Polyhedron 38 (2012) 162–168

Contents lists available at SciVerse ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

Preparation of methylhydrazine and methyldiazene complexes of molybdenum and tungsten

Gabriele Albertin *, Stefano Antoniutti, Chiara Girardi

Dipartimento di Scienze Molecolari e Nanosistemi, Università Ca' Foscari Venezia, Dorsoduro 2137, 30123 Venezia, Italy

ARTICLE INFO

Article history:
Received 23 January 2012
Accepted 2 March 2012
Available online 16 March 2012

Keywords:
Carbonyl and nitrosyl complexes
Methylhydrazine
Methyldiazene
Phosphonite and phosphinite ligands
Molybdenum and tungsten

ABSTRACT

Nitrosyl complexes $[M(CO)_3(NO)L_2]BPh_4$ (**2**, **5**) [M = Mo, W; L = $PPh(OEt)_2$, PPh_2OEt] were prepared by allowing carbonyl compounds $M(CO)_4L_2$ (**1**, **4**) to react with $NOPF_6$ in CH_2Cl_2. Dicarbonyl complex $[W(CO)_2(NO)\{PPh(OEt)_2\}_3]BPh_4$ (**7**) was also prepared by reacting $W(CO)_3[PPh(OEt)_2]_3$ (**6**) with $NOPF_6$. Treatment of nitrosyl complexes **2**, **5** with $[NEt_4]Br$ gave bromide derivative $[MBr(CO)_2(NO)L_2]BPh_4$ (**3**). Hydrazine complexes $[M(CO)(RNHNH_2)(NO)L_3]BPh_4$ (**8**, **9**, **10**) (R = H, CH_3) were prepared by allowing nitrosyl complexes **2**, **5** to react with hydrazine $RNHNH_2$ in CH_2Cl_2. Reaction of methylhydrazine complexes $[M(CO)(CH_3NHNH_2)(NO)L_3]BPh_4$ (**8**, **10**) with $Pb(OAc)_4$ at −30 °C resulted in selective oxidation of hydrazine, affording the corresponding methyldiazene derivatives $[M(CO)(CH_3N{=}NH)(NO)L_3]BPh_4$ (**11**, **12**). The complexes were characterised spectroscopically (IR and NMR), and a geometry in solution was also established.

1. Introduction

The chemistry of transition-metal coordinated hydrazine and substituted hydrazines continues to be studied, primarily for its relevance in the nitrogen fixation process [1,2] and also for the rich and varied chemistry shown by the metal bond hydrazine system [3–6].

Hydrazine may behave either as a mono (η^1) or bidentate (η^2) ligand or as a bridging group (μ) between two metal fragments [3–6]. Coordinated hydrazine can be selectively oxidised to 1,2-diazene [2] or, alternatively, reduced to ammonia [1,7,8]. Hydrazine has also been shown to be a substrate of nitrogenase and has been trapped as an intermediate during enzyme turnover [9].

A number of hydrazine complexes were thus prepared for several central metals, with different types of supporting ligands including tertiary phosphines, carbonyl, and cyclopentadienyl [3–6]. Less attention has been paid to phosphites and for molybdenum [10] – a metal present in nitrogenase – no hydrazine complex stabilised by phosphonite or phosphinite as supporting ligand has ever been reported.

We have been interested for several years in the chemistry of diazo complexes of transition metals and have reported the synthesis and reactivity of mono- and bis(hydrazine) complexes of Mn and Fe triads with phosphite ligands, of the type $[M(RNHNH_2)(CO)_nL_{5-n}]^+$ (M = Mn, Re; $n = 2,3$), $[MH(RNHNH_2)L_4]^+$ and $[M(RNHNH_2)_2L_4]^{2+}$ (M = Fe, Ru, Os; L = phosphites) [11,12]. We have now extended these studies to molybdenum and tungsten and report here the synthesis and reactivity of hydrazine complexes of these metals, stabilised by phosphonite and phosphinite ligands.

2. Experimental

2.1. General comments

All synthetic work was carried out under Ar using standard Schlenk techniques or an inert atmosphere dry-box. All solvents were dried over appropriate drying agents, degassed on a vacuum line, and distilled into vacuum-tight storage flasks. $Mo(CO)_6$ and $W(CO)_6$ were STREM products, used as received. Phosphines $PPh(OEt)_2$ and PPh_2OEt were prepared by the method of Rabinowitz and Pellon [13]. Hydrazines $C_6H_5NHNH_2$ and CH_3NHNH_2 were Aldrich products and were used as received. Hydrazine NH_2NH_2 was prepared by decomposition of hydrazine cyanurate (Fluka) following the reported method [14]. High-grade (99.99%) lead(IV) acetate was purchased from Aldrich. Other reagents were purchased from commercial sources in the highest available purity and used as received. Infrared spectra (KBr pellets) were recorded on Perkin-Elmer Spectrum-One FT-IR spectrophotometer. NMR spectra (^1H, ^{31}P, ^{13}C) were obtained on AVANCE 300 Bruker spectrometer (300 MHz) at temperatures between +20 and −80 °C, unless otherwise noted. ^1H and $^{13}C\{^1H\}$ spectra are referred to internal tetramethylsilane; $^{31}P\{^1H\}$ chemical shifts are reported with respect to 85% H_3PO_4, with downfield shifts considered positive. *J* values are given in Hz. COSY, HMQC and HMBC NMR

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* Corresponding author.
E-mail address: albertin@unive.it (G. Albertin).

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http://dx.doi.org/10.1016/j.poly.2012.03.004

experiments were performed with standard programs. iNMR software package [15] was used to treat NMR data. The conductivity of 10^{-3} mol dm^{-3} solutions of the complexes in CH_3NO_2 at 25 °C was measured on a Radiometer CDM 83. Elemental analyses were determined in the Microanalytical Laboratory of the Dipartimento di Scienze Farmaceutiche, University of Padova (Italy).

2.2. Synthesis of precursor complexes

Complexes $Mo(CO)_4(pip)_2$ (pip = piperidine) and $W(CO)_3(CH_3CN)_3$ were prepared following the previously reported methods [16,17].

2.3. Synthesis of complexes

2.3.1. $Mo(CO)_4L_2$ (**1**) [L = $PPh(OEt)_2$ (**a**), PPh_2OEt (**b**)]

An excess of the appropriate phosphite (12 mmol) was added to a solution of $Mo(CO)_4(pip)_2$ (1.5 g, 3.97 mmol) in toluene (40 mL) and the reaction mixture was refluxed for 2 h. The solvent was removed under reduced pressure to give an oil which was triturated with ethanol (3 mL). A yellow solid slowly separated out which was filtered and crystallised from ethanol; Yield: 75%. **1a**: IR (KBr pellet) ν_{CO}: 1921 (m), 1893 (s); (Nujol mull) ν_{CO}: 1897 (s) cm^{-1}. ^1H NMR (CD_2Cl_2, 25 °C) δ: 7.63–7.36 (m, 10H, Ph), 3.99, 3.82 (m, 8H, CH_2), 1.31 (t, 12H, CH_3) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ: A_2 spin syst, 184.2 (s) ppm. *Anal.* Calc. for $C_{24}H_{30}MoO_8P_2$ (604.38): C, 47.69; H, 5.00. Found: C, 47.48; H, 5.13%. **1b**: IR (KBr pellet) ν_{CO}: 1900 (s) cm^{-1}. ^1H NMR [$(CD_3)_2CO$, 25 °C] δ: 7.67, 7.48 (m, 20H, Ph), 3.75 (m, 4H, CH_2), 1.27 (t, 6H, CH_3) ppm. $^{31}P\{^1H\}$ NMR [$(CD_3)_2CO$, 25 °C] δ: A_2 spin syst, 152.3 (s) ppm. *Anal.* Calc. for $C_{32}H_{30}MoO_6P_2$ (668.46): C, 57.50; H, 4.52. Found: C, 57.72; H, 4.65%.

2.3.2. $[Mo(CO)_3(NO)L_2]BPh_4$ (**2**) [L = $PPh(OEt)_2$ (**a**), PPh_2OEt (**b**)]

A slight excess of solid $NOPF_6$ (0.16 g, 0.91 mmol) was added to a solution of the appropriate complex $Mo(CO)_4L_2$ (**1**) (0.83 mmol) in dichloromethane (15 mL). The reaction mixture was stirred at room temperature for 90 min and then the solvent removed under reduced pressure. The oil obtained was treated with ethanol (2 mL) containing an excess of $NaBPh_4$ (0.565 g, 1.65 mmol). A yellow solid slowly separated out which was filtered and crystallised from dichloromethane and ethanol; Yield: 80%. **2a**: IR (KBr pellet) ν_{CO}: 2108 (m), 2039, 2016 (s); ν_{NO}: 1739 (s) cm^{-1}. ^1H NMR (CD_2Cl_2, 25 °C) δ: 7.70–6.88 (m, 30H, Ph), 3.97, 3.92 (qnt, 8H, CH_2), 1.39, 1.38 (t, 12H, CH_3) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ: AB spin syst, δ_A 157.2, δ_B 142.9 ppm, J_{AB} = 43.0 Hz. Λ_M = 51.7 Ω^{-1} mol^{-1} cm^2. *Anal.* Calc. for $C_{47}H_{50}BMoNO_8P_2$ (925.60): C, 60.99; H, 5.44; N, 1.51. Found: C, 60.76; H, 5.32; N, 1.59%. **2b**: IR (KBr pellet) ν_{CO}: 2106 (m), 2037, 2010 (s); ν_{NO}: 1747 (s) cm^{-1}. ^1H NMR (CD_2Cl_2, 25 °C) δ: 7.70–6.86 (m, 40H, Ph), 3.58, 3.49 (qnt, 4H, CH_2), 1.15, 1.13 (t, 6H, CH_3) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ: AB spin syst, δ_A 129.4, δ_B 115.6 ppm, J_{AB} = 82.0 Hz. Λ_M = 54.8 Ω^{-1} mol^{-1} cm^2. *Anal.* Calc. for $C_{55}H_{50}BMoNO_6P_2$ (989.69): C, 66.75; H, 5.09; N, 1.42. Found: C, 66.59; H, 5.21; N, 1.53%.

2.3.3. $MoBr(CO)_2(NO)L_2$ (**3**) [L = $PPh(OEt)_2$ (**a**), PPh_2OEt (**b**)]

An equimolar amount of solid $[NEt_4]Br$ (0.173 g, 0.82 mmol) was added to a solution of the appropriate complex $[Mo(CO)_3(NO)L_2]BPh_4$ (**2**) (0.82 mmol) in dichloromethane (10 mL) and the reaction mixture was stirred at room temperature for 4 h. The solvent was removed under reduced pressure leaving an oil which was treated with ethanol (2 mL). A yellow solid separated out from the resulting stirring solution, which was filtered and crystallised from dichloromethane and ethanol; Yield: 75%. **3a**: IR (KBr pellet) ν_{CO}: 1993 (s); ν_{NO}: 1635 (s) cm^{-1}. ^1H NMR (CD_2Cl_2, 25 °C) δ: 7.74–6.38 (m, 10H, Ph), 4.16, 3.99 (m, 8H, CH_2), 1.35 (t, 12H, CH_3) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ: A_2 spin syst, 161.7 (s) ppm. *Anal.* Calc. for $C_{22}H_{30}BrMoNO_7P_2$ (658.27): C, 40.14; H, 4.59; N, 2.13. Found: C, 40.29; H, 4.42; N, 2.00%. **3b**: IR (KBr pellet) ν_{CO}: 1967 (s), 1916 (m); ν_{NO}: 1622 (s); (Nujol mull) ν_{CO}: 1972 (s); ν_{NO}: 1624 (s) cm^{-1}. ^1H NMR (CD_2Cl_2, 25 °C) δ: 7.75, 7.47 (m, 20H, Ph), 3.91 (m, 4H, CH_2), 1.29 (t, 6H, CH_3) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ: A_2 spin syst, 131.1 (s) ppm. *Anal.* Calc. for $C_{30}H_{30}BrMoNO_5P_2$ (722.35): C, 49.88; H, 4.19; N, 1.94. Found: C, 49.66; H, 4.32; N, 2.05%.

2.3.4. $W(CO)_4[PPh(OEt)_2]_2$ (**4a**)

An excess of $PPh(OEt)_2$ (0.59 mL g, 2.98 mmol) was added to a solution of $W(CO)_6$ (0.5 g, 1.42 mmol) in toluene (80 mL) and the reaction mixture was irradiated at room temperature for 15 min in a Pyrex Schlenk-flask using a standard 125-W medium-pressure mercury arc lamp. The solvent was removed under reduced pressure to give an oil which was triturated with ethanol (2 mL). The white solid which slowly separated out was filtered and crystallised from ethanol; Yield: 25%. IR (KBr pellet) ν_{CO}: 1920 (m), 1887 (s); (Nujol mull) ν_{CO}: 1898 (s) cm^{-1}. ^1H NMR (CD_2Cl_2, 25 °C) δ: 7.61, 7.44 (m, 10H, Ph), 3.97, 3.81 (m, 8H, CH_2), 1.32 (t, 12H, CH_3) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ: A_2 spin syst, 156.3 (s) ppm, $J_{^{31}P^{183}W}$ = 363.0 Hz. *Anal.* Calc. for $C_{24}H_{30}O_8P_2W$ (692.28): C, 41.64; H, 4.37. Found: C, 41.51; H, 4.28%.

2.3.5. $[W(CO)_3(NO)\{PPh(OEt)_2\}_2]BPh_4$ (**5a**)

A slight excess of solid $NOPF_6$ (0.14 g, 0.79 mmol) was added to a solution of $W(CO)_4[PPh(OEt)_2]_4$ (**4a**) (0.50 g, 0.72 mmol) in dichloromethane (10 mL) and the reaction mixture was stirred at room temperature for 60 min. The solvent was removed under reduced pressure to leave an oil which was triturated with ethanol (2 mL) containing an excess of $NaBPh_4$ (0.49 g, 1.44 mmol). A yellow solid slowly separated out from the solution, which was filtered and crystallised from dichloromethane and ethanol; Yield: 80%. IR (KBr pellet) ν_{CO}: 2096 (m), 2025, 2001 (s); ν_{NO}: 1734 (s) cm^{-1}. ^1H NMR (CD_2Cl_2, 25 °C) δ: 7.62, 7.31, 7.02, 6.87 (m, 30H, Ph), 3.98, 3.93 (qnt, 8H, CH_2), 1.40, 1.39 (t, 12H, CH_3) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ: AB spin syst, δ_A 139.4, δ_B 131.8 ppm, J_{AB} = 37.0, $J_{^{31}PA^{183}W}$ = 358.0, $J_{^{31}PB^{183}W}$ = 242.8 Hz. Λ_M = 53.5 Ω^{-1} mol^{-1} cm^2. *Anal.* Calc. for $C_{47}H_{50}BNO_8P_2W$ (1013.50): C, 55.70; H, 4.97; N, 1.38. Found: C, 55.56; H, 5.08; N, 1.29%.

2.3.6. $W(CO)_3[PPh(OEt)_2]_3$ (**6a**)

An excess of $PPh(OEt)_2$ (1.52 mL, 7.67 mmol) was added to a solution of $W(CO)_3(CH_3CN)_3$ (1 g, 2.56 mmol) in dichloromethane (20 mL) and the reaction mixture was refluxed for 2 h. The solvent was removed under reduced pressure to give an oil which was triturated with ethanol (2 mL). A dark-blue solid separated out, which was filtered and crystallised from ethanol; Yield: 55%. IR (KBr pellet) ν_{CO}: 1974 (m), 1893, 1862 (s) cm^{-1}. ^1H NMR (CD_2Cl_2, 25 °C) δ: 7.70–7.25 (m, 15H, Ph), 3.98, 3.83, 3.67 (m, 12H, CH_2), 1.33, 1.27 (t, 18H, CH_3) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ: A_2B spin syst, δ_A 156.3, δ_B 154.4 ppm, J_{AB} = 25.8, $J_{^{31}PA^{183}W}$ = 363.4, $J_{^{31}PB^{183}W}$ = 317.3 Hz. Anal. Calc. for $C_{33}H_{45}O_9P_3W$ (862.47): C, 45.96; H, 5.26. Found: C, 45.74; H, 5.37%.

2.3.7. $[W(CO)_2(NO)\{PPh(OEt)_2\}_3]BPh_4$ (**7a**)

A slight excess of solid $NOPF_6$ (0.112 g, 0.64 mmol) was added to a solution of complex $W(CO)_3[PPh(OEt)_2]_3$ (**6a**) (0.50 g, 0.58 mmol) in dichloromethane (15 mL) and the reaction mixture was stirred at room temperature for 60 min. The solvent was removed under reduced pressure leaving an oil which was treated with ethanol (2 mL) containing an excess of $NaBPh_4$ (0.60 g, 1.75 mmol). A yellow solid slowly separated out which was filtered and crystallised from dichloromethane and ethanol; Yield: 90%. IR (KBr pellet) ν_{CO}: 2037, 1970 (s); ν_{NO}: 1694 (s) cm^{-1}. ^1H NMR

(CD_2Cl_2, 25 °C) δ: 7.60–6.87 (m, 35H, Ph), 3.90, 3.80 (m, 12H, CH_2), 1.35, 1.34 (t, 18H, CH_3) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ: A_2B spin syst, δ_A 144.8, δ_B 134.2 ppm, J_{AB} = 40.5, $J_{^{31}PA^{183}W}$ = 359.4, $J_{^{31}PB^{183}W}$ = 239.8 Hz. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ: 205.9 (dt, CO, J_{CP} = 9.8, J_{CP} = 17.4 Hz), 165–122 (m, Ph), 65.9 (d), 64.4 (t) (CH_2), 16.4 (t, CH_3) ppm. $\Lambda_M = 53.6\ \Omega^{-1}\ mol^{-1}\ cm^2$. *Anal.* Calc. for $C_{56}H_{65}BNO_9P_3W$ (1183.69): C, 56.82; H, 5.53; N, 1.18. Found: C, 56.58; H, 5.40; N, 1.26%.

*2.3.8. [Mo(CO)(CH_3NHNH_2)(NO)L_3]BPh_4 (**8**) [L = PPh($OEt)_2$ (**a**), PPh_2OEt (**b**)]*

An excess of methylhydrazine CH_3NHNH_2 (144 μL, 2.70 mmol) was added to a solution of the appropriate complex [Mo$(CO)_3$(NO)L_2]BPh_4 (**2**) (0.54 mmol) in dichloromethane (15 mL) and the reaction mixture was stirred at room temperature for 2 h. The solvent was removed under reduced pressure leaving an oil which was treated with ethanol (2 mL) containing an excess of $NaBPh_4$ (0.55 g, 1.62 mmol). A yellow solid separated out from the resulting solution, which was filtered and crystallised from dichloromethane and ethanol; Yield: 45%. **8a**: IR (KBr pellet) ν_{NH}: 3334, 3277 (m); ν_{CO}: 1977 (s); ν_{NO}: 1658 (s) cm^{-1}. ^1H NMR (CD_2Cl_2, 25 °C) δ: 7.51, 7.33 (m, 35H, Ph), 4.05, 3.95 (m, 12H, CH_2), 2.17 (br, 2H, NH_2), 1.90 (m, 1H, NH), 1.64 (d, 3H, CH_3N, J_{HH} = 4 Hz), 1.42, 1.41, 1.39 (t, 18H, CH_3 phos) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ: A_2B spin syst, δ_A 173.7, δ_B 169.2 ppm, J_{AB} = 37.3 Hz. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ: 219.5 (dt, CO, J_{CP} = 50.6, J_{CP} = 11.3 Hz), 165–122 (m, Ph), 64.2 (m, CH_2), 43.3 (s, CH_3N), 16.7 (m, CH_3 phos) ppm. $\Lambda_M = 49.5\ \Omega^{-1}\ mol^{-1}\ cm^2$. Anal. Calc. for $C_{56}H_{71}BMoN_3O_8P_3$ (1113.85): C, 60.39; H, 6.42; N, 3.77. Found: C, 60.20; H, 6.28; N, 3.91%. **8b**: IR (KBr pellet) ν_{NH}: 3323, 3255 (m); ν_{CO}: 1983 (s); ν_{NO}: 1629 (s) cm^{-1}. ^1H NMR (CD_2Cl_2, 25 °C) δ: 7.55–6.88 (m, 50H, Ph), 3.55 (m), 3.30 (qnt) (6H, CH_2), 1.75 (m, br, 2H, NH_2), 1.58 (br, 1H, NH), 1.34 (d, 3H, CH_3N, J_{HH} = 4 Hz), 0.94, 0.64 (t, 9H, CH_3 phos) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ: A_2B spin syst, δ_A 142.4, δ_B 139.4 ppm, J_{AB} = 32.0 Hz. $\Lambda_M = 54.1\ \Omega^{-1}\ mol^{-1}\ cm^2$. *Anal.* Calc. for $C_{68}H_{71}BMoN_3O_5P_3$ (1209.98): C, 67.50; H, 5.91; N, 3.47. Found: C, 67.32; H, 5.77; N, 3.33%.

*2.3.9. [Mo(CO)(NH_2NH_2)(NO){PPh($OEt)_2$}$_3$]BPh_4 (**9a**)*

A slight excess of hydrazine NH_2NH_2 (7.6 μL, 0.24 mmol) was added to a solution of [Mo$(CO)_3$(NO){PPh($OEt)_2$}$_2$]BPh_4 (**2a**) (0.20 g, 0.22 mmol) in dichloromethane (10 mL) and the reaction mixture was stirred at room temperature for 2 h. The solvent was removed under reduced pressure leaving an oil which was treated with ethanol (2 mL) containing an excess of $NaBPh_4$ (0.144 g, 0.42 mmol). A yellow solid slowly separated out from the resulting solution, which was filtered and crystallised from dichloromethane and ethanol; Yield: 15%. IR (KBr pellet) ν_{NH}: 3338, 3278, 3255 (m); ν_{CO}: 1978 (s); ν_{NO}: 1651 (s) cm^{-1}. ^1H NMR (CD_2Cl_2, 25 °C) δ: 7.52–6.84 (m, 35H, Ph), 4.10–3.85 (m, 12H, CH_2), 2.30 (m, 2H, Mo-NH_2), 1.55 (m, 2H, N-NH_2), 1.38, 1.36, 1.34 (t, 18H, CH_3 phos) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ: A_2B spin syst, δ_A 172.7, δ_B 168.8 ppm, J_{AB} = 37.3 Hz. $\Lambda_M = 53.4\ \Omega^{-1}\ mol^{-1}\ cm^2$. *Anal.* Calc. for $C_{55}H_{69}BMoN_3O_8P_3$ (1099.82): C, 60.06; H, 6.32; N, 3.82. Found: C, 59.84; H, 6.45; N, 3.70%.

*2.3.10. [W(CO)(CH_3NHNH_2)(NO){PPh($OEt)_2$}$_3$]BPh_4 (**10a**)*

An excess of methylhydrazine CH_3NHNH_2 (26 μL, 0.49 mmol) was added to a solution of complex [W$(CO)_3$(NO){PPh($OEt)_2$}$_2$]BPh_4 (**5a**) (0.100 g, 0.1 mmol) in dichloromethane (15 mL) and the reaction mixture was stirred at room temperature for 3 h. The solvent was removed under reduced pressure to give an oil which was treated with ethanol (2 mL) containing an excess of $NaBPh_4$ (68 mg, 0.20 mmol). An orange solid separated out which was filtered and crystallised from dichloromethane and ethanol; Yield: 35%. IR (KBr pellet) ν_{NH}: 3328, 3272 (m); ν_{CO}: 1963 (s); ν_{NO}: 1648 (s) cm^{-1}. ^1H NMR (CD_2Cl_2, 25 °C) δ: 7.65–6.87 (m, 35H, Ph), 4.06, 3.89 (m, 12H, CH_2), 2.29 (br, 2H, NH_2), 1.86 (m, 1H, NH), 1.58 (d, 3H, CH_3N, J_{HH} = 4 Hz), 1.42, 1.38, 1.35 (t, 18H, CH_3 phos) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ: A_2B spin syst, δ_A 156.5, δ_B 156.0 ppm, J_{AB} = 28.2 Hz. $\Lambda_M = 55.1\ \Omega^{-1}\ mol^{-1}\ cm^2$. *Anal.* Calc. for $C_{56}H_{71}BN_3O_8P_3W$ (1201.75): C, 55.97; H, 5.95; N, 3.50. Found: C, 55.76; H, 5.83; N, 3.61%.

*2.3.11. [Mo(CO)($CH_3N{=}NH$)(NO)L_3]BPh_4 (**11**) [L = PPh($OEt)_2$ (**a**), PPh_2OEt (**b**)]*

A solid sample of the appropriate methylhydrazine complex [Mo(CO)(CH_3NHNH_2)(NO)L_3]BPh_4 (**8**) (0.16 mmol) was placed in a 25-mL three-necked round-bottomed flask fitted with a solid-addition side-arm containing a slight excess of Pb$(OAc)_4$ (80 mg, 0.18 mmol). Dichloromethane (10 mL) was added, the solution cooled to −30 °C and lead acetate added portion wise to the cold stirring solution over 20–30 min. The reaction mixture was allowed to reach 0 °C and stirred for 15 min and then the solvent removed under reduced pressure. The oil obtained was treated with ethanol (2 mL) containing a slight excess of $NaBPh_4$ (68 mg, 0.20 mmol). An orange solid slowly separated out from the resulting solution, which was filtered and crystallised from dichloromethane and ethanol; Yield: 65%. **11a**: IR (KBr pellet) ν_{CO}: 1987 (s); ν_{NO}: 1661 (s) cm^{-1}. ^1H NMR (CD_2Cl_2, 25 °C) δ: 11.06 (s, br, 1H, NH), 7.55–6.84 (m, 35H, Ph), 4.16, 4.01, 3.89 (m, 12H, CH_2), 2.57 (q, 3H, CH_3N), 1.46, 1.40, 1.39 (t, 18H, CH_3 phos) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ: A_2B spin syst, δ_A 174.6, δ_B 170.7 ppm, J_{AB} = 35.5 Hz. $\Lambda_M = 52.9\ \Omega^{-1}\ mol^{-1}\ cm^2$. *Anal.* Calc. for $C_{56}H_{69}BMoN_3O_8P_3$ (1111.83): C, 60.49; H, 6.26; N, 3.78. Found: C, 60.25; H, 6.15; N, 3.91%. **11b**: IR (KBr pellet) ν_{CO}: 1982 (s); ν_{NO}: 1633 (s) cm^{-1}. ^1H NMR (CD_2Cl_2, 25 °C) δ: 10.44 (s, br, 1H, NH), 7.79–7.86 (m, 50H, Ph), 3.43 (m), 3.34 (qnt) (6H, CH_2), 2.21 (q, 3H, CH_3N), 0.87, 0.63 (t, 9H, CH_3 phos) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ: A_2B spin syst, δ_A 143.8, δ_B 140.9 ppm, J_{AB} = 31.0 Hz. $\Lambda_M = 54.4\ \Omega^{-1}\ mol^{-1}\ cm^2$. *Anal.* Calc. for $C_{68}H_{69}BMoN_3O_5P_3$ (1207.96): C, 67.61; H, 5.76; N, 3.48. Found: C, 67.44, H 5.89, N 3.37%.

*2.3.12. [W(CO)($CH_3N{=}NH$)(NO){PPh($OEt)_2$}$_3$]BPh_4 (**12a**)*

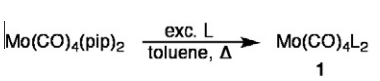
This complex was prepared exactly like the related molybdenum compounds **11** and crystallised from dichloromethane and ethanol; Yield: 70%. IR (KBr pellet) ν_{CO}: 1960 (s); ν_{NO}: 1648 (s) cm^{-1}. ^1H NMR (CD_2Cl_2, 25 °C) δ: 12.13 (s, br, 1H, NH), 7.70–6.86 (m, 35H, Ph), 4.10, 3.87 (m, 12H, CH_2), 2.18 (q, 3H, CH_3N), 1.36, 1.34, 1.30 (t, 18H, CH_3 phos) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ: A_2B spin syst, δ_A 155.0, δ_B 149.5 ppm, J_{AB} = 30.1 Hz. $\Lambda_M = 50.7\ \Omega^{-1}\ mol^{-1}\ cm^2$. *Anal.* Calc. for $C_{56}H_{69}BN_3O_8P_3W$ (1199.73): C, 56.06; H, 5.80; N, 3.50. Found: C, 55.87; H, 5.72; N, 3.37%.

3. Results and discussion

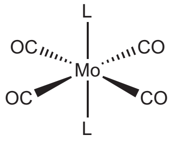
3.1. Preparation of precursor complexes

Mixed-ligands complexes Mo$(CO)_4L_2$ with carbonyl and phosphine were prepared by substituting piperidine ligands in the compound Mo$(CO)_4(pip)_2$, as shown in Scheme 1.

Complexes **1** were isolated in good yields as stable yellow solids and characterised by analytical and spectroscopic data (IR and NMR). *Trans* geometry **I** in solution was also established (Chart 1).



Scheme 1. pip = piperidine; L = PPh($OEt)_2$ (**a**), PPh_2OEt (**b**).



(I) 1

Chart 1.

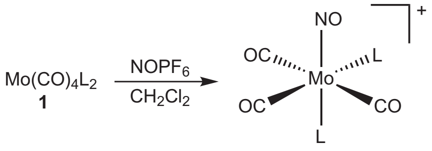
The IR spectrum of complex $Mo(CO)_4(PPh_2OEt)_2$ (**1b**) shows only one ν_{CO} band at 1900 cm^{-1} (KBr), indicating a *trans* arrangement of the ligands [18], as in geometry **I**. Instead, the related complex $Mo(CO)_4[PPh(OEt)_2]_2$ (**1a**) shows, in KBr, two ν_{CO} bands, one of medium intensity at 1921 and one strong at 1893 cm^{-1}, which may suggest a mutually *cis* position of the two groups. However, in Nujol mull, the spectra show only one strong band at 1897 cm^{-1} suggesting, in this case too, a *trans* arrangement of the ligands. The $^{31}P\{^1H\}$ NMR spectra of both carbonyls **1** support geometry **I**, showing a sharp singlet at 184.2 ppm, for **1a**, and at 152.3 ppm, for **1b**, due to the two magnetically equivalent phosphine ligands.

Carbonyl complexes $Mo(CO)_4L_2$ (**1**) react with $NOPF_6$ in CH_2Cl_2 to give cationic nitrosyl derivatives $[Mo(CO)_3(NO)L_2]^+$ (**2**), which were isolated as BPh_4^- salts and characterised (Scheme 2).

The reaction proceeds with substitution of one carbonyl ligand by NO^+ affording the mixed-ligand nitrosyl derivatives **2**. Treatment of these complexes with $[NEt_4]Br$ in CH_2Cl_2 gives the bromo-nitrosyl derivatives $MoBr(CO)_2(NO)L_2$ (**3**), which were isolated in good yield and characterised. Bromide substitutes one carbonyl ligand in **2**, yielding the neutral complex **3** (Scheme 3).

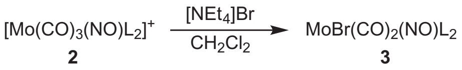
Related triphenylphosphine complexes $Mo(CO)_4(PPh_3)_2$ have been reported [19] to give $MoF_2(NO)_2(PPh_3)_2$ by treatment with $NOPF_6$, whereas the dinitrosyl complex $MoBr_2(NO)_2(PPh_3)_2$ was obtained in the presence of $NOPF_6$ and $[NBu_4]Br$. The tris(phosphine) complexes $MoX(CO)(NO)(PMePh_2)_3$ were also described [20].

The new nitrosyl complexes $[Mo(CO)_3(NO)L_2]BPh_4$ (**2**) and $MoBr(CO)_2(NO)L_2$ (**3**) were separated as yellow solids, stable in air and in solution of polar solvents, where they behave as either 1:1 (**2**) or non-electrolytes (**3**) [21]. Analytical and spectroscopic data (IR, NMR) support the proposed formulations and geometries in solution were also established. The IR spectra of nitrosyl complexes $[Mo(CO)_3(NO)L_2]BPh_4$ (**2**) show three ν_{CO} bands – one of medium intensity and two strong – suggesting a *mer* arrangement of the three carbonyl ligands. The spectra also show one strong absorption at 1739 (**2a**) and 1747 cm^{-1} (**2b**) attributed to the ν_{NO} of the nitrosyl ligand. By comparison with literature data [22], the value of the ν_{NO} also suggest the presence of a linear NO^+ group, with the metal centre in a formal oxidation state of zero [Mo(0)]. In the temperature range +20 to −80 °C, the $^{31}P\{^1H\}$ NMR spectra of complexes **2** appear as AB quartets, which can be simulated with the parameters reported in Section 2 and suggesting the magnetic non-equivalence of the two phosphines. On the basis of these data, *mer–cis* geometry **II** (Scheme 2) may be proposed for nitrosyl complexes **2**.



(II) 2

Scheme 2. L = $PPh(OEt)_2$ (**a**), PPh_2OEt (**b**).



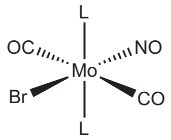
Scheme 3. L = $PPh(OEt)_2$ (**a**), PPh_2OEt (**b**).

The IR spectrum of $MoBr(CO)_2(NO)[PPh(OEt)_2]_2$ (**3a**) shows only one ν_{CO} band at 1993 cm^{-1} indicating a mutually *trans* position of the two carbonyl ligands. One strong band at 1635 cm^{-1}, attributed to the ν_{NO} of the nitrosyl ligand, is also present. Instead, the IR spectrum of the related complex $MoBr(CO)_2(NO)(PPh_2OEt)_2$ (**3b**) shows, in KBr, two ν_{CO} bands, one strong at 1967 and one of medium intensity at 1916 cm^{-1}. A strong band at 1622 cm^{-1} of the nitrosyl ligand is also present. However, in Nujol, the spectrum shows only one strong ν_{CO} band at 1972 cm^{-1}, suggesting the mutually *trans* position of the two carbonyl ligands. In the temperature range +20 to −80 °C, the $^{31}P\{^1H\}$ NMR spectrum is a sharp singlet suggesting the magnetic equivalence of the two phosphonite ligands. The ^1H NMR spectrum also suggests a mutually *trans* position of the two phosphines, based on the complicated multiplets at 4.16 and 3.99 ppm, for **3a**, and at 3.91 ppm, for **3b**, of the methylene protons of the substituents, due to virtual coupling [23] of two phosphorus atoms in a mutually *trans* position. On the basis of these data, *trans–trans* geometry **III** (Chart 2) may be proposed for phenyldiethoxyphosphine derivatives **3**.

Tungsten bis(phosphonite) complex $W(CO)_4[PPh(OEt)_2]_2$ (**4**) was prepared by photochemical substitution of carbonyls by phosphonites in $W(CO)_6$, as shown in Scheme 4.

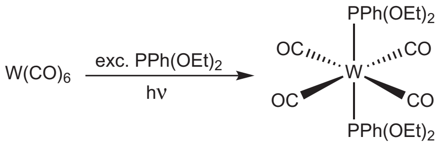
Treatment of compound $W(CO)_4[PPh(OEt)_2]_2$ (**4**) with $NOPF_6$ in CH_2Cl_2 gave the cationic nitrosyl complex $[W(CO)_3(NO)\{PPh(OEt)_2\}_2]^+$ (**5**), which was separated as tetraphenylborate salt and characterised (Scheme 5).

The reaction proceeds with substitution of one carbonyl ligand, yielding the tricarbonyl-nitrosyl derivative **5**. A similar reaction



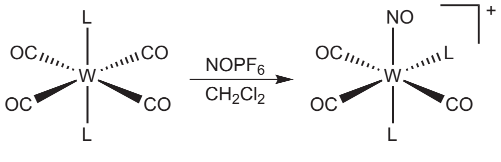
(III) 3

Chart 2.



(IV) 4

Scheme 4.



4 (V) 5

Scheme 5. L = $PPh(OEt)_2$.

[19] was observed in the related complex $W(CO)_4(PPh_3)_2$ [24], yielding the cation $[W(CO)_3(NO)(PPh_3)_2]^+$.

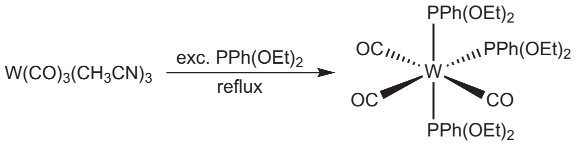
New tungsten complexes **4** and **5** were isolated as white (**4**) or yellow (**5**) solids, stable in air and in solution of polar organic solvents, where they behave as either non-electrolyte (**4**) or 1:1 electrolytes (**5**) [21]. Analytical and spectroscopic data support the proposed formulation and a geometry in solution was also established. The IR spectrum in KBr of the tetracarbonyl complex $W(CO)_4[PPh(OEt)_2]_2$ (**4**) shows one strong ν_{CO} band at 1887 cm^{-1} and one of medium intensity at 1920 cm^{-1}. However, in Nujol, only one strong ν_{CO} band at 1898 cm^{-1} was observed, suggesting *trans* geometry **IV** for the compound [18]. The ^{31}P NMR spectrum shows a sharp singlet at 156.7 ppm, with the characteristic satellites due to coupling with ^{183}W ($J_{^{31}P^{183}W}$ = 363.0 Hz), indicating the magnetic equivalence of the two phosphines, as expected for **IV**-type geometry.

The IR spectrum of the tricarbonyl-nitrosyl complex $[W(CO)_3(NO)\{PPh(OEt)_2\}_2]BPh_4$ (**5**) shows three ν_{CO} bands – one of medium intensity and two strong – suggesting *mer* arrangement of the three carbonyl ligands. The spectrum also shows a strong band at 1734 cm^{-1}, attributed to the ν_{NO} of the nitrosyl group. In the temperature range between +20 and −80 °C, the ^{31}P NMR spectrum is an AB quartet, which can be simulated with the parameters reported in the Section 2 and indicating that the two phosphines are not magnetically equivalent. On the basis of these data, *mer–cis* geometry **V** may be proposed for the nitrosyl complex **5**.

Tricarbonyl complex $W(CO)_3[PPh(OEt)_2]_3$ (**6**) was prepared by substituting the nitrile ligands with phosphonites in the acetonitrile precursor $W(CO)_3(CH_3CN)_3$, as shown in Scheme 6.

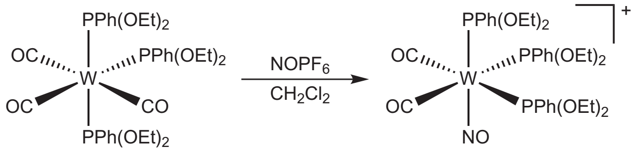
The phosphine complex [25] $W(CO)_3[PPh(OEt)_2]_3$ (**6**) reacts with $NOPF_6$ in CH_2Cl_2 to give the nitrosyl derivative $[W(CO)_2(NO)\{PPh(OEt)_2\}_3]^+$ (**7**), which was isolated as BPh_4 salt and characterised (Scheme 7).

The new complexes **6** and **7** were separated as green (**6**) or yellow (**7**) solids stable in air and in solution of polar organic solvents where they behave as either non-electrolyte (**6**) or 1:1 electrolyte (**7**) [21]. Analytical and spectroscopic data (IR, NMR) support the proposed formulation and allows geometry in solution to be proposed. In the ν_{CO} region, the IR spectrum of tricarbonyl compound $W(CO)_3[PPh(OEt)_2]_3$ (**6**) shows one band of medium intensity and two strong ones, suggesting *mer* arrangement of the three carbonyl ligands. The ^{31}P NMR spectrum appears as an A_2B multiplet, which can be simulated with the parameters reported in the Section 2 and indicating that two phosphines are magnetically equivalent and different from the third. On the basis of these data, *mer* geometry **VI** may be proposed for complex **6**.



(VI) 6

Scheme 6.



6 (VII) 7

Scheme 7.

The IR spectrum of the nitrosyl complex $[W(CO)_2(NO)\{PPh(OEt)_2\}_3]BPh_4$ (**7**) shows two ν_{CO} bands, at 2037 and 1970 cm^{-1}, indicating a mutually *cis* position of the two carbonyl ligands. A strong absorption at 1694 cm^{-1} is also present, due to the ν_{NO} of the nitrosyl group. The ^{31}P NMR spectrum appears as an A_2B multiplet, which can be simulated with the parameters reported in the Section 2 and indicating that two phosphines are magnetically equivalent and different from the third. As the ^{13}C NMR spectrum shows only one multiplet (doublet of triplets) in the carbonyl carbon region at 205.9 ppm, due to the magnetic equivalence of the two CO ligands, *fac–cis* geometry **VII** is proposed in solution for the nitrosyl derivative **7**.

3.2. Preparation and reactivity of hydrazine complexes

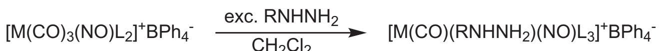
All carbonyl complexes of molybdenum and tungsten **1**–**7** were reacted with hydrazine, in an attempt to prepare $RNHNH_2$ derivatives. The results showed that only cationic nitrosyl complexes $[M(CO)_3(NO)L_2]BPh_4$ (**2**, **5**) (M = Mo, W) react with hydrazines $RNHNH_2$ to give the related complexes $[M(CO)(RNHNH_2)(NO)L_3]BPh_4$ (**8**–**10**), which were isolated in the solid state and characterised (Scheme 8).

The other complexes, **1**, **3**, **4**, **6** and **7**, do not react with hydrazines at room temperature and the starting complexes were recovered unchanged even after some days of reaction. Instead, in reflux conditions only some decompositions were observed and no hydrazine complexes could be obtained.

The reaction of tricarbonyl species **2** and **5** with hydrazines is rather surprising, because it does not involve the simple substitution of one ligand with hydrazine, but is followed by a redistribution of ligands between the molecules, yielding the probably more stable tris(phosphine) complexes $[M(CO)(RNHNH_2)(NO)L_3]BPh_4$ (**8**–**10**).

It is worth noting that only with methylhydrazine were both Mo and W complexes obtained as solids in moderate yields, whereas with phenylhydrazine no derivative was separated in pure form. At room temperature, the reaction with $PhNHNH_2$ was very slow, but reflux conditions caused only decomposition, preventing the separation of phenylhydrazine derivatives. Instead, hydrazine NH_2NH_2 gives the stable molybdenum complex **9a** in low yield, and only a mixture of products, which were not separated, was obtained with tungsten.

The new hydrazine complexes **8**–**10** were isolated as yellow solids, stable in air and in solution of polar organic solvents, where they behave as 1:1 electrolytes [21]. The elemental analysis and spectroscopic data (IR, NMR) support the proposed formulation. The IR spectra of methylhydrazine complexes **8** and **10** show three bands of medium intensity between 3334 and 3255 cm^{-1} attributed to the ν_{NH} of the hydrazine ligand. The spectra also show one strong band at 1983–1963 cm^{-1}, attributed to the ν_{CO} of the carbonyl group, and a strong one at 1663–1629 cm^{-1} due to the ν_{NO} of the nitrosyl ligand. Beside the signals of the phosphines and BPh_4 anion, the ^1H NMR spectra of $[M(CO)(CH_3NHNH_2)(NO)L_3]BPh_4$ (**8**, **10**) show one slightly broad multiplet at 2.29–1.75 ppm, attributed to the metal-bonded NH_2 group, and one multiplet at 1.90–1.58 ppm, due to the NH moiety of the hydrazine ligand. In the spectra, a doublet at 1.64–1.34 ppm is also present



$$\underset{\mathbf{2,\ 5}}{[M(CO)_3(NO)L_2]^+BPh_4^-} \xrightarrow[CH_2Cl_2]{exc.\ RNHNH_2} \underset{\mathbf{8–10}}{[M(CO)(RNHNH_2)(NO)L_3]^+BPh_4^-}$$

Scheme 8. M = Mo (**8**, **9**), W (**10**); L = $PPh(OEt)_2$ (**a**), PPh_2OEt (**b**); R = CH_3 (**8**, **10**), H (**9**).

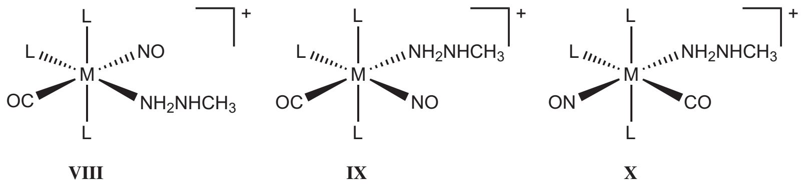
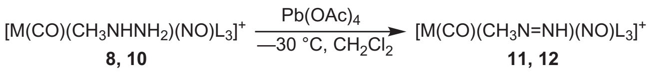


Chart 3.

and was attributed to the methyl substituent of the CH_3NHNH_2 ligand. These attributions were supported by integrations of the proton signals, ^1H–^1H and ^1H–^{31}P decoupling and COSY experiments, which strongly support the presence of the hydrazine ligand. In the temperature range between +20 and −80 °C, the ^{31}P NMR spectra are A_2B multiplets, indicating that two phosphines are magnetically equivalent and different from the third. However, spectroscopic data alone do not allow us to decide unambiguously between the three geometries of Chart 3 for methylhydrazine complexes **8** and **10**.

Unfortunately, any attempt to determine the crystal structure by X-ray diffraction studies failed, owing to the poor quality of the crystals obtained, and therefore no geometry can reasonably be proposed.

The IR spectrum of hydrazine complex $[Mo(CO)(NH_2NH_2)(NO)\{PPh(OEt)_2\}_3]BPh_4$ (**9a**) shows one ν_{CO} band at 1978 cm^{-1}, one ν_{NO} at 1651 cm^{-1} and three medium intensity absorptions at 3338, 3278, 3255 cm^{-1}, attributed to the ν_{NH} of the hydrazine ligand. However, its presence is confirmed by the ^1H NMR spectrum, which shows a broad multiplet at 2.30 ppm, due to the metal-bonded NH_2 group, and the multiplet of the end-on NH_2 moiety at 1.55 ppm. The ^{31}P NMR spectrum was an A_2B multiplet, indicating that two phosphites are magnetically equivalent and different from the third. However, like methylhydrazine complexes **8** and **10**, the spectroscopic data do not allow us to decide between the three geometries of Chart 3.



$$\underset{\textbf{8, 10}}{[M(CO)(CH_3NHNH_2)(NO)L_3]^+} \xrightarrow[-30\ ^\circ C,\ CH_2Cl_2]{Pb(OAc)_4} \underset{\textbf{11, 12}}{[M(CO)(CH_3N{=}NH)(NO)L_3]^+}$$

Scheme 9. M = Mo (**11**), W (**12**); L = $PPh(OEt)_2$ (**a**), PPh_2OEt (**b**).

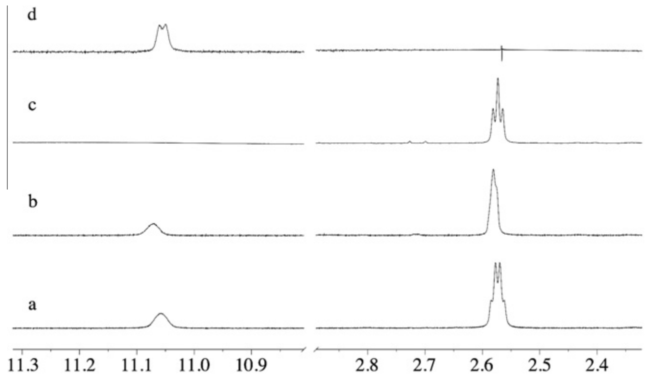


Fig. 1. ^1H NMR spectra of complex **11a** in CD_2Cl_2 at 298 K, signals of the $HN{=}NCH_3$ moiety: (a) ^1H spectrum; (b) $^1H\{^{31}P\}$ spectrum; (c) ^1H with homodecoupling at 11.06 δ; (d) ^1H with homodecoupling at 2.57 δ.

Reactivity studies on hydrazine complexes $[M(CO)(RNHNH_2)(NO)L_3]BPh_4$ (**8**–**10**) towards oxidation reaction were undertaken and the results are summarised in Scheme 9.

Methylhydrazine complexes $[M(CO)(CH_3NHNH_2)(NO)L_3]BPh_4$ (**8**, **10**) react with $Pb(OAc)_4$ at −30 °C to give methyldiazene derivatives $[M(CO)(CH_3N{=}NH)(NO)L_3]BPh_4$ (**11**, **12**), which were isolated as solids and characterised. The reaction proceeds with selective oxidation of the coordinated methylhydrazine to methyldiazene, which turned out to be stable and could be isolated.

Instead, the related hydrazine complex $[Mo(CO)(NH_2NH_2)(NO)\{PPh(OEt)_2\}_3]BPh_4$ (**9a**) reacts with $Pb(OAc)_4$ at −30 °C with a colour change of the solution, but no stable product was isolated.

The new diazene complexes **11** and **12** were isolated as yellow-orange solids, stable in air and in solution of polar organic solvents, where they behave as 1:1 electrolytes [21]. The analytical and spectroscopic data (IR, NMR) support the proposed formulation. Diagnostic for the presence of the methyldiazene moiety are ^1H NMR spectra, which show the characteristic signal [3] of the diazene hydrogen atom at 12.13–10.44 ppm. The spectra also showed a quartet at 2.57–2.18 ppm and was attributed – by decoupling and COSY experiments – to the methyl substituent of the diazene ligand $CH_3N{=}NH$. The multiplicity of this signal was due both to the H-H coupling with the diazene NH proton (see Fig. 1b) and to "long range" H-P coupling with the phosphorus nuclei of only two phosphines (see Fig. 1c). Coupling with the third phosphine is probably small and was not observed.

The IR spectra show the expected strong bands due to the ν_{CO} at 1987–1960 cm^{-1} and to the ν_{NO} at 1661–1633 cm^{-1}, whereas the ^{31}P NMR spectra was an A_2B multiplet, suggesting the magnetic equivalence of two phosphines, different from the third. However, these spectroscopic data do not allow us to decide between the three geometries of Chart 4, although ^1H NMR spectra of methyldiazene complexes may suggest **XI**-type geometry.

4. Conclusions

In this paper we prove that hydrazine complexes of molybdenum and tungsten, stabilised by phosphonite and phosphinite L ligands, can be prepared with nitrosyl compounds $[M(CO)_3(NO)L_2]BPh_4$ as precursors. Among the properties shown by these

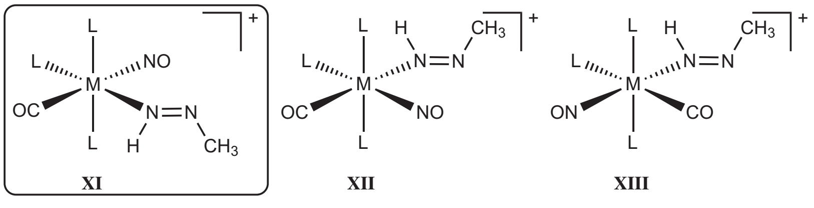


Chart 4.

hydrazine complexes is easy oxidation with Pb(OAc)$_4$, yielding methyldiazene derivatives.

Acknowledgment

The financial support of MIUR (Rome)-PRIN 2009 is gratefully acknowledged. We thank Mrs. Daniela Baldan for her technical assistance.

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