Inorg. Chem. **2006**, *45*, 3816–3825

Synthesis and Characterization of Triazenide and Triazene Complexes of Ruthenium and Osmium

Gabriele Albertin,*,† Stefano Antoniutti,† Marco Bedin,† Jesús Castro,‡ and Soledad Garcia-Fontán‡

Dipartimento di Chimica, Università Ca' Foscari di Venezia, Dorsoduro 2137, 30123 Venezia, Italy, and Departamento de Química Inorgánica, Universidade de Vigo, Facultade de Química, Edificio de Ciencias Experimentais, 36310 Vigo, Galicia, Spain

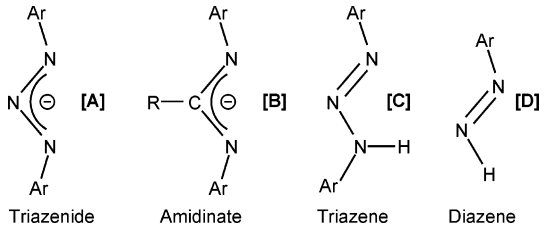
Received December 1, 2005

Triazenide [M(η^2-1,3-ArNNNAr)P_4]BPh_4 [M = Ru, Os; Ar = Ph, *p*-tolyl; P = $P(OMe)_3$, $P(OEt)_3$, $PPh(OEt)_2$] complexes were prepared by allowing triflate [M(κ^2-OTf)P_4]OTf species to react first with 1,3-ArN═NN(H)Ar triazene and then with an excess of triethylamine. Alternatively, ruthenium triazenide [Ru(η^2-1,3-ArNNNAr)P_4]BPh_4 derivatives were obtained by reacting hydride [RuH(η^2-H_2)P_4]$^+$ and RuH(κ^1-OTf)P_4 compounds with 1,3-diaryltriazene. The complexes were characterized by spectroscopy and X-ray crystallography of the [Ru(η^2-1,3-PhNNNPh){$P(OEt)_3$}$_4$]BPh_4 derivative. Hydride triazene [OsH(η^1-1,3-ArN═NN(H)Ar)P_4]BPh_4 [P = $P(OEt)_3$, $PPh(OEt)_2$; Ar = Ph, *p*-tolyl] and [RuH{η^1-1,3-*p*-tolyl-N═NN(H)-*p*-tolyl}{$PPh(OEt)_2$}$_4$]BPh_4 derivatives were prepared by allowing κ^1-triflate MH(κ^1-OTf)P_4 to react with 1,3-diaryltriazene. The [Os(κ^1-OTf){η^1-1,3-PhN═NN(H)Ph}{$P(OEt)_3$}$_4$]BPh_4 intermediate was also obtained. Variable-temperature NMR studies were carried out using ^{15}N-labeled triazene complexes prepared from the 1,3-$Ph^{15}N{=}N^{15}N(H)Ph$ ligand. Osmium dihydrogen [OsH(η^2-H_2)P_4]BPh_4 complexes [P = $P(OEt)_3$, $PPh(OEt)_2$] react with 1,3-ArN═NN(H)Ar triazene to give the hydride–diazene [OsH(ArN═NH)P_4]BPh_4 derivatives. The X-ray crystal structure determination of the [OsH(PhN═NH){$PPh(OEt)_2$}$_4$]BPh_4 complex is reported. A reaction path to explain the formation of the diazene complexes is also reported.

Introduction

The 1,3-diaryltriazenide [ArNNNAr]$^-$ anion (Chart 1, **A**) is a "small-bite" ligand that can act as a monodentate,[1] a chelate,[2] or a bridging ligand,[3] giving numerous examples of transition metal complexes.[1−3] Its use in coordination chemistry, however, is less developed when compared to related ligands, such as amidinate [ArNC(R)NAr]$^-$ (**B**),[4] or anionic N−C−X-type (X = N, O, S) ligands,[5] even though

Chart 1



* To whom correspondence should be addressed. E-mail:albertin@unive.it.

† Università Ca' Foscari di Venezia.

‡ Universidade de Vigo.

(1) (a) Brown, L. D.; Ibers, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 1957−1958. (b) Immirzi, A.; Porzio, W.; Bombieri, G.; Toniolo, L. *J. Chem. Soc. Dalton Trans.* **1980**, 1098−1100.

(2) (a) Laing, K. R.; Robinson, S. D.; Uttley, M. F. *J. Chem. Soc. Dalton Trans.* **1974**, 1205−1214. (b) Rossi, R.; Duatti, A.; Magon, L.; Toniolo, L. *Inorg. Chim. Acta* **1981**, *48*, 243−246. (c) Rossi, R.; Duatti, A.; Magon, L.; Casellato, W.; Graziani, R.; Toniolo, L. *J. Chem. Soc., Dalton Trans.* **1982**, 1949−1952. (d) Marchi, A.; Rossi, R.; Duatti, A.; Magon, L.; Bertolasi, V.; Ferretti, V.; Gilli, G. *Inorg. Chem.* **1985**, *24*, 4744−4748. (e) Hillhouse, G. L.; Haymore, B. L. *Inorg. Chem.* **1987**, *26*, 1876−1885. (f) Colson, S. F.; Robinson, S. D. *Polyhedron* **1988**, *7*, 417−418. (g) Colson, S. F.; Robinson, S. D. *Inorg. Chim. Acta* **1988**, *149*, 13−14. (h) Carriedo, C.; Connelly, N. G.; Hettrich, R.; Orpen, A. G.; White, J. M. *J. Chem. Soc., Dalton Trans.* **1989**, 745−748. (i) Menon, M.; Pramanik, A.; Chattopadhyay, S.; Bag, N.; Chakravorty, A. *Inorg. Chem.* **1995**, *34*, 1361−1367. (j) Westhusin, S.; Gantzel, P.; Walsh, P. J. *Inorg. Chem.* **1998**, *37*, 5956−5959.

(3) (a) Connelly, N. G.; Garcia, G. *J. Chem. Soc., Dalton Trans.* **1987**, 2737−2749. (b) Ang, H. G.; Koh, L. L.; Yang, G. Y. *J. Chem. Soc., Dalton Trans.* **1996**, 1573−1581. (c) Ang, H. G.; Koh, L. L.; Ang, S. G.; Ng, S. Y.; Yang, G. Y. *J. Chem. Soc., Dalton Trans.* **1996**, 4083−4088. (d) Connelly, N. G.; Einig, T.; Garcia Herbosa, G.; Hopkins, P. M.; Mealli, C.; Orpen, A. G.; Rosair, G. M.; Viguri, F. *J. Chem. Soc., Dalton Trans.* **1994**, 2025. (e) Ruiz, J.; López, J. F. J.; Rodriguez, V.; Perez, J.; Ramirez de Arellano, M. C.; Lopez, G. *J. Chem. Soc., Dalton Trans.* **2001**, 2683−2689. (f) Connelly, N. G.; Hayward, O. D.; Klangsinsirikul, P.; Orpen, A. G. *J. Chem. Soc., Dalton Trans.* **2002**, 305. (g) Tejel, C.; Ciriano, M. A.; Rios-Moreno, G.; Dobrinovitch, I. T.; Lahoz, F. J.; Oro, L. A.; Porra-Hake, M. *Inorg. Chem.* **2004**, *43*, 4719−4726.

10.1021/ic052063u CCC: $33.50
Published on Web 04/05/2006

triazenide is a donor ligand which has shown its ability to stabilize mono- and dinuclear derivatives.[1−3]

Triazene 1,3-ArN═NN(H)Ar (Chart 1, **C**), instead, has been mainly used as a precursor for the triazenide complexes, resulting in its very limited use as a ligand. Only two examples[3a,g] of IrCl(η^4-cod){RN═NN(H)R} (cod = cycloocta-1,5-diene)- and RhCl{ArN═NN(H)Ar}$(CO)_2$-type complexes, containing triazene as a ligand, are reported in the literature. This result is somewhat surprising because triazene may be compared to the substituted-diazene ArN═NH (**D**), whose coordination chemistry has been extensively developed over the past twenty-five years, leading to the synthesis of several complexes with interesting properties.[6]

We are interested in the chemistry of "diazo" complexes of transition metals and have reported on the synthesis and the reactivity of aryldiazene and aryldiazenido complexes of manganese and iron triads.[7,8] The broadening of these studies to "triazo" species such as triazene and triazenide should be of interest not only for a comparison between "diazo" and "triazo" ligands toward the same metal fragment but also for extending the knowledge of the chemistry of triazene and triazenide complexes. A glance through literature, in fact, shows that, except for the pioneer work of Robinson et al.[2a,f,g] on the chemistry of triazenide complexes of ruthenium(II) and osmium(II), only some cluster compounds[3b,c] with the triazenide ligand have been reported for these metals. In this paper, we report some studies on the reactivity of 1,3-diaryltriazene molecules toward classical and nonclassical hydride complexes of ruthenium and osmium, which allow the synthesis of new triazenides and of the first triazene complexes of Ru and Os to be achieved.

Experimental Section

All synthetic work was carried out in an appropriate atmosphere (Ar, N_2) using standard Schlenk techniques or a vacuum atmosphere drybox. Once isolated, the complexes were found to be relatively stable in air but were stored in an inert atmosphere at −25 °C. All solvents were dried over appropriate drying agents, degassed on a vacuum line, and distilled into vacuum-tight storage flasks. $RuCl_3 \cdot 3H_2O$ and $(NH_4)_2OsCl_6$ salts were obtained from Pressure Chemical Co. and were used as received. Phosphite $PPh(OEt)_2$ was prepared by the method of Rabinowitz and Pellon,[9] while $P(OEt)_3$ was an Aldrich product purified by distillation under nitrogen. 1,3-Diaryltriazenes, 1,3-ArN═NN(H)Ar (Ar = Ph, *p*-tolyl), were prepared following the literature method.[10] The labeled triazene 1,3-$Ph^{15}N{=}N^{15}N(H)Ph$ was prepared from labeled aniline $Ph^{15}NH_2$ (99% enriched, CIL) and $NaNO_2$. Other reagents were purchased from commercial sources in the highest available purity and used as received. Infrared spectra were recorded on a Nicolet Magna 750 or Perkin-Elmer Spectrum One FT-IR spectrophotometers. NMR spectra (^1H, ^{31}P, ^{15}N) were obtained on AC 200 or AVANCE 300 Bruker spectrometers at temperatures between −90 and +30 °C, unless otherwise noted. ^1H spectra are referred to internal tetramethylsilane; $^{31}P\{^1H\}$ chemical shifts are reported with respect to 85% H_3PO_4, while ^{15}N is reported with respect to $CH_3{}^{15}NO_2$. In both cases, downfield shifts are considered positive. The COSY, HMQC, and HMBC NMR experiments were performed using their standard programs. The SwaN-MR software package[11] 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 were measured with a CDM 83 radiometer.

Synthesis of Complexes. The classical[12] MH_2P_4 and nonclassical[13] $[MH(\eta^2\text{-}H_2)P_4]Y$ [M = Ru, Os; P = $P(OMe)_3$, $P(OEt)_3$, $PPh(OEt)_2$; Y = BF_4, BPh_4] hydride complexes were prepared according to the procedure previously reported. The triflate species, $MH(\kappa^1\text{-}OTf)P_4$ and $[M(\kappa^2\text{-}OTf)P_4]OTf$, were prepared in solution by reacting hydride MH_2P_4 complexes with CF_3SO_3H (HOTf) or $CF_3SO_3CH_3$ (CH_3OTf), following the reported method.[14]

$[Ru(\eta^2\text{-}1,3\text{-}ArNNNAr)P_4]BPh_4$ (1, 2) [P = $P(OMe)_3$ (1), $P(OEt)_3$ (2); Ar = Ph (a), *p*-tolyl (b)]. Method 1. An equimolar amount of $HBF_4 \cdot Et_2O$ (0.26 mmol, 37 μL) was added to a solution of the appropriate hydride RuH_2P_4 (0.26 mmol) complex in 6 mL of CH_2Cl_2 cooled to −196 °C. The reaction mixture was brought to −30 °C and stirred for about 1 h, and then an excess of the appropriate 1,3-ArN═NN(H)Ar triazene (0.52 mmol) in 2 mL of CH_2Cl_2 was added. The solution was brought to room temperature and then refluxed for about 1 h. The solvent was removed under reduced pressure yielding an oil which was treated with ethanol (2 mL). The addition of an excess of $NaBPh_4$ (0.78 mmol, 0.27 g) in 2 mL of ethanol caused the separation of a brown solid which was filtered and crystallized from CH_2Cl_2 and ethanol: yield from 65 to 80%.

Method 2. An equimolar amount of CF_3SO_3H (0.26 mmol, 23 μL) was added to a solution of the appropriate hydride RuH_2P_4 (0.26 mmol) complex in 6 mL of CH_2Cl_2 cooled to −196 °C. The reaction mixture was allowed to reach room temperature, was stirred for 1 h, and then was cooled again to −196 °C. Triflic acid (0.27

(4) (a) Edelmann, F. T. *Coord. Chem. Rev.* **1994**, *137*, 403−481. (b) Barker, J.; Kilner, M. *Coord. Chem. Rev.* **1994**, *133*, 219−300. (c) Oro, L. A.; Ciriano, M. A.; Perez-Torrente, J. J.; Villaroya, B. E. *Coord. Chem. Rev.* **1999**, *193*−*195*, 941−975.

(5) Zhang, Z.-Z.; Cheng, H. *Coord. Chem. Rev.* **1996**, *147*, 1.

(6) (a) Sutton, D. *Chem. Rev.* **1993**, *93*, 995−1022. (b) Kisch, H.; Holzmeir, P. *Adv. Organomet. Chem.* **1992**, *34*, 67−109. (c) Zollinger, H. In *Diazo Chemistry II*; VCH: Weinheim, Germany, 1995.

(7) (a) Albertin, G.; Antoniutti, S.; Bortoluzzi, M.; Castro-Fojo, J.; Garcia-Fontán, S. *Inorg. Chem.* **2004**, *43*, 4511−4522. (b) Albertin, G.; Antoniutti, S.; Bacchi, A.; Fregolent, B.; Pelizzi, G. *Eur. J. Inorg. Chem.* **2004**, 1922−1938. (c) Albertin, G.; Antoniutti, S.; Bacchi, A.; Boato, M.; Pelizzi, G. *J. Chem. Soc., Dalton Trans*. **2002**, 3313−3320. (d) Albertin, G.; Antoniutti, S.; Bacchi, A.; Bordignon, E.; Giorgi, M. T.; Pelizzi, G. *Angew. Chem., Int. Ed.* **2002**, *41*, 2192−2194. (e) Albertin, G.; Antoniutti, S.; Bordignon, E.; Visentin, E. *Inorg. Chem.* **2001**, *40*, 5465−5467. (f) Albertin, G.; Antoniutti, S.; Bordignon, E.; Perinello, G. *J. Organomet. Chem.* **2001**, *625*, 217−230.

(8) (a) Albertin, G.; Antoniutti, S.; Bacchi, A.; Bordignon, E.; Miani, F.; Pelizzi, G. *Inorg. Chem.* **2000**, *39*, 3283−3293. (b) Albertin, G.; Antoniutti, S.; Bacchi, A.; Ballico, G. B.; Bordignon, E.; Pelizzi, G.; Ranieri, M.; Ugo, P. *Inorg. Chem.* **2000**, *39*, 3265−3279. (c) Albertin, G.; Antoniutti, S.; Bordignon, E.; Menegazzo, F. *J. Chem. Soc., Dalton Trans.* **2000**, 1181−1189. (d) Albertin, G.; Antoniutti, S.; Bacchi, A.; Barbera, D.; Bordignon, E.; Pelizzi, G.; Ugo, P. *Inorg. Chem.* **1998**, *37*, 5602−5610. (e) Albertin, G.; Antoniutti, S.; Bacchi, A.; Bordignon, E.; Busatto, F.; Pelizzi, G. *Inorg. Chem.* **1997**, *36*, 1296−1305. (f) Albertin, G.; Antoniutti, S.; Bacchi, A.; Bordignon, E.; Pelizzi, G.; Ugo, P. *Inorg. Chem.* **1996**, *35*, 6245−6253.

(9) Rabinowitz, R.; Pellon, J. *J. Org. Chem.* **1961**, *26*, 4623−4626.

(10) Hartman. W. W.; Dickey, J. B. *Org. Synth.* **1943**, *2*, 163−165.

(11) Balacco, G. *J. Chem. Inf. Comput. Sci.* **1994**, *34*, 1235−1241.

(12) (a) Gerlach, D. H.; Peet, W. G.; Muetterties, E. L. *J. Am. Chem. Soc.* **1972**, *94*, 4545−4549. (b) Peet, W. G.; Gerlach, D. H. *Inorg. Synth.* **1974**, *15*, 38−42. (c) Albertin, G.; Antoniutti, S.; Bordignon, E. *J. Chem. Soc., Dalton Trans*. **1989**, 2353−2358.

(13) (a) Amendola, P.; Antoniutti, S.; Albertin, G.; Bordignon, E. *Inorg. Chem.* **1990**, *29*, 318−324. (b) Albertin, G.; Antoniutti, S.; Baldan, D.; Bordignon, E. *Inorg. Chem.* **1995**, *34*, 6205−6210.

(14) (a) Albertin, G.; Antoniutti, S.; Bacchi, A.; Bordignon, E.; Dolcetti, P. M.; Pelizzi, G. *J. Chem. Soc., Dalton Trans*. **1997**, 4435−4444. (b) Albertin, G.; Antoniutti, S.; Bacchi, A.; Bergamo, M.; Bordignon, E.; Pelizzi, G. *Inorg. Chem.* **1998**, *37*, 479−489. (c) Albertin, G.; Antoniutti, S.; Beraldo, S.; Chimisso, F. *Eur. J. Inorg. Chem.* **2003**, 2845−2854.

mmol, 24 μL) was added, and the reaction mixture was stirred for 1 h at room temperature. A solution of the appropriate 1,3-ArN═NN(H)Ar triazene (0.28 mmol) in 2 mL of CH_2Cl_2 was added to the resulting solution, which was stirred for 4 h, and then an excess of NEt_3 (1.04 mmol, 145 μL) was added. The reaction mixture was stirred for 3 h and filtered to remove the $(NHEt_3)CF_3SO_3$ salt, and then the solution was evaporated to dryness under reduced pressure. The oil obtained was treated with ethanol (2 mL) containing an excess of $NaBPh_4$ (0.78 mmol, 0.27 g). A brown solid slowly separated out, and it was filtered and crystallized from CH_2Cl_2 and ethanol: yield ≥ 80%.

Anal. Calcd for $C_{48}H_{66}BN_3O_{12}P_4Ru$ (**1a**): C, 51.81; H, 5.98; N, 3.78. Found: C, 52.03; H, 6.11; N, 3.67. Λ_M: 51.5 Ω^{-1} mol^{-1} cm^2. ^{1}H NMR (CD_2Cl_2, 20 °C): δ 7.40−6.87 (m, 30 H, Ph), 3.77 {virtual triplet (vt), J_{HP} = 5.3 Hz, 18 H, CH_3}, 3.51 (vt, J_{HP} = 5.3 Hz, 18 H, CH_3). ^{31}P{^{1}H} NMR (CD_2Cl_2, 20 °C): δ A_2B_2 spin syst, δ_A 139.0, δ_B 129.2, J_{AB} = 57.0 Hz. Anal. Calcd for $C_{50}H_{70}BN_3O_{12}P_4Ru$ (**1b**): C, 52.64; H, 6.18; N, 3.68. Found: C, 52.48; H, 6.23; N, 3.56. Λ_M: 50.6 Ω^{-1} mol^{-1} cm^2. ^{1}H NMR (CD_2Cl_2, 20 °C): δ 7.38−6.86 (m, 28 H, Ph), 3.74 (vt, J_{HP} = 5.3 Hz, 18 H, CH_3 phos), 3.53 (vt, J_{HP} = 5.3 Hz, 18 H, CH_3 phos), 2.35 (s, 6 H, CH_3 *p*-tolyl). ^{31}P{^{1}H} NMR (CD_2Cl_2, 20 °C): δ A_2B_2 spin syst, δ_A 138.8, δ_B 129.5, J_{AB} = 57.0 Hz. Anal. Calcd for $C_{60}H_{90}BN_3O_{12}P_4Ru$ (**2a**): C, 56.25; H, 7.08; N, 3.28. Found: C, 56.36; H, 7.14; N, 3.20. Λ_M: 53.3 Ω^{-1} mol^{-1} cm^2. ^{1}H NMR (CD_2Cl_2, 20 °C): δ 7.56−6.87 (m, 30 H, Ph), 4.12, 3.85 (m, 24 H, CH_2), 1.33 (t, J_{HH} = 7 Hz, 18 H, CH_3), 1.06 (t, J_{HH} = 7 Hz, 18 H, CH_3). ^{31}P{^{1}H} NMR (CD_2Cl_2, 20 °C): δ A_2B_2 spin syst, δ_A 134.5, δ_B 125.2, J_{AB} = 58.1 Hz.

[Ru(η^2-1,3-Ph^{15}NN^{15}NPh){P(OEt)$_3$}$_4$]BPh$_4$ (2a$_1$). This complex was prepared exactly like the related unlabeled compound **2a** following Method 1 and using the labeled 1,3-Ph^{15}NN^{15}N(H)Ph triazene ligand: yield ≥60%. ^{1}H NMR (CD_2Cl_2, 20 °C): δ 7.55−6.87 (m, 30 H, Ph), 4.13, 3.87 (m, 24 H, CH_2), 1.33 (t, J_{HH} = 7 Hz, 18 H, CH_3), 1.06 (t, J_{HH} = 7 Hz, 18 H, CH_3). ^{31}P{^{1}H} NMR (CD_2Cl_2, 20 °C): δ AA′B_2XX′ spin syst (X, X′ = ^{15}N), δ_A 135.3, δ_B 126.0, $J_{AA'}$ = 63.5, J_{AB} = $J_{A'B}$ = 57.3, J_{AX} = $J_{A'X'}$ = 46.6, $J_{AX'}$ = $J_{A'X}$ = 4.95, J_{BX} = $J_{BX'}$ = 5.20, $J_{XX'}$ = 4.05 Hz.

[Ru(η^2-1,3-PhNNNPh){PPh(OEt)$_2$}$_4$]BPh$_4$ (3a). An equimolar amount of methyltriflate ($CF_3SO_3CH_3$, 0.33 mmol, 37 μL) was added to a solution of $RuH_2\{PPh(OEt)_2\}_4$ (0.33 mmol, 0.30 g) in 6 mL of toluene cooled to −196 °C. The reaction mixture was brought to room temperature and stirred for 1 h, and then an excess of 1,3-PhNNN(H)Ph (0.70 mmol, 0.138 g) in toluene (2 mL) was added. Dichloromethane (10 mL) was added to the reaction mixture which was refluxed for about 30 min. The solvent was removed under reduced pressure to give an oil which was treated with ethanol (3 mL) containing an excess of $NaBPh_4$ (0.66 mmol, 0.23 g). A brown solid separated out which was filtered and crystallized from CH_2Cl_2 and ethanol: yield ≥75%. Anal. Calcd for $C_{76}H_{90}BN_3O_8P_4Ru$: C, 64.77; H, 6.44; N, 2.98. Found: C, 64.55; H, 6.35; N, 3.10. Λ_M: 51.9 Ω^{-1} mol^{-1} cm^2. ^{1}H NMR (CD_2Cl_2, 20 °C): δ 8.04−6.66 (m, 50 H, Ph), 4.30−3.60 (m, 16 H, CH_2), 1.50 (t, J_{HH} = 7 Hz, 6 H, CH_3), 1.25 (t, J_{HH} = 7 Hz, 6 H, CH_3), 1.09 (t, J_{HH} = 7 Hz, 12 H, CH_3). ^{31}P{^{1}H} NMR [$(CD_3)_2CO$/$CDCl_3$, −100 °C): δ A_2B_2 spin syst, δ_A 163.0, δ_B 153.8, J_{AB} = 44.4 Hz.

[Os(η^2-1,3-ArNNNAr)P$_4$]BPh$_4$ (4, 5) [P = P(OEt)$_3$ (4), PPh(OEt)$_2$ (5); Ar = Ph (a), *p*-tolyl (b)]. An equimolar amount of methyltriflate (0.11 mmol, 12 μL) was added to a solution of the appropriate hydride OsH_2P_4 (0.11 mmol) in 6 mL of toluene cooled to −196 °C. The reaction mixture was brought to room temperature, stirred for 1 h, and then cooled again to −196 °C. An equimolar amount of triflic acid (0.11 mmol, 10 μL) was added, and the solution stirred for 1 h at room temperature. An excess of the appropriate triazene (0.44 mmol) in 2 mL of toluene was added to the resulting solution which, after the further addition of CH_2Cl_2 (5 mL), was stirred at room temperature for 4 h. An excess of triethylamine (0.44 mmol, 61 μL) was added to the reaction mixture, which was stirred for 3 h, and then the solvent was removed under reduced pressure. The oil obtained was treated with ethanol (2 mL) containing an excess of $NaBPh_4$ (0.44 mmol, 0.15 g). A brown solid slowly separated out which was filtered and crystallized from CH_2Cl_2 and ethanol: yield ≥75%. Anal. Calcd for $C_{60}H_{90}BN_3O_{12}OsP_4$ (**4a**): C, 52.59; H, 6.62; N, 3.07. Found: C, 52.42; H, 6.68; N, 3.01. Λ_M: 51.5 Ω^{-1} mol^{-1} cm^2. ^{1}H NMR (CD_2Cl_2, 20 °C): δ 7.98−6.87 (m, 30 H, Ph), 4.10, 3.83 (m, 24 H, CH_2), 1.34 (t, J_{HH} = 7 Hz, 18 H, CH_3), 1.06 (t, J_{HH} = 7 Hz, 18 H, CH_3). ^{31}P{^{1}H} NMR (CD_2Cl_2, 20 °C): δ A_2B_2 spin syst, δ_A 91.8, δ_B 79.1, J_{AB} = 40.5 Hz. Anal. Calcd for $C_{62}H_{94}BN_3O_{12}OsP_4$ (**4b**): C, 53.25; H, 6.78; N, 3.00. Found: C, 53.41; H, 6.73; N, 2.88. Λ_M: 52.7 Ω^{-1} mol^{-1} cm^2. ^{1}H NMR (CD_2Cl_2, 20 °C): δ 7.50−6.86 (m, 28 H, Ph), 4.21, 3.82 (m, 24 H, CH_2), 2.33 (s, 6 H, CH_3 *p*-tolyl), 1.31 (t, J_{HH} = 7 Hz, 18 H, CH_3 phos), 1.04 (t, J_{HH} = 7 Hz, 18 H, CH_3 phos). ^{31}P{^{1}H} NMR (CD_2Cl_2, 20 °C): δ A_2B_2 spin syst, δ_A 92.3, δ_B 80.2, J_{AB} = 41.0 Hz. Anal. Calcd for $C_{76}H_{90}BN_3O_8OsP_4$ (**5a**): C, 60.92; H, 6.05; N, 2.80. Found: C, 60.79; H, 6.16; N, 2.67. Λ_M: 50.9 Ω^{-1} mol^{-1} cm^2. ^{1}H NMR (CD_2Cl_2, −30 °C): δ 7.55−6.86 (m, 50 H, Ph), 4.05, 3.60, 3.35 (m, 16 H, CH_2), 1.29, 1.27, 1.17, 1.15, 1.05, 0.84 (t, J_{HH} = 7 Hz, 24 H, CH_3). ^{31}P{^{1}H} NMR (CD_2Cl_2, −30 °C): δ ABC_2 spin syst, δ_A 122.7, δ_B 122.2, δ_C 111.2, J_{AB} = 24.2, J_{AC} = 26.7, J_{BC} = 30.5 Hz.

[Os(κ^1-OTf){η^1-1,3-PhN═NN(H)Ph}{P(OEt)$_3$}$_4$]BPh$_4$ (6a). An equimolar amount of methyltriflate (0.11 mmol, 12 μL) was added to a solution of $OsH_2\{P(OEt)_3\}_4$ (0.12 mmol, 0.10 g) in 6 mL of toluene cooled to −196 °C. The reaction mixture was brought to room temperature, stirred for 1 h, and then cooled again to −196 °C. A slight excess of CF_3SO_3H (0.13 mmol, 12 μL) was added, and the solution was stirred for 1 h at room temperature. An excess of 1,3-PhN═NN(H)Ph (0.22 mmol, 44 mg) in 2 mL of CH_2Cl_2 was added, and the reaction mixture, after the addition of 5 mL of CH_2Cl_2, was stirred for 2 h. The solvent was removed under reduced pressure to give an oil which was treated with ethanol containing an excess of $NaBPh_4$ (0.44 mmol, 0.15 g). A brown solid slowly separated out which was filtered and crystallized from CH_2Cl_2 and ethanol: yield ≥ 45%. Anal. Calcd for $C_{61}H_{91}BF_3N_3O_{15}OsP_4S$: C, 48.19; H, 6.03; N, 2.76. Found: C, 48.06; H, 6.14; N, 2.63. Λ_M: 51.2 Ω^{-1} mol^{-1} cm^2. ^{1}H NMR (CD_2Cl_2): δ (−80 °C) 11.65 (s, 1 H, NH); (−50 °C) 11.2 (s, br, 1 H, NH), 7.34−6.90 (m, 30 H, Ph), 4.18 (m, 24 H, CH_2), 1.33 (t, J_{HH} = 7 Hz, 15 H, CH_3), 1.12 (t, J_{HH} = 7 Hz, 21 H, CH_3). ^{31}P{^{1}H} NMR (CD_2Cl_2, −80 °C): δ A_2BC spin syst, δ_A 84.6, δ_B 74.2, δ_C 63.5, J_{AB} = 41.8, J_{AC} = 44.9, J_{BC} = 48.7 Hz. IR (KBr, cm^{-1}): 3327 w (νNH).

[OsH{η^1-1,3-ArN═NN(H)Ar}P$_4$]BPh$_4$ (7, 8) [P = P(OEt)$_3$ (7), PPh(OEt)$_2$ (8); Ar = Ph (a), *p*-tolyl (b)]. A solid sample of the appropriate OsH_2P_4 hydride (0.1 mmol) in 6 mL of toluene was placed in a 25 mL three-necked round-bottomed flask, and the resulting solution was cooled to −196 °C. An equimolar amount of methyltriflate (0.11 mmol, 12 μL) was added, and the reaction mixture was brought to room temperature and stirred for 1 h. An excess of the appropriate triazene 1,3-ArN═NN(H)Ar (0.20 mmol) in 2 mL of toluene was added, and the reaction mixture, after the addition of 5 mL of CH_2Cl_2, was stirred at room temperature for 4 h. The solvent was removed under reduced pressure to give an oil which was treated with ethanol containing an excess of $NaBPh_4$ (0.44 mmol, 0.15 g). A dark-green solid slowly separated out which

was filtered and crystallized from CH_2Cl_2 and ethanol: yield from 60 to 75%. Anal. Calcd for $C_{60}H_{92}BN_3O_{12}OsP_4$ (**7a**): C, 52.51; H, 6.76; N, 3.06. Found: C, 52.42; H, 6.88; N, 3.14. Λ_M: 52.6 Ω^{-1} mol^{-1} cm^2. ^1H NMR (CD_2Cl_2, −90 °C): δ 10.84 (s, br, 1 H, NH), 7.90−6.67 (m, 30 H, Ph), 4.12−3.60 (m, 24 H, CH_2), 1.24 (t, J_{HH} = 7 Hz, 9 H, CH_3), 1.17 (t, J_{HH} = 7 Hz, 9 H, CH_3), 1.15 (t, J_{HH} = 7 Hz, 18 H, CH_3), −8.19 to −8.66 (m, 1 H, OsH). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −90 °C): δ A_2BC spin syst, δ_A 107.0, δ_B 102.5, δ_C 100.2, J_{AB} = 32.3, J_{AC} = 44.4, J_{BC} = 29.0 Hz. IR (KBr, cm^{-1}): 3345 w (νNH). Anal. Calcd for $C_{76}H_{92}BN_3O_8OsP_4$ (**8a**): C, 60.84; H, 6.18; N, 2.80. Found: C, 60.67; H, 6.28; N, 2.72. Λ_M: 55.8 Ω^{-1} mol^{-1} cm^2. ^1H NMR (CD_2Cl_2, −90 °C): δ 11.04 (s, br, 1 H, NH), 7.90−6.55 (m, 50 H, Ph), 4.10−3.34 (m, 16 H, CH_2), 1.27 (t, J_{HH} = 7 Hz, 3 H, CH_3), 1.20 (t, J_{HH} = 7 Hz, 6 H, CH_3), 1.14 (t, J_{HH} = 7 Hz, 9 H, CH_3), 1.04 (t, J_{HH} = 7 Hz, 6 H, CH_3), −7.92 to −8.36 (m, 1 H, OsH). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −90 °C): δ AB_2C spin syst, δ_A 124.6, δ_B 123.5, δ_C 120.4, J_{AB} = 19.3, J_{AC} = 29.7, J_{BC} = 20.4 Hz. IR (KBr, cm^{-1}): 3358 w (νNH), 1975 w (νOsH). Anal. Calcd for $C_{78}H_{96}BN_3O_8OsP_4$ (**8b**): C, 61.29; H, 6.33; N, 2.75. Found: C, 61.44; H, 6.26; N, 2.69. Λ_M: 55.3 Ω^{-1} mol^{-1} cm^2. ^1H NMR (CD_2Cl_2, −80 °C): δ 10.12 (s, br, 1 H, NH), 7.46−6.47 (m, 48 H, Ph), 4.05−3.40 (m, 16 H, CH_2), 2.35 (s, 6 H, CH_3 *p*-tolyl), 1.23 (t, J_{HH} = 7 Hz, 6 H, CH_3 phos), 1.19 (t, J_{HH} = 7 Hz, 6 H, CH_3 phos), 1.10 (t, J_{HH} = 7 Hz, 12 H, CH_3 phos), −7.83 to −8.46 (m, 1 H, OsH). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −80 °C): δ AB_2C spin syst, δ_A 126.7, δ_B 121.6, δ_C 121.2, J_{AB} = 20.1, J_{AC} = 29.6, J_{BC} = 22.1 Hz. IR (KBr, cm^{-1}): 3359 w (νNH), 1990 w (νOsH).

[OsH{η^1-1,3-Ph^{15}N═N^{15}N(H)Ph}{PPh(OEt)$_2$}$_4$]BPh$_4$ (8a$_1$). This complex was prepared exactly like the related unlabeled compound **8a** using the 1,3-Ph^{15}NN^{15}NPh triazene ligand: yield ≥65%. ^1H NMR (CD_2Cl_2, −80 °C): δ 11.05 (d, 1 H, NH, $J_{^{15}NH}$ = 92 Hz), 7.90−6.58 (m, 50 H, Ph), 4.11−3.34 (m, 16 H, CH_2), 1.27 (t, J_{HH} = 7 Hz, 3 H, CH_3), 1.20 (t, J_{HH} = 7 Hz, 6 H, CH_3), 1.14 (t, J_{HH} = 7 Hz, 9 H, CH_3), 1.04 (t, J_{HH} = 7 Hz, 6 H, CH_3), −7.91 to −8.38 (m, 1 H, OsH). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −80 °C): δ AB_2CX spin syst (X = ^{15}N), δ_A 124.7, δ_B 123.7, δ_C 120.4, J_{AB} = 19.2, J_{AC} = 29.7, J_{AX} = 1.0, J_{BC} = 20.6, J_{BX} = 1.0, J_{CX} = 6.30 Hz. IR (KBr, cm^{-1}): 3347 w (νNH), 1972 w (νOsH).

[RuH{η^1-1,3-*p*-tolyl-N═NN(H)-*p*-tolyl}{PPh(OEt)$_2$}$_4$]BPh$_4$ (9b). An equimolar amount of methyltriflate ($CF_3SO_3CH_3$, 0.33 mmol, 37 μL) was added to a solution of $RuH_2\{PPh(OEt)_2\}_4$ (0.33 mmol, 0.30 g) in 6 mL of toluene cooled to −196 °C. The reaction mixture was brought to room temperature and stirred for 1 h, and then an excess of 1,3-*p*-tolyl-N═NN(H)-*p*-tolyl (0.70 mmol, 0.158 g) in toluene (2 mL) was added. Dichloromethane (10 mL) was added, and the reaction mixture was stirred at room temperature for 3 h. The solvent was removed under reduced pressure giving an oil which was triturated with ethanol (2 mL) containing an excess of $NaBPh_4$ (0.60 mmol, 0.21 g). A green solid slowly separated out which was filtered and crystallized from CH_2Cl_2 and ethanol: yield ≥70%. Anal. Calcd for $C_{78}H_{96}BN_3O_8P_4Ru$: C, 65.09; H, 6.72; N, 2.92. Found: C, 65.31; H, 6.85; N, 2.79. Λ_M: 49.5 Ω^{-1} mol^{-1} cm^2. ^1H NMR (CD_2Cl_2): δ (20 °C) 9.84 (s, br, 1 H, NH), 8.10−6.85 (m, 48 H, Ph), 4.15−3.50 (m, 16 H, CH_2), 2.43 (s, 3 H, CH_3 *p*-tolyl), 2.40 (s, 3 H, CH_3 *p*-tolyl), 1.51 (t, J_{HH} = 7 Hz, 3 H, CH_3 phos), 1.35 (t, J_{HH} = 7 Hz, 6 H, CH_3 phos), 1.27 (t, J_{HH} = 7 Hz, 9 H, CH_3 phos), 1.10 (t, J_{HH} = 7 Hz, 6 H, CH_3), −6.70 to −7.30 (m, 1 H, RuH); (−90 °C) 11.97 (s, 1 H, NH), 8.00−6.60 (m, 48 H, Ph), 4.10−3.50 (m, 16 H, CH_2), 2.41 (s, 3 H, CH_3 *p*-tolyl), 2.38 (s, 3 H, CH_3 *p*-tolyl), 1.35−1.15 (m, 24 H, CH_3 phos), −6.78 to −7.15 (m, 1 H, RuH). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −90 °C): δ AB_2C spin syst, δ_A 172.2, δ_B 165.2, δ_C 160.4, J_{AB} = 44.5, J_{AC} = 29.5, J_{BC} = 27.9 Hz. IR (KBr, cm^{-1}): 3331 m (νNH).

[OsH(PhN═NH)P$_4$]BPh$_4$ (10a, 11a) [P = P(OEt)$_3$ (10), PPh(OEt)$_2$ (11)]. An equimolar amount of CF_3SO_3H (0.1 mmol, 9 μL) was added to a solution of the appropriate OsH_2P_4 hydride (0.1 mmol) in 5 mL of dichloromethane cooled to −196 °C. The reaction mixture was stirred for 1 h at room temperature, and then an excess of 1,3-PhN═NN(H)Ph (0.3 mmol, 59 mg) was added. The resulting solution was stirred at room temperature for 10 h, and then the solvent removed under reduced pressure to give a brown oil which was treated with ethanol containing an excess of $NaBPh_4$ (0.2 mmol, 68 mg). An orange solid slowly separated out which was filtered and crystallized from CH_2Cl_2 and ethanol: yield ≥ 45%. Anal. Calcd for $C_{54}H_{87}BN_2O_{12}OsP_4$ (**10a**): C, 50.62; H, 6.84; N, 2.19. Found: C, 50.54; H, 6.96; N, 2.05. Λ_M: 54.7 Ω^{-1} mol^{-1} cm^2. ^1H NMR (CD_2Cl_2, 20 °C): δ 14.47 (s, br, 1 H, NH), 7.30−6.97 (m, 25 H, Ph), 4.02 (m, 24 H, CH_2), 1.27 (t, J_{HH} = 7 Hz, 9 H, CH_3), 1.24 (t, J_{HH} = 7 Hz, 9 H, CH_3), 1.18 (t, J_{HH} = 7 Hz, 18 H, CH_3), −8.28 to −8.68 (m, 1 H, OsH). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −90 °C): δ AB_2C spin syst, δ_A 102.4, δ_B 100.5, δ_C 99.5, J_{AB} = 32.5, J_{AC} = 42.8, J_{BC} = 31.7 Hz. Anal. Calcd for $C_{70}H_{87}BN_2O_8OsP_4$ (**11a**): C, 59.66; H, 6.22; N, 1.99. Found: C, 59.84; H, 6.30; N, 1.91. Λ_M: 50.4 Ω^{-1} mol^{-1} cm^2. ^1H NMR (CD_2Cl_2, 20 °C): δ 13.42 (s, br, 1 H, NH), 8.05−6.67 (m, 45 H, Ph), 4.02−3.20 (m, 16 H, CH_2), 1.30 (t, J_{HH} = 7 Hz, 6 H, CH_3), 1.12 (t, J_{HH} = 7 Hz, 6 H, CH_3), 1.08 (t, J_{HH} = 7 Hz, 12 H, CH_3), −7.78 to −8.45 (m, 1 H, OsH). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −90 °C): δ AB_2C spin syst, δ_A 125.8, δ_B 123.7, δ_C 119.8, J_{AB} = 19.2, J_{AC} = 22.7, J_{BC} = 30.0 Hz.

[OsH(Ph^{15}N═NH){PPh(OEt)$_2$}$_4$]BPh$_4$ (11a$_1$). This compound was prepared exactly like the related unlabeled **11a** complex, using 1,3-Ph^{15}N═N^{15}N(H)Ph as a reagent: yield ≥ 45%. ^1H NMR (CD_2Cl_2, 20 °C): δ 13.40 (s, br, 1 H, NH), 8.04−6.67 (m, 45 H, Ph), 4.00−3.20 (m, 16 H, CH_2), 1.30 (t, J_{HH} = 7 Hz, 6 H, CH_3), 1.14 (t, J_{HH} = 7 Hz, 6 H, CH_3), 1.08 (t, J_{HH} = 7 Hz, 12 H, CH_3), −7.78 to −8.45 (m, 1 H, OsH). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −90 °C): δ AB_2C spin syst, δ_A 125.9, δ_B 123.6, δ_C 119.8, J_{AB} = 19.2, J_{AC} = 22.7, J_{BC} = 30.2 Hz.

X-ray Crystal Structure Determinations. The data collection was taken on a SIEMENS Smart CCD area-detector diffractometer with graphite-monochromated Mo Kα radiation at room temperature for **2a** and at −100 °C for **11a**. Absorption corrections were carried out using SADABS.[15]

The structure of [Ru(η^2-1,3-PhNNNPh){P(OEt)$_3$}$_4$]BPh$_4$ (**2a**) was solved by the Patterson method, and the structure of [OsH(PhN═NH){PPh(OEt)$_2$}$_4$]BPh$_4$ (**11a**) was solved by direct methods. Both were refined by a full-matrix least-squares methods based on F^2.[16] Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in idealized positions and refined with isotropic displacement parameters, except for those labeled as H1, bonded to the Os atom, and H11, bonded to a nitrogen atom, in [OsH(PhN═NH){PPh(OEt)$_2$}$_4$]BPh$_4$ (**11a**). H1 and H11 were located on a difference electron-density map. H11 was refined with isotropic displacement parameters, but for H1, the positions were not refined. Atomic-scattering factors and anomalous dispersion corrections for all atoms were taken from International Tables for X-ray Crystallography.[17] Details of the crystal data and structural refinement are given in Table 1.

(15) Sheldrick, G. M. *SADABS. An empirical absorption correction program for area detector data*; University of Göttingen: Göttingen, Germany, 1996.

(16) Sheldrick, G. M. *SHELX-97. Program for the solution and refinement of crystal structures*; University of Göttingen: Göttingen, Germany, 1997.

(17) *International Tables for X-ray Crystallography*; Kluwer: Dordrecht, The Netherlands, 1992; Vol. C.

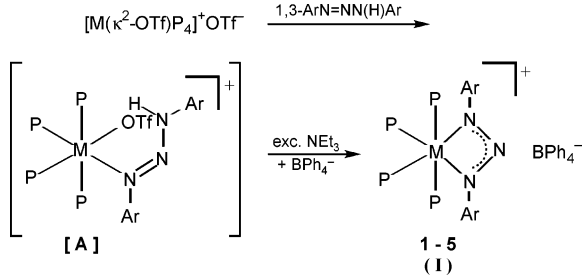
Table 1. Crystal Data and Structure Refinement

	2a	11a
empirical formula	$C_{60}H_{90}BN_3O_{12}P_4Ru$	$C_{70}H_{87}BN_2O_8OsP_4$
fw	1281.11	1409.31
temp	293(2) K	173(2) K
wavelength	0.71073 Å	0.71073 Å
cryst syst	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
unit cell dimensions	$a = 12.5801(13)$ Å	$a = 12.5264(6)$ Å
	$b = 14.8211(16)$ Å	$b = 15.1969(7)$ Å
	$c = 18.7249(19)$ Å	$c = 18.0865(8)$ Å
	$\alpha = 88.894(2)°$	$\alpha = 87.1340(10)°$
	$\beta = 85.266(2)°$	$\beta = 83.7010(10)°$
	$\gamma = 75.550(2)°$	$\gamma = 82.9620(10)°$
vol	3369.3(6) Å^3	3394.1(3) Å^3
Z	2	2
density (calcd)	1.263 Mg/m^3	1.379 Mg/m^3
abs coeff	0.385 mm^{-1}	2.027 mm^{-1}
F(000)	1352	1452
cryst size	0.42 × 0.39 × 0.20 mm	0.36 × 0.32 × 0.27 mm
θ range	1.42−28.03°	1.65−28.01°
index ranges	$-16 \le h \le 16$	$-16 \le h \le 13$
	$-17 \le k \le 19$	$-19 \le k \le 16$
	$-19 \le l \le 24$	$-19 \le l \le 23$
reflns collected	19 562	21 481
independent reflns	13 683 [R(int) = 0.0293]	14 976 [R(int) = 0.0291]
reflns obsd (>2σ)	6917	12 163
data completeness	0.839	0.912
max. and min. transmission	1.000 and 0.883	1.000 and 0.900
data/restraints/params	13 683/0/742	14 976/0/788
GOF on F^2	0.821	0.864
final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0506$	$R_1 = 0.0351$
	wR2 = 0.0945	wR2 = 0.0567
R indices (all data)	$R_1 = 0.1088$	$R_1 = 0.0481$
	wR2 = 0.1078	wR2 = 0.0591
largest diff. peak and hole	0.572 and −0.381 e Å^{-3}	2.025 and −1.254 e Å^{-3}

Results and Discussion

Triazenide Complexes. Triazenide [M(η^2-1,3-ArNNNAr)P_4]BPh_4 complexes of ruthenium (**1**−**3**) and osmium (**4** and **5**) were easily prepared by reacting triflate [M(κ^2-OTf)P_4]$^+$ cations with 1,3-diaryltriazene and then with an excess of NEt_3, as shown in Scheme 1.

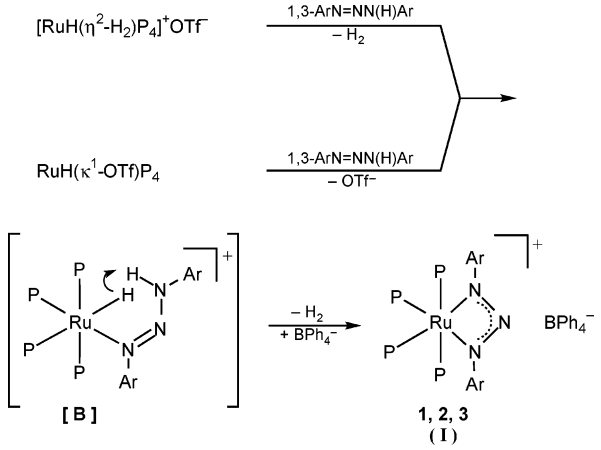
Scheme 1



M = Ru (**1**, **2**, **3**), Os (**4**, **5**); P = $P(OMe)_3$ (**1**), $P(OEt)_3$ (**2**, **4**, **6**), $PPh(OEt)_2$ (**3**, **5**); Ar = Ph (**a**), *p*-tolyl (**b**); $OTf^- = CF_3SO_3^-$ and when M = Os, P = $P(OEt)_3$, Ar = Ph, [**A**] = **6a.**

Furthermore, in the case of ruthenium, the reactions of both [RuH(η^2-H_2)P_4]$^+$ and RuH(κ^1-OTf)P_4 hydride complexes with 1,3-diaryltriazene give the triazenide [Ru(η^2-1,3-ArNNNAr)P_4]$^+$ (**1** and **2**) derivatives, which were isolated as BPh_4 salts and characterized (Scheme 2).

Scheme 2



P = $P(OMe)_3$ (**1**), $P(OEt)_3$ (**2**), $PPh(OEt)_2$ (**3**); Ar = Ph (**a**), *p*-tolyl (**b**).

The reaction of the κ^2-triflate [M(κ^2-OTf)P_4]$^+$ cations with 1,3-diaryltriazene (Scheme 1) proceeds with the initial coordination of the triazene to give the [M(κ^1-OTf){η^1-1,3-ArN═NN(H)Ar}P_4]$^+$ **(A)** intermediate which, in the case of the [Os(κ^1-OTf){η^1-1,3-PhN═NN(H)Ph}{$P(OEt)_3$}$_4$]$^+$ cation, was isolated in the solid state and characterized (**6a**). Treatment of these η^1-triazenes **(A)** with an excess of NEt_3 gives the final triazenide derivatives (**1**−**5**). Triethylamine, in fact, deprotonates the η^1-triazene allowing η^2-coordination of the 1,3-ArNNNAr triazenide ligand.

The reaction of the ruthenium hydrides (Scheme 2) was followed by NMR spectroscopy and showed that the addition of triazene to both the [RuH(η^2-H_2)P_4]$^+$ and RuH(κ^1-OTf)-P_4 hydride precursors causes the substitution of the labile[18] η^2-H_2 or κ^1-OTf ligand and the formation of a new complex formulated as the hydride−triazene intermediate **(B)**. This complex was not isolated in pure form, but its formulation is supported both by the NMR data and by the separation, as solids, of the related hydride−triazene [MH{η^1-1,3-ArN═NN(H)Ar}P_4]BPh_4 complexes of both ruthenium (**9b**) and osmium (**7**−**8**) (see below). In fact, the ^{1}H NMR spectrum of the reaction mixture shows, starting from the triflate complex, the disappearance of the signals of the RuH(κ^1-OTf)P_4 precursors and the appearance of a new hydride multiplet at −8.10 to −8.60 ppm. Furthermore, at −40 °C a broad signal near +9.2 ppm also appears and is attributable to the NH proton of the η^1-coordinate triazene ligand. Finally, the ^{31}P NMR spectra show a nonsymmetric AB_2C type multiplet, in agreement with the presence of an intermediate-type **(B)** compound. As the reaction proceeds, the ^{31}P spectra show the appearance of the A_2B_2 multiplet of the final triazenide [Ru(η^2-1,3-ArNNNAr)P_4]$^+$ (**1**−**2**) derivatives. At room temperature, however, the formation of the triazenide complex is slow and needs higher temperatures (40 °C) to be completed in a reasonable time. The formation of the final complexes (**1**−**2**) from the hydride−triazene intermediate **(B)** is not surprising and can be explained by taking into account

(18) In the case of the [RuH(η^2-H_2){$PPh(OEt)_2$}$_4$]OTf complex, the known stability[13a] to the loss of the H_2 ligand prevented the preparation of triazenide **3a** in pure form, which was obtained as a byproduct in a mixture of compounds.

the increased acidity of the triazene N-H hydrogen atom caused by the η^1-coordination of the 1,3-ArN═NN(H)Ar group[19] and the protonation of the hydride [Ru]−H ligand to give a H_2 molecule. Thus, an intramolecular acid−base reaction between the triazene NH proton of η^1-1,3-ArN═NN(H)Ar ligand and the Ru−H hydride group in the intermediate species **(B)** may result in evolution of H_2 and formation of the chelate η^2-triazenide ligand. Support for this hypothesis comes from the ^{1}H NMR spectra of the reaction mixture of RuH(κ^1-OTf)P_4 with 1,3-PhN═NN(H)Ph in CD_2Cl_2, which show a weak signal at 4.6 ppm characteristic[20] of the presence of free dihydrogen, in agreement with the path proposed in Scheme 2.

The 1,3-triazenide complexes of ruthenium and osmium can be isolated with both the 1,3-diphenyl and 1,3-di-*p*-tolyl ligands. However, complexes **1a**−**5a** can only be prepared with the 1,3-PhNNNPh group with all the phosphites used. With the 1,3-*p*-tolyl-NNN-*p*-tolyl ligand, instead, triazenide complexes **1b** and **4b** were obtained only with the good π-accepting[21] $P(OMe)_3$ and $P(OEt)_3$ phosphite ligands. The use of the less π-acidic[21] $PPh(OEt)_2$ ligand probably makes the NH hydrogen atom of the [RuH{η^1-*p*-tolyl-N═NN(H)-*p*-tolyl}P_4]$^+$ and the [M(κ^1-OTf){η^1-*p*-tolyl-N═NN(H)-*p*-tolyl}P_4]$^+$ intermediates less acidic, preventing the intramolecular acid−base reaction between RuH and the triazene NH hydrogen atom, in one case, and the deprotonation by NEt_3 in the other. As a result, samples of pure hydride−triazene [RuH{η^1-*p*-tolyl-N═NN(H)-*p*-tolyl}{$PPh(OEt)_2$}$_4$]BPh_4 (**9b**) complex can be isolated (see below). We have also used LiOH as a base, instead of NEt_3, in the reaction of the triflate−triazene intermediate **(A)** (Scheme 1), but with both the $PPh(OEt)_2$ and the *p*-tolyltriazene ligands, only intractable mixtures were obtained.

The triazenide [M(η^2-1,3-ArNNNAr)P_4]BPh_4 (**1**−**5**) complexes are red-brown microcrystalline solids stable in air and in a solution of polar organic solvents where they behave like 1:1 electrolytes.[22] Their formulation is supported by analytical and spectroscopic data and by the X-ray crystal structure determination of [Ru(η^2-1,3-PhNNNPh){$P(OEt)_3$}$_4$]BPh_4 (**2a**) for which the ORTEP diagram of the cation is shown in Figure 1.

Selected bond distances and angles for **2a** are in Table 2. The cation complex contains the Ru(II) atom in a distorted octahedral environment which is coordinated to N1 and N3 of the triazenide ligand [RuNN bite angle of 58.4(1)°] and to four phosphorus atoms of four monodentated phosphite ligands $P(OEt)_3$. The octahedron can be described as having the nitrogen atoms in the distorted equatorial plane, with the dihedral angle between the RuPP and the RuNN planes being 11.5(2)°. The N1−N2−N3 angle takes a value of 107.0(3)°, similar to that of previously reported complexes with triazenide ligands[3b,c,e] but slightly larger than that for the Ru(II) complex [Ru($PhNNNPh)_2(PPh_3)_2$][2i] with an average value of 104.0(4)°. The N−N distances, 1.319(4) and 1.312(4) Å, are well within the range expected for this ligand and, together with the Ru−N distances of 2.163(3) and 2.170(3) Å, show an important delocalization over the ring and its strained nature. The Ru−P distances are in two different sets, since those in the equatorial plane are shorter than those in axial positions. This could be an effect of the electron withdrawal of the triazenide ligand added to the mutually trans effect of the phosphites in the axial positions. Those last values are not very different from those found in the already mentioned complex [Ru($PhNNNPh)_2(PPh_3)_2$],[2i] in which the phosphine ligands are also mutually in trans positions.

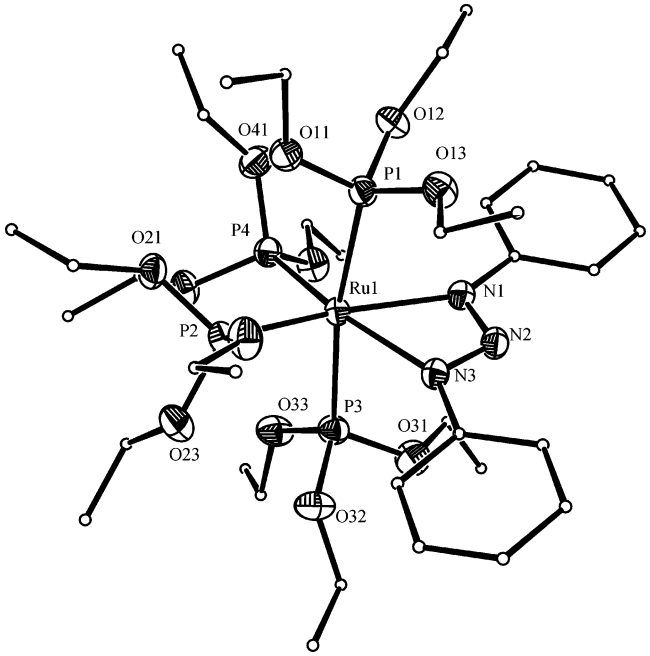


Figure 1. Cation [Ru(η^2-1,3-PhNNNPh){$P(OEt)_3$}$_4$]BPh_4 (**2a**) (30% probability level), where the carbon atoms have been drawn as small spheres. Hydrogen atoms have been omitted.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **2a**

Ru(1)−N(3)	2.163(3)	Ru(1)−N(1)	2.170(3)
Ru(1)−P(4)	2.2538(10)	Ru(1)−P(2)	2.2621(11)
Ru(1)−P(1)	2.3363(11)	Ru(1)−P(3)	2.3392(12)
N(1)−N(2)	1.319(4)	N(2)−N(3)	1.312(4)
N(3)−Ru(1)−N(1)	58.43(11)	N(3)−Ru(1)−P(4)	162.35(9)
N(1)−Ru(1)−P(4)	105.71(9)	N(3)−Ru(1)−P(2)	104.47(9)
N(1)−Ru(1)−P(2)	161.14(9)	P(4)−Ru(1)−P(2)	92.24(4)
N(3)−Ru(1)−P(1)	90.30(8)	N(1)−Ru(1)−P(1)	81.59(8)
P(4)−Ru(1)−P(1)	95.06(4)	P(2)−Ru(1)−P(1)	91.25(4)
N(3)−Ru(1)−P(3)	82.01(8)	N(1)−Ru(1)−P(3)	90.59(8)
P(4)−Ru(1)−P(3)	91.06(4)	P(2)−Ru(1)−P(3)	94.91(4)
P(1)−Ru(1)−P(3)	171.14(4)	N(1)−N(2)−N(3)	107.0(3)

In the temperature range between +20 and −80 °C, the $^{31}P\{^1H\}$ NMR spectra of the $P(OMe)_3$ and $P(OEt)_3$ complexes **1a**, **1b**, **2a**, **4a**, and **4b** appear as an A_2B_2 multiplet, in agreement with a geometry of type **I** (Schemes 1 and 2), like that observed in the solid state. We have also prepared the labeled [Ru(η^2-1,3-$Ph^{15}NN^{15}NPh$){$P(OEt)_3$}$_4$]BPh_4 (**2a**$_1$) complex using the 1,3-$Ph^{15}N{=}N^{15}N(H)Ph$ ligand and ob-

(19) (a) Sutherland, J. W. *J. Phys. Chem.* **1979**, *83*, 789−795. (b) Sawicki, E.; Hauser, T. R.; Stanley, T. W. *Anal. Chem.* **1959**, *31*, 2063−2065. (c) Hansen, L. D.; West, B. D.; Baca, E. J.; Black, C. L. *J. Am. Chem. Soc.* **1968**, *90*, 6588−6592.
(20) Crabtree, R. H.; Lavin, M.; Bonneviot, L. *J. Am. Chem. Soc.* **1986**, *108*, 4032.
(21) (a) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313−348. (b) Rahaman, M. M.; Liu, H.-Y.; Eriks, K.; Prock, A.; Giering, W. P. *Organometallics* **1989**, *8*, 1−7.
(22) Geary, W. J. *Coord. Chem. Rev.* **1971**, *7*, 81−122.

Table 3. ^{15}N NMR Data for Selected Triazene and Triazenide Complexes

	compound	^{15}N NMR[a,b] δ (J/Hz)	assignment
	$Ph^{15}N{=}N{-}^{15}N(H)Ph$	−20.5 s[c] −198.0 d $J_{^{15}NH} = 92$	$Ph^{15}N{=}^{15}NH$
2a$_1$	[Ru(η^2-1,3-$Ph^{15}NN^{15}NPh$) {P(OEt)$_3$}$_4$]BPh_4	AA′B$_2$XX′ spin syst X = X′ = ^{15}N δ_X −140.0 $J_{AX} = J_{A'X'}$ = 46.6 $J_{BX} = J_{BX'}$ = 5.20 $J_{AX'} = J_{A'X}$ = 4.95 $J_{XX'} = 4.05$	
11a$_1$	[OsH{$Ph^{15}N{=}NH$) {PPh(OEt)$_2$}$_4$]BPh_4	−10.7 s	$Ph^{15}N{=}$
8a$_1$	[OsH{η^1-1,3-$Ph^{15}N{=}N^{15}N(H)Ph$} {PPh(OEt)$_2$}$_4$]BPh_4	−15.6 m[c] −199.2 d $J_{^{15}NH} = 92$	$Ph^{15}N{=}^{15}NH$

[a] From $CH_3{}^{15}NO_2$. [b] In CD_2Cl_2 at 20 °C unless otherwise noted. [c] At −90 °C.

served a complicated multiplet in the ^{31}P spectra. A simulation using an AA′B$_2$XX′ (X, X′ = ^{15}N) model, however, gave an excellent agreement between the simulated and the experimental spectra, allowing the NMR parameters to be calculated. The ^{15}N NMR spectrum of **2a$_1$** was also recorded and appears as an AA′B$_2$XX′ (X, X′ = ^{15}N) multiplet at −140.0 ppm whose parameters are reported in Table 3.

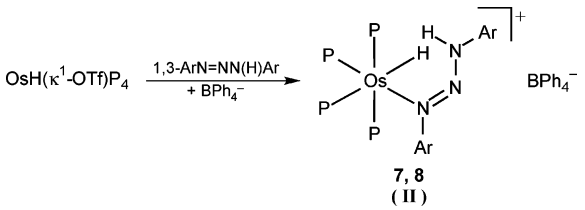
The $^{31}P\{^1H\}$ NMR spectra of the PPh(OEt)$_2$ derivatives **3a** and **5a** are temperature-dependent and result partially different from those of the related compounds **1**, **2**, and **4**. The broad multiplet observed at room temperature for both **3a** and **5a** changes as the temperature is lowered and, for the ruthenium complex (**3a**), resolves at −100 °C into an A$_2$B$_2$ multiplet, in agreement with a type-**I** geometry. In the case of the osmium compound **5a**, instead, a well-resolved multiplet appears at −30 °C which remains unchanged until −100 °C and was simulated using an ABC$_2$ model with the parameters reported in the Experimental Section. A ^{31}P spectrum of this type is not in agreement with the proposed formulation of the compound, which should give a symmetric A$_2$B$_2$-type spectrum. However, taking into account that the values of the chemical shifts of A and B are very close and that the PPh(OEt)$_2$ ligand can give rotational isomers,[23] the VT ^{31}P spectra of **5a** may be explained on the basis of the restricted rotation of the phosphine ligand around the Os−P bond. At −30 °C, two PPh(OEt)$_2$ phosphites are magnetically equivalent, while the other two can be made virtually inequivalent by the different arrangement of the phenyl and ethoxy groups of one phosphite with respect to the other. The steric requirements of the PPh(OEt)$_2$, as compared to the P(OEt)$_3$ phosphite ligand in our η^2-triazenide complexes, probably lead to the asymmetric ABC$_2$ ^{31}P spectra in the [Os(η^2-1,3-PhNNNPh){PPh(OEt)$_2$}$_4$]BPh_4 (**5a**) derivative.

(23) Examples of inequivalent phosphorus nuclei in octahedral complexes containing four PPh(OEt)$_2$ or PPhMe$_2$ ligands in a plane have recently been reported for FeHCl{PPh(OEt)$_2$}$_4$,[24] [IrCl$_2$(PPhMe$_2$)$_4$]ClO$_4$,[25] and MnH(CO){PPh(OEt)$_2$}$_4$ [26] derivatives.

Triazenide complexes of ruthenium(II) and osmium(II) have been reported with carbonyl and triphenylphosphine ligands and are neutral species of the MX(ArNNNAr)(CO)-(PPh$_3$)$_2$ (X = H, Cl) and M(ArNNNAr)$_2$(PPh$_3$)$_2$ types.[2a,i] The use of both the dihydrogen [RuH(η^2-H$_2$)P$_4$]$^+$ and the triflate [M(κ^2-O$_2$SOCF$_3$)P$_4$]$^+$ (M = Ru, Os) cations as precursors allows new cationic [M(η^2-ArNNNAr)P$_4$]$^+$ triazenide complexes stabilized by phosphite ligands to be prepared.

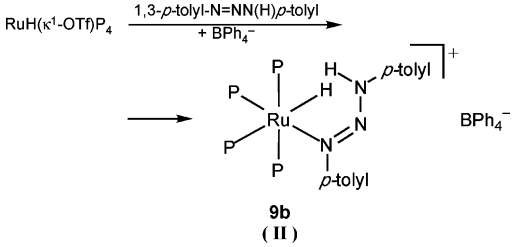
Triazene Complexes. Hydride−triflate OsH(κ^1-OTf)P$_4$ complexes react with an excess of 1,3-diaryltriazene to give the hydride−triazene [OsH{η^1-1,3-ArN=NN(H)Ar}P$_4$]$^+$ derivatives, which were isolated as BPh_4 salts and characterized (Scheme 3).

Scheme 3



P = P(OEt)$_3$ (**7**), PPh(OEt)$_2$ (**8**); Ar = Ph (**a**), *p*-tolyl (**b**)

Scheme 4



P = PPh(OEt)$_2$

Related ruthenium triazene complexes were also prepared in only one case, using both the 1,3-di-*p*-tolyltriazene and the PPh(OEt)$_2$ phosphite ligands, as shown in Scheme 4.

The hydride−triazene [OsH{η^2-1,3-ArN=NN(H)Ar}P$_4$]$^+$ (**7, 8**) cations are very stable and do not give rise to evolution of H_2 nor to formation of the related triazenide [Os(η^2-1,3-ArNNNAr)P$_4$]$^+$ cations under any conditions. This unreactivity of the osmium species is rather surprising (see Scheme 2) and may be attributed to a different reactivity of the Os−H as compared to that of Ru−H toward the NH of the coordinate η^1-1,3-triazene.

The hydrogen atom in the [Os]−H group probably has less hydridic character[13a,27] than the related [Ru]−H and needs a stronger acid than the NH of the η^1-triazene for its protonation. The absence of this acid−base reaction between the hydride and the triazenic NH group prevents the

(24) Albertin, G.; Antoniutti, S.; Bordignon, E. *J. Organomet. Chem.* **1996**, *513*, 147−153.
(25) Deeming, A. J.; Doherty, S.; Marshall, J. E.; Powell, N. I. *J. Chem. Soc., Chem. Commun.* **1989**, 1351.
(26) Albertin, G.; Antoniutti, S.; Bettiol, M.; Bordignon, E.; Busatto, F. *Organometallics* **1997**, *16*, 4959−4969.
(27) (a) Dedieu, A. *Transition Metal Hydrides*; Wiley-VCH: New York, 1992. (b) Peruzzini, M.; Poli, R. *Recent Advances in Hydride Chemistry*; Elsevier: Amsterdam, 2001.

formation of the triazenide complexes and, for the first time, allows the preparation of 1,3-diaryltriazene complexes.

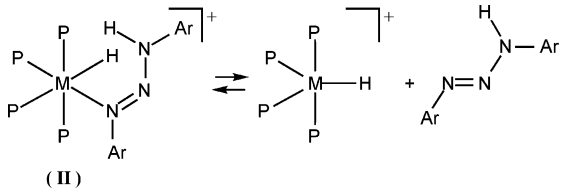
The absence of the acid−base reaction is also observed in ruthenium complex **9b**, in which the nature of both the phosphite and the triazene ligands prevents the formation of the η^2-triazenide derivative.

The hydride−triazene [MH{η^1-1,3-ArN═NN(H)Ar}P_4]-BPh_4 (**7**−**9**) compounds are green or yellow-green solids stable both as solids and in solutions of polar organic solvents, where they behave like 1:1 electrolytes.[22] The infrared spectra show a weak band at 3359−3331 cm^{-1} attributed to the NH of the triazene and, for **7** and **8**, a weak band at 1990−1975 cm^{-1} from ν_{M-H}. The presence of both the triazene and the hydride ligands is confirmed by the ^1H NMR spectra, which also indicate that the complexes are fluxional (see Figure S1). The broad signals that appear at room temperature in the proton spectra of complexes **7**−**9** change as the temperature is lowered, and at −90 °C, a slightly broad singlet attributed to the NH of the triazene ligand appears at 11.97−10.12 ppm. At this temperature, a well-resolved multiplet of the hydride ligand between −6.70 and −8.66 ppm is also present, as well as the signal of the phosphite groups. At −90 °C, the ^{31}P NMR spectra also resolve into an AB_2C or A_2BC pattern, which was simulated with the parameters reported in the Experimental Section.

Further information on the behavior in solution of the hydride−triazene complexes come from VT-NMR studies of the labeled [OsH{1,3-Ph^{15}N═N^{15}N(H)Ph}{PPh(OEt)$_2$}$_4$]-BPh_4 (**8a**$_1$) derivative (see Figure S2). The broad signal at 10.5 ppm that appears at −30 °C in the proton spectra of the [OsH{1,3-PhN═NN(H)Ph}P_4]$^+$ (**8a**) cation is now a broad doublet in the spectra of the labeled compound **8a**$_1$ and resolves into a sharp doublet (11.05 ppm) with $^1J_{^{15}NH}$ of 92 Hz at −80 °C. These results strongly support the formulation proposed for the triazene complexes **7**−**9** and suggest that a geometry of the type **II**, with the hydride and the triazene ligands in a mutually cis position, is also present at −80 °C. The AB_2C or A_2BC pattern of the ^{31}P spectra, in fact, and the complicated multiplet of the hydride ligand observed in the ^1H NMR spectra, with one large J_{PH} value and three small ones, agree with this arrangement.

Furthermore, the absence of a detectable coupling[28] between the NH proton and the ^{31}P nuclei of the phosphine seems to suggest that structure **II**, with the diazene nitrogen atom bonded to the central metal, is present in the low exchange-limit conditions. The proton coupled ^{15}N NMR spectrum (Table 3) supports this hypothesis showing, at −80 °C, a doublet at −199.2 ppm with a $^1J_{^{15}NH}$ value of of 92 Hz from the ^{15}NH triazene nitrogen atom and a multiplet at −15.6 ppm attributed to the Ar^{15}N═N−^{15}N diazenic atom coupling with the phosphorus nuclei of the phosphine, in agreement with a geometry of type **II**. The coupling between the ^{15}N and the ^{31}P nuclei is also observed in the spectra of the ^{31}P NMR which appears as an AB_2CX (X = ^{15}N) multiplet and was simulated using the parameters reported in the Experimental Section, thus confirming the proposed geometry (**II**) for the hydride−triazene derivative **8a**$_1$.

Scheme 5



Further support for geometry **II** comes from a comparison of the ^{15}N NMR spectra of **8a**$_1$ with those of the free 1,3-Ph^{15}N═N^{15}N(H)Ph ligand (Table 3), which shows that, while the chemical shift of the diazenic Ph^{15}N═ nitrogen atom changes by about 5 ppm upon coordination, that of the NH group remains practically the same, in agreement with a type-**II** coordination.

The fluxional behavior shown by triazene complexes **7**−**9** may be explained by an intermolecular process involving, as suggested by a reviewer, the dissociation of the triazene ligand, as shown in Scheme 5. This dynamic process, which involves both dissociation of the 1,3-triazene and hydrogen exchange between the two N atoms of the free 1,3-ArN═NN(H)Ar species,[30] may explain the VT NMR spectra observed.

Strong support for such a dissociation equilibrium of the triazene ligand in the complexes has been obtained by adding the ^{15}N-labeled free triazene to the unlabeled **7a**, **8a**, and **9b** compounds in a NMR tube and observing that exchange between the labeled and unlabeled triazene does take place. On the basis of these results, the dissociation process of Scheme 5, which slows at −80 °C, can reasonably be proposed to explain the VT behavior of our triazene derivatives.

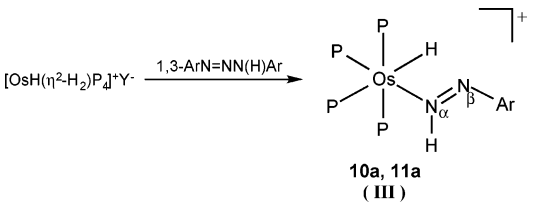
The IR spectrum of the triflate−triazene [Os(κ^1-OTf)-{η^1-1,3-PhN═NN(H)Ph}{P(OEt)$_3$}$_4$]BPh_4 (**6a**) complex shows a weak band at 3327 cm^{-1} attributed to the νNH of the triazene ligand. The ^1H NMR spectra confirm the presence of this ligand and also indicate that the compound is fluxional. The NH signal of the triazene, in fact, begins to appear at −40 °C as a very broad signal near 11 ppm, which sharpens as the temperature is lowered and becomes a slightly broad signal at 11.6 ppm at −80 °C. The $^{31}P\{^1H\}$ NMR spectrum also changes as the temperature is lowered, and the broad multiplet that appears at room temperature resolves into an A_2BC multiplet at −80 °C. On the basis of these data, a dissociation equilibrium of the type shown in Scheme 5 probably also occurs for this complex containing the η^1-triazene and the triflate ligand in a mutually cis position.

(28) Values between 2 and 10 Hz for the $^3J_{HP}$ were observed both in diazene [Ru(ArN═NH)$_2P_4$](BPh$_4$)$_2$ and [Re(NH═NH)(CO)P_4]BPh_4 complexes and in hydroxylamine [M(NH$_2$OH)$_2P_4$](BPh$_4$)$_2$ (M = Ru, Os) derivatives.[14c,29,31b]

(29) Albertin, G.; Antoniutti S.; Giorgi, M. T. *Eur. J. Inorg. Chem.* **2003**, 2855−2866.

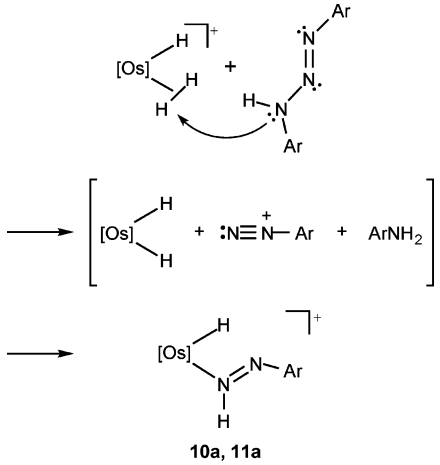
(30) It can be noted that the labeled 1,3-Ph^{15}N═N^{15}N(H)Ph free diazene molecule is fluxional (see Figure S3), and at room temperature, no NH signal was observed in the proton NMR spectra. At −30 °C a broad signal appears which splits into two humps at −70 °C, and at −90 °C, a well-resolved doublet with $^1J_{^{15}NH}$ of 92 Hz appears. This behavior may be explained on the basis of a proton exchange between the two ^{15}N nitrogen atoms in the molecule, which is fast at room temperature and prevents the observation of the $^1J_{^{15}NH}$.

Scheme 6



P = P(OEt)$_3$ (**10**), PPh(OEt)$_2$ (**11**); Y$^-$ = OTf$^-$, BPh$_4^-$; Ar = Ph (**a**)

Scheme 7



[Os] = OsP$_4$

Aryldiazene Derivatives. Dihydrogen [OsH(η^2-H$_2$)P$_4$]Y (Y = OTf$^-$, BPh$_4^-$) complexes slowly react with 1,3-diaryltriazene to give the aryldiazene [OsH(ArN═NH)P$_4$]-BPh$_4$ (**10a** and **11a**) derivatives which were isolated in about a 60% yield and characterized (Scheme 6).

The formation of an aryldiazene complex from the reaction of a 1,3-triazene species is rather surprising because coordinate aryldiazenes are generally obtained[6−8] from the insertion reaction of an aryldiazonium cation, ArN$_2^+$, into the M−H bond of a hydride derivative. However, when the properties of both the osmium η^2-H$_2$ complexes[13] and of the 1,3-diaryltriazene molecule are taken into account, a reaction path to explain the synthesis of hydride−diazene complexes **10** and **11** can be proposed (Scheme 7). Although the η^2-H$_2$ ligand in the osmium [OsH(η^2-H$_2$)P$_4$]$^+$ cations is stable to the substitution by other ligands, such as triazene, it is sufficiently acidic[13a] to be able to protonate the aminic nitrogen atom of the 1,3-ArN═NN(H)Ar molecule. The protonation of the triazene to the amine nitrogen atom can result in cleavage of the N−N bond with formation of both the amine, ArNH$_2$, and the aryldiazonium cation, ArN$_2^+$. The reaction of ArN$_2^+$ with the dihydride OsH$_2$P$_4$, formed from the deprotonation of the [OsH(η^2-H$_2$)P$_4$]$^+$ cation, can give the final aryldiazene derivatives **10a** and **11a**.

The presence of free ArNH$_2$ amine (detected by ^{1}H NMR) in the reaction mixture and the known reactivity[12c] of the dihydride OsH$_2$P$_4$ complexes toward aryldiazonium cations ArN$_2^+$, which gives the same [OsH(ArN═NH)P$_4$]$^+$ derivatives, support the path proposed in Scheme 7.

The osmium aryldiazene complexes, **10** and **11**, were isolated as stable diamagnatic yellow solids, soluble in polar organic solvents, where behave like 1:1 electrolytes.[22] Good

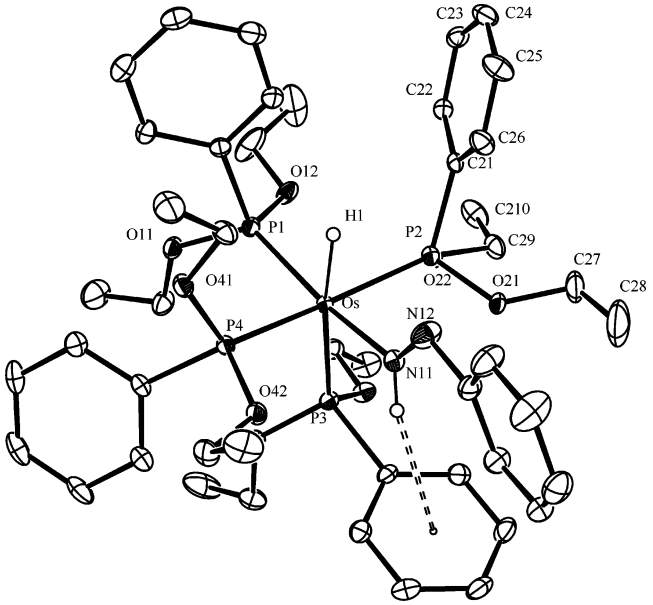


Figure 2. Cation of [OsH(PhN═NH){PPh(OEt)$_2$}$_4$]BPh$_4$ (**11a**) (30% probability level). Hydrogen atoms, except for two, were omitted for clarity.

analytical data have been obtained for the two complexes, which were characterized spectroscopically (IR and NMR data) and by the X-ray crystal structure determination of [OsH(PhN═NH){PPh(OEt)$_2$}$_4$]BPh$_4$ (**11a**). The ORTEP diagram of the cation of **11a** is shown in Figure 2.

The osmium atom in the cationic complex is coordinated by four phosphonite ligands, a phenyl diazene group, and a hydride ligand, which is cis to the diazene ligand. Unfortunately, the position of the hydride ligand was not refined, so its geometrical parameters are not precise. The coordination polyhedron can be described as a distorted octahedron where the hydride and the diazene ligands are in the equatorial positions. The other two equatorial position and the axial positions are occupied by four PPh(OEt)$_2$ phosphonite ligands. The main source of the distortion is the usual bend of the ligand toward the position occupied by the hydride ligand, as is shown by the value of the axial P−Os−P angle of 166.70(3)° or the N11−Os−P1 angle of 165.91(9)°. The Os−P distances show that the phosphonite trans to the diazene ligand is about 0.04 Å shorter than the other three. The Os−N and C−N distances are as expected for single bonds, although there are not any structural studies on Os(II) complexes with diazene ligands to our knowledge. The N(11)−N(12) distance, 1.241(4) Å, is typical for a double bond and is within the range expected for aryldiazene complexes.[8b,e,31,32]

The phosphonite ligand being trans to the hydride ligand allows a hydrogen bond to be established between the NH group of the diazene ligand and the π-cloud of the phenyl ring bond to the phosphorus atom, with parameters N−Ct

(31) (a) Albertin, G.; Antoniutti, S.; Pelizzi, G.; Vitali, F.; Bordignon, E. *J. Am. Chem. Soc.* **1986**, *108*, 6627−6634. (b) Albertin, G.; Antoniutti, S.; Pelizzi, G.; Vitali, F.; Bordignon, E. *Inorg. Chem.* **1988**, *27*, 829−835.

(32) Melenkivitz, R.; Southern, J. S.; Hillhouse, G. L.; Concolino, T. E.; Liable-Sands, L. M.; Rheingold, A. L. *J. Am. Chem. Soc.* **2002**, *124*, 12068−12069.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for **11a**

Os−N(11)	2.104(3)	Os−P(1)	2.2716(9)
Os−P(3)	2.3296(9)	Os−P(4)	2.3297(9)
Os−P(2)	2.3382(9)	Os−H(1)	1.7848(2)
N(12)−C(51)	1.423(4)	N(11)−N(12)	1.241(4)
N(11)−Os−P(1)	165.91(9)	N(11)−Os−P(3)	90.91(9)
P(1)−Os−P(3)	103.01(3)	N(11)−Os−P(4)	85.08(8)
P(1)−Os−P(4)	90.67(3)	P(3)−Os−P(4)	98.15(3)
N(11)−Os−P(2)	86.35(8)	P(1)−Os−P(2)	95.24(3)
P(3)−Os−P(2)	92.13(3)	P(4)−Os−P(2)	166.70(3)

= 2.90(4) Å, H−Ct = 3.694(3) Å, and N−H···Ct = 149(4)°, where Ct represents the centroid of the ring.

The ^{1}H NMR spectra of the aryldiazene complexes, **10** and **11** show, in addition to the signals of the phosphite and the BPh_4 anion, slightly broad signals at 14.47 (**10a**) and 13.42 (**11a**) ppm, attributed to the NH diazene proton, and a multiplet between −7.78 and −8.68 ppm from the hydride ligand. In the temperature range between +20 and −80 °C, the ^{31}P NMR data appear, for both compounds **10a** and **11a**, as an AB_2C multiplet, in agreement with a mutually cis position of the hydride and the diazene ligand. On the basis of these data, a geometry of type **III** (Scheme 6) like that observed in the solid state can be reasonably proposed for diazene complexes **10a** and **11a**. We have also prepared the labeled $[OsH(Ph^{15}N{=}NH)P_4]BPh_4$ (**11a$_1$**) complex from the reaction of $Ph^{15}N{=}N^{15}N(H)Ph$ with $[OsH(\eta^2\text{-}H_2)P_4]^+$ and recorded both the ^{1}H and ^{15}N NMR spectrum. In the proton spectra, only one signal of the diazene ^{15}NH proton is present in the high region of the spectra at 13.4 ppm, and although the broadness of this signal prevents the determination of the $J_{^{15}NH}$, the spectrum indicates that a value lower than 7−8 Hz for $J_{^{15}NH}$ can be estimated. These data confirm that the ^{15}N-labeled atom is in the β position, in further agreement with the path proposed in Scheme 7 for the formation of the diazene derivative.

Conclusions

In this paper we report the synthesis of unprecedented complexes of ruthenium and osmium containing 1,3-diaryltriazene as a monodentate ligand. The complexes are fluxional, and at −90 °C, a geometry with the diazene nitrogen atom of the 1,3-ArN═NN(H)Ar ligand bonded to the metal was proposed. The hydride−triazene $[MH\{\eta^1\text{-}1,3\text{-}ArN{=}NN(H)Ar\}P_4]^+$ species are unstable in some cases and lead to the η^2-triazenide $[M(\eta^2\text{-}1,3\text{-}ArNNNAr)P_4]BPh_4$ derivatives. However, a route for the facile synthesis of this type of triazenide complexes of ruthenium and osmium can be achieved using the κ^2-triflate $[M(\kappa^2\text{-}O_2SOCF_3)P_4]^+$ cation as a precursor. The structural parameters for the chelate triazenide $[Ru(\eta^2\text{-}1,3\text{-}PhNNNPh)\{P(OEt)_3\}_4]BPh_4$ complex were also obtained. Finally, we also report a new reaction shown by the dihydrogen $[OsH(\eta^2\text{-}H_2)P_4]^+$ cation which yields the aryldiazene $[OsH(ArN{=}NH)P_4]^+$ derivative when treated with diaryltriazene 1,3-ArN═NN(H)Ar molecules. A reaction path for this reaction, involving a N−N cleavage of the triazene, is also proposed.

Acknowledgment. The financial support of MIUR (Rome), PRIN 2004, is gratefully acknowledged. We thank Daniela Baldan for technical assistance.

Supporting Information Available: Crystallographic data in CIF format for complexes **2a** and **11a** and NMR data in Figures S1, S2, and S3. This material is available free of charge via the Internet at http://pubs.acs.org.

IC052063U