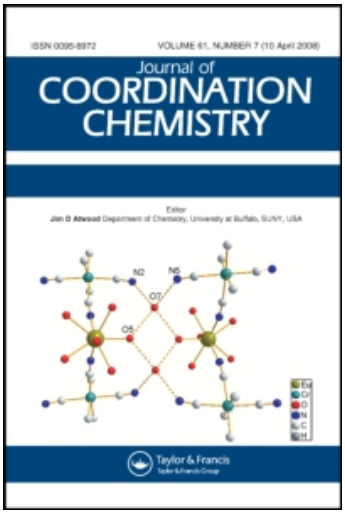

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Reactivity of organohydrazidomolybdenum(VI) complexes toward tertiary phosphines

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The reactivity of mixed [organohydrazido(1-)][organohydrazido(2-)]molybdenum(VI) complexes $[Mo(NHNRPh)(NNRPh)(acac)X_2]$ {R = Ph, X = Br (**1**); R = Ph, X = I (**2**) and R = Me; X = I (**3**)} with the tertiary phosphines PPh_3, $[PMePh_2$ and PMe_2Ph has been investigated. The syntheses of $[Mo(NNPh_2)_2Br_2(PPh_3)]$ (**4**), $[Mo(NNPh_2)_2Br_2(PMePh_2)_2]$ (**5**), $[Mo(NNPh_2)_2Br_2(PMe_2Ph)_2]$ (**6**), $[Mo(NNPh_2)_2(acac)I(PPh_3)]$ (**7**), $[Mo(NNPh_2)_2(acac)(PMePh_2)_2]^+I^-$ (**8**) and $[Mo(NNMePh)_2(acac)(PMePh_2)_2]^+I^-$ (**9**) are reported. Complexes were characterized by analysis, and electronic, IR, ^1H and $^{31}P\{H\}$ NMR spectroscopy.

Keywords: Molybdenum complexes; Phosphine derivatives; Hydrazido(2-) complexes

1. 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 H_2NN^{2-} species as an intermediate [1, 2]. The most commonly employed synthesis methods involve protonation and alkylation of organodiazenido complexes, the reaction of a metal halide with either asymmetrically disubstituted hydrazine, $RR'NNH_2$ or a trimethylsilyl derivative, $Me_3SiNHNRR'$, or a condensation of asymmetrically disubstituted hydrazines with oxometal complexes, especially oxomolybdenum complexes [2, 3]. Many complexes containing the *cis*-$[MoO(NNRR')]^{2+}$ and *cis*-$[Mo(NNRR')_2]^{2+}$ moieties have been synthesized and some 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) [4], (O,S) [5], (S,S) [5–9], (N,N) [9, 10], and (O,O) [11] chelated ligands,

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while the *cis*-$[MoO(NNRR')]^{2+}$ unit is found in a number of mononuclear complexes, containing monodentate thiolate [11, 12] or (O,O) [5, 13, 15], (O,S) [6], (S,S) [15], (N,O) [16], (N,S) [4], (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-derivative polyoxomolybdates [21–23] have also been described. The $[Mo(NNRR')]^{4+}$ moiety is also known [17, 24]. Although most of the structurally characterized complexes of NNH_2^{2-} contain phosphines, there have been comparatively few studies of [organohydrazido(2-)]molybdenum complexes containing phosphines as ancillary ligands [7, 9, 25–29]. This report deals with the reactivity of mixed [organohydrazido(1-)][organohydrazido(2-)]molybdenum(VI) complexes with tertiary phosphines. The syntheses and spectroscopic characterization of $[Mo(NNPh_2)_2Br_2(PPh_3)]$ (**4**), $[Mo(NNPh_2)_2Br_2(PMePh_2)_2]$ (**5**), $[Mo(NNPh_2)_2Br_2(PMe_2Ph)_2]$ (**6**), $[Mo(NNPh_2)_2(acac)I(PPh_3)]$ (**7**), $[Mo(NNPh_2)_2(acac)(PMePh_2)_2]^+I^-$ (**8**) and $[Mo(NNMePh)_2(acac)(PMePh_2)_2]^+I^-$ (**9**), obtained by the reaction of [Mo(NHNRPh (NNRPh)(acac)X_2] {R = Ph, X = Br (**1**); R = Ph, X = I (**2**) and R = Me; X = I (**3**)} with the appropriate phosphine (PPh_3, $PMePh_2$ and PMe_2Ph) are reported.

2. Experimental

Acetylacetone, 1-methyl-1-phenylhydrazine, 1,1-diphenylhydrazine hydrochloride, triphenylphosphine, methyldiphenylphosphine, dimethylphenylphosphine, $Na_2MoO_4 \cdot 2H_2O$, concentrated solutions of HBr, HI and reagent grade solvents were obtained from commercial sources and used without further purification. Precursor complexes $[Mo(NHNPh_2)(NNPh_2)(acac)Br_2]$ (**1**), $[Mo(NHNPh_2)(NNPh_2)(acac)I_2]$ (**2**) and [Mo(NHNMePh)(NNMePh)(acac)I_2] (**3**) were obtained as previously described [30]. All reactions were performed under an N_2 atmosphere using Schlenk techniques.

Melting points were determined using a Kofler apparatus. Microanalytical data were obtained on a Perkin-Elmer Model 2400 system. Magnetic properties were recorded in the solid state using $[HgCo(CN)_4]$ as reference on a Faraday Cahn Ventron RTL balance (6000 Gauss). IR spectra were recorded on a Perkin Elmer 599 spectrophotometer (KBr discs) and electronic spectra (1.0×10^{-5} M dichloromethane solutions) on a Hewlett Packard 8452A spectrophotometer. ^1H and ^{31}P NMR were recorded in $CDCl_3$ solutions on a Bruker AC-200P spectrometer at room temperature using TMS and H_3PO_4 as internal and external standards, respectively.

2.1. *Dibromobis{diphenylhydrazido(2-)}(triphenylphosphine)molybdenum(VI), $[Mo(NNPh_2)_2Br_2(PPh_3)]$ (4)*

To a Schlenk tube containing 6 cm^3 of acetonitrile, 0.17 g (0.64 mmol) of PPh_3 and 0.23 g (0.32 mmol) of $[Mo(NHNPh_2)(NNPh_2)(acac)Br_2]$ (**1**) were added. After stirring and gently heating the mixture for 5 min and cooling at room temperature, a green microcrystalline solid was filtered off by suction, washed with diethylether and dried under vacuum. The complex was dissolved in dichloromethane and crystallized by diffusion of diethylether into it. Yield: 74%. M.p. 163–164°C. Anal. Calcd for $C_{42}H_{35}N_4PBr_2Mo$ (%): C, 57.2; H, 4.00. Found: C, 57.30; H, 4.28. Electronic spectrum,

λ_{max}, nm (log ε): 408 (4.08), 360 (4.08), 296(sh) (4.30), 238 (>4.50). IR (cm^{-1}): 3040 (w), ν(C–H) arom. 1595 (s), ν(NN); 1490 (s), ν(C=C). ^{1}H NMR, δ ppm: 7.52–6.99 (m, C_6H_5–). ^{31}P{H} NMR, δ ppm: 34.8 (s, Mo-PPh_3).

2.2. *Dibromobis{diphenylhydrazido(2-)}*bis*(methyldiphenylphosphine) molybdenum(VI), [Mo(NNPh$_2$)$_2$Br$_2$(PMePh$_2$)$_2$] (5)*

Some 0.2 g (0.28 mmol) of [Mo(NHNPh$_2$)(NNPh$_2$)(acac)Br$_2$] (**1**) was mixed with 0.17 g (0.84 mmol) of $PMePh_2$ in 7 cm^3 of acetonitrile. After gentle heating under stirring during 10 min and cooling to room temperature, a yellow microcrystalline solid was filtered off, washed with diethylether, and dried under vacuum. Complex **5** crystallizes from a mixture of dichloromethane/*n*-hexane, while in dichloromethane/diethylether [Mo(NNPh$_2$)$_2$Br$_2$(PMePh$_2$)$_2$] · Et_2O (**5′**), was obtained. Both crystalline solids, **5** and **5′**, were filtered off and dried under vacuum. Yield: 81%. M.p. 120–121°C. Anal. Calcd for $C_{50}H_{46}N_4P_2Br_2Mo$ (**5**) (%): C, 58.90; H, 4.54. Found: C, 58.60; H, 4.61. Electronic spectrum, λ_{max}, nm (log ε): 404 (4.07), 354 (4.12), 300(sh) (4.13), 238 (>4.5). IR (cm^{-1}): 3080 (w), ν(C–H) arom. 2990 (w), ν(C–H) aliph. 1590 (s), ν(NN); 1490 (s), ν(C=C). ^{1}H NMR for **5′**, δ ppm: 1.20 (t, CH_3–, Et_2O), 1.81 (d, broad, free $PMePh_2$), 2.28 (d, CH_3–, Mo-$PMePh_2$), 2.40 (v t, CH_3–, *trans*-Ph_2MeP-Mo-$PMePh_2$), 3.47 (q, –CH_2O–, Et_2O), 6.47–7.67 (m, C_6H_5–). ^{31}P{H} NMR for **5′**, δ ppm: 23.34 (s) 11.00 (s), −27.72 (s, broad, free $PMePh_2$).

2.3. *Dibromobis{diphenylhydrazido(2-)}*bis*(phenyldimethylphosphine) molibdenum(VI), [Mo(NNPh$_2$)$_2$Br$_2$(PMe$_2$Ph)$_2$] (6)*

Some 0.25 g, (0.34 mmol) of [Mo(NHNPh$_2$)(NNPh$_2$)(acac)Br$_2$] (**1**) was mixed with 0.14 g (1.02 mmol) of PMe_2Ph in 10 cm^3 acetonitrile. The mixture was gently heated and stirred for 10 min and cooled to room temperature. The solvent was removed under vacuum, and the solid dispersed in diethylether, filtered off, washed with diethylether and dried under vacuum. The complex was dissolved in chloroform and crystallized by diffusion of diethylether into the solution. Pure crystalline product was filtered off and dried under vacuum. Yield: 80%. M.p. 165–166°C. Anal. Calcd for $C_{40}H_{42}N_4P_2Br_2Mo$ (%): C, 53.60; H, 4.72. Found: C, 52.90; H, 4.94. Electronic spectrum, λ_{max}, nm (log ε): 396 (3.97), 348(sh) (4.14), 304 (4.27), 240 (>4.5). IR (cm^{-1}): 3070 (w), ν(C–H) arom. 2900 (w), ν(C–H) aliph. 1590 (s), ν(NN); 1490 (s), ν(C=C). ^{1}H NMR, δ ppm: 1.99 (v t, CH_3, 12 H, CH_3-P), 6.5–7.6 (m, 30 H, C_6H_5–). ^{31}P{H} NMR, δ ppm: −3.85 (s, Mo-PMe_2Ph).

2.4. *Acetilacetonateiodinebis{diphenylhydrazido(2-)} triphenylphosphinemolibdenum(VI), Mo(NNPh$_2$)$_2$(acac)I(PPh$_3$)] (7)*

In a Schlenk tube containing 5 cm^3 of acetonitrile, 0.20 g (0.25 mmol) of [Mo(NHNPh$_2$)(NNPh$_2$)(acac)I$_2$] (**2**) and 0.066 g (0.50 mmol) of $PMePh_3$ were added. The mixture was gently heated and stirred for 5 min and cooled to room temperature. The solvent was removed under vacuum, and the residue washed twice with diethylether and dried under vacuum. The complex was dissolved in a minimum

quantity of CH_2Cl_2 and chromatographed on an Al_2O_3 column (8 cm × 6 mm). Impurities were eluted with *n*-hexane, and the yellow product with acetonitrile. Recrystallization was from a 1 : 1 CH_2Cl_2/*n*-hexane mixture at −15°C. Yield: 95%. M.p. 145–146°C. Anal. Calcd for $C_{47}H_{42}N_4PO_2IMo$ (%): C, 59.50; H, 4.46. Found: C, 59.50; H, 4.63. Electronic spectrum, λ_{max}, nm ($\log \varepsilon$): 392 (4.01), ~360(sh) (~4.02), 280(sh) (4.56), 234 (>4.5). IR (cm^{-1}): 3060 (w), ν(C–H) arom. 2970 (w), ν(C–H) aliph. 1590 (s), ν(NN); 1530(s) ν(CO), 1490 (s), ν(C=C). ^{1}H NMR, δ ppm: 1.63 (s, 6H, CH_3-CO), 5.28 (s, 1H, H-methine), 6.99–7.37 (m, 35H, C_6H_5–). ^{31}P{H} NMR, δ ppm: 34.29 (s, Mo-PPh_3).

2.5. *Acetylacetonatebis{diphenylhydrazido(2-)}*bis*(diphenylmethylphosphine) molybdate(VI) iodide, [Mo(NNPh$_2$)$_2$(acac)(PMePh$_2$)$_2$]$^+$I$^-$ (8)*

To a Schlenk tube containing 10 cm^3 of acetonitrile, 0.20 g (0.25 mmol) of [Mo(NHNPh$_2$)(NNPh$_2$)(acac)I$_2$] (**2**) and 0.10 g (0.5 mmol) of Ph_2MeP were added. The reaction mixture was heated gently and stirred for 5 min and cooled to room temperature. The solvent was eliminated under vacuum and the yellow solid was dissolved in a minimum quantity of dichloromethane and chromatographed as above with *n*-hexane. Following washing with dichloromethane/*n*-hexane (1 : 1), the pure complex was eluted with acetonitrile. The eluate was dried under high vacuum and the solid transferred to a flask and kept in a vacuum desiccator. Yield: 44%. M.p. 105–106°C. Anal. Calcd for $C_{55}H_{53}N_4P_2O_2IMo$ (%): C, 60.80; H, 4.92. Found: C, 61.10; H, 5.03. Electronic spectrum, λ_{max}, nm ($\log \varepsilon$): 380 (4.06), 328 (sh) (4.36), 290(sh) (>4.50), 240 (>4.50). IR (cm^{-1}): 3060 (w), ν(C–H) arom. 2970 (w), ν(C–H) aliph. 1590 (s), ν(NN); 1530(s), ν(CO), 1495 (s), ν(C=C). ^{1}H NMR, δ ppm: 1.64 (s, 6H, CH_3-CO), 1.75 (v t, 6H, CH_3-P), 5.30 (s, H-methine), 6.62–7.37 (m, 40H, C_6H_5–). ^{31}P{H} NMR, δ ppm: 16.82 (s, Mo-$PMePh_2$).

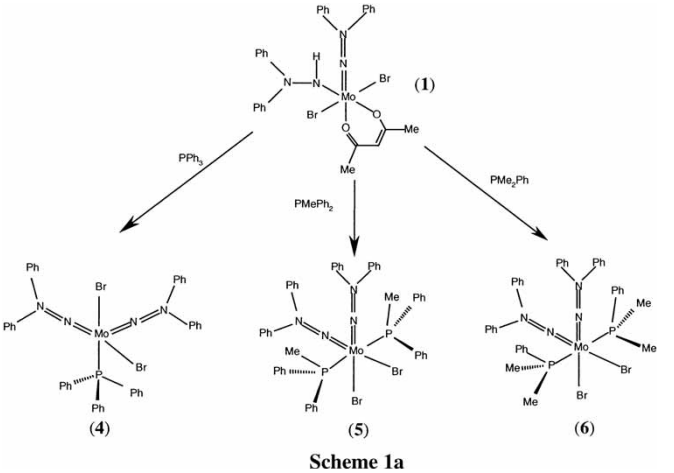
2.6. *Acetylacetonatebis{phenymethyllhydrazido(2-)}*bis*(diphenylmethylphosphine) molybdate(VI) iodide, [Mo(NNMePh$_2$)(acac)(PMePh$_2$)$_2$]$^+$I$^-$ (9)*

To a Schlenk tube containing 10 cm^3 of acetonitrile, 0.50 g (0.72 mmol) of complex [Mo(NHNMePh)(NNMePh)(acac)I$_2$] (**3**) and 0.29 g (0.5 mmol) of Ph_2MeP were added. The reaction mixture was heated gently and stirred for 5 min and cooled to room temperature. The solvent was eliminated under vacuum and the yellow solid dispersed in 20 cm 3L of diethylether for 12 h. The solid was filtered off, washed with diethylether and dried under vacuum. The product was dissolved in a minimum quantity of dichloromethane and chromatographed as above. The solution was completely dried under high vacuum and the solid recrystallized in dichloromethane/*n*-hexane (1 : 1) at −15°C. The pure complex was filtered off, washed with diethylether, transferred to a flask and kept in a vacuum desiccator. Yield: 95%. M.p. 130−131°C. Anal. Calcd for $C_{35}H_{45}N_4P_2O_2IMo$ (%): C, 56.10, H, 5.41. Found: C, 56.80; H, 5.22. Electronic spectrum, λ_{max}, nm ($\log \varepsilon$): 380 (4.12), 320(sh) (4.36), 276(sh) (>4.50), 243 (>4.50). IR (cm^{-1}): 3060 (w), ν(C–H) arom. 2950 (w), ν(C–H) aliph. 1585 (s), ν(NN); 1530(s) ν(CO), 1495 (s), ν(C=C). ^{1}H NMR, δ ppm: 1.74 (v t, 6H, CH_3-P), 1.84 (s, 6H, CH_3-CO), 3.64 (s, 6H, CH_3-N), 5.28 (s, 1H methine C–H), 5.30 (s, traces of CH_2Cl_2), 7.18−7.75 (m, 30H, C_6H_5–). ^{31}P{H} NMR, δ ppm: 16.51 and 16.74 (s, Mo-$PMePh_2$).

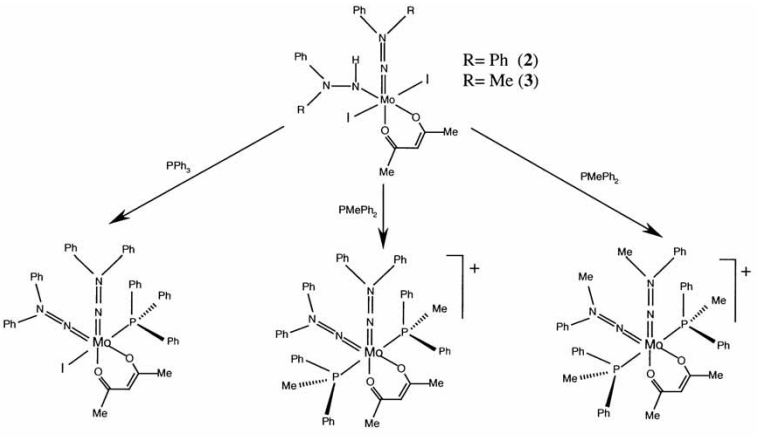
3. Results and dicussion

In acetonitrile, the precursor complex $[Mo(NHNPh_2)(NNPh_2)(acac)Br_2]$ (**1**) reacts with excess tertiary phosphine, PPh_3, $PMePh_2$ and PMe_2Ph, to give neutral mononuclear *cis-bis*[organohydrazido(2-]-molybdenum(VI) complexes (see scheme 1a). These complexes contain either one $[Mo(NNPh_2)_2(PhPh_3)Br_2]$ (**4**), or two $[Mo(NNPh_2)_2Br_2(PMePh_2)_2]$ (**5**), $[Mo(NNPh_2)_2Br_2(PMePh_2)_2] \times Et_2O$ (**5′**) and $[Mo(NNPh_2)_2Br_2(PMe_2Ph)_2]$ (**6**), phosphine molecules coordinated to molybdenum. The precursor complex **1** reacts similarly to $[Mo(NHNPh_2)(NNPh_2)(acac)Cl_2]$, whose reactivity towards phosphines has been described [29]. In this case, complex **4** and the analogous five-coordinate chloro complex, $[Mo(NNPh_2)_2(PPh_3)Cl_2]$, confirm that both steric and electronic effects are operative [29], impeding any attempt to obtain six-coordinate species $[Mo(NNPh_2)_2(PPh_3)_2Br_2]$. Experimentally, it has been found that in $CDCl_3$ solution, complex **5** undergoes partial de-coordination of a phosphine molecule (~12%). However, complex **6** maintains both phosphine molecules coordinated to molybdenum. The observed behaviour agrees with the increase of the steric bulk of the phosphines in the order $PMe_2Ph < PMePh_2 < PPh_3$. Additionally, these reactions differ from those of cationic complexes $[M(NNMe_2)_2Cl(PR_3)_2]^+$ obtained by reaction of $[MCl_4(PR_3)]^+$ (M = Mo, W; $PR_3 = PPh_3$, $PMePh_2$) with $Me_3SiNHNMe_2$ in MeCN, as described in the literature [9, 25], were the instability of $[M(NNMe_2)_2Cl_2(PR_3)_2]$ in relation to $[M(NNMe_2)_2Cl(PR_3)_2]^+$ may be explained by the higher basicity of the Me_2NN^{2-} ligand [29] compared to Ph_2NN^{2-}.

Under similar conditions, the precursor $[Mo(NHNPh_2)(NNPh_2)(acac)I_2]$ (**2**) reacts with PPh_3 yielding $[Mo(NNPh_2)_2(acac)(PPh_3)I]$ (**7**), while with $PMePh_2$ it gives $[Mo(NNPh_2)_2(acac)(PMePh_2)_2]^+I^-$ (**8**). Likewise, the precursor $[Mo(NHNMePh)(NNMePh)(acac)I_2]$ (**3**) reacts with $PMePh_2$ to give $[Mo(NNMePh)_2(acac)(PMePh_2)_2]^+I^-$ (**9**) (see scheme 1b). These complexes **7**–**9**, are mononuclear with 18 (**7**) and 20 (**8**, **9**) electrons per Mo atom. The results contrast with those obtained for **4**–**6** and those reported earlier in the literature [29]. Although these complexes contain the *cis-bis*[organohydrazido(2-)]-molybdenum(VI) core, they retains acetylacetonate ligands in the coordination sphere, eliminating one, in **7**, or two iodide ligands, in **8** and **9**. This behaviour may be explained using the HSAB concept [31]. It is commonly



Scheme 1a



Scheme 1b

known that the relative hardness of the halide anions decreases in the order $Cl^- > Br^- > I^-$, which predicts that Cl^- and Br^- are hard enough to remain bonded to the hard Mo(VI) centre and, consequently, phosphines may displace the softest anion, $acac^-$ in **4**–**6**. On the contrary, the reactions of phosphines with precursors $[Mo(NHNPh_2)(NNPh_2)(acac)I_2]$ (**2**) and [Mo(NHNMePh)(NNMePh)(acac)I_2] (**3**) that contain the softest anion I^-, allow partial displacement of the iodide ligands in **7**, or completely in **8** and **9**. The observed behaviour establishes the relative hardness of the implicated ligands decreasing in the order $Cl^- > Br^- > : PR_3 > acac^- > I^-$. The presence of only one phosphine in the neutral complex **7** is due to the steric effects [29] as mentioned for **4**. Complex **9** shows the presence of two isomers in $CDCl_3$ solution, probably formed by different dispositions of the methyl and phenyl groups [29] located on the hydrazido(2-) ligands.

Finally, all synthesized complexes are diamagnetic properties and elemental analyses agree with proposed formulae. Attempts in order to obtain a most extensive series of complexes from compounds **2** and **3** were unsuccessful, probably due to that under the conditions used the oxidative power of the reaction mixture is sufficiently high to oxidize liberated iodide to molecular iodine identified by its typical violet colour in organic solvents.

Complexes **3**–**9** have been studied by electronic, IR, ^1H and $^{31}P\{H\}$ NMR spectroscopy. As a rule [29] electronic spectra in CH_2Cl_2 solutions show four absorption bands between 230−410 nm. The highest energy bands can be attributed to an internal transition within the phenyl groups of the hydrazido and phosphine ligands, while the lower energy band arises from the *cis-bis*$[Mo(NNRPh)]^{2+}$ chromophore [13, 14, 21, 29]. IR spectra in general show a weak band due to aromatic ν(C–H) stretching in the 3040−3070 cm^{-1} range, and a weak band in the 2990−2950 cm^{-1} region attributed to aliphatic ν(C–H) stretching of CH_3– groups. Two intense and sharp absorptions were observed, the first in the 1595−1590 cm^{-1} range tentatively attributed to ν(NN) stretching of the *cis-bis*$[Mo(NNRPh)]^{2+}$ moiety [9, 10, 18, 27, 29, 32]. The second, located in the 1495–1490 cm^{-1} range, has been attributed to ν(C=C) stretching in aromatic rings. Furthermore, the weak band at *ca* 3255 cm^{-1} characteristic of the ν(N–H) stretching of PhRNNH(1-) ligands and the

strong band at *ca* 1570 cm^{-1} attributed to chelated ν(C=O), both present in precursors **1**–**3** [30], are notably absent in the IR spectra of complexes **4**–**6**; the first is also absent in complexes **7**–**9**. However, complexes **7**–**9** exhibit an intense absorption located at 1530 cm^{-1} that may be assigned to ν(C=O) stretching, in agreement with the presence of the $acac^-$ anion in the coordination sphere [30, 35].

^1H and $^{31}P\{H\}$ NMR spectra of complexes **4**–**9** in CH_2Cl_2 have been considered in order to complement the information about the structure, stereochemistry and stability of each compound. In $[Mo(NNPh_2)_2Br_2(PPh_3)]$ (**4**) the position of the multiplet, 6.99–7.52 ppm, in the ^1H NMR spectrum and one singlet, 34.80 ppm in $^{31}P\{H\}$ NMR, assigned to aromatic protons and coordinated phosphine, respectively, are typical of a complex with distorted trigonal bipyramidal geometry [29]. This is corroborated by the $^{31}P\{H\}$ signal located at 36.98 ppm for the analogous complex $[Mo(NNPh_2)_2Cl_2(PPh_3)]\cdot 0.5CH_2Cl_2$ whose crystalline structure has been previously described [29]. The ^1H NMR spectrum of **5′** shows that the complex suffers partial de-coordination of one phosphine molecule in $CDCl_3$ solution. The most abundant species is the six-coordinate $[Mo(NNPh_2)_2Br_2(PMePh_2)_2]$ (**5**) complex, which displays a virtual triplet [27, 33–34] centred at 2.40 ppm and assigned to the mutually *trans*-Ph_2MeP-Mo-$PMePh_2$ moiety. On the other hand, the five-coordinate species $[Mo(NNPh_2)_2Br_2(PMePh_2)]$ with ~12% abundance, exhibits a doublet corresponding to only one coordinated $PMePh_2$ ligand at 2.28 ppm. The mixture exhibits a complicated multiplet in the 6.47–7.67 ppm range attributed to the protons connected to the phenyl groups. Additionally, the spectrum shows a triplet centred at 1.20 ppm, a quartet centred at 3.47 ppm, both corresponding to diethylether of crystallization, and a broad signal at 1.81 ppm due to free $PMePh_2$. The information is confirmed by the $^{31}P\{H\}$ NMR spectrum, that shows a major singlet at 11.00 ppm attributed to the mutually *trans*-Ph_2MeP-Mo-$PMePh_2$ moiety present in the original complex **5′**, another singlet at 23.34 ppm corresponding to coordinated $PMePh_2$ in $[Mo(NNPh_2)_2Br_2(PMePh_2)]$ species and a broad singlet at −27.72 ppm located exactly in the position for free $PMePh_2$. The ^1H NMR spectrum of **6** displays a virtual triplet centred at 1.99 ppm, attributed to the mutually *trans*-$PhMe_2$P-Mo-PMe_2Ph moiety and a multiplet assigned to all protons linked to the phenyl groups of the hydrazido(2-) and phosphine ligands, in the 6.5–7.6 range. $^{31}P\{H\}$ NMR exhibits only one singlet at −3.85 ppm, showing the presence of only one species in $CDCl_3$ solution.

In ^1H NMR of complexes **7**–**9** the $acac^-$ ligand displays two singlets the first at 1.63, 1.64 and 1.84 ppm, respectively, due to the equivalent methyl groups and the second at 5.28, 5.30 and 5.28 ppm, respectively, assigned to the methine groups. In addition, a complex multiplet located in the ranges 6.99–7.37, 6.62–7.37 and 7.18–7.75 ppm, respectively, were attributed to protons linked to the phenyl groups of the hydrazido(2-) and phosphine ligands. Additionally, complexes **8** and **9** exhibit a virtual triplet [27, 33–34] corresponding to the mutually *trans*-Ph_2MeP-Mo-$PMePh_2$ moieties centred at 1.75 and 1.74 ppm, respectively. Moreover, **9** shows a singlet at 3.64 ppm due to methyl groups on the hydrazido(2-) ligand. The ^1H NMR spectrum of **9** shows evidence of the presence of small quantities of another isomer in solution that is not possible to quantify. Complexes **7** and **8** exhibit only one signal in the $^{31}P\{H\}$ NMR spectrum at 34.29 and 16.82 ppm, respectively, due to the presence of only one species in $CDCl_3$ solution. On the contrary, complex **9** displays two resonances with slightly different chemical shifts, the most intense at 16.51 ppm and the other of very low abundance at 16.7 ppm, indicating the presence of two isomers in $CDCl_3$ solution. Spectroscopic and

crystallographic studies of $[Mo(NNMePh)Cl_2(PPh_3)_2]$ [29] show that second isomer formed by **9** may be generated by the different disposition (inner or outer) of methyl groups located on the hydrazido(2-) ligands.

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