5. Views[33] of the molecular structures of **3** and **4** with the atom-labeling scheme are shown in Figures 1 and 2, respectively.

Results and Discussion

Syntheses and Reactivity. In acetonitrile, the complexes $[Mo(NHNRPh)(NNRPh)(acac)Cl_2)]$ (R = Me, **1**; R = Ph, **2**) react cleanly with phosphines, $PMe_{3-n}Ph_n$ (n = 1−3) to yield neutral diamagnetic mononuclear bis[organohydrazido(2−)]-molybdenum(VI) complexes in good yields (see Scheme 1). These species contain either one, *e.g.* **3** and **11**, or two, *e.g.* complexes **4−8**, phosphines. They react similarly with 1,2-bis(diphenylphosphino)ethane affording the mononuclear complexes **9** and **10**. Complexes **4−10** differ from the cationic complexes $[M(NNMe_2)_2Cl(PR'_3)_2]^+$ obtained by reaction of $[MCl_4(PR'_3)_2]$ (M = Mo, W; PR'_3 = PPh_3, $PMePh_2$) with $Me_3SiNHNMe_2$ in MeCN.[10,25] The instability of $[M(NNMe_2)_2Cl_2(PR'_3)_2]$ *versus* $[M(NNMe_2)_2Cl(PR'_3)_2]^+$ could arise from the higher basicity of the Me_2NN^{2-} ligand compared to Ph_2NN^{2-} and $PhMeNN^{2-}$. It is noteworthy that the complexes $[Mo(NNRPh)_2Cl_2(PR'_3)_2]$ (R = Me, R′ = Ph, **4**; R = Ph, PR'_3 = $PMePh_2$, **5**) undergo dissociation in $CDCl_3$ to give complexes $[Mo(NNRPh)_2Cl_2(PR'_3)]$ instead of $[Mo(NNRPh)_2Cl(PR'_3)_2]^+$, while complexes $[Mo(NNRPh)_2Cl_2(PR'_3)_2]$ (R = Me, PR'_3 = $PMePh_2$, **6**; R = Ph, PR'_3 = PMe_2Ph, **7**; R = Me, PR'_3 = PMe_2Ph, **8**) are stable toward dissociation. On the other hand, all attempts to synthesize $[Mo(NNPh_2)_2Cl_2(PPh_3)_2]$ were unsuccessful. This indicates that steric effects are operative besides electronic effects. In refluxing acetonitrile, the five-coordinated complexes **3** and **11** and the unstable six-coordinated complex **4** react with acetylacetone to give back complexes **1** and **2**. This shows that the interconversion of hydrazido(2−) and hydrazido(1−) ligands may be forced back and forth by use of suitable ancillary ligands.

X-ray Structures. The asymmetric units of both **3** and **4**$\cdot$0.5CH_2Cl_2 contain two crystallographically independent molybdenum complexes a and b. Moreover that of **4**$\cdot$0.5CH_2Cl_2 contains a molecule of CH_2Cl_2. The geometry about the molybdenum centers in **3** is best described as distorted trigonal bipyramidal with the triphenylphosphine and one chloro ligand occupying the axial positions and the equatorial plane defined by the second chloro group and the α-nitrogen atoms of the two diphenylhydrazido(2−) ligands. The Mo−P and Mo−Cl distances compare well with those of related complexes,[10,25] and the overall geometry of the hydrazido ligands is similar to that in most organohydrazido(2−) complexes.[8,10,25] The short Mo−N [1.76(1) Å in (a), 1.75(1) Å in (b)] and N−N distances [1.30(1) and 1.33(1) Å in (a), 1.33(1) and 1.34(1) Å in (b)], the near linearity of the Mo−N−N grouping [Mo-N-N = 172.9(9) and 176.8(8)° in (a), 169.3(8) and 172.7(8)° in (b)], and the near planarity of the Mo−N−N−C_2 moieties indicate extensive electronic delocalization throughout the Mo−N−NPh_2 systems. Accordingly, the diphenylhydrazido(2−) ligands may be considered as four-electron donors, and the molybdenum center attains a 18-electron count. The small differences between (a) and (b) probably arise from intra- and intermolecular nonbonding contact interactions rather than from electronic effects.

Molecules a and b in **4**$\cdot$0.5CH_2Cl_2 display similar distorted octahedral geometries. The phosphines occupy two *trans*-axial

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Table 2. Atomic Positional[a] and Temperature Factors[b] for [Mo(NNPh$_2$)$_2$Cl$_2$(PPh$_3$)]

atom	*x*/*a*	*y*/*b*	*z*/*c*	*U*(eq), Å^2	atom	*x*/*a*	*y*/*b*	*z*/*c*	*U*(eq), Å^2
Mo(1)	0.67479(5)	0.22964(6)	0.15279(5)	0.0425	Mo(51)	0.82718(5)	0.71446(6)	0.36706(5)	0.0414
Cl(1)	0.7561(2)	0.1559(2)	0.2154(2)	0.0618	Cl(51)	0.7414(2)	0.6435(2)	0.3087(2)	0.0609
Cl(2)	0.6466(2)	0.2618(2)	0.2613(1)	0.0661	Cl(52)	0.8605(2)	0.7301(2)	0.2581(1)	0.0651
P(1)	0.5786(2)	0.3031(2)	0.1137(2)	0.0499	P(51)	0.9266(2)	0.7850(2)	0.4013(1)	0.0461
N(1)	0.6474(4)	0.1500(6)	0.1059(4)	0.0418	N(51)	0.8480(5)	0.6358(6)	0.4178(4)	0.0457
N(2)	0.6275(5)	0.0874(6)	0.0735(5)	0.0533	N(52)	0.8584(5)	0.5711(6)	0.4514(5)	0.0475
N(11)	0.7243(4)	0.2897(5)	0.1126(4)	0.0435	N(61)	0.7818(4)	0.7825(5)	0.4031(4)	0.0429
N(12)	0.7611(5)	0.3275(6)	0.0774(5)	0.0538	N(62)	0.7454(5)	0.8244(5)	0.4390(5)	0.0502
C(1)	0.6457(4)	0.0709(5)	0.0086(4)	0.0496	C(51)	0.8389(4)	0.5612(5)	0.5161(4)	0.0497
C(2)	0.6447(5)	−0.0038(4)	−0.0136(5)	0.0683	C(52)	0.8070(4)	0.4965(5)	0.5321(5)	0.0577
C(3)	0.6622(5)	−0.0209(5)	−0.0767(5)	0.0873	C(53)	0.7894(4)	0.4871(5)	0.5964(5)	0.0795
C(4)	0.6807(5)	0.0367(7)	−0.1178(4)	0.0832	C(54)	0.8037(5)	0.5424(7)	0.6447(4)	0.0790
C(5)	0.6817(5)	0.1114(6)	−0.0956(5)	0.0787	C(55)	0.8355(5)	0.6072(6)	0.6287(4)	0.0961
C(6)	0.6642(5)	0.1285(4)	−0.0325(5)	0.0634	C(56)	0.8532(5)	0.6166(5)	0.5643(5)	0.0790
C(7)	0.5932(5)	0.0370(5)	0.1102(5)	0.0557	C(57)	0.8911(4)	0.5126(5)	0.4194(4)	0.0523
C(8)	0.6193(4)	0.0076(7)	0.1706(6)	0.0889	C(58)	0.8837(5)	0.5045(5)	0.3502(4)	0.0723
C(9)	0.5862(6)	−0.0432(7)	0.2063(4)	0.1002	C(59)	0.9181(6)	0.4509(7)	0.3191(4)	0.0952
C(10)	0.5270(6)	−0.0647(7)	0.1816(6)	0.1023	C(60)	0.9599(5)	0.4053(6)	0.3573(6)	0.0907
C(11)	0.5009(4)	−0.0353(7)	0.1212(7)	0.0933	C(61)	0.9673(4)	0.4134(5)	0.4265(6)	0.0808
C(12)	0.5340(5)	0.0155(6)	0.0855(5)	0.0779	C(62)	0.9329(5)	0.4670(5)	0.4575(4)	0.0513
C(13)	0.7780(4)	0.2967(5)	0.0148(3)	0.0439	C(63)	0.7299(4)	0.7951(5)	0.5015(3)	0.0515
C(14)	0.8075(4)	0.2270(5)	0.0129(4)	0.0680	C(64)	0.7073(5)	0.7217(5)	0.5060(4)	0.0788
C(15)	0.8237(5)	0.1984(5)	−0.0476(6)	0.0861	C(65)	0.6939(6)	0.6932(5)	0.5676(6)	0.1052
C(16)	0.8103(5)	0.2396(7)	−0.1063(4)	0.0816	C(66)	0.7031(5)	0.7379(7)	0.6246(4)	0.0920
C(17)	0.7808(5)	0.3093(6)	−0.1044(3)	0.0698	C(67)	0.7257(5)	0.8113(7)	0.6201(4)	0.0815
C(18)	0.7646(4)	0.3379(4)	−0.0438(5)	0.0599	C(68)	0.7391(5)	0.8398(4)	0.5585(5)	0.0664
C(19)	0.7917(5)	0.3950(5)	0.1046(5)	0.0531	C(69)	0.7214(4)	0.8931(4)	0.4115(4)	0.0459
C(20)	0.8460(5)	0.4224(6)	0.0824(5)	0.0641	C(70)	0.6682(4)	0.9243(6)	0.4332(4)	0.0606
C(21)	0.8741(5)	0.4864(7)	0.1120(6)	0.0860	C(71)	0.6438(4)	0.9907(6)	0.4042(6)	0.0821
C(22)	0.8478(7)	0.5229(5)	0.1637(6)	0.0881	C(72)	0.6727(5)	1.0258(4)	0.3536(5)	0.0771
C(23)	0.7934(7)	0.4955(6)	0.1859(5)	0.1049	C(73)	0.7259(5)	0.9946(5)	0.3319(4)	0.0784
C(24)	0.7653(4)	0.4316(7)	0.1563(5)	0.0848	C(74)	0.7503(4)	0.9283(6)	0.3609(5)	0.0643
C(25)	0.5569(4)	0.2901(5)	0.0247(3)	0.0453	C(75)	0.9470(4)	0.7894(5)	0.4916(3)	0.0380
C(26)	0.5012(4)	0.2572(6)	0.0007(5)	0.0742	C(76)	1.0076(3)	0.7830(5)	0.5193(4)	0.0552
C(27)	0.4878(4)	0.2456(6)	−0.0677(5)	0.0877	C(77)	1.0211(3)	0.7874(5)	0.5883(4)	0.0669
C(28)	0.5301(6)	0.2669(6)	−0.1120(3)	0.0797	C(78)	0.9740(5)	0.7982(5)	0.6295(3)	0.0625
C(29)	0.5858(5)	0.2998(6)	−0.0880(4)	0.0714	C(79)	0.9134(4)	0.8046(5)	0.6017(4)	0.0594
C(30)	0.5992(4)	0.3115(5)	−0.0196(5)	0.0630	C(80)	0.8999(3)	0.8002(5)	0.5328(4)	0.0558
C(31)	0.5110(4)	0.2708(6)	0.1530(4)	0.0562	C(81)	0.9928(4)	0.7408(6)	0.3675(4)	0.0546
C(32)	0.4603(6)	0.3177(5)	0.1580(5)	0.0717	C(82)	1.0390(5)	0.7810(5)	0.3396(5)	0.0711
C(33)	0.4084(4)	0.2901(8)	0.1853(5)	0.0863	C(83)	1.0886(4)	0.7427(8)	0.3165(5)	0.0773
C(34)	0.4072(4)	0.2156(8)	0.2077(5)	0.0813	C(84)	1.0921(4)	0.6641(8)	0.3213(5)	0.0838
C(35)	0.4578(6)	0.1687(5)	0.2027(5)	0.0959	C(85)	1.0459(6)	0.6239(5)	0.3493(6)	0.0843
C(36)	0.5097(5)	0.1963(5)	0.1754(5)	0.0680	C(86)	0.9963(4)	0.6623(6)	0.3723(5)	0.0682
C(37)	0.5809(5)	0.4066(4)	0.1250(5)	0.0552	C(87)	0.9261(5)	0.8852(4)	0.3757(5)	0.0552
C(38)	0.5602(5)	0.4560(6)	0.0737(4)	0.0842	C(88)	0.9271(6)	0.9427(5)	0.4232(3)	0.0719
C(39)	0.5636(6)	0.5339(6)	0.0840(5)	0.0979	C(89)	0.9230(7)	1.0180(5)	0.4030(5)	0.1122
C(40)	0.5876(6)	0.5624(4)	0.1456(6)	0.0866	C(90)	0.9178(7)	1.0359(4)	0.3352(6)	0.1043
C(41)	0.6083(5)	0.5131(6)	0.1968(5)	0.0729	C(91)	0.9168(6)	0.9785(7)	0.2877(4)	0.0888
C(42)	0.6050(5)	0.4352(5)	0.1865(4)	0.0687	C(92)	0.9209(5)	0.9031(6)	0.3080(4)	0.0705

[a] Estimated standard deviations in the least significant digits are given in parentheses. [b] $U(\mathrm{eq}) = [U(11) \cdot U(22) \cdot U(33)]^{1/3}$.

sites, while the equatorial positions are occupied by two *cis*-hydrazido(2−) ligands and two *cis*-chloro ligands. This arrangement appears to maximize π-bonding interactions. Again, the structural features of the [organohydrazido(2−)]molybdenum moieties fall in the usual ranges.[8,10,25] However, a small increase in the Mo-N distances, a concomitant decrease in the N−N distances, and a somewhat larger departure from linearity are observed in octahedral [Mo(NNMePh)$_2$Cl$_2$(PPh$_3$)$_2$] compared to trigonal bipyramidal [Mo(NNPh$_2$)$_2$Cl$_2$(PPh$_3$)]. Thus, complex **4** achieves a 20-electron count. As a simple molecular orbital scheme might account for the accommodation of the 20 electrons,[10] the unstability of complex **4** toward dissociation probably reflects steric rather than electronic strain.

Spectroscopic Studies. Complexes **3**−**11** have been studied by IR, UV−visible, ^{1}H, and ^{31}P NMR spectroscopy. As a rule, the IR spectra exhibit a strong and sharp band in the 1600−1590 cm^{-1} region, which is tentatively attributed to the ν(NN) stretching mode of the hydrazido(2−) ligands,[10,18,27,34] and a strong band at *ca.* 1495 cm^{-1} assigned to a ν(CC) mode of the phenyl groups. The weak band at *ca.* 3255 cm^{-1} characteristic of the ν(NH) stretching mode of the PhRNNH(1−) ligands[29] and the strong band at *ca.* 1570 cm^{-1} due to the chelated acetylacetonate ligand[29,35] are notably absent from the IR spectra of complexes **3**−**11**.

The UV−visible spectra of complexes **3**−**11** in CH$_2$Cl$_2$ solutions show, in general, four absorption bands between 220 and 480 nm. The highest-energy band can be attributed to an internal transition within the phenyl groups, while the other arise from the [Mo(NNRPh)$_2$]$^{2+}$ chromophore.[13,14,21]

^{1}H and ^{31}P solution NMR studies of complexes **3**−**11** have been undertaken to obtain information about their stereochemistry and stability. From the solid-state studies of complexes **3** and **4**·0.5CH$_2$Cl$_2$, it was anticipated that complexes **3** and **11** should possess distorted trigonal bipyramidal geometry in solution, while complexes **4**−**8** should display distorted octa-

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Table 3. Atomic Positional[a] and Temperature Factors[b] for $[Mo(NNMePh)_2Cl_2(PPh_3)_2]\cdot 0.5CH_2Cl_2$

atom	*x*/*a*	*y*/*b*	*z*/*c*	*U*(eq), Å^2	atom	*x*/*a*	*y*/*b*	*z*/*c*	*U*(eq), Å^2
Mo(1)	0.3101(1)	0.41442(9)	0.28882(6)	0.0377	P(52)	0.0689(4)	−0.0132(3)	0.3050(2)	0.0472
Cl(1)	0.2142(3)	0.3640(3)	0.2360(2)	0.0545	N(51)	0.1602(9)	−0.0837(8)	0.1807(5)	0.0358
Cl(2)	0.1907(3)	0.5663(3)	0.2438(2)	0.0503	N(52)	0.163(1)	−0.1538(9)	0.1623(6)	0.0448
P(1)	0.1687(3)	0.4448(3)	0.3778(2)	0.0442	N(61)	0.117(1)	0.0984(9)	0.1867(5)	0.0462
P(2)	0.4409(3)	0.3942(3)	0.1955(2)	0.0423	N(62)	0.067(1)	0.1853(9)	0.1789(6)	0.0449
N(1)	0.3743(9)	0.4681(8)	0.3134(5)	0.0390	C(51)	0.0793(9)	−0.1422(9)	0.1343(5)	0.0460
N(2)	0.412(1)	0.5198(9)	0.3258(6)	0.0512	C(52)	0.088(1)	−0.2107(7)	0.1063(6)	0.0654
N(11)	0.372(1)	0.2988(8)	0.3216(5)	0.0356	C(53)	0.009(1)	−0.199(1)	0.0766(5)	0.0730
N(12)	0.395(1)	0.2140(9)	0.3417(6)	0.0462	C(54)	−0.079(1)	−0.118(1)	0.0750(5)	0.0759
C(1)	0.480(1)	0.485(1)	0.3690(5)	0.0560	C(55)	−0.0880(8)	−0.0492(9)	0.1030(6)	0.0755
C(2)	0.496(1)	0.3993(9)	0.3983(7)	0.0741	C(56)	−0.009(1)	−0.0614(7)	0.1326(5)	0.0559
C(3)	0.560(1)	0.363(1)	0.4417(1)	0.1041	C(57)	0.256(1)	−0.240(1)	0.1647(8)	0.0551
C(4)	0.606(1)	0.412(2)	0.4557(6)	0.1192	C(58)	−0.0093(8)	0.2216(9)	0.1406(5)	0.0466
C(5)	0.590(1)	0.498(2)	0.4264(8)	0.0966	C(59)	−0.018(1)	0.1664(7)	0.1075(6)	0.0617
C(6)	0.526(1)	0.5350(9)	0.3831(8)	0.0881	C(60)	−0.094(1)	0.202(1)	0.0711(6)	0.0763
C(7)	0.384(2)	0.614(1)	0.2953(9)	0.0658	C(61)	−0.161(1)	0.293(1)	0.0678(6)	0.0961
C(8)	0.4868(8)	0.1636(7)	0.3696(5)	0.0423	C(62)	−0.153(1)	0.3477(8)	0.1008(7)	0.0911
C(9)	0.494(1)	0.0859(8)	0.4081(6)	0.0733	C(63)	−0.077(1)	0.3122(8)	0.1372(6)	0.0764
C(10)	0.581(1)	0.0371(7)	0.4361(5)	0.0717	C(64)	0.085(1)	0.243(1)	0.2121(8)	0.0524
C(11)	0.6615(9)	0.0660(9)	0.4256(6)	0.0699	C(65)	0.3095(9)	0.1013(6)	0.0867(5)	0.0408
C(12)	0.6545(9)	0.144(1)	0.3871(6)	0.0732	C(66)	0.289(1)	0.1274(9)	0.0298(5)	0.0700
C(13)	0.567(1)	0.1924(7)	0.3591(5)	0.0591	C(67)	0.266(1)	0.216(1)	0.0042(5)	0.0804
C(14)	0.325(1)	0.172(1)	0.3374(9)	0.0579	C(68)	0.263(1)	0.2790(6)	0.0353(7)	0.0810
C(15)	0.184(1)	0.3476(7)	0.4346(4)	0.0472	C(69)	0.283(1)	0.2529(8)	0.0922(6)	0.0735
C(16)	0.1017(8)	0.3229(9)	0.4604(6)	0.0618	C(70)	0.3067(9)	0.1640(9)	0.1179(4)	0.0443
C(17)	0.116(1)	0.253(1)	0.5063(6)	0.0909	C(71)	0.4722(7)	−0.0592(8)	0.1329(5)	0.0439
C(18)	0.212(1)	0.2078(8)	0.5264(5)	0.0794	C(72)	0.534(1)	−0.0119(7)	0.1080(5)	0.0504
C(19)	0.294(1)	0.2325(8)	0.5006(6)	0.0772	C(73)	0.6385(9)	−0.0494(9)	0.1152(6)	0.0646
C(20)	0.2796(9)	0.3024(9)	0.4547(6)	0.0611	C(74)	0.6812(7)	−0.134(1)	0.1473(6)	0.0791
C(21)	0.1691(9)	0.5290(7)	0.4168(5)	0.0459	C(75)	0.619(1)	−0.1814(8)	0.1722(6)	0.0932
C(22)	0.1726(9)	0.6088(8)	0.3852(4)	0.0542	C(76)	0.515(1)	−0.1440(8)	0.1650(6)	0.0720
C(23)	0.175(1)	0.6729(6)	0.4131(6)	0.0639	C(77)	0.339(1)	−0.0751(7)	0.0661(4)	0.0489
C(24)	0.1739(9)	0.6573(8)	0.4727(6)	0.0639	C(78)	0.2438(8)	−0.0609(7)	0.0515(5)	0.0549
C(25)	0.1704(9)	0.578(1)	0.5044(4)	0.0618	C(79)	0.241(1)	−0.1040(9)	0.0084(6)	0.0597
C(26)	0.1680(9)	0.5134(7)	0.4764(5)	0.0568	C(80)	0.334(1)	−0.1615(9)	−0.0200(5)	0.0765
C(27)	0.0335(7)	0.4878(8)	0.3653(5)	0.0531	C(81)	0.429(1)	−0.1757(8)	−0.0053(5)	0.0740
C(28)	−0.041(1)	0.5691(8)	0.3819(5)	0.0512	C(82)	0.4311(8)	−0.1325(8)	0.0377(6)	0.0547
C(29)	−0.1428(9)	0.5999(8)	0.3706(6)	0.0740	C(83)	−0.0102(9)	−0.0736(8)	0.3030(5)	0.0480
C(30)	−0.1695(8)	0.549(1)	0.3427(6)	0.0747	C(84)	0.0438(7)	−0.1609(8)	0.2895(5)	0.0482
C(31)	−0.095(1)	0.468(1)	0.3261(6)	0.0796	C(85)	−0.010(1)	−0.2115(6)	0.2864(5)	0.0607
C(32)	0.007(1)	0.4372(7)	0.3374(6)	0.0713	C(86)	−0.118(1)	−0.1747(9)	0.2969(6)	0.0768
C(33)	0.402(1)	0.4240(8)	0.1235(4)	0.0497	C(87)	−0.1725(7)	−0.087(1)	0.3105(6)	0.0684
C(34)	0.4764(8)	0.3898(8)	0.0772(6)	0.0610	C(88)	−0.1183(9)	−0.0368(6)	0.3135(5)	0.0635
C(35)	0.450(1)	0.4157(9)	0.0214(5)	0.0760	C(89)	0.109(1)	−0.0562(8)	0.3773(4)	0.0566
C(36)	0.350(1)	0.476(1)	0.0120(4)	0.0750	C(90)	0.0420(9)	−0.0807(8)	0.4221(7)	0.0620
C(37)	0.2753(9)	0.5098(9)	0.0583(7)	0.0878	C(91)	0.068(1)	−0.1079(9)	0.4779(5)	0.0732
C(38)	0.3013(9)	0.4839(9)	0.1141(5)	0.0658	C(92)	0.160(2)	−0.111(1)	0.4890(5)	0.0910
C(39)	0.5322(9)	0.2746(6)	0.1953(5)	0.0441	C(93)	0.227(1)	−0.086(1)	0.4443(7)	0.0928
C(40)	0.640(1)	0.2467(9)	0.1843(5)	0.0609	C(94)	0.201(1)	−0.059(1)	0.3885(6)	0.0868
C(41)	0.7040(7)	0.155(1)	0.1862(6)	0.0695	C(95)	−0.0263(9)	0.1032(6)	0.3140(6)	0.0552
C(42)	0.661(1)	0.0919(6)	0.1991(6)	0.0684	C(96)	−0.099(1)	0.1492(9)	0.2757(5)	0.0520
C(43)	0.553(1)	0.1198(7)	0.2100(5)	0.0599	C(97)	−0.1711(9)	0.2366(9)	0.2820(6)	0.0673
C(44)	0.4890(7)	0.2112(9)	0.2082(5)	0.0515	C(98)	−0.171(1)	0.2781(6)	0.3265(7)	0.0711
C(45)	0.5205(9)	0.4580(8)	0.1897(6)	0.0469	C(99)	−0.098(1)	0.232(1)	0.3648(5)	0.0759
C(46)	0.588(1)	0.4340(7)	0.2299(5)	0.0537	C(100)	−0.026(1)	0.1446(9)	0.3585(5)	0.0728
C(47)	0.6462(9)	0.484(1)	0.2273(6)	0.0697	C(200)[c]	0.993(3)	0.561(2)	0.177(2)	0.06(1)[e]
C(48)	0.637(1)	0.557(1)	0.1845(7)	0.0821	Cl(201)[c]	0.997(2)	0.524(1)	0.119(1)	0.208(8)[e]
C(49)	0.569(1)	0.5813(8)	0.1443(6)	0.0840	Cl(202)[c]	0.889(1)	0.650(1)	0.1943(7)	0.148(6)[e]
C(50)	0.511(1)	0.5316(9)	0.1469(5)	0.0638	Cl(300)[c]	0.502(3)	0.842(3)	0.335(2)	0.08(1)[e]
Mo(51)	0.2007(1)	−0.01758(9)	0.21279(6)	0.0394	Cl(301)[c]	0.566(2)	0.895(1)	0.3387(9)	0.176(7)[e]
Cl(51)	0.2984(4)	0.0397(3)	0.2572(2)	0.0589	Cl(302)[d]	0.595(2)	0.744(2)	0.328(1)	0.102(8)[e]
Cl(52)	0.3150(4)	−0.1639(3)	0.2672(2)	0.0595	Cl(303)[d]	0.515(2)	0.760(2)	0.391(1)	0.113(8)[e]
P(51)	0.3363(3)	−0.0144(3)	0.1235(2)	0.0453					

[a] Estimated standard deviations in the least significant digits are given in parentheses. [b] U(eq) = $[U(11)\cdot U(22)\cdot U(33)]^{1/3}$. [c] Occupancy factor 0.5. [d] Occupancy factor 0.25. [e] U(iso).

hedral geometry with *trans*-phosphine ligands. Then, a virtual triplet[27,36,37] was expected for the ^{1}H NMR spectra of complexes **5** and **6**, which contain *trans*-$PMePh_2$ ligands, and those of complexes **7** and **8**, which contain PMe_2Ph ligands. Indeed, the spectrum of complex **5** exhibits a pseudotriplet centered at 2.38 ppm but also two doublets at 2.20 and 1.63 ppm, which indicates partial dissociation of **5** into $PMePh_2$ and a five-coordinated species. On the other hand, that of complex **6** shows two virtual triplets, in relative intensities 4:1, centered at 2.37 and 2.31 ppm, which are assigned to the methyl proton resonances of the phosphines, and three singlets at 3.21, 3.19, and 3.02 ppm, which arise from the methyl proton resonances of the hydrazido ligands. The signals at 3.19 and 2.37 ppm

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(36) Crabtree, R. H. *Organometallic Chemistry of the Transition Metals*; Wiley: New York, 1988; pp 212−217.

(37) Ali, H. M.; Leigh, G. J. *J. Chem. Soc., Dalton Trans.* **1986**, 213.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for [Mo(NNPh$_2$)$_2$Cl$_2$(PPh$_3$)]

Mo(1)−Cl(1)	2.448(4)	Mo(51)−Cl(51)	2.454(4)
Mo(1)−Cl(2)	2.384(3)	Mo(51)−Cl(52)	2.383(3)
Mo(1)−P(1)	2.526(4)	Mo(51)−P(51)	2.537(4)
Mo(1)−N(1)	1.76(1)	Mo(51)−N(51)	1.75(1)
Mo(1)−N(11)	1.76(1)	Mo(51)−N(61)	1.75(1)
P(1)−C(25)	1.820(6)	P(51)−C(87)	1.840(7)
P(1)−C(31)	1.824(8)	P(51)−C(75)	1.827(6)
P(1)−C(37)	1.840(8)	P(51)−C(81)	1.825(7)
N(1)−N(2)	1.33(1)	N(51)−N(52)	1.33(1)
N(2)−C(1)	1.43(1)	N(52)−C(51)	1.41(1)
N(2)−C(7)	1.41(1)	N(52)−C(57)	1.44(1)
N(11)−N(12)	1.30(1)	N(61)−N(62)	1.34(1)
N(12)−C(13)	1.45(1)	N(62)−C(63)	1.43(1)
N(12)−C(19)	1.45(1)	N(62)−C(69)	1.41(1)
Cl(2)−Mo(1)−Cl(1)	83.9(1)	Cl(52)−Mo(51)−Cl(51)	84.5(1)
P(1)−Mo(1)−Cl(1)	161.3(1)	P(51)−Mo(51)−Cl(51)	166.5(1)
P(1)−Mo(1)−Cl(2)	83.4(1)	P(51)−Mo(51)−Cl(52)	82.3(1)
N(1)−Mo(1)−Cl(1)	92.5(3)	N(51)−Mo(51)−Cl(51)	91.0(3)
N(1)−Mo(1)−Cl(2)	125.0(3)	N(51)−Mo(51)−Cl(52)	122.6(3)
N(1)−Mo(1)−P(1)	90.7(3)	N(51)−Mo(51)−P(51)	93.6(3)
N(11)−Mo(1)−Cl(1)	96.4(3)	N(61)−Mo(51)−Cl(51)	96.4(3)
N(11)−Mo(1)−Cl(2)	119.7(3)	N(61)−Mo(51)−Cl(52)	122.1(3)
N(11)−Mo(1)−P(1)	94.3(3)	N(61)−Mo(51)−P(51)	93.0(3)
N(11)−Mo(1)−N(1)	115.2(4)	N(61)−Mo(51)−N(51)	115.3(4)
N(2)−N(1)−Mo(1)	176.8(8)	N(52)−N(51)−Mo(51)	172.7(8)
C(1)−N(2)−N(1)	120.6(10)	C(51)−N(52)−N(51)	121.2(9)
C(7)−N(2)−N(1)	115.6(10)	C(57)−N(52)−N(51)	117.2(9)
C(7)−N(2)−C(1)	123.6(9)	C(57)−N(52)−C(51)	121.6(9)
N(12)−N(11)−Mo(1)	172.9(9)	N(62)−N(61)−Mo(51)	169.3(8)
C(13)−N(12)−N(11)	119.8(10)	C(63)−N(62)−N(61)	118.2(9)
C(19)−N(12)−N(11)	120.2(9)	C(69)−N(62)−N(61)	118.6(9)
C(19)−N(12)−C(13)	119.5(9)	C(69)−N(62)−C(63)	123.0(9)

Table 5. Selected Bond Lengths (Å) and Angles (deg) for [Mo(NNMePh)$_2$Cl$_2$(PPh$_3$)$_2$]·0.5CH$_2$Cl$_2$

Mo(1)−Cl(1)	2.532(5)	Mo(51)−Cl(51)	2.500(5)
Mo(1)−Cl(2)	2.519(4)	Mo(51)−Cl(52)	2.529(5)
Mo(1)−P(1)	2.575(5)	Mo(51)−P(51)	2.570(5)
Mo(1)−P(2)	2.568(5)	Mo(51)−P(52)	2.570(5)
Mo(1)−N(1)	1.78(1)	Mo(51)−N(51)	1.80(1)
Mo(1)−N(11)	1.81(1)	Mo(51)−N(61)	1.83(1)
P(1)−C(15)	1.84(1)	P(51)−C(65)	1.84(1)
P(1)−C(21)	1.844(9)	P(51)−C(71)	1.813(9)
P(1)−C(27)	1.83(1)	P(51)−C(77)	1.858(9)
P(2)−C(33)	1.83(1)	P(52)−C(83)	1.83(1)
P(2)−C(39)	1.848(9)	P(52)−C(89)	1.83(1)
P(2)−C(45)	1.83(1)	P(52)−C(95)	1.85(1)
N(1)−N(2)	1.30(2)	N(51)−N(52)	1.31(2)
N(2)−C(1)	1.43(2)	N(52)−C(51)	1.42(2)
N(2)−C(7)	1.50(2)	N(52)−C(57)	1.48(2)
N(11)−N(12)	1.30(2)	N(61)−N(62)	1.30(2)
N(12)−C(8)	1.44(2)	N(62)−C(58)	1.43(2)
N(12)−C(14)	1.48(2)	N(62)−C(64)	1.50(2)
Cl(2)−Mo(1)−Cl(1)	80.7(1)	Cl(52)−Mo(51)−Cl(51)	80.3(2)
P(1)−Mo(1)−Cl(1)	94.2(2)	P(51)−Mo(51)−Cl(51)	83.5(2)
P(1)−Mo(1)−Cl(2)	84.6(1)	P(51)−Mo(51)−Cl(52)	96.9(2)
P(2)−Mo(1)−Cl(1)	84.0(2)	P(52)−Mo(51)−Cl(51)	92.5(2)
P(2)−Mo(1)−Cl(2)	91.1(1)	P(52)−Mo(51)−Cl(52)	83.6(2)
P(2)−Mo(1)−P(1)	175.6(2)	P(52)−Mo(51)−P(51)	175.8(2)
N(1)−Mo(1)−Cl(1)	168.0(4)	N(51)−Mo(51)−Cl(51)	165.7(4)
N(1)−Mo(1)−Cl(2)	89.3(4)	N(51)−Mo(51)−Cl(52)	87.5(4)
N(1)−Mo(1)−P(1)	91.5(4)	N(51)−Mo(51)−P(51)	90.6(4)
N(1)−Mo(1)−P(2)	89.5(4)	N(51)−Mo(51)−P(52)	93.6(4)
N(11)−Mo(1)−Cl(1)	88.7(4)	N(61)−Mo(51)−Cl(51)	89.8(4)
N(11)−Mo(1)−Cl(2)	167.5(4)	N(61)−Mo(51)−Cl(52)	167.9(4)
N(11)−Mo(1)−P(1)	89.7(4)	N(61)−Mo(51)−P(51)	89.0(4)
N(11)−Mo(1)−P(2)	94.3(4)	N(61)−Mo(51)−P(52)	89.8(4)
N(11)−Mo(1)−N(1)	102.0(6)	N(61)−Mo(51)−N(51)	103.1(6)
N(2)−N(1)−Mo(1)	170.2(11)	N(52)−N(51)−Mo(51)	159.4(11)
C(1)−N(2)−N(1)	119.4(13)	C(51)−N(52)−N(51)	118.5(12)
C(7)−N(2)−N(1)	119.9(15)	C(57)−N(52)−N(51)	120.6(13)
C(7)−N(2)−C(1)	120.7(14)	C(57)−N(52)−C(51)	120.6(13)
N(12)−N(11)−Mo(1)	163.9(11)	N(62)−N(61)−Mo(51)	164.7(12)
C(8)−N(12)−N(11)	118.4(13)	C(58)−N(62)−N(61)	116.9(13)
C(14)−N(12)−N(11)	120.4(14)	C(64)−N(62)−N(61)	120.6(14)
C(14)−N(12)−C(8)	121.1(13)	C(64)−N(62)−C(58)	122.4(13)

have the same integrated intensity, while the sum of the intensities of the signals at 3.21 and 3.02 equals the intensity of the signal at 2.31 ppm. This is consistent with a 4:1 mixture of two isomers A and B, which respectively display equivalent and inequivalent hydrazido-methyl groups. Actually there are two possible isomers A and A′ with equivalent hydrazido ligands (see Chart 1); it is noteworthy that arrangement A (outer methyl groups) is found in the solid-state structure of **4**, rather than the alternate arrangement A′ (inner methyl groups). The spectra of complexes **7** and **8** exhibit a pseudotriplet centered at 1.92 and 1.83 ppm, respectively, arising from the *trans*-PMe$_2$Ph ligands, and in the case of **8** a singlet at 3.70 ppm, attributed to the methyl proton resonance of the equivalent hydrazido ligands, indicating that a single isomer is present. The spectra of complexes **4** and **11** show a singlet at the same position, which is in agreement with the transformation of **4** into **11** (see below). The spectra of complexes **9** and **10** exhibit in the 3.60−2.15 ppm range an asymmetrical multiplet due to the nonequivalent methylene groups of the coordinated dppe ligand. In addition, that of **10** shows also a singlet at 3.54 ppm corresponding to the methyl proton resonance of the hydrazido ligands and a weak singlet at 4.14 ppm attributed to a minor isomer (see below). In addition, the ^{1}H NMR spectra of all complexes show a complex multiplet in the 7.94−6.60 ppm range, corresponding to the phenyl proton resonances of the hydrazido(2−) and phosphine ligands.

As expected, the ^{31}P{^{1}H} NMR spectra of **3** and **11** exhibit a singlet at 36.98 and 38.05 ppm, respectively. The spectra of complexes **7** and **8** also show a single resonance at 1.24 and 1.44 ppm, respectively, indicating the equivalence of the *trans*-phosphine ligands. However, the behavior of complexes **4**−**6** is less simple. The spectrum of **4** exhibits two signals with equal intensities at 38.02 and −6.19 ppm; the latter can be unambiguously assigned to free triphenylphosphine, which indicates that **4** undergoes complete dissociation to give **11** and PPh$_3$. The spectrum of complex **5** shows three singlets in different intensities, indicating partial dissociation (*ca.* 12%) in CDCl$_3$; the more intense singlet at 13.05 ppm corresponds to the nondissociated species **5**, while the other two, with equal intensities, at 25.89 and −27.60 ppm are assigned to a five-coordinated complex similar to **3** and **11** and to free PMePh$_2$, respectively. This is in agreement with the ^{1}H NMR data (see above). The spectrum of complex **6** two singlets at 14.17 and 13.92 ppm in 1:2.8 ratio, which are assigned to isomers. Finally, the spectra of **9** and **10** display two doublets centered at 38.35 and 3.60 ppm with $^2J_{\mathrm{P-P}} = 28.0$ Hz for the former and 42.62 and 9.35 ppm with $^2J_{\mathrm{P-P}} = 35.0$ Hz for the latter, indicating unsymmetrical coordination of the dppe ligand.[37] Additionally, complex **10** shows two supplementary doublets of low intensity at 37.78 and 1.06 ppm, $^2J_{\mathrm{P-P}} = 19.8$ Hz, attributed to a minor isomer.

Electrochemical Studies. Cyclic voltammetry (CV) studies of complexes **3**−**11** were carried out in CH$_2$Cl$_2$ at a platinum electrode at scan rates varying from 10 to 300 mV s^{-1}. The CV data are summarized in Table 6. The number of electrons transferred in the various steps was estimated to be 1 by comparison to the ferrocene oxidation under the same experimental conditions. The five-coordinated complexes **3** and **11** show an oxidation peak at +1.09 and +1.01 V, respectively, associated with a weak reduction peak at *ca.* +0.5 and +0.1 V, respectively. On the other hand, they display a reduction peak at −1.80 and −1.51 V, respectively, associated with a weak oxidation peak at *ca.* −0.2 V. This indicates that both oxidation and reduction processes are irreversible, the oxidized species,

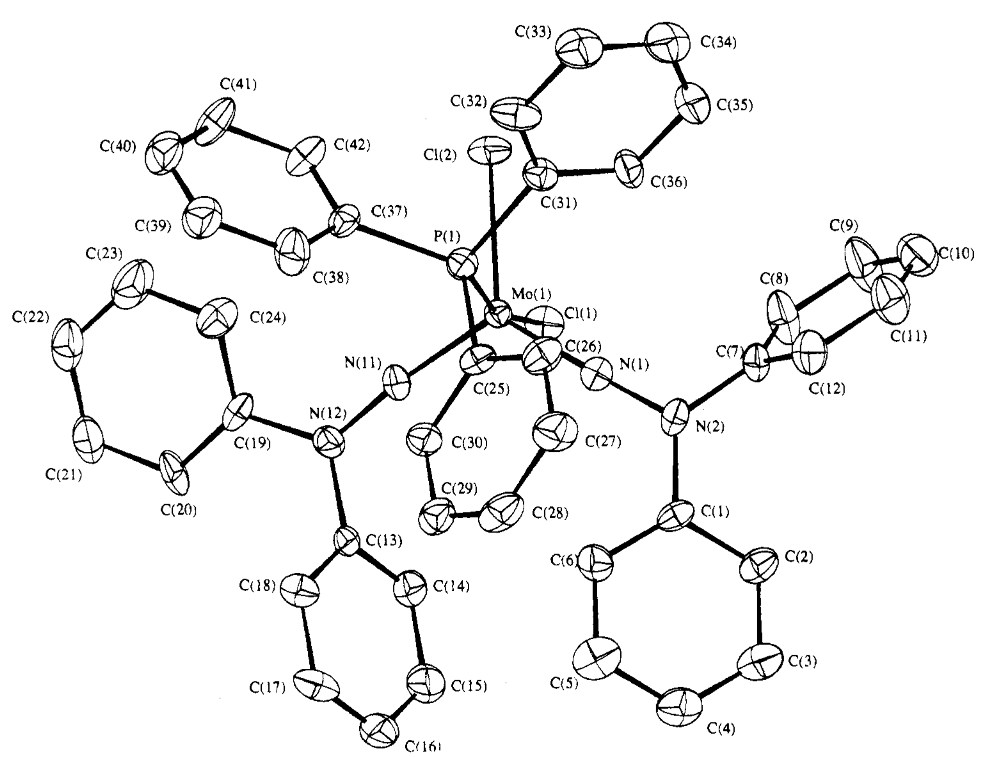

Figure 1. View of the molecular structure of one of the independent molecules of [Mo(NNPh$_2$)Cl$_2$(PPh$_3$)] in **3**, with the atom-labeling scheme. (Chemically equivalent atoms in the independent molecules are labeled X$_n$ and X$_{50+n}$, respectively.)

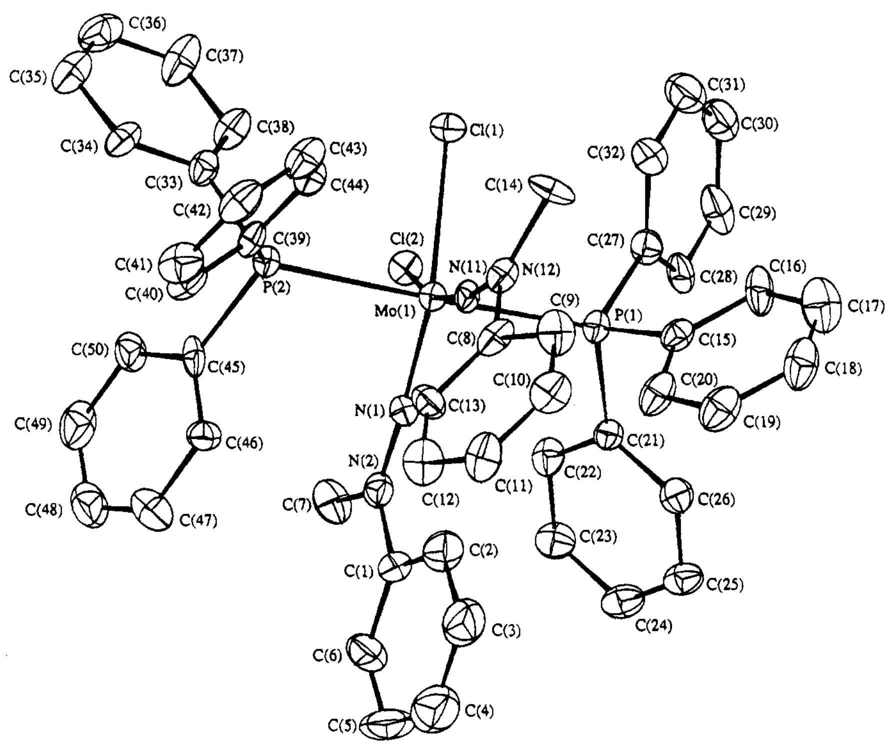

Figure 2. View of the molecular structure of one of the independent molecules of [Mo(NNMePh)Cl$_2$(PPh$_3$)$_2$] in **4**·0.5CH$_2$Cl$_2$, with the atom-labeling scheme. (Chemically equivalent atoms in the independent molecules are labeled X$_n$ and X$_{50+n}$, respectively.)

[Mo(NNRPh)$_2$(PPh$_3$)Cl$_2$]$^+$, and the reduced species, [Mo(NNRPh)$_2$(PPh$_3$)Cl$_2$]$^-$, being unstable in solution. The electrochemical behavior of **4** is more complicated due to the presence of **11** and free PPh$_3$ in solution. The six-coordinated complexes **5**–**8** exhibit a nearly-reversible one-electron oxidation process at *ca.* +0.87 V (ΔE_p = 120 mV at 100 mV s^{-1}) and an irreversible one-electron reduction process in the −1.42 to −1.72 V range. Finally, the oxidation and reduction processes of complexes **9** and **10** are also irreversible; however, the dppe ligand shifts the oxidation and the reduction potentials to more positive and more negative values, respectively. In the broad lines, the electrochemical behavior of complexes **3** and **5**–**11** is similar to that of [organohydrazido(2−)]molybdenum complexes containing dithiocarbamate[38] and acetylacetonate[13] ancillary ligands.

Conclusion. Mixed [organohydrazido(1−)][organohydrazido(2−)]molybdenum complexes [(MoNHNRPh)(NNRPh)(acac)-

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[38] Crichton, B. A. L.; Dilworth, J. R.; Pickett, C. J.; Chatt, J. *J. Chem. Soc., Dalton Trans.* **1981**, 419.

Scheme 1

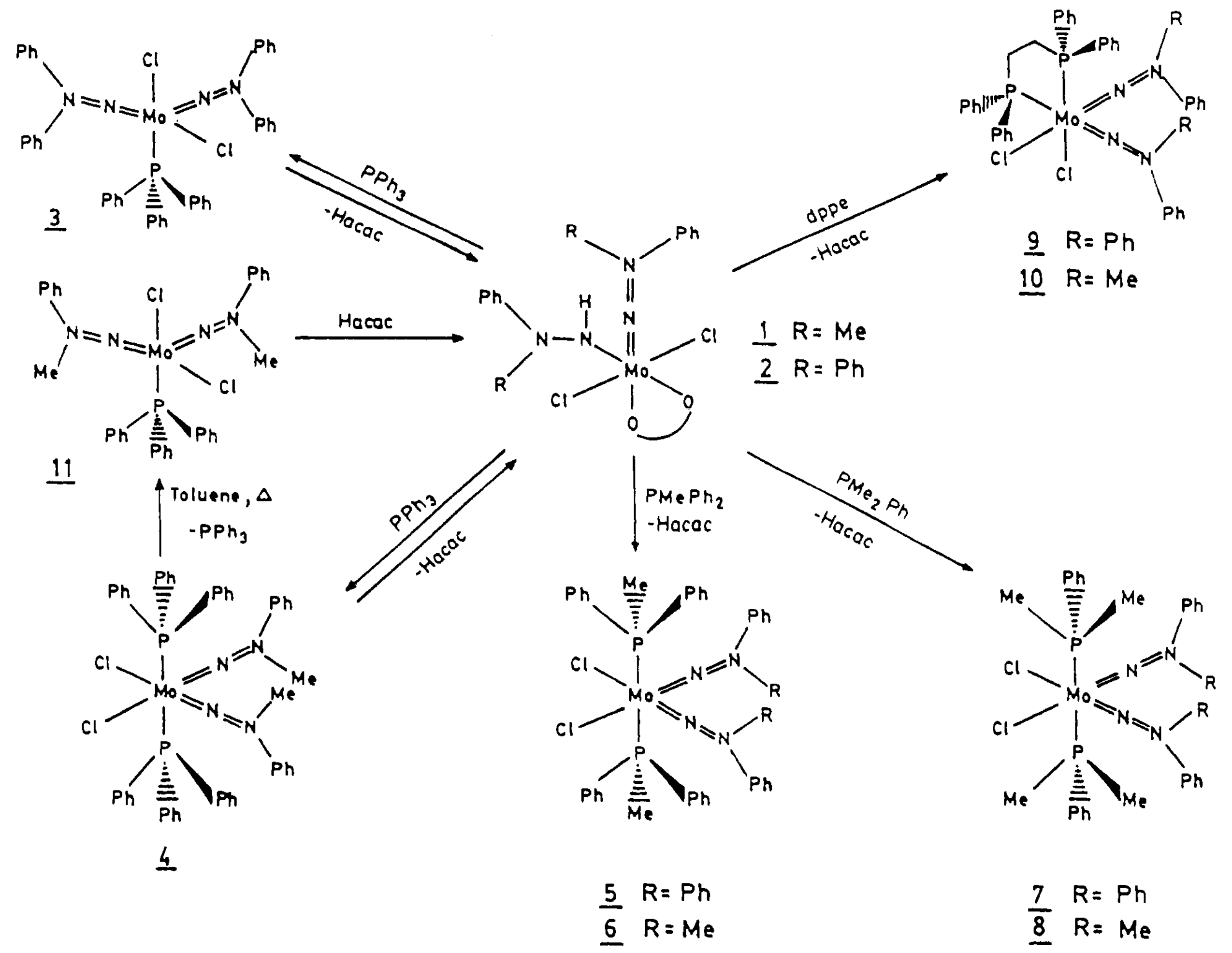

Chart 1

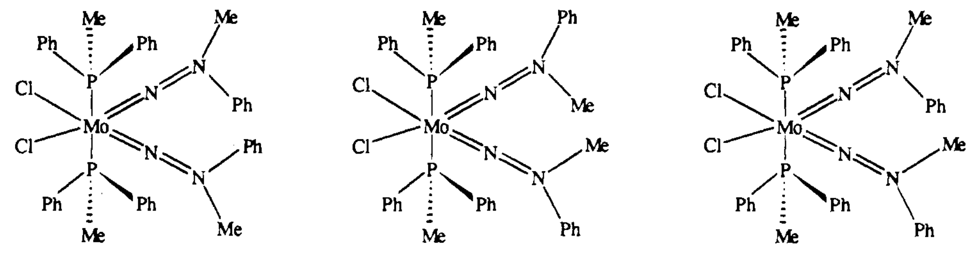
A A' B

Table 6. Cyclic Voltammetric Data (V *vs* SCE) in CH_2Cl_2 Solution

complex	E_p, V redn	E_p, V oxidn
3	−1.80	1.09
5	−1.42	0.93
6	−1.62	0.86
7	−1.44	0.83
8	−1.72	0.86
9	−1.71	1.37
10	−1.77	1.31
11	−1.51	1.01

Cl_2] (R = Me, Ph) have proved to be suitable precursors in the synthesis of a number of five- and six-coordinated bis[organohydrazido(2−)]molybdenum complexes containing ancillary tertiary phosphine ligands. The product stoichiometry appears to be dictated mainly by steric effects. The five-coordinated complexes and the most strained six-coordinated complex react with acetylacetone, giving back the precursors. These results demonstrate the reversible behavior of the [Mo(NHNRPh)(NNRPh)]$^{3+}$/[Mo(NNRPh)$_2$]$^{2+}$ couple.

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Supplementary Material Available: Tables giving crystal data, anisotropic thermal parameters, and bond lengths and bond angles for compounds **3** and **4**·0.5CH_2Cl_2 (7 pages). Ordering information is given on any current masthead page.