

The First Example of Tetraosmium Carbonyl Clusters Containing (μ_3 -NH) Nitrene Ligands: Syntheses and Crystal Structures

Yat Li and Wing-Tak Wong*

Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong, People's Republic of China

Zhen-Yang Lin

Department of Chemistry, The University of Science and Technology, Clear Water Bay, Hong Kong, People's Republic of China

Received September 16, 2002

The reaction of $[\text{Os}_4(\mu\text{-H})_4(\text{CO})_{12}]$ with *o*-tert-butylhydroxylamine hydrochloride (${}^t\text{BuONH}_2\cdot\text{HCl}$) in the presence of trimethylamine-*N*-oxide (Me_3NO) in dichloromethane afforded $[\text{Os}_4(\mu\text{-H})_4(\text{CO})_{11}\{\eta^1\text{-NH}_2\text{O}^t\text{Bu}\}]$ (**1**) in high yield. Upon the addition of tetrafluoroboric acid (HBF_4) into the solution of **1** in acetonitrile, the novel cationic cluster $[\text{Os}_4(\mu\text{-H})_4(\text{CO})_{11}(\mu\text{-NH}_2)(\text{NCMe})][\text{BF}_4]$ (**2**) formed. Reaction of **1** with HBF_4 in the presence of diphenylacetylene gave two geometric isomers, $[\text{Os}_4(\mu\text{-H})_2(\text{CO})_{11}(\mu\text{-NH}_2)\{\mu\text{-}\eta^3\text{-Ph}(\text{CHC})\text{Ph}\}]$ (**3**) and $[\text{Os}_4(\mu\text{-H})_2(\text{CO})_{11}(\mu\text{-NH}_2)(\eta^1\text{-Ph}(\text{CH}=\text{C})\text{Ph})]$ (**4**). Treatment of **2** with excess Me_3NO in acetonitrile gave $[\text{Os}_4(\mu\text{-H})_4(\text{CO})_{10}(\mu\text{-NH}_2)(\text{NCMe})_2][\text{BF}_4]$ (**5**). The carbonylation of **2** in the refluxing chloroform afforded the neutral clusters $[\text{Os}_3(\mu\text{-H})_2(\text{CO})_9(\mu\text{-NH}_2)\text{Cl}]$ (**6**) and $[\text{Os}_4(\mu\text{-H})_3(\text{CO})_{12}(\mu\text{-NH}_2)]$ (**7**). Protonation of **7** with trifluoromethylsulfonic acid, $\text{CF}_3\text{SO}_3\text{H}$, gave another cationic cluster, $[\text{Os}_4(\mu\text{-H})_4(\text{CO})_{12}(\mu\text{-NH}_2)][\text{CF}_3\text{SO}_3]$ (**8**), which is an analogue of **2**. Refluxing of **7** in toluene under an argon atmosphere afforded $[\text{Os}_4(\mu\text{-H})_2(\text{CO})_{12}(\mu_3\text{-NH})]$ (**9**), which is the first example of (μ_3 -NH) nitrene ligands containing tetraosmium carbonyl clusters. The solid-state structures of **2**–**9** were established by X-ray analysis. The ${}^1\text{H}$ NMR properties of these clusters were studied, and a correlation between the chemical shift and the structural geometry was established.

Introduction

The chemistry of late transition metal carbonyl clusters possessing amino,¹ amido,² and nitrene ligands^{3–5} has been extensively investigated in recent years. Much of the interest in those species stems from the comparison of their reactivity to that of nitrogen atoms bound to metal surfaces. The formation and cleavage of N–H bonds on metal surfaces is believed to be an integral part of several important heterogeneously catalyzed

reactions, such as the Haber process⁶ and the oxidation of ammonia.⁷ In some of these reactions, surface-coordinated nitrogen atoms are the key intermediates. The Haber process has been shown to involve the dissociative chemisorption of molecular nitrogen to give surface-adsorbed nitrogen atoms, which further react with molecular hydrogen to form N–H bonds, followed by the desorption of ammonia.⁸ The bonding relationship between coordinated transition metal clusters and the surface-adsorbed NH_x moieties is illustrated in Scheme 1.^{9–12}

* Corresponding author. Fax: (+852)25472933. E-mail: wt Wong@hkucc.hku.hk.

(1) Lin, Y. W.; Gau, H. M.; Wen, Y. S.; Lu, K. L. *Organometallics* **1992**, *11*, 1445. Lu, K. L.; Chen, C. J.; Lin, Y. W.; Gau, H. M.; Hong, F. E.; Wen, Y. S. *Organometallics* **1993**, *12*, 2188.

(2) Cabeza, J. A.; Rto, I. D.; Grepioni, F.; Riera, V. *Organometallics* **2000**, *19*, 4643. Cabeza, J. A.; Nöth, H.; Rosales-Hoz, M. D. J.; Sánchez-Cabrera, G. *Eur. J. Inorg. Chem.* **2000**, 2327. Cabeza, J. A.; Fernández-Colinas, J. M.; García-Granda, S.; Riera, V.; Van der Maelen, J. F. *Inorg. Chem.* **1992**, *31*, 1233. Hui, B. K. M.; Wong, W. T. *J. Chem. Soc., Dalton Trans.* **1998**, 3977.

(3) Scoles, L.; Sterenberg, B. T.; Udachin, K. A.; Carty, A. J. *Chem. Commun.* **2002**, 320.

(4) Lee, K. K. H.; Wong, W. T. *J. Chem. Soc., Dalton Trans.* **1996**, 1707. Lee, K. K. H.; Wong, W. T. *Inorg. Chem.* **1996**, *35*, 5393. Lee, K. K. H.; Wong, W. T. *J. Organomet. Chem.* **1995**, *503*, C43. Lee, K. K. H.; Wong, W. T. *J. Organomet. Chem.* **1999**, *577*, 323. Ho, E. N. M.; Lin, Z. Y.; Wong, W. T. *Eur. J. Inorg. Chem.* **2001**, 1321. Ho, E. N. M.; Lin, Z. Y.; Wong, W. T. *Chem. Eur. J.* **2001**, *7*, 258.

(5) Ramage, D. L.; Geoffroy, G. L.; Rheingold, A. L.; Haggerty, B. D. *Organometallics* **1992**, *11*, 1242. Wang, D.; Shen, H.; Richmond, M. G.; Schwartz, M. *Organometallics* **1995**, *14*, 3636. Song, J. S.; Geoffroy, G. L.; Rheingold, A. L. *Inorg. Chem.* **1992**, *31*, 1505. Yeh, W. Y.; Stern, C. L.; Shriver, D. F. *Inorg. Chem.* **1997**, *36*, 4408.

(6) Smith, J. M.; Lachicotte, R. J.; Pittard, K. A.; Cundari, T. R.; Lukat-Rodgers, G.; Rodgers, K. R.; Holland, P. L. *J. Am. Chem. Soc.* **2001**, *123*, 9222. Yiokari, C. G.; Pitselis, G. E.; Polydoros, D. G.; Katsaounis, A. D.; Vayenas, C. G. *J. Phys. Chem. A* **2000**, *104*, 10600. Vettrano, M.; Trudeau, M.; Lo, A. Y. H.; Schurko, R. W.; Antonelli, D. *J. Am. Chem. Soc.* **2002**, *124*, 9567.

(7) Coia, G. M.; Devenney, M.; White, P. S.; Meyer, T. J.; Wink, D. A. *Inorg. Chem.* **1997**, *36*, 2341. Kuo, C.-H.; Yuan, F.; Hill, D. O. *Ind. Eng. Chem. Res.* **1997**, *36*, 4108. Ding, Z. Y.; Li, L.; Wade, D.; Gloyna, E. F. *Ind. Eng. Chem. Res.* **1998**, *37*, 1707.

(8) Guan, S.; Liu, H. Z. *Ind. Eng. Chem. Res.* **2000**, *39*, 2891. Izumi, Y.; Iwata, Y.; Aika, K. *J. Phys. Chem.* **1996**, *100*, 9421. Joly, J.-P.; Perrard, A. *Langmuir* **2001**, *17*, 1538.

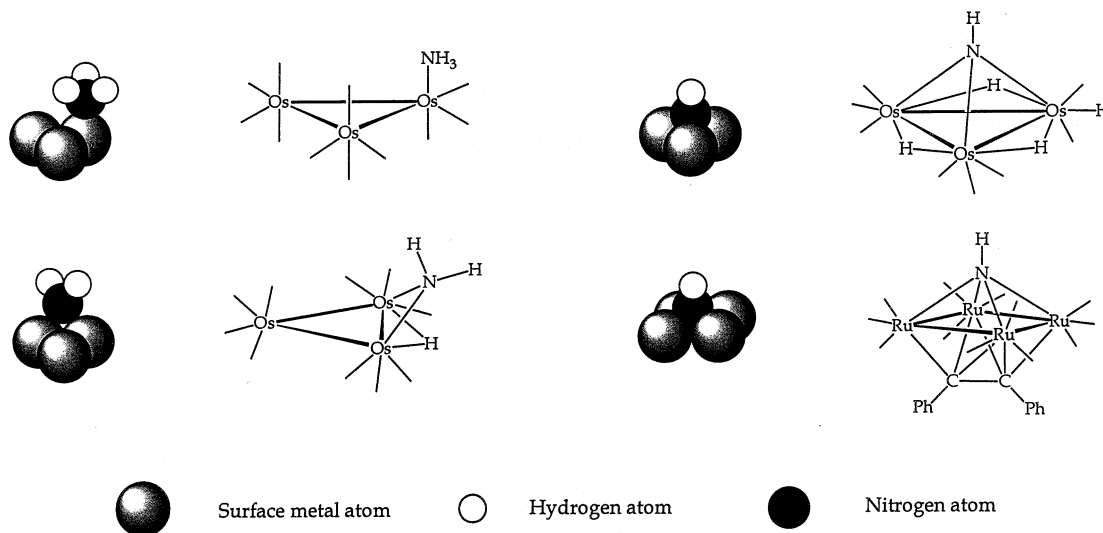
(9) Süss-Fink, G. *Z. Naturforsch.* **1980**, *B35*, 454. Aime, S.; Dastrù, W.; Gobetto, R.; Krause, J.; Sappa, E. *Organometallics* **1995**, *14*, 3224.

(10) Bryan, E. G.; Johnson, B. F. G.; Lewis, J. J. *J. Chem. Soc., Dalton Trans.* **1977**, 1328. Johnson, B. F. G.; Lewis, J.; Raitby, P. R.; Sankey, S. W. *J. Organomet. Chem.* **1982**, *228*, 135.

(11) Smieja, J. A.; Gladfelter, W. L. *J. Organomet. Chem.* **1985**, *297*, 349.

(12) Bolhm, M. L.; Gladfelter, W. L. *Organometallics* **1986**, *5*, 1049.

Scheme 1



The examples of transition metal carbonyl clusters containing nitrene ligands are rare compared to those clusters containing imido groups (μ_3 -NR or μ_4 -NR). Several efficient routes to the isolation of (μ_3 -NH and μ_4 -NH) nitrene clusters have been reported. These include protonation of nitrido complexes,^{12,13} thermolysis, and pyrolysis of nitrosyl complexes.⁴ However, these synthetic methodologies are limited to the iron and ruthenium systems only. To our knowledge, there is no structurally established example of an osmium cluster containing (μ_3 -NH and μ_4 -NH) nitrene ligands. Herein, we report the preparation and characterization of a series of new novel osmium metal clusters containing amino and (μ -NH₂) amido ligands and the first example of (μ_3 -NH) nitrene ligands containing osmium clusters. The new synthetic methodology of nitrene metal clusters from amino metal clusters through amido metal clusters is demonstrated.

Experimental Section

All reactions and manipulations were carried out under argon using standard Schlenk techniques, except for the chromatographic separations. Solvents were purified by standard procedures and distilled prior to use.¹⁴ Reactions were monitored by analytical thin-layer chromatography (Merck Kieselgel 60 F₂₅₄), and the products were separated by thin-layer chromatography on plates coated with silica (Merck Kieselgel 60 F₂₅₄). All chemicals, unless otherwise stated, were purchased commercially and used as received. [Os₄(μ -H)₄(CO)₁₂]¹⁵ was prepared by the literature methods.

Infrared spectra were recorded on a Bio-Rad FTS-135 IR spectrometer, using 0.5 mm calcium fluoride solution cells, and ¹H NMR spectra were recorded on a Bruker DPX300 spectrometer using CD₂Cl₂ and referenced to SiMe₄ (δ 0). Variable-temperature ¹H NMR spectra were obtained on a Bruker DPX500 spectrometer. Positive ionization fast atom bombardment (FAB) mass spectra were recorded on a Finnigan MAT

95 mass spectrometer, using *m*-nitrobenzyl alcohol as matrix solvent. Microanalyses were performed by Butterworth Laboratories, UK.

Preparation of [Os₄(μ -H)₄(CO)₁₁{ η^1 -NH₂O^tBu}] (1). The complex [Os₄(μ -H)₄(CO)₁₂] (110 mg, 0.1 mmol) was dissolved in dichloromethane (30 mL) and mixed with 1 equiv of *o*-tert-butylhydroxylamine hydrochloride (^tBuONH₂·HCl) at 0 °C. One equivalent of trimethylamine-*N*-oxide was added dropwise. Upon stirring for 1 h, the solution turned dark yellow. The solvent was removed under reduced pressure. Chromatography of the residue on preparative TLC plates eluting with *n*-hexane/dichloromethane (1:1, v/v) afforded the complex [Os₄(μ -H)₄(CO)₁₁{ η^1 -NH₂O^tBu}] (**1**) (40 mg, 34%). Anal. Calcd for C₁₅H₁₅NO₁₂Os₄: C, 15.50; H, 1.30; N, 1.20. Found: C, 15.4; H, 1.3, N, 1.2. IR (*n*-hexane): ν (CO) 2093(w), 2060(s), 2033-(s), 2010(m), 2003(m), 1983(w). ¹H NMR (CD₂Cl₂, 298 K): δ -18.65 (s, br, 4H, hydride), 1.25 (s, 9H, methyl), 6.08 (s, 2H, NH₂); at 233K, **1a** -13.64 (s, 1H, hydride), -15.36 (s, 1H, hydride), -18.28 (s, 1H, hydride), -18.41 (s, 1H, hydride); **1b** -14.28 (s, 1H, hydride), -14.93 (s, 1H, hydride), -18.18 (s, 1H, hydride), -20.86 (s, 1H, hydride). FAB-MS (*m/z*): 1162.

Reaction of 1 with Tetrafluoroboric Acid (HBF₄·Et₂O). Three drops of tetrafluoroboric acid were added into a solution of **1** (23 mg, 0.02 mmol) in acetonitrile (30 mL) under an argon atmosphere. The yellow solution was stirred for 1 h, and the solvent then reduced in vacuo. The residue was separated by preparative TLC on silica, with an eluent of *n*-hexane/dichloromethane (1:1, v/v). The yellow band was isolated as [Os₄(μ -H)₄(CO)₁₁(μ -NH₂)(NCMe)][BF₄] (**2**) (18 mg, 80%). Anal. Calcd for C₁₃H₉BF₄N₂O₁₁Os₄: C, 12.83; H, 0.75; N, 2.30. Found: C, 12.6; H, 0.7, N, 2.2. IR (CH₂Cl₂): ν (CN) 2132(m); ν (CO) 2105(s), 2078(s), 2062(s), 2041(w), 2032(w), 2008(w), 1993(w). ¹H NMR (CD₂Cl₂): δ -21.25 (s, 1H, hydride), -16.78 (s, 1H, hydride), -16.14 (s, 1H, hydride), -15.55 (s, 1H, hydride), 1.10 (s, br, 1H, NH₂), 1.84 (s, br, 1H, NH₂), 2.72 (s, 3H, methyl). FAB-MS (*m/z*): 1130.

Reaction of 1 with HBF₄ in the Presence of Diphenylacetylene. A solution of **1** (23 mg, 0.02 mmol) in dichloromethane (30 mL) was mixed with an excess amount of diphenylacetylene under an argon atmosphere. Several drops of tetrafluoroboric acid were added, and the resultant solution was stirred for 2 h. The solvent was concentrated under reduced pressure and subjected to TLC separation using *n*-hexane/dichloromethane (1:1, v/v) as eluent. Two consecutive yellow bands afforded [Os₄(μ -H)₂(CO)₁₁(μ -NH₂){ μ - η^3 -Ph(CHC-Ph)}] (**3**) (4 mg) and [Os₄(μ -H)₂(CO)₁₁(μ -NH₂)(η^1 -Ph(CH=C)Ph)] (**4**) (3 mg) in 15 and 12% yields, respectively. **3** Anal. Calcd for C₂₅H₁₅NO₁₁Os₄: C 23.71; H 1.19; N 1.11. Found: C, 23.6;

(13) Fjare, D. E.; Gladfelter, W. L. *Inorg. Chem.* **1981**, *20*, 3533. Fjare, D. E.; Gladfelter, W. L. *J. Am. Chem. Soc.* **1981**, 1573.

(14) Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*, 4th ed.; Butterworth Heinemann: Bath, 1996.

(15) Kaesz, H. D.; Knox, S. A. R.; Koepke, J. W.; Saillant, R. B. *J. Chem. Soc., Chem. Commun.* **1971**, 477. Johnson, B. F. G.; Lewis, J.; Raithby, P. R.; Scheldrick, G. M.; Wong, K. *J. Chem. Soc., Dalton Trans.* **1978**, 673. Zuccaro, C.; Pampaloni, G.; Calderazzo, F. *Inorg. Synth.* **1989**, *26*, 293.

H, 1.2, N, 1.1. IR (CH₂Cl₂): $\nu(\text{CO})$ 2095(w), 2064(s), 2047(s), 2032(m), 1997(w). ¹H NMR (CD₂Cl₂): δ -16.79 (s, 1H, hydride), -13.35 (s, 1H, hydride), -0.03 (s, br, 1H, NH₂), 0.32 (s, br, 1H, NH₂), 2.60 (s, 1H, methyl), 6.73 (dd, $J_{\text{HH}} = 7.8$, 2H, phenyl), 7.24 (m, 6H, phenyl), 7.43 (m, 2H, phenyl). FAB-MS (m/z): 1266. **4** Anal. Calcd for C₂₅H₁₅NO₁₁Os₄: C, 23.71; H, 1.19; N 1.11. Found: C, 23.7; H, 1.2, N, 1.2. IR (CH₂Cl₂): $\nu(\text{CO})$ 2103(w), 2074(s), 2055(s), 2029(s), 2008(w). ¹H NMR (CD₂Cl₂): δ -19.10 (s, 1H, hydride), -15.90 (s, 1H, hydride), 4.00 (s, br, 1H, NH₂), 4.83 (s, br, 1H, NH₂), 2.12 (s, 1H, methyl), 6.81 (d, $J_{\text{HH}} = 6.9$, 2H, phenyl), 7.02 (m, 6H, phenyl), 7.31 (t, $J_{\text{HH}} = 7.9$, 2H, phenyl). FAB-MS (m/z): 1087. [M - Ph(CH=O)Ph]⁺.

Preparation of [Os₄(μ -H)₄(CO)₁₀(μ -NH₂)(NCMe)₂][BF₄] (**5**). Solid **2** (23 mg, 0.02 mmol) was dissolved in acetonitrile (30 mL) to give a yellow solution. One equivalent of trimethylamine-*N*-oxide was added dropwise into the yellow solution. Upon stirring for 3 h, the yellow solution darkened. The solvent was removed under reduced pressure. The residue was redissolved in dichloromethane and separated by TLC eluting with *n*-hexane/dichloromethane (1:3, v/v) affording [Os₄(μ -H)₄(CO)₁₀(μ -NH₂)(NCMe)₂][BF₄] (**5**) (15 mg, 66%). Anal. Calcd for C₁₄H₁₂BF₄N₃O₁₀Os₄: C, 13.67; H, 0.98; N, 3.42. Found: C, 13.8; H, 1.0, N, 3.5. IR (CH₂Cl₂): $\nu(\text{CN})$ 2107(m); $\nu(\text{CO})$ 2072(s), 2059(s), 2022(m), 2001(w), 1989(w). ¹H NMR (CD₂Cl₂): δ -21.98 (s, 2H, hydride), -15.53 (s, 2H, hydride), 0.64 (s, 2H, NH₂), 2.69 (s, 6H, methyl). FAB-MS (m/z): 1143.

Carbonylation of 2. A solution of **2** (23 mg, 0.02 mmol) in chloroform (30 mL) was heated to refluxing temperature with carbon monoxide bubbled through the solution for 10 h. With the aid of IR monitoring, the reaction was halted until all of **2** was consumed. The solvent was then removed in vacuo, and the residue was chromatographed on TLC using *n*-hexane/dichloromethane (1:1, v/v) as eluent. A minor yellow band of [Os₃(μ -H)₂(CO)₉(μ -NH₂)Cl] (**6**) (2 mg, 10%) and a pale yellow band of [Os₄(μ -H)₃(CO)₁₂(μ -NH₂)] (**7**) (12 mg, 55%) were isolated. **6**: Anal. Calcd for C₁₀H₄ClNO₉Os₃: C, 13.52; H, 0.45; N, 1.58. Found: C, 13.4; H, 0.44, N, 1.59. IR (CH₂Cl₂): $\nu(\text{CO})$ 2124(w), 2116(w), 2091(m), 2063(s), 2049(m), 2005(m). ¹H NMR (CD₂Cl₂): δ -15.37 (t, $J_{\text{HH}} = 2.0$, 2H, hydride), 5.30 (s, br, 2H, NH₂). FAB-MS (m/z): 876. **7**: Anal. Calcd for C₁₂H₅NO₁₂Os₄: C, 12.91; H, 0.45; N, 1.25. Found: C, 12.8; H, 0.46, N, 1.25. IR (CH₂Cl₂): $\nu(\text{CO})$ 2107(w), 2078(s), 2060(s), 2014(s), 1989(m). ¹H NMR (CD₂Cl₂): δ -16.38 (s, 3H, hydride), -0.57 (s, br, 2H, NH₂). FAB-MS (m/z): 1116.

Reaction of 7 with Trifluoromethylsulfonic Acid (CF₃SO₃H). To a yellow dichloromethane solution of **7** (22 mg, 0.02 mmol) were added several drops of trifluoromethylsulfonic acid (CF₃SO₃H). The yellow solution was stirred at ambient temperature for 3 h, and then the solvent was reduced in vacuo. Some colorless precipitate appeared and was characterized as [Os₄(μ -H)₄(CO)₁₂(μ -NH₂)](CF₃SO₃) (**8**) (8 mg, 36%). Anal. Calcd for C₁₃H₆F₃NO₁₅Os₄S: C, 12.33; H, 0.48; N, 1.11. Found: C, 12.4; H, 0.46, N, 1.09. IR (CH₂Cl₂): $\nu(\text{CO})$ 2126(s), 2105(s), 2084(vs), 2049(s), 2018(w). ¹H NMR (CD₂Cl₂): δ -17.20 (s, 4H, hydride), 2.63 (s, br, 2H, NH₂). FAB-MS (m/z): 1117.

Thermolysis of [Os₄(μ -H)₃(CO)₁₂(μ -NH₂)]. A solution of **7** (22 mg, 0.02 mmol) in toluene (30 mL) was refluxed under an argon atmosphere for 24 h. After cooling, the solvent was removed in vacuo and the residue was separated by preparative TLC on silica, with an eluent of *n*-hexane/dichloromethane (1:1, v/v). The pale yellow band was isolated and identified as [Os₄(μ -H)₂(CO)₁₂(μ -NH)] (**9**) (5 mg, 24%). Anal. Calcd for C₁₂H₃NO₁₂Os₄: C, 12.94; H, 0.27; N, 1.26. Found: C, 12.9; H, 0.26; N, 1.27. IR (CH₂Cl₂): $\nu(\text{CO})$ 2078(s), 2030(s), 2006(m). ¹H NMR (CD₂Cl₂): δ -16.82 (d, $J_{\text{HH}} = 0.8$, 2H, hydride), 9.35 (s, br, 1H, NH). FAB-MS (m/z): 1115.

X-ray Crystallography. Single crystals of **2–9** were grown from their appropriate solvent systems under favorable conditions. Intensity data were collected at ambient temperature

using a Bruker SMART CCD 1000 diffractometer with graphite-monochromated Mo K α radiation using ω scan type. Details of the intensity data collection and crystal data are given in Table 1. The data were corrected for Lorentz and polarization effects. The structures were solved by direct methods (SIR92 or SHELXS86)¹⁶ and expanded using Fourier techniques (DIRDIF94),¹⁷ refined by full-matrix least-squares analysis. Refinements for all non-hydrogen atoms anisotropically have been attempted for all the structures. However, some thermal parameters of these atoms were found to be nonpositive definite, and their thermal parameters were refined in an isotropical manner. This is a common problem encountered for strongly absorbing crystals, as the absorption correction is imperfect. Hydrogen atoms on the organic moieties were introduced in their idealized position, while hydride atoms were located either by difference Fourier syntheses using low angle data or from potential energy calculations.¹⁸ They were included in the structure factors but not refined. The absolute structures of **8** and **9** were also established from the refined Flack parameters. All calculations were performed using the teXsan¹⁹ crystallographic software package of the Molecular Structure Corporation.

Results and Discussion

Synthesis. The preparation of **1–9** is summarized in Scheme 2. The parent amino cluster **1** was simply prepared by the reaction of [Os₄(μ -H)₄(CO)₁₂] with *o*-tert-butylhydroxylamine hydrochloride ('BuONH₂·HCl). An amino transfer to the cluster can be achieved upon elimination of the 'BuO group as 'BuOH in acidic medium. This would result in the further coordination of NH₂ ligand to the metal core. The novel cationic amido cluster **2** was isolated by using this strategy. The amido-supported butterfly geometry of **2** is thought to be favorable for the formation of a nitrene cluster after removing the labile acetonitrile ligand. The carbonylation of **2** in the refluxing chloroform afforded the neutral clusters **6** and **7**. The formation of trinuclear cluster **7** is attributed to the decomposition of **2**. Cluster **7**, the deprotonated analogue of **2**, was protonated with trifluoromethylsulfonic acid (CF₃SO₃H) to give the cationic **8**. Clusters **2** and **8** are isoelectronic, and the protonation and deprotonation processes are found to be reversible. The first example of a (μ -3-NH) nitrene osmium cluster **9** was isolated by the thermolysis of **7** in toluene. The transformation of an amino ligand to a nitrene ligand through an amido ligand was established. In addition, the reaction of **2** with excess Me₃NO in acetonitrile gave another cationic cluster, **5**.

The main stimulus for the study of **1** toward diphenylacetylene stems from the success of the isolation of a series of μ -4-nitrene clusters in the reaction of [Ru₃(CO)₁₀(μ -3-NOMe)] with diphenylacetylene.²⁰ The diphenylacetylene is suggested to be important structural stabilizers in the formation of a square planar metal core that contains a μ -4-NH ligand. However, only two

(16) Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, M.; Giacovazzo, C.; Guagliardi A.; Polidori, G. *SIR92, J. Appl. Crystallogr.* **1994**, *27*, 435.

(17) SHELXS 86, Program for Crystal Structure Solution: Sheldrick, G. M. *Acta Crystallogr., Sect. A* **1990**, *46*, 467.

(18) Orpen, A. G. *J. Chem. Soc., Dalton Trans.* **1980**, 2509.

(19) DIRDIF94: Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; Gelder, R. de.; Israel, R.; Smits, J. M. M. *The DIRDIF-94 program system*; Technical Report of the Crystallography Laboratory; University of Nijmegen: The Netherlands, 1994.

(20) Ho, E. N. M.; Wong, W. T. *J. Chem. Soc., Dalton Trans.* **1998**, 4215.

Table 1. Crystal Data and Data Collection Parameters for 2–9

	2	3	4	5	6	7	8	9
empirical formula	[BC ₁₃ F ₄ H ₉ N ₂ O ₁₁ Os ₄] 1/2CHCl ₃	C ₂₅ H ₁₇ NO ₁₁ Os ₄	C ₂₃ H ₁₅ NO ₁₁ Os ₄	[BC ₁₄ F ₄ H ₁₂ N ₃ O ₁₀ Os ₄] 2C ₄ H ₈ O	[C ₁₀ H ₄ NO ₉ ClO ₃] CHCl ₃	C ₁₂ H ₅ NO ₁₂ Os ₄	C ₁₃ F ₃ H ₆ NO ₁₅ SO ₄	C ₁₂ H ₃ NO ₁₂ Os ₄
fw	1276.51	1268.21	1266.19	1374.08	995.56	1115.97	1266.04	1113.96
cryst color, habit	yellow, plate	orange, block	orange, block	yellow, block	yellow, plate	yellow, block	orange, block	yellow, plate
cryst dimens/mm	0.07 × 0.12 × 0.16	0.32 × 0.31 × 0.29	0.19 × 0.18 × 0.11	0.21 × 0.19 × 0.11	0.22 × 0.21 × 0.07	0.22 × 0.21 × 0.11	0.26 × 0.25 × 0.17	0.23 × 0.21 × 0.09
cryst syst	monoclinic	triclinic	monoclinic	monoclinic	monoclinic	hexagonal	orthorhombic	orthorhombic
space group	P2 ₁ /n (no. 14)	P1 (no. 2)	P2 ₁ /c (no. 14)	P2 ₁ /n (no. 14)	P2 ₁ /n (no. 14)	P6 ₅ (no. 170)	Pna2 ₁ (no. 33)	Pnma (no. 62)
a/Å	20.380(1)	9.405(1)	9.668(2)	12.020(1)	12.535(1)	8.993(1)	14.561(1)	15.404(2)
b/Å	9.9997(5)	9.439(1)	25.949(7)	12.533(1)	9.5150(9)	8.993(1)	17.096(2)	15.727(2)
c/Å	27.705(1)	16.746(2)	12.453(3)	24.337(2)	18.405(1)	43.190(4)	10.391(1)	16.359(2)
α/°	106.530(9)	77.28(1)	110.38(2)	101.33(2)	99.82(1)			
β/°	86.67(1)	84.47(1)	2928(1)	3594.8(6)	2163.0(3)	3025.0(5)	2586.7(4)	3963.1(8)
γ/°	84.47(1)	1442.3(3)	4	4	4	6	4	8
Z	8	2	4	4	4	6	4	8
D _x /g cm ⁻³	3.133	2.915	2.872	2.539	3.057	3.675	3.251	3.734
μ(Mo Kα)/cm ⁻¹	189.35	176.10	173.46	141.60	181.01	251.65	197.43	256.11
no. of reflns collected	34 087	8868	18 226	22 414	13 679	18 968	16 300	24 918
no. of unique reflns	12 846	6182	6786	8500	5169	4589	3339	5048
no. of obsd reflns	6250	4862	3367	5171	3506	4042	2403	3226
[I > 1.5σ(I)]								
R	0.071	0.060	0.077	0.043	0.046	0.039	0.040	0.059
R _w	0.045	0.074	0.071	0.043	0.035	0.039	0.028	0.063
goodness of fit, S	1.53	1.98	1.43	0.96	1.71	1.08	1.09	1.42

amido clusters, **3** and **4**, were isolated in the reaction of **1** and diphenylacetylene and no μ_4 -NH nitrene osmium cluster can be detected under a similar reaction condition employed for the ruthenium system.

Solid-State Structures of 2–9. The solid-state structures of **2–9** were established by single-crystal X-ray diffraction analyses, and the selected bond parameters are illustrated in Table 2. The novel cationic cluster [Os₄(μ -H)₄(CO)₁₁(μ -NH₂)(NCMe)][BF₄], **2**, is the sole product isolated in the reaction of **1** toward tetrafluoroboric acid (HBF₄) in acetonitrile at ambient temperature, where the *tert*-butylhydroxy ligand (tBuO) is eliminated. This amido metal cluster is significant, in part because it is one of the very rare cationic carbonyl cluster complexes, and more importantly because it is believed to be a good candidate for synthesizing nitrene metal clusters. It is anticipated that the acetonitrile ligand can be removed under mild conditions, which might trigger the amido nitrogen to further coordinate to the other two metal centers.

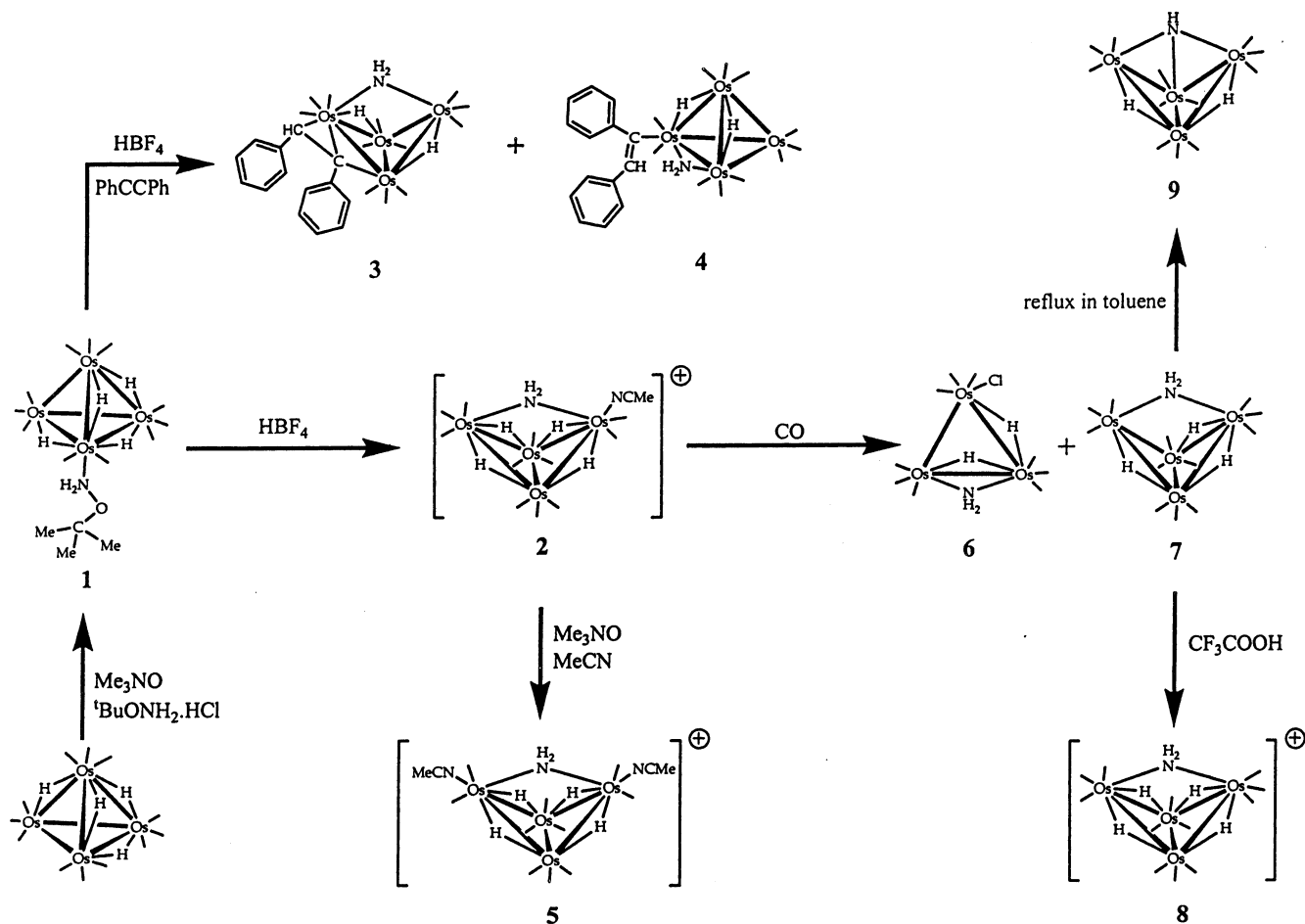
The molecular structure of **2** is illustrated in Figure 1. Four osmium atoms of **2** adopt the butterfly geometry, coordinated with 11 terminal carbonyl ligands. The two triosmium triangles share the common Os(1)–Os(3) hinge edge, and the dihedral angle between the Os(1)–Os(2)–Os(3) and the Os(1)–Os(3)–Os(4) planes is 95.51°. This is similar to the corresponding value of 97.7° observed in [Os₄(μ -H)₄(CO)₁₂(OH)]⁺.²¹ The hinge Os(1)–Os(3) bond distance [2.839(2) Å] is the shortest, while the four hydride-bridged “hinge” to “wingtip” Os–Os bond distances are within the range 2.983(2)–3.041(2) Å. The butterfly geometry is supported by the amido ligand through two wingtip atoms Os(2) and Os(4), having Os–N bond distances of 2.17(2) and 2.08(3) Å, respectively. The terminal acetonitrile ligand coordinated to the Os(4) atom with a distance of 2.06(2) Å, showing only a slight deviation from linearity, with Os(4)–N(1)–C(12) and N(1)–C(12)–C(13) angles of 173° and 174°, respectively.

The success of the isolation of a series of μ_4 -nitrene clusters in the reaction of [Ru₃(CO)₁₀(μ_3 -NOMe)] with diphenylacetylene or phenylacetylene suggests that the alkynes are important structural stabilizers. Several drops of tetrafluoroboric acid were added to a mixture of **1** and diphenylacetylene in dichloromethane, leading to the formation of two new clusters, [Os₄(μ -H)₂(CO)₁₁(μ -NH₂){ μ - η^3 -Ph(ChC)Ph}], **3**, and [Os₄(μ -H)₂(CO)₁₁(μ -NH₂){ η^1 -Ph(CH=C)Ph}], **4**, in moderate yields. These are geometric isomers; the diphenylacetylene ligand acts as a three-electron and one-electron donor in **3** and **4**, respectively.

The solid-state structures of **3** and **4** are depicted in Figures 2 and 3, respectively. X-ray analysis of **3** illustrates that the amido-supported butterfly geometry of **2** is retained. The dihedral angle between the two wings of the triosmium planes Os(1)–Os(2)–Os(3) and Os(2)–Os(3)–Os(4) is 86.97°, which is slightly smaller than the value observed in **2**. The diphenylacetylene bridges Os(3) and Os(4) with a μ - η^3 coordination mode have an Os(3)–Os(4) bond distance of 2.856(1) Å, which is comparable to the value observed in [HOs₃(CO)₁₀{ μ - η^3 -Ph(ChC)Ph}].²² Cluster **4** has a distorted tetrahedron

(21) Johnson, B. F. G.; Lewis, J.; Raithby, P. R.; Zuccaro, C. *J. Chem. Soc., Dalton Trans.* **1980**, 716.

Scheme 2



metal framework with a characteristic 60 cluster valence electron count. The amido ligand asymmetrically bridges Os(3) and Os(4) with Os–N distances of 2.12(3) and 2.03(2) Å, respectively. The dihedral angle between planes Os(3)–N(1)–Os(4) and Os(1)–Os(3)–Os(4) is 172.35°. The diphenylacetylene is terminally bonded to Os(4), with a Os(4)–C(18) bond of 2.12(4) Å. A similar bonding mode was observed in $[\text{Ir}_4(\text{CO})_{11}\{\eta^1\text{-Ph}(\text{CH}=\text{C})\text{Ph}\}][\text{NEt}_4]$.²³

Through the treatment of an acetonitrile solution of **2** with an excess of trimethylamine-*N*-oxide, the orange cluster $[\text{Os}_4(\mu\text{-H})_4(\text{CO})_{10}(\mu\text{-NH}_2)(\text{NCMe})_2][\text{BF}_4]$, **5**, was isolated. Cluster **5** is another example of a cationic metal cluster, which is structurally similar to the unbridged butterfly cluster $[\text{Os}_4(\mu\text{-H})_4(\text{CO})_{10}(\text{NCMe})_2]^+$.²⁴ It seems that the acetonitrile group is a good stabilizer for the cationic metal cluster because it is a good σ -donor and a poor π -acceptor. The metal–carbon bonds can be strengthened, as more back- π -electrons can be shared by the remaining carbonyl ligands.

The molecular architecture of **5** is very similar to that of **2**, where one more carbonyl ligand is replaced by the acetonitrile ligand. Two labile acetonitrile ligands are terminally bonded to two wingtip osmium atoms, which show only a slight deviation from linearity, and the Os–

(1)–N(2)–C(11) and Os(3)–N(3)–C(13) angles are 174° and 176°, respectively. The molecular structure of **5** possesses a C_s symmetry, where the mirror plane bisects the atoms O(8), C(8), Os(4), N(1), Os(2), C(4), O(4).

A chloroform solution of **2** was heated to reflux with carbon monoxide bubbling for 10 h, and the new clusters $[\text{Os}_3(\mu\text{-H})_2(\text{CO})_9(\mu\text{-NH}_2)\text{Cl}]$, **6**, and $[\text{Os}_4(\mu\text{-H})_3(\text{CO})_{12}(\mu\text{-NH}_2)]$, **7**, were isolated. Cluster **6** is believed to be a fragment of **2**, and the chloride atom probably originates from the chloroform solution. The molecular structure of **6** is depicted in Figure 5, which consists of an isosceles triangle of osmium metal atoms. The three Os–Os bond distances are within the range 2.826(1)–3.0551(9) Å, where the nonbridged Os(1)–Os(2) edge is the shortest one. The dihedral angle of the plane Os(2)–Os(3)–N(1) with reference to the triosmium plane is 101.41°. The characteristic 48 cluster valence electron count is observed.

The amido-supported butterfly geometry is also observed in **7** (Figure 6), which has a dihedral angle of 94.49° between the planes Os(1)–Os(2)–Os(4) and Os(2)–Os(3)–Os(4). Each osmium metal center is coordinated by three terminal carbonyl ligands. The characteristic 62 cluster valence electron count was observed for **7**. The labile acetonitrile group of **2** is substituted by a carbonyl ligand, together with metal hydride elimination. It is noteworthy that the deprotonation occurs preferentially at the metal hydride sites instead of at the hydrogen atoms of the amido ligand. The ^1H NMR spectrum of **2** reveals that the significantly

(22) Clauss, A. D.; Tachikawa, M.; Shapely, J. R.; Pierpont, C. G. *Inorg. Chem.* **1981**, *20*, 1528.

(23) Della Pergola, R.; Garlaschelli, L.; Martinengo, S.; Manassero, M.; Sansoni, M. *J. Organomet. Chem.* **2000**, *593*, 63.

(24) Johnson, B. F. G.; Lewis, J.; Nelson, W. J. H.; Puga, J.; Raithby, P. R.; Whitmore, K. H. *J. Chem. Soc., Dalton Trans.* **1983**, 1339.

Table 2. Selected Bond Distances [Å] and Angles [deg] for 2–9

	2	3	4	5	6	7	8	9
Os(1)–Os(2)	3.025(2)	2.827(1)	2.770(2)	3.0727(7)	2.826(1)	2.8367(9)	3.024(1)	2.762(1)
Os(1)–Os(3)	2.839(2)	3.028(1)	2.908(2)		3.0551(9)		3.028(1)	2.851(2)
Os(1)–Os(4)	3.041(2)		2.752(2)	3.0001(7)		2.977(1)		
Os(2)–Os(3)	3.015(2)	2.899(1)	2.964(2)	3.0622(7)	2.8178(9)	3.0263(9)	2.834(1)	2.958(1)
Os(2)–Os(4)		2.888(1)	2.972(2)	2.8178(7)		2.812(1)	3.036(1)	
Os(3)–Os(4)	2.983(2)	2.856(1)	2.791(2)	3.0005(7)		3.0490(9)	3.020(1)	
Os(4)–Os(5)								2.764(1)
Os(4)–Os(6)								2.856(2)
Os(5)–Os(6)								2.969(1)
Os(4)–N(1)	2.06(2)	2.09(1)	2.03(2)				2.11(2)	
Os(3)–N(1)			2.12(3)	2.113(10)	2.11(1)	2.15(1)		
Os(4)–N(2)	2.08(3)							
Os(2)–N(2)	2.17(2)							
Os(3)–N(3)				2.06(1)				
Os(1)–N(2)				2.08(1)				
Os(2)–N(1)					2.14(1)			2.05(1)
Os(1)–N(1)		2.13(1)		2.132(9)		2.15(2)	2.12(1)	2.16(2)
Os(4)–N(2)								2.15(3)
Os(5)–N(2)								2.05(1)
Os(3)–C(12)		2.19(2)						
Os(4)–C(12)		2.18(2)						
Os(4)–C(18)			2.12(4)					
Os(1)–Cl(1)					2.472(4)			
Os(1)–N(2)–C(11)				174(1)				
Os(3)–N(3)–C(13)				176(1)				
Os(4)–N(1)–C(12)		109.9(7)						
Os(3)–C(12)–Os(4)		81.8(6)						
Os(3)–N(1)–Os(4)			84.5(9)					
Os(1)–N(1)–Os(4)	114(1)						115.0(6)	
Os(1)–N(1)–Os(3)				114.1(4)		111.5(6)		
Os(2)–N(1)–Os(3)					83.1(4)			
Os(2)–N(1)–Os(2*)								130(1)
Os(1)–N(1)–Os(2)								81.9(7)
Os(5)–N(1)–Os(5*)								130(1)
Os(4)–N(1)–Os(5)								82.1(7)

shielded amido proton signals are located at $\delta = 1.10$ and 1.84. The electron-rich amido ligand lowers the polarity of the NH bond to a certain extent, so that the elimination of the NH proton becomes very difficult. This is probably the reason for the deprotonation process in the synthesis of **7** occurring preferentially at metal

hydride sites instead of at the amido ligand, which might disfavor the formation of μ_3 - or μ_4 -nitrene clusters.

To investigate the properties of the bridging amido ligand, molecular orbital calculations at the B3LYP level of density functional theory based on the experimental geometry of **7** were performed to examine its orbital bonding characteristics in the HOMO–LUMO region.

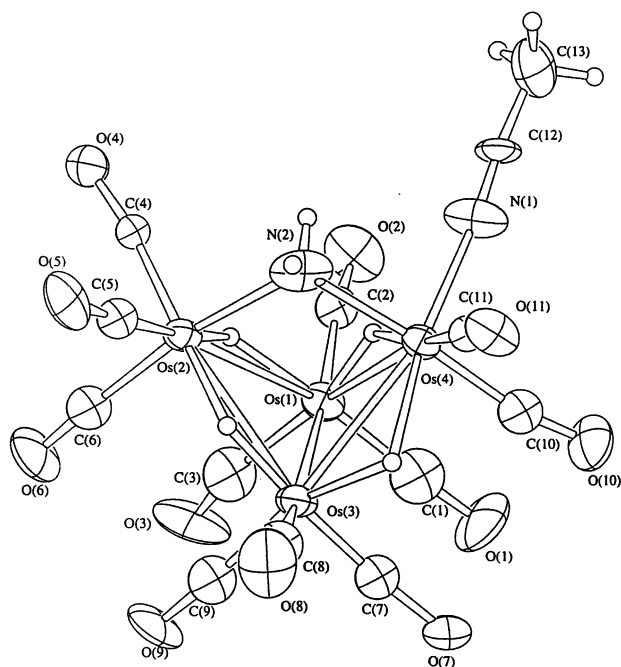


Figure 1. Molecular structure of $[\text{Os}_4(\mu\text{-H})_4(\text{CO})_{11}(\mu\text{-NH}_2)(\text{NCMe})][\text{BF}_4]$ (**2**) with the atom-numbering scheme.

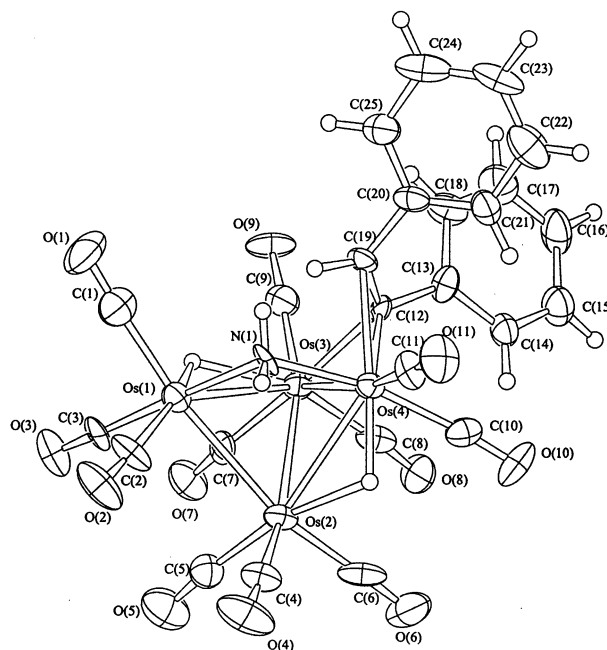


Figure 2. Molecular structure of $[\text{Os}_4(\mu\text{-H})_2(\text{CO})_{11}(\mu\text{-NH}_2)\{\mu\text{-}\eta^3\text{-Ph(ChC)Ph}\}]$ (**3**) with the atom-numbering scheme.

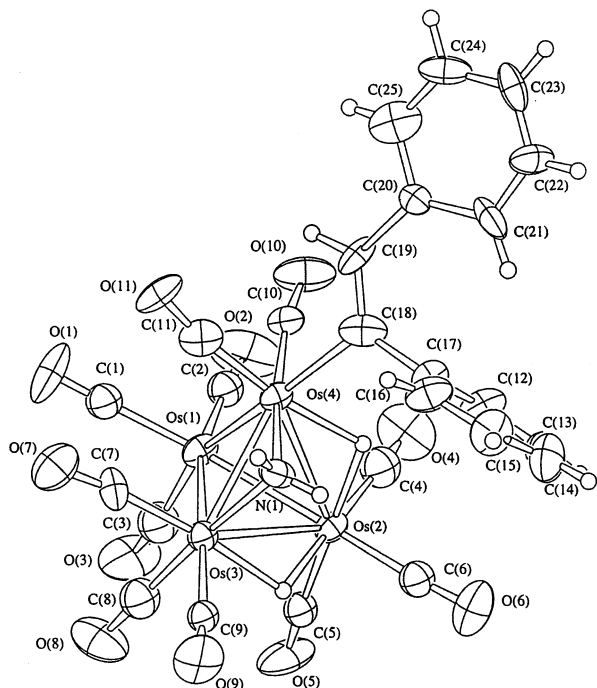


Figure 3. Molecular structure of $[\text{Os}_4(\mu\text{-H})_2(\text{CO})_{11}(\mu\text{-NH}_2)(\eta^1\text{-Ph}(\text{CH}=\text{C})\text{Ph})]$ (**4**) with the atom-numbering scheme.

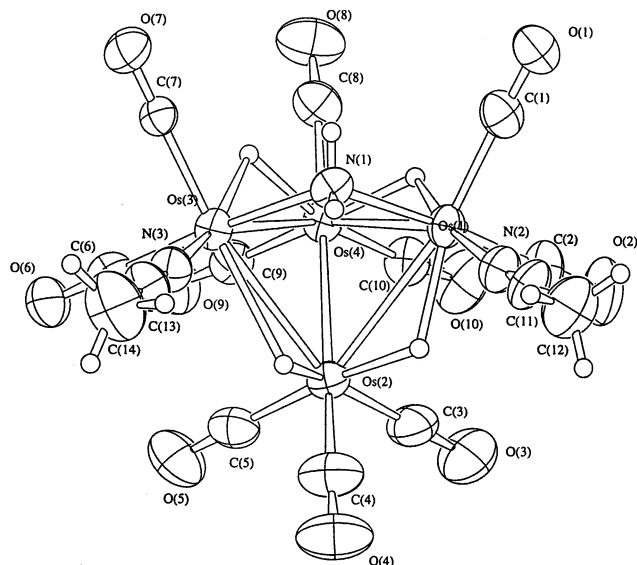


Figure 4. Molecular structure of $[\text{Os}_4(\mu\text{-H})_4(\text{CO})_{10}(\mu\text{-NH}_2)(\text{NCMe})_2][\text{BF}_4]$ (**5**) with the atom-numbering scheme.

It was observed that the highest occupied molecular orbitals (HOMOs) correspond to the σ bonds of the unbridged Os–Os bonds, followed by the “ t_{2g} ” set d orbitals of the four metal centers. The lowest unoccupied molecular orbitals (LUMOs) are π^* of the carbonyl ligands, together with the Os–Os/Os–CO σ^* antibonding orbitals. The spatial plots²⁵ of the two highest occupied and one lowest unoccupied orbital are shown in Figure 7. The natural bond order (NBO) analysis,²⁶ based on the molecular orbital calculations, indeed shows that the Os–H bonds are much weaker than the NH bonds. The Wiberg bond indices²⁷ for the Os–H

(25) Schaftenaar, G. *Molden v3.5*, CAOS/CAMM Center Nijmegen: Toernooiveld, Nijmegen, Netherlands, 1999.

(26) Glendening, E. D.; Reed, A. E.; Carpenter, J. E.; Weinhold, F. *NBO* version 3.1.

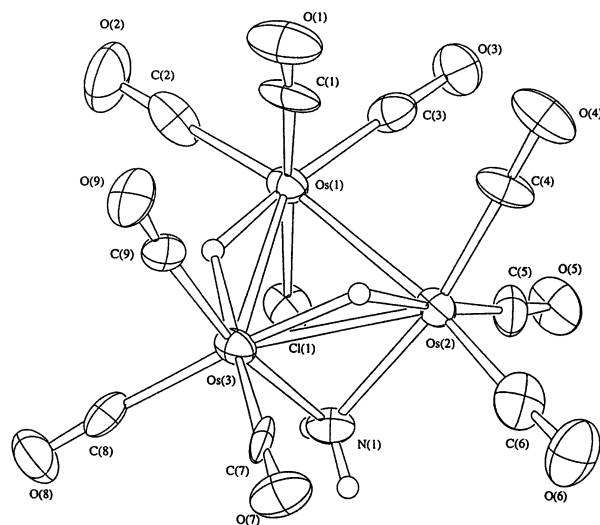


Figure 5. Molecular structure of $[\text{Os}_3(\mu\text{-H})_2(\text{CO})_9(\mu\text{-NH}_2)\text{Cl}]$ (**6**) with the atom-numbering scheme.

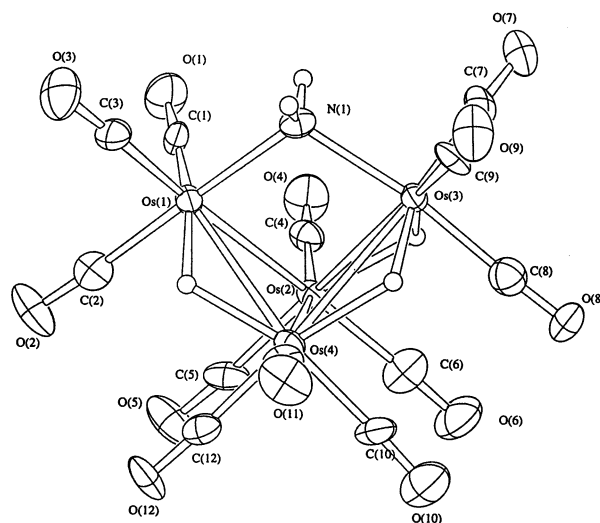


Figure 6. Molecular structure of $[\text{Os}_4(\mu\text{-H})_3(\text{CO})_{12}(\mu\text{-NH}_2)]$ (**7**) with the atom-numbering scheme.

bonds range from 0.18 to 0.32, while the indices for the N–H bonds are about 0.85. Clearly, the preference for the protonation or deprotonation site depends heavily on the relative bond strength.

Protonation of **7** with a few drops of trifluoromethylsulfonic acid in dichloromethane gave some colorless crystalline materials, which were identified as $[\text{Os}_4(\mu\text{-H})_4(\text{CO})_{12}(\mu\text{-NH}_2)][\text{CF}_3\text{SO}_3]$, **8**. As expected, the protonation occurs at the metal hydride sites, which is consistent with molecular orbital calculations. They are the analogue of **2** and **5** (Figure 8). Each osmium metal is bonded with three carbonyl ligands, and four hydrides are bridged on the “hinge to wing” Os–Os bond. The dihedral angle between the wings of Os(1)–Os(2)–Os(3) and Os(2)–Os(3)–Os(4) is 83.67° . It is a highly symmetric structure in comparison to **2** and **5** and possesses C_2 symmetry. The C_2 axis passes through the amido nitrogen to the center point of the hinge osmium–osmium edge. This cationic cluster experiences orbital contraction due to the electron deficiency, which makes the orbital overlapping less efficient. Therefore, the

(27) Wiberg, K. B. *Tetrahedron* **1968**, *24*, 1083.

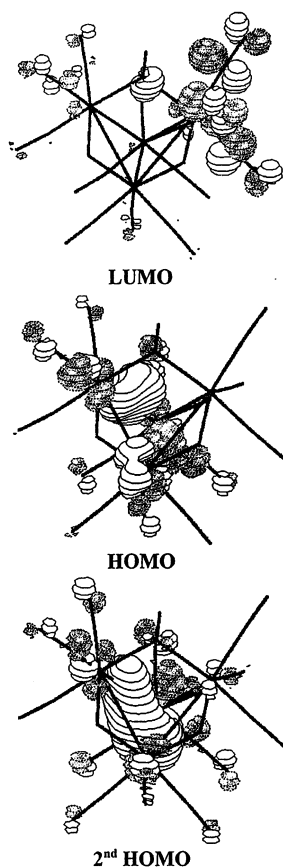


Figure 7. Spatial plots of the two highest occupied and the lowest unoccupied molecular orbitals for $[\text{Os}_4(\mu\text{-H})_3(\text{CO})_{12}(\mu\text{-NH}_2)]$ (**7**).

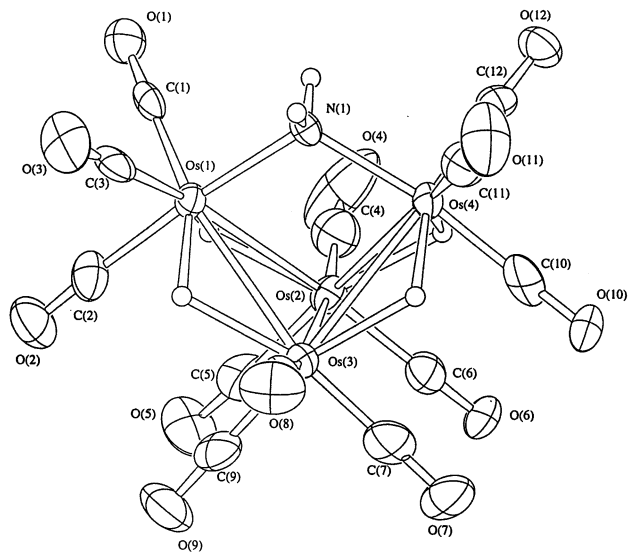


Figure 8. Molecular structure of $[\text{Os}_4(\mu\text{-H})_4(\text{CO})_{12}(\mu\text{-NH}_2)][\text{CF}_3\text{SO}_3]$ (**8**) with the atom-numbering scheme.

metal–metal bond strength decreases and the average bond distances of **8** are relatively lengthened. A similar observation is also found in **2** and **5**. This probably suggests that **8** is more likely to form clusters with a 64 valence electron count under nucleophilic attack, by breaking the relatively weak metal–metal bond.

The novel cluster $[\text{Os}_4(\mu\text{-H})_2(\text{CO})_{12}(\mu_3\text{-NH})]$, **9**, was isolated in the thermolysis of **7** in toluene. To the best of our knowledge, this is the first example of a $\mu_3\text{-NH}$

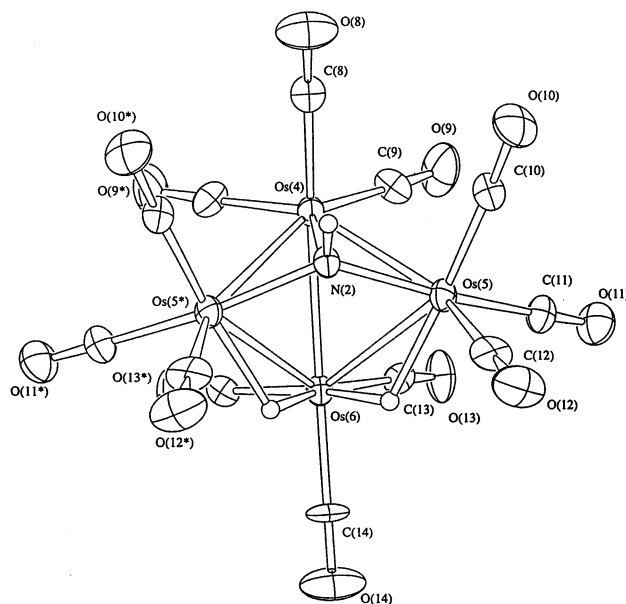


Figure 9. Molecular structure of $[\text{Os}_4(\mu\text{-H})_2(\text{CO})_{12}(\mu_3\text{-NH})]$ (**9**) with the atom-numbering scheme.

osmium nitrene cluster. The nitrene ligand acts as a four-electron donor, and an amido proton and a metal hydride are eliminated during the thermolysis. The characteristic 62 cluster valence electron count of butterfly geometry is retained. The ^1H NMR spectrum of **9** shows that the nitrene proton signal is located at $\delta = 9.35$, which is highly deshielded in comparison to amido protons. This implies that the nitrene ligand is relatively electron deficient, which makes the NH bond polar, suggesting that the deprotonation process may occur more preferentially on the nitrene ligand as compared to **7**. This might be a good precursor for the formation of the nitrido or μ_4 -nitrene clusters.

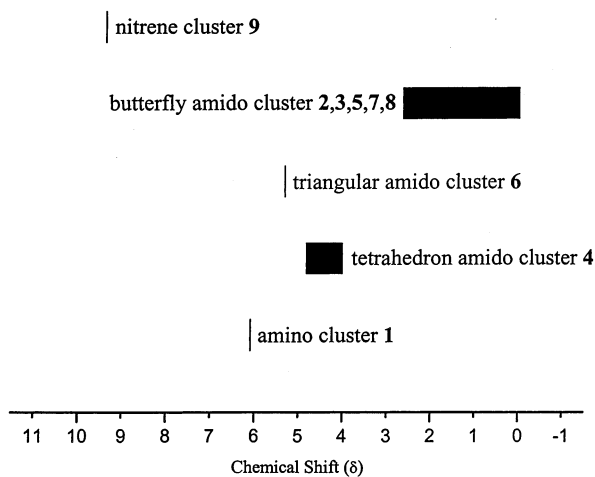
X-ray analyses show that there are two crystallographically independent, but essentially identical, molecules in each asymmetric unit. The molecular structure of only one of these will be described and is shown in Figure 9. The molecule consists of a butterfly arrangement of four osmium atoms with a triply bridging nitrene ligand spanning one of the open triangular faces, $\text{Os}(1)\text{--Os}(2)\text{--Os}(2^*)$. This kind of coordination moiety is also observed in $[\text{Os}_4(\mu\text{-H})_2(\text{CO})_{12}(\mu_3\text{-PC}_6\text{H}_{11})]$,²⁸ $[\text{Os}_4(\text{CO})_{12}(\mu\text{-SCH}_2\text{CMe}_2\text{CH}_2\text{Cl})(\mu\text{-H})]$,²⁹ and $[\text{Os}_4(\text{CO})_{12}(\mu\text{-H})_2(\mu_3\text{-S})]$.³⁰ The molecule contains a plane of symmetry that is imposed by the crystal lattice and passes through the atoms $\text{N}(1)$, $\text{H}(2)$, $\text{O}(1)$, $\text{C}(1)$, $\text{Os}(1)$, $\text{Os}(3)$, $\text{C}(7)$, and $\text{O}(7)$. The dihedral angle between the two wings of the butterfly, $\text{Os}(1)\text{--Os}(2)\text{--Os}(3)$ and $\text{Os}(1)\text{--Os}(2^*)\text{--Os}(3)$, is 97.90° , which is similar to the values observed in other amido butterfly clusters. The dihedral angles of the planes $\text{Os}(1)\text{--Os}(2)\text{--Os}(3)$ and $\text{Os}(1)\text{--N}(1)\text{--Os}(2^*)$ with reference to the plane $\text{Os}(1)\text{--N}(1)\text{--Os}(2)$ are 95.56° and 133.14° , respectively. The observed dihedral angle is probably a consequence of the preferred bite of the coordinatively flexible capping nitrene ligand, rather than an electronic requirement of the bonding within

(28) Colbran, S. B.; Johnson, B. F. G.; Lahoz, F. J.; Lewis, J.; Raithby, P. R. *J. Chem. Soc., Dalton Trans.* **1988**, 1199.

(29) Adams, R. D.; Belinski, J. A.; Pompeo, M. P. *Organometallics* **1992**, *11*, 3129.

(30) Adams, R. D.; Wang, S. *Inorg. Chem.* **1986**, *25*, 2534.

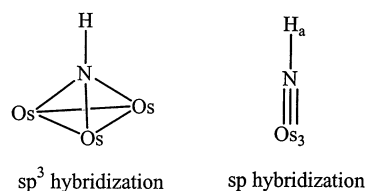
Scheme 3



the cluster core. The trend of Os–N bond distances in **9** for the hinge Os(1)–N(1) [2.05(1) Å] is marginally shorter than wingtip Os(2)–N(1) [2.16(2) Å]. The Os(2)–N(1)–Os(2*) and Os(1)–N(1)–Os(2) angles are 130(1)° and 81.9(7)°, respectively, which are slightly larger than those values observed in other similar systems.^{28–30}

¹H NMR Properties of Tetraosmium Carbonyl Clusters Containing Amino, Amido, and Nitrene Ligands. The range of chemical shifts of the ¹H NMR signals of amino, amido, and nitrene protons in **1–9** is illustrated in Scheme 3. Clearly, there is a negative shift of NH signal as the amino clusters are transformed to amido clusters. This is probably because the electron-rich osmium metal center tends to donate electrons to the electronegative nitrogen atom. Therefore, the electron density around the amido nitrogen increases as it bonds to more metal centers; the ¹H NMR signal of NH becomes relatively upfield. The amido clusters are believed to have similar chemical shifts for NH signals. However, highly shielded amido proton signals of the supported butterfly clusters are observed in the ¹H NMR spectrum in comparison to other amido clusters. There is no obvious explanation for this observation, but it suggests that the chemical shift of the NH protons, at least to a certain extent, depends on their coordination geometry. In contrast to the supported butterfly amido clusters, the NH signal of the triply bridged nitrene cluster is highly deshielded. This suggests that the nitrene nitrogen might involve sp hybridization, in which the p_x and p_y orbitals of nitrogen are not involved in hybridization, but overlap directly with the d orbitals of the osmium metal; see Scheme 4. Under this circumstance, the H_a is significantly influenced by the anisotropic-induced magnetic field of the Os₃–N triple bond,

Scheme 4



which might cause a positive shift in the ¹H NMR signal of the NH group. A similar highly deshielded NH signal (δ 9.50) was observed in [Fe₃(CO)₉(μ_3 -CO)(μ_3 -NH)].³¹

The ¹H NMR signal of the NH group can serve as a reference showing the electronic environment of amino, amido, and nitrene ligands in the cluster, to determine the polarity of the NH bond. The results might provide some information on possible reactivities of these clusters.

Conclusion

Osmium metal clusters containing (μ -NH₂) amido and (μ_3 -NH or μ_4 -NH) nitrene are relatively rare. They are believed to be important cluster analogues for the reactivity study of surface-bound nitrogen atoms toward molecular hydrogen. In light of this, the syntheses, structural characterization, and various reactivities of a series of amino, amido, and nitrene tetraosmium metal clusters have been examined and discussed in this paper.

The first example of a tetraosmium cluster containing a (μ_3 -NH) nitrene ligand was reported. The transformation of an amino cluster into a nitrene cluster through an amido cluster has also been demonstrated in this work and seems to be a good synthetic route to the formation of nitrene clusters. The ¹H NMR properties of these clusters were studied, and a correlation between the chemical shift and the structural geometry has been established.

Acknowledgment. We gratefully acknowledge financial support from the Hong Kong Research Grants Council and the University of Hong Kong. Y. Li acknowledges the receipt of a postgraduate studentship (1999–2002) and the Li Po Chun Scholarship (2001–2002) administered by the University of Hong Kong and the Sir Edward Youde Memorial Fellowship (2001–2002) awarded by the Sir Edward Youde Memorial Trustees.

Supporting Information Available: Details of data collection parameters, bond lengths, bond angles, fractional atomic coordinates, and anisotropic thermal parameters for **2–9** are available free of charge via the Internet at <http://pubs.acs.org>.

(31) Fjare, D. E.; Gladfelter, W. L. *J. Am. Chem. Soc.* **1981**, *103*, 1573.