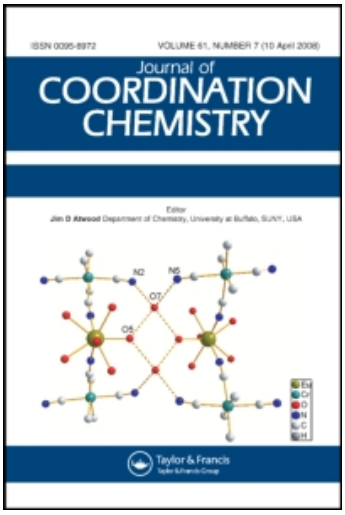

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Reactivity of [Mo(NHNRPh)(NNRPh)(acac)X_2] (R = Ph, Me; X = Br, I) toward tertiary phosphines

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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 tertiary phosphines as PPh_3, $PMePh_2$ and PMe_2Ph are examined. 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. All complexes were characterized by elemental analysis, UV-visible, 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 interest as models of intermediates in nitrogen fixation. Indeed, 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 (i) protonation and alkylation of organodiazenido complexes, (ii) the reaction of a metal halide with either asymmetrically disubstituted hydrazine, e.g. RR′NNH_2 or their trimethylsilyl derivatives, e.g. $Me_3SiNHNRR'$ and (iii) a condensation type reaction of asymmetrically disubstituted hydrazines with oxometal complexes, especially oxomolybdemun complexes [2, 3]. Many complexes containing *cis*-$[MoO(NNRR')]^{2+}$ and *cis*-$[Mo(NNRR')_2]^{2+}$ cores have been synthesized and some 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, while the *cis*-$[MoO(NNRR')]^{2+}$ unit is found in a number of mononuclear

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complexes, containing monodentate thiolate [11] 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 synthesis and analytic and spectroscopic characterization of complexes 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 a appropriate phosphine (PPh_3, $PMePh_2$ and PMe_2Ph) is reported here.

2. Results and discussion

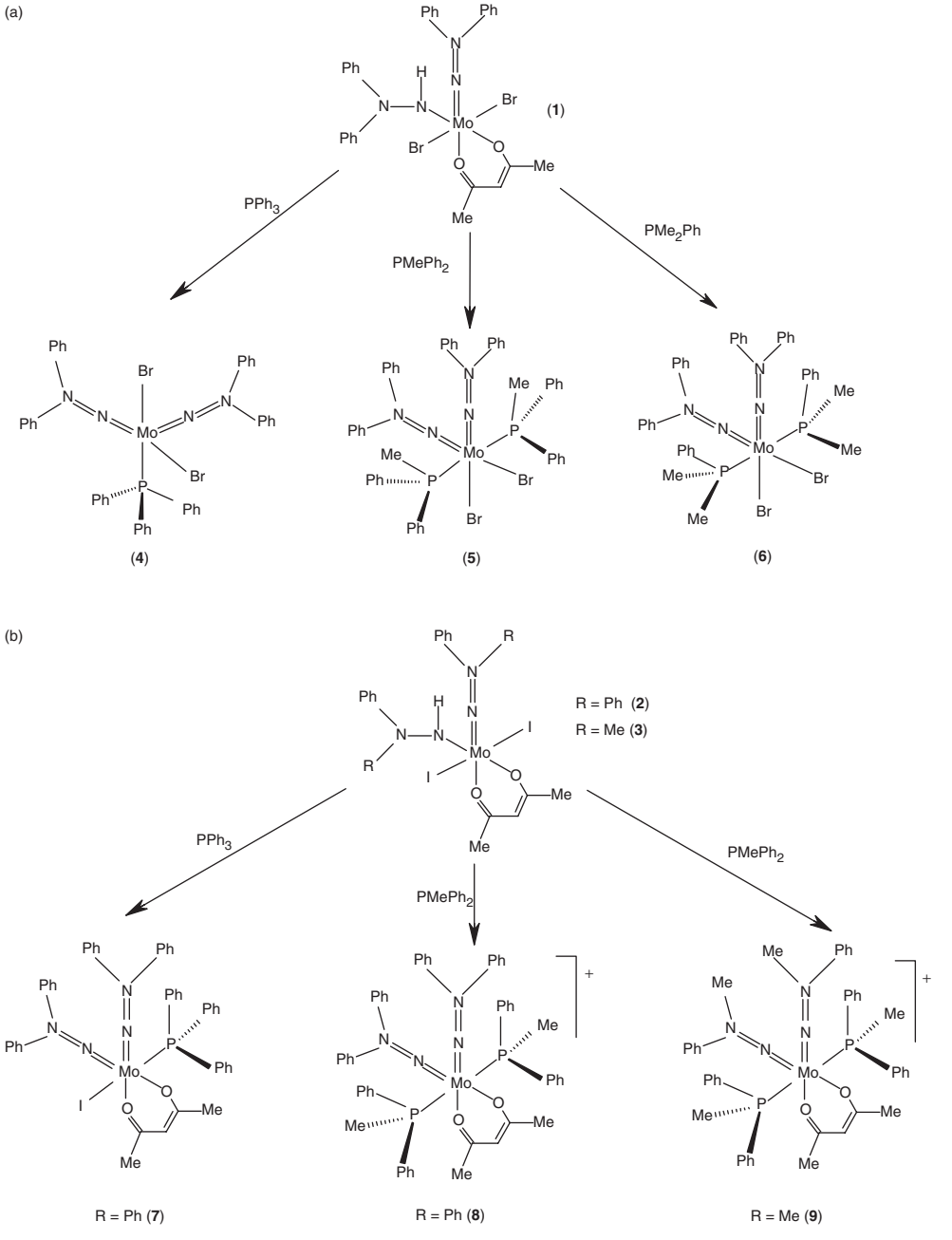
2.1. *Synthesis*

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, $[Mo(NNPh_2)_2(PPh_3)Br_2]$ (**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 the molybdenum atom with 18 (**4**) and 20 (**5**, **5′**, **6**) electron-count, respectively. The precursor complex **1** reacts similarly to $[Mo(NHNPh_2)(NNPh_2)(acac)Cl_2]$, whose reactivity towards phosphine has been described in a previous study [29]. In this case, complex **4** and the analogous five-coordinated 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 the six-coordinated species $[Mo(NNPh_2)_2(PPh_3)_2Br_2]$. In $CDCl_3$ solutions, complex **5′** suffers partial dissotiation of one phosphine molecule, ~12%, equation (1), but complex **6** always maintains coordination to both phosphines. The observed behaviour agrees with the increase of the steric effect of these phosphines in the following order: $PMe_2Ph < PMePh_2 < PPh_3$. Additionally, these reactions differ from the 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 described in the literature [9, 25], where 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 compared to Ph_2NN^{2-} and $PhMeNN^{2-}$ [29].

$$[Mo(NNPh_2)_2Br_2(PMePh_2)_2] \cdot Et_2O \overset{CDCL_3}{\rightleftharpoons} [Mo(NNP_2)_2Br_2(PMePh_2)] + PMePh_2 + Et_2O \quad (1)$$

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 $PMePh_2$ gives the cationic $[Mo(NNPh_2)_2(acac)(PMePh_2)_2]^+I^-$ (**8**). Likewise, the precursor

[Mo(NHNMePh)(NNMePh)(acac)I_2] (**3**) reacts with $PMePh_2$ to give the analogous cationic complex $[Mo(NNMePh)_2(acac)(PMePh_2)_2]^+I^-$ (**9**) (see scheme 1b). These complexes **7**–**9**, are mononuclear with 18 (**7**) and 20 (**8**, **9**) electron-count around each Mo atom. The results contrast with those obtained for **4**–**6** and with those reported



Scheme 1. Chemical reactivity of molybdenum(VI) complexes toward tertiary phosphines.

earlier in the literature [29]. Although these complexes contain the *cis*-bis[organohydrazido(2-)]-molybdenum(VI) core, they differ from complexes **4–6** by retaining acetylacetonate in the coordination sphere of the metal, eliminating one, in **7**, or two iodide ligands, in **8** and **9**. This behaviour may be explained using the HSAB concept [31]. In fact, it is commonly known that the relative hardness of the halide anions decreases in the order $Cl^- > Br^- > I^-$, predicting that Cl^- and Br^- are hard enough to remain bonded to the hard Mo(VI) centre and, consequently, phosphines displace the softest anion, $acac^-$ in **4–6**. Contrarily, the reactions of phosphines with the precursors $[Mo(NHNPh_2)(NNPh_2)(acac)I_2]$ (**2**) and $[Mo(NHNMePh)(NNMePh)(acac)I_2]$ (**3**) that contain the soft anion I^-, allows a partial displacement of the iodide ligands in **7**, or completely in **8** and **9**. The observed behaviour establishes the relative hardness of the ligands as: $Cl^- > Br^- > :PR_3 > acac^- > I^-$. The presence of only one phosphine molecule in the neutral **7** is due to steric effects [29] as mentioned previously for **4**. Complex **9** shows the presence of two isomers in $CDCl_3$ solution, probably from different disposition of the methyl and phenyl groups (inner and outer) [29] located on the hydrazido(2-) ligands.

Finally, the NMR spectra confirm the diamagnetic behaviour of these complexes and the elemental analysis agrees with the proposed formula. Attempts to obtain an extensive series of complexes from **2** and **3** were unsuccessful, probably, due to the conditions used; the oxidative power of the reaction mixture is sufficiently high to oxidize the liberated iodide anion yielding molecular iodine that was identified by the typical violet colour in organic solvents.

2.2. *Spectroscopic studies*

Complexes **3–9** have been studied by UV-visible, IR, ^1H and $^{31}P\{H\}$ NMR spectroscopy. As a rule [29] the UV-visible spectra in CH_2Cl_2 solution 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$[Mo(NNRPh)_2]^{2+}$ chromophore [13, 14, 21, 29]. The IR spectra in general, shows a weak band due to the aromatic ν(C–H) stretching mode in the 3040–3070 cm^{-1} range, and a weak absorption band in the 2990–2950 cm^{-1} region attributed to the aliphatic ν(C–H) stretching mode of CH_3- groups. In addition, two intense and sharp absorption bands were observed; the first one in the 1595–1590 cm^{-1} range which has been tentatively attributed to the ν(NN) stretching mode of the *cis*-bis$[Mo(NNRPh)]^{2+}$ moiety [9, 10, 18, 27, 29, 32]. The second one located in the 1495–1490 cm^{-1} range has been attributed to ν(C=C) stretching mode in the aromatic rings. Furthermore, the weak band at ca 3255 cm^{-1} characteristic of the ν(N–H) stretching mode of the PhRNNH(1-) ligands and the strong band at ca 1570 cm^{-1} attributed to the chelated ν(C=O), both present in the precursors **1–3** [30], are 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), in agreement with the presence of the $acac^-$ anion in the coordination sphere of the Mo centre [30, 35].

^1H NMR spectra, table 1, and $^{31}P\{H\}$ NMR spectra, figure 1, of complexes **4–9** complement the information about the structure, stereochemistry and stability of each compound. In $[Mo(NNPh_2)_2Br_2(PPh_3)]$ (**4**) a multiplet at 6.99–7.52 ppm found in the

Table 1. ^{1}H NMR spectra of complexes **4**–**9** in $CDCl_3$ solutions.

	H-signals assignment, δ (ppm)					
	C_6H_{5-}	CH_3–N	CH_3–P	CH_3–CO	–CH	Et_2O
4	6.99–7.52m	–	–	–	–	–
5′	6.47–7.67m		2.40vt[1] 2.28d[2] 1.81bs[3]			1.20t, 3H 3.47q, 2H
6	6.50–7.60m, 30H	–	1.99vt (12H)	–	–	–
7	6.99–7.37m, 35H	–	–	1.63s, 6H	5.28s, 1H	–
8	6.62–7.37m, 40H	–	1.75vt, 6H	1.64s, 6H	5.30s, 1H	–
9	7.18–7.75m	3.64s[4] 3.42s[5] 3.76s[5] 3.95s[5]	1.74vt	1.84s	5.28s[4] 5.32s[5]	

[1]vt: Virtual triplet, [2]doublet attributed to five-coordinated complex, [3]broad singlet attributed to free $PMePh_2$, [4]majority signal, [5]low abundance signals.

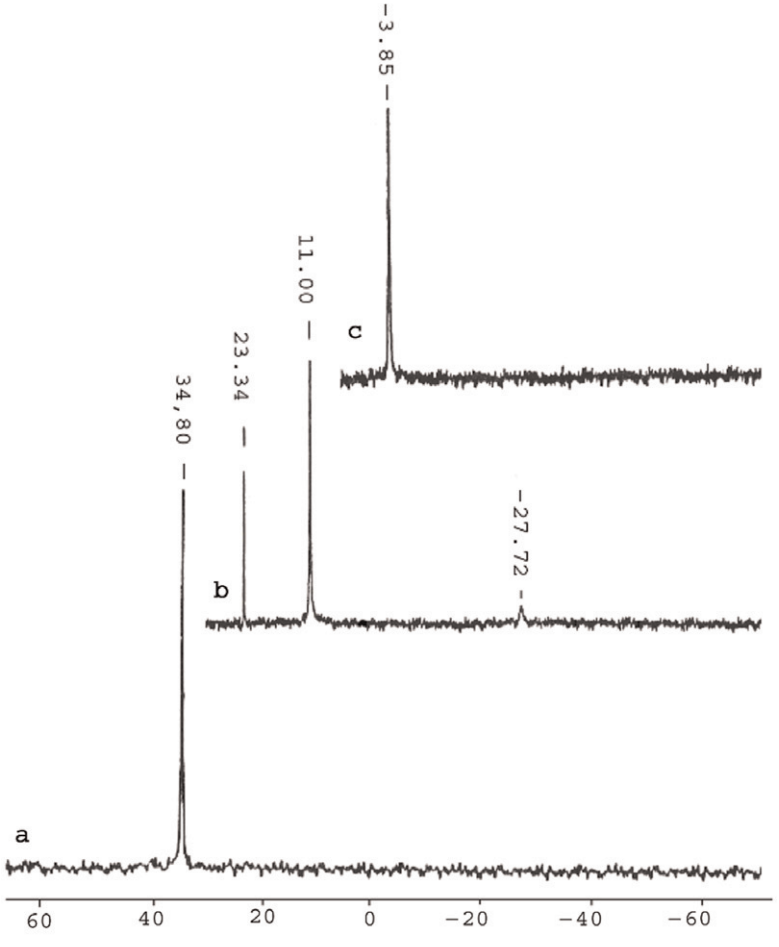


Figure 1. ^{31}P{H} NMR spectra of (a) $[Mo(NNPh_2)_2Br_2(PPh_3)]$ (**4**), (b) $[Mo(NNPh_2)_2Br_2(PMePh_2)_2]$ (**5′**) and (c) $[Mo(NNPh_2)_2Br_2(PMePh)_2]$ (**6**).

^{1}H NMR spectrum and one singlet at 34.80 ppm in the ^{31}P{H} NMR spectrum, figure 1(a), were assigned to the aromatic protons and the phosphine molecule, respectively. X-ray studies on $[Mo(NNPh_2)_2Cl_2(PPh_3)] \cdot 0.5CH_2Cl_2$ showed a distorted trigonal bipyramidal geometry; comparing with **4**, their similar multiplet in ^{1}H NMR at 6.91–7.50 ppm and the singlet in the ^{31}P{^{1}H} NMR at 36.98 ppm suggest that both complexes are isostructural [29]. The ^{1}H NMR spectrum of **5′** shows clearly that the complex suffers partial loss of one phosphine molecule in $CDCl_3$ solution, equation (1). In fact, the most abundant species, ~88%, is the six-coordinate $[Mo(NNPh_2)_2Br_2(PMePh_2)_2]$ (**5**) complex, that displays a virtual triplet [27, 33–34] centered at 2.40 ppm assigned to the mutually *trans*-Ph_2MeP-Mo-P$MePh_2$ moiety. On the other hand, the five-coordinated species, $[Mo(NNPh_2)_2Br_2(PMePh_2)]$ ~12% abundance, exhibits a doublet corresponding to only one coordinated $PMePh_2$ ligand at 2.28 ppm. This mixture exhibits a complicated multiplet in 6.47–7.67 ppm range attributed to the protons connected to all the phenyl groups. Additionally, the spectrum shows a triplet centered at 1.20 ppm and one quartet centered at 3.47 ppm, both corresponding to the crystallization diethylether. The relative area of all hydrogen signals indicate that complex **5′** is $[Mo(NNPh_2)_2Br_2(PMePh_2)_2] \cdot Et_2O$. A wide signal at 1.81 ppm due to the methyl of free $PMePh_2$ shows that this ligand in $CDCl_3$ solution is in equilibrium with the five- and six-coordinated species, equation (1). The information is confirmed by the ^{31}P{H} NMR spectrum, figure 1(b), that shows a majority singlet at 11.00 ppm attributed to the mutually *trans*-Ph_2MeP-Mo-P$MePh_2$ moiety present in the original complex, **5′**, another singlet at 23.34 ppm corresponding to the coordinated $PMePh_2$ in five-coordinated $[Mo(NNPh_2)_2Br_2(PMePh_2)]$ and the wide singlet at −27.72 ppm for free $PMePh_2$. The ^{1}H NMR spectrum of **6**, displays a virtual triplet centered at 1.99 ppm, attributed to the mutually *trans*-$PhMe_2$P-Mo-PMe_2Ph 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. The ^{31}P{H} NMR, figure 1(c), exhibits only one singlet at −3.85 ppm that agrees with the presence of only one species in $CDCl_3$ solution.

In the ^{1}H NMR of complexes **7**–**9** the $acac^-$ ligand displays two singlets the first one at 1.63, 1.64 and 1.84 ppm, respectively due to the equivalent methyl groups and the second one 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 of 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-P$MePh_2$ centered at 1.75 and 1.74 ppm, respectively. Moreover, **9** shows a singlet located at 3.64 ppm due to the methyl groups on the hydrazido(2-) ligand. The presence of other signals of low-intensity in the ^{1}H RMN spectrum of **9**, table 1, indicates the presence of another complex in $CDCl_3$ solution, probably a conformer that we could not quantify and identify (*vide infra*). Complexes **7** (figure 2a) and **8** (figure 2b) exhibit only one signal in the ^{31}P{H} NMR spectrum at 34.29 and 16.82 ppm, respectively, indicating presence of only one species in $CDCl_3$ solution. On the contrary, complex **9**, figure 2(c), displays two resonances with a slight difference of chemical shift, the most intense at 16.51 ppm, the other with very low intensity at 16.70 ppm, suggesting the presence of two very similar complexes in $CDCl_3$ solution,

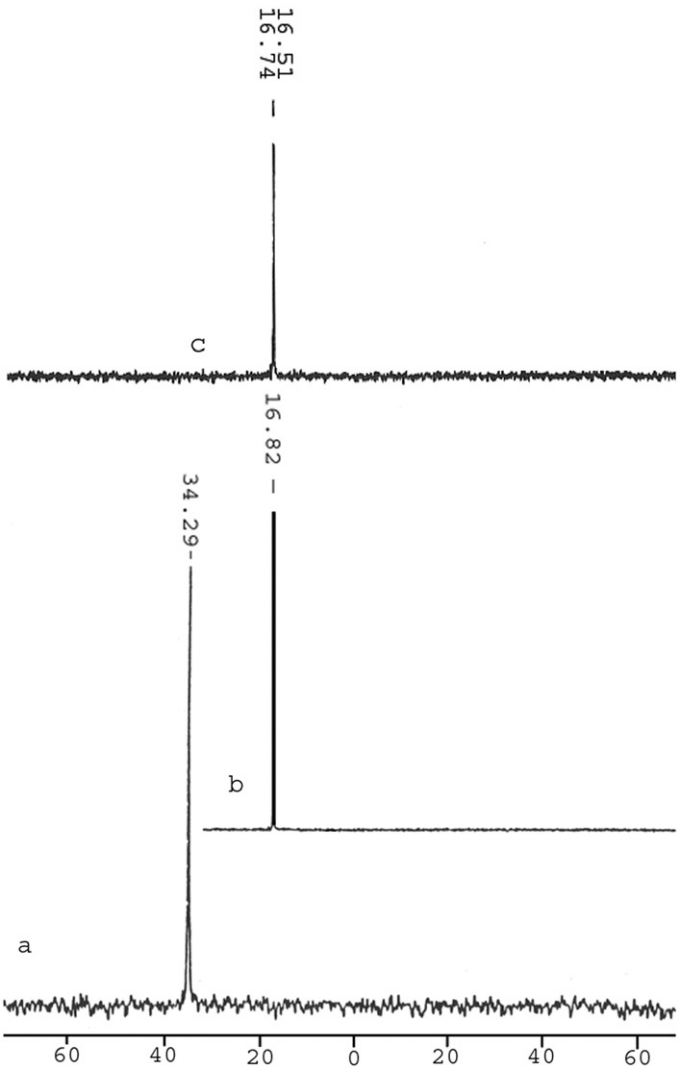


Figure 2. $^{31}P\{H\}$ NMR spectra of (a) $[Mo(NNPh_2)_2(acac)I(PPh_3)]$ (**7**), (b) $[Mo(NNPh_2)_2(acac)(PMePh_2)_2]^+I^-$ (**8**) and (c) $[Mo(NNMeph)_2(acac)(PMePh_2)_2]^+I^-$ (**9**).

probably, generated by the asymmetric disposition of methyl and phenyl groups connected to the hydrazido(2-) ligands [29].

3. Experimental

3.1. *Chemicals*

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 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 described previously [30].

3.2. *Physical measurements*

Melting points were determined by using a Kofler apparatus. Microanalytical data were obtained on a Perkin-Elmer Model 2400 elemental analyzer. Magnetic properties were registered in solid state using $[Hg(SCN)_4]$ as reference in a Faraday Cahn Ventron RTL equipment with a permanent magnet of 6000 Gauss intensity, using a sample of around 5 mg. The infrared spectra were recorded on Perkin-Elmer Model 599 equipment in KBr discs. Electronic spectra were recorded in dichloromethane solutions on a Hewlet Packard, Model 8452A spectrophotometer with diode arrangement, using stock solution 1.0×10^{-3} mol L^{-1} diluted to 1.0×10^{-5} mol L^{-1}. ^1H NMR and ^{31}P NMR were recorded in $CDCl_3$ solutions on Bruker AC-200P equipment at room temperature using TMS and H_3PO_4 as internal and external standards, respectively.

3.3. *Synthesis*

All reactions were performed under N_2 using Schlenk tubes connected to the vacuum line.

3.3.1. Dibromo bis{diphenylhydrazido(2-)}(triphenylphosphine)molybdenum(VI)

$[Mo(NNPh_2)_2Br_2(PPh_3)]$ (**4**). In 6 mL 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, then cooling at room temperature, a green microcrystalline solid was filtered by suction, washed with diethylether and dried under vacuum. The complex was dissolved in dichloromethane and crystallized by diffusion of diethylether into this solution. Anal. yield: 74%. M.p.: 163–164°C. E.A. found (%): C 57.3, H 4.3. $C_{42}H_{35}N_4PBr_2Mo$ (**4**) required (%) C 57.2, H 4.0. UV-visible (CH_2Cl_2) λ_{max}, nm ($\log \varepsilon$): 408 (4.08), 360 (4.08), 296 (sh) (4.30) and 238 (>4.50). IR (KBr disc, cm^{-1}): 3040 (w), ν(C–H) arom.; 1595 (s), ν(NN); 1490 (s), ν(C=C).

3.3.2. Dibromo bis{diphenylhydrazido(2-)}bis(methyldiphenylphosphine)molybdenum(VI)

$[Mo(NNPh_2)_2Br_2(PMePh_2)_2]$ (**5**). 0.2 g, (0.28 mmol) of $[Mo(NHNPh_2)(NNPh_2)(acac)Br_2]$ (**1**) were mixed with 0.17 g (0.84 mmol) of $PMePh_2$ in 7 mL of acetonitrile. After gentle heating under stirring during 10 min and cooling at room temperature, a yellow microcrystalline solid was obtained and filtered, washed with diethylether, and dried under vacuum. Complex **5** crystallizes from a mixture of dichloromethane/hexane, while in dichloromethane/diethylether $[Mo(NNPh_2)_2Br_2(PMePh_2)_2] \cdot Et_2O$ (**5′**), was obtained. Both crystalline solids, **5** and **5′**, were filtered and dried under vacuum. Anal. yield: 81%. M.p.: 120–121°C. E.A. found (%): C 58.6, H 4.6. $C_{50}H_{46}N_4P_2Br_2Mo$ (**5**) requires (%) C 58.9, H 4.5. UV-visible for **5** (CH_2Cl_2) λ_{max}, nm ($\log \varepsilon$): 404 (4.07), 354 (4.12), 300 (sh) (4.13) and 238 (>4.5). IR for **5** (KBr disc, cm^{-1}): 3080 (w), ν(C–H) arom.; 2990 (w), ν(C–H) aliph. 1590 (s), ν(NN); 1490 (s), ν(C=C).

3.3.3. Dibromo bis{diphenylhydrazido(2-)}bis(phenyldimethylphosphine)molybdenum(VI)

$[Mo(NNPh_2)_2Br_2(PMe_2Ph)_2]$ (**6**). 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 mL acetonitrile. The mixture was gently heated and stirred for 10 min and cooled at room temperature. The solvent was eliminated under vacuum and the obtained solid was dispersed by vigorous stirring with diethylether, then filtered and washed with diethyl ether and dried in vacuum. The complex dissolved in chloroform was crystallized by diffusion of diethyl ether into this solution and the pure crystalline product was filtered and dried in vacuum. Anal. yield: 80%. M.p.: 165–166°C. E.A. found (%): C 52.9, H 4.9. $C_{40}H_{42}N_4P_2Br_2Mo$ (**6**) requires (%) C 53.6, H 4.7. UV-visible (CH_2Cl_2) λ_{max}, nm ($\log \varepsilon$): 396 (3.97), 348 (sh) (4.14), 304 (4.27) and 240 (>4.5). IR (KBr disc, cm^{-1}): 3070 (w), ν(C–H) arom.; 2900 (w), ν(C–H) aliph. 1590 (s), ν(NN); 1490 (s), ν(C=C).

3.3.4. Acetylacetonateiodinebis{diphenylhydrazido(2-)}triphenylphosphine molybdenum(VI)

$[Mo(NNPh_2)_2(acac)I(PPh_3)]$ (**7**). In 5 mL 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 under stirring during 5 min and cooled at room temperature. The solvent was eliminated under vacuum and the residue was washed twice with diethylether, eliminating the supernatant with a Pasteur's pipette and the product was dried under vacuum. Chromatography on an Al_2O_3 column (8 × 6 mm) was used for purification. The complex was dissolved in minimal CH_2Cl_2 and fixed in the column with hexane, following the elution of all impurities with CH_2Cl_2, the yellow pure product was eluted with acetonitrile. Finally, recrystallization was carried out in a 1 : 1 CH_2Cl_2/hexane mixture at −15°C and the product was filtered by suction and dried in vacuum. Anal. yield: 95% M.p.: 145–146°C. E.A. found (%): C 59.5, H 4.6. $C_{47}H_{42}N_4PO_2IMo$ (**7**) requires (%) C 59.5, H 4.4. UV-visible (CH_2Cl_2) λ_{max}, nm ($\log \varepsilon$): 392 (4.01), 360 (sh) (4.02), 280 (sh) (4.56), 234 (>4.5). IR (KBr disc, 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).

3.3.5. Acetylacetonatebis{diphenylhydrazido(2-)}bis(diphenylmethylphosphine) molybdenum(VI)iodide

$[Mo(NNPh_2)_2(acac)(PMePh_2)_2]^+I^-$ (**8**). In 10 mL 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 under stirring for 5 min and cooled at room temperature. The solvent was eliminated under vacuum and the yellow solid was dissolved in minimum dichloromethane and fixed on a chromatographic Al_2O_3 column (8 × 6 mm) with hexane. Following washing with dichloromethane/hexane (1 : 1), the pure complex was eluted with acetonitrile. The eluate was completely dried under high vacuum and the solid was transferred to a flask and kept in a vacuum desiccator. Anal.: Yield: 44% (after chromatography) m.p.: 105–106°C. E.A. found (%): C 61.1, H 5.0. $C_{55}H_{53}N_4P_2O_2IMo$ (**8**) requires (%) C 60.8, H 4.9. UV-visible (CH_2Cl_2) λ_{max}, nm ($\log \varepsilon$): 380 (4.06), 328 (sh) (4.36), 290 (sh) (>4.50). 240 (>4.50).

IR (KBr disc, 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).

3.3.6. Acetylacetonatebis{phenylmethylhydrazido(2-)}bis(diphenylmethylphosphine) molybdenum(VI)iodide

$[Mo(NNMePh)_2(acac)(PMePh_2)_2]^+I^-$ (**9**). In 10 mL of acetonitrile 0.50 g (0.72 mmol) of $[Mo(NHNMePh)(NNMePh)(acac)I_2]$ (**3**) and 0.29 g (0.5 mmol) Ph_2MeP, were added. The reaction mixture was heated gently under stirring for 5 min and cooled at room temperature. The solvent was eliminated under vacuum and the yellow solid was dispersed by vigorous stirring with 20 mL of diethyl ether for 12 h. Then, the solid was filtered by suction, washed with diethylether and dried in vacuum. The product was dissolved in a minimal quantity of dichloromethane and fixed in a chromatographic Al_2O_3 column (8×6 mm) with hexane. Following washing with dichloromethane/hexane (1 : 1), the pure complex was eluted with acetonitrile. The obtained solution was completely dried under high vacuum and the solid was recrystallized in dichloromethane/hexane 1 : 1 at $-15°C$. The pure complex was filtered, washed with diethylether, transferred to a flask and kept in a vacuum desiccator. Anal. yield: 95% M.p.: 130–131°C. E.A. found (%): C 56.8, H 5.2. $C_{35}H_{45}N_4P_2O_2IMo$ (**9**) requires (%) C 56.1, H 5.4. UV-visible (CH_2Cl_2) λ_{max}, nm ($\log \varepsilon$): 380 (4.12), 320 (sh) (4.36), 276 (sh) (>4.50), 243 (>4.50). IR (KBr disc, 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).

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