Table IV. ^{31}P NMR Shifts[a] of Various Primary and Secondary Phosphines and Phosphides

Primary Phosphines

R	H_2PR	LiHPR	LiHPR + 12-crown-4
Mes	-153.8	-154.1	line broadening
Ph	-124.81	-111.9	line broadening

Secondary Phosphines

R	HPR_2	$LiPR_2$	$LiPR_2$ + 12-crown-4
Mes	-93.6	-62.9	-42.8
Ph	-39.9	-21.4	-7.5
C_6H_{11}	-27.2	-9.5	-7.1
t-Bu	20.7	41.9	

[a] All values are given in ppm relative to H_3PO_4. Plus and minus signs designate downfield and upfield chemical shifts, respectively.

One possible clue for these unusual trends may lie in the difference in coordination number between the starting material (three-coordinate) and the lithium derivative (four-coordinate). The crystal structures of $LiPR_2$ solvates (R = Ph, C_6H_{11}, Mes) all show the phosphorus to be four-coordinate, and there is a significant ^{31}P chemical shift on lithiation. In contrast, the ^{31}P signal for $[(THF)_3LiPHMes]$, which has three- rather than four-coordinate phosphorus, is only slightly shifted from the parent three-coordinate phosphine H_2PMes.

The addition of 12-crown-4 to $LiPR_2$ complexes in THF solution results in a further downfield shift to the ^{31}P signal. This is illustrated in Figure 5 for the case of the title compound, $HPMes_2$. Addition of *n*-BuLi to $HPMes_2$ (^{31}P -93.6 ppm), results in the appearance of a new signal 30.7 ppm downfield at -62.9 ppm. Further addition of 12-crown-4 gives a new resonance at -42.8 ppm. The latter downfield shift is difficult to explain since it is expected that the free $[PMes_2]^-$ anion having a full negative charge on phosphorus would be more shielded and thus appear upfield. In addition, there is no structural evidence of significant charge delocalization over the mesityl rings of $[PMes_2]^-$ to account for the downfield chemical shift. However, a $p\pi$–$p\pi$ interaction between phosphorus and the aromatic ring has been proposed elsewhere to account for the anomalous ^{31}P shifts.[27,29] Similar trends are seen in the $HPPh_2$ system.

Addition of 12-crown-4 to the primary lithium phosphides results in no significant changes in chemical shift, but broadening of the peaks is observed. This might be interpreted as the inability of 12-crown-4 to achieve cation–anion separation in the case of the more nucleophilic primary phosphides. Crystallization and subsequent structural characterization of these species are currently under way.

Acknowledgment. We thank the National Science Foundation (Grant CHE-811-6355) and the Committee of Research at the University of California, Davis, for financial support.

Supplementary Material Available: Full listings (Tables S1a–S4d) of bond distances and angles, anisotropic thermal parameters, and hydrogen coordinates (10 pages); tables of observed and calculated structure factors (55 pages). Ordering information is given on any current masthead page.

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(29) Grim, S. O.; Molenda, R. P. *Phosphorus* **1974**, *4*, 189.

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Osmium Azo Oxime Chemistry. Facial Tris Chelate and Trinuclear OsMOs Species

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The reaction of ammonium hexabromoosmate(IV) with excess alkaline (NaOH) (phenylazo)acetaldoxime in aqueous methanol affords the facial tris chelate anion $Os^{II}A_3^-$ isolated as $NaOsA_3{\cdot}3H_2O$ (**4**; A^- = PhN=NC(=NO$^-$)Me). The corresponding tetraphenylarsonium salt, Ph_4AsOsA_3 (**7**), has also been isolated by reacting **4** with Ph_4AsCl. In chloroform solution, the arsenic atom of **7** is covalently bonded to one of the oximato oxygen atoms of facial OsA_3^-. The conversion **7** → **4** can be achieved with $NaPh_4B$. Stereochemical identification is made with the help of ^1H NMR spectra. Complex **4** reacts with metal perchlorates, furnishing trinuclear complexes (**5**) of types $(OsA_3)_2M^{II}$ (M = Mg (**5a**), Mn (**5b**), Co (**5d**), Ni (**5e**)) and $[(OsA_3)_2M^{III}]ClO_4$ (M = Fe (**5c**)). The reconversion **5** → **4** is achieved by selective extrusion of M^{n+} (n = 2, 3) as the hydroxide with the help of NaOH. The osmometric molecular weights of the $(OsA_3)_2M$ complexes confirm their trinuclear nature. In **5** the six oximato oxygen atoms of the two facial OsA_3^- units provide octahedral O_6 coordination for the central metal atom (M^{n+}). In **5b–e** the MO_6 octahedron is high spin. The EPR spectra of the $S = {}^5/_2$ species, viz. **5b** ($g_\parallel = 6.28$; $g_\perp = 1.99$) and **5c** (intense $g = 4.2$ signal), respectively correspond to primary axial and rhombic distortions of MO_6. In voltammetry characteristic responses due to osmium(III)–osmium(II) (**4**, **7**), M(III)–M(II) (**5b–d**), and the two successive ligand (azo) redox processes $(OsA_3)_2M$–$(OsA_2A^-)(OsA_3)M$–$(OsA_2A^-)_2M$ (**5a–e**) are observed. The spectral and electrochemical properties of **4** and **5** are compared with those of the iron(II) complexes, and the strong ligand field and bonding strengths of A^- are underscored. It is proposed that the binding of M^{n+} is significantly stronger in **5** than in the iron(II) congeners. Attempted synthesis of RuA_3^- has not succeeded so far.

Introduction

Platinum metal complexes of azo ligands are of current interest to us.[1-4] Azo-coordinated osmium is rare. The only reports available to us deal with certain diimine[5] and azo dicarboxylic ester[6] species, an azobenzene complex[7] and certain 2-(arylazo)pyridine chelates.[8,9] In contrast, ruthenium has a substantive azo

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(1) Goswami, S.; Mukherjee, R. N.; Chakravorty, A. *Inorg. Chem.* **1983**, *22*, 2825–2832 and references therein. Seal, A.; Ray, S. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1984**, *C40*, 929–932. Ghosh, P.; Chakravorty, A. *J. Chem. Soc., Dalton Trans.* **1985**, 361–367.

(2) Mahapatra, A. K.; Datta, S.; Goswami, S.; Mukherjee, M.; Mukherjee, A. K.; Chakravorty, A. *Inorg. Chem.* **1986**, *25*, 1715–1721 and references therein. Mukherjee, A. K.; Mukherjee, M.; Das, P. K.; Mahapatra, A. K.; Goswami, S.; Chakravorty, A. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1986**, *C42*, 793–796.

(3) Mahapatra, A. K.; Bandyopadhyay, D.; Bandyopadhyay, P.; Chakravorty, A. *Inorg. Chem.* **1986**, *25*, 2214–2221. Mahapatra, A. K.; Bandyopadhyay, D.; Bandyopadhyay, P.; Chakravorty, A. *J. Chem. Soc., Chem. Commun.* **1984**, 999–1000. Bandyopadhyay, P.; Bandyopadhyay, D.; Chakravorty, A.; Cotton, F. A.; Falvello, L. R.; Han, S. *J. Am. Chem. Soc.* **1983**, *105*, 6327–6329.

(4) Bandyopadhyay, D.; Bandyopadhyay, P.; Chakravorty, A.; Cotton, F. A.; Falvello, L. R. *Inorg. Chem.* **1983**, *22*, 1315–1321 and references therein.

(5) Laing, K. R.; Robinson, S. D.; Uttley, M. F. *J. Chem. Soc., Dalton Trans.* **1973**, 2713–2722.

(6) Einstein, F. W. B.; Nussbaum, S.; Sutton, D.; Willis, A. C. *Organometallics* **1984**, *3*, 568–574.

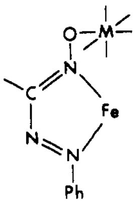
(7) Dawoodi, Z.; Mays, M. J.; Raithby, P. R. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1981**, *B37*, 252–254. Dawoodi, Z.; Mays, M. J.; Raithby, P. R. *J. chem. soc., Chem. Commun.* **1980**, 712–714.

(8) Ghosh, B. K.; Goswami, S.; Chakravorty, A. *Inorg. Chem.* **1983**, *22*, 3358–3360. Mukhopadhyay, A.; Ray, S. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, in press.

(9) Ghosh, B. K.; Mukhopadhyay, A.; Goswami, S.; Ray, S.; Chakravorty, A. *Inorg. Chem.* **1984**, *23*, 4633–4639.

0020-1669/87/1326-1946$01.50/0

chemistry.[1,2,10-13] We describe herein osmium species chelated by azo and oxime functions of the arylazo oxime ligand[14-16] PhN=NC(=NOH)Me, abbreviated HA. The virtual nonexistence of osmium oximates in the literature and the recorded disparity of the HA chemistries of iron and ruthenium has provided additional incentives for this work. Thus with HA iron(II) affords[17-19] the facial tris chelate FeA_3^-, which can sequester 3d ions, M^{n+} (n = 2,3), furnishing linear FeMFe species of type $[(FeA_3)_2M]^{(n-2)+}$ wherein A^- is both chelating and bridging as shown schematically in **1**. On the other hand, the arylazo oxime chemistry of ruthenium is dominated by the hydrogen-bonded halo species *trans*-$RuX_2(HA)(A)$ (**2**)[10] and *cis*-$RuX_2(HA)_2$ (**3**)[11] (X = Cl, Br).



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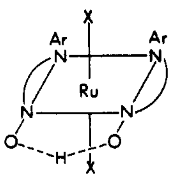

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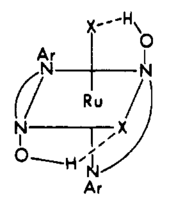


3

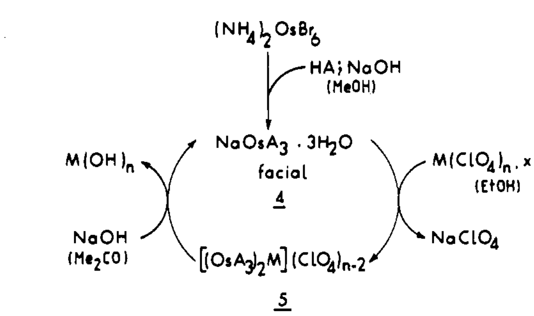
In the present work we show that an HA chemistry of osmium similar to that of iron can be developed. Facial OsA_3^- and its trinuclear adduct $[(OsA_3)_2M]^{(n-2)+}$ (M^{n+} = Mg^{2+}, Mn^{2+}, Fe^{3+}, Co^{2+}, and Ni^{2+}) have been synthesized and characterized. We have not encountered the osmium analogues of the ruthenium species **2** and **3**, and the attempted synthesis of RuA_3^- has failed.

Results and Discussion

A. Synthesis. The main reactions utilized and the compounds isolated and their number designations are stated in Scheme I. The formation of the green tris complex **4** (*fac*-OsA_3^-, see below) from hexabromoosmate occurs by reductive (Os(IV) → Os(II)) chelation in boiling aqueous methanol in the presence of a 10-fold excess of an equimolecular mixture of HA and NaOH. The trinuclear aggregation of **4** into **5** by M^{n+} and the reversal of the process by selective extrusion of bound M^{n+} by OH^- constitute a cycle in which the reactions proceed smoothly in excellent yields at room temperature. The cycle provides an obvious way of interconverting complexes of type **5**.

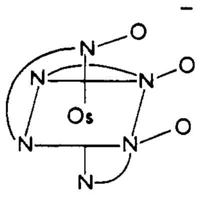
B. Facial Tris Complex. The hygroscopic complex **4** is the precursor of all trinuclear species. It is soluble in water as well as in many organic solvents, including benzene. Solubility in nonpolar solvents strongly suggests that intimate association of Na^+ with OsA_3^- can occur presumably via oximato bridging. Significantly, the molar conductance (Λ_M = 90 mho cm^2 M^{-1}) of **4** in acetonitrile is lower than the 1:1 electrolytic value.[20]

Scheme I



	M	n
5a	Mg	2
5b	Mn	2
5c	Fe	3
5d	Co	2
5e	Ni	2

The facial stereochemistry (**6**) of the OsA_3^- moiety in **4** is revealed by the single ^1H NMR signal for the three methyl groups in $CDCl_3$ (δ_{Me} = 2.71). The other possible isomer would have meridional geometry in which the three chelate rings would be in three different environments. The complex RhA_3 occurs in two isomeric forms, which are readily distinguished by ^1H NMR.[21] We have no evidence that meridional OsA_3^- exists. The diamagnetic nature of **4** is in accord with the t_{2g}^6 configuration of the metal in OsA_3^-. The presence of a strong oximato NO stretch at ~1240 cm^{-1} is diagnostic of a five-membered arylazo oximato chelate ring.[4,15] Such a stretch is present in **4** as well as in all complexes of type **5**.



6

Attempted synthesis of the tetraphenylarsonium salt of OsA_3^- via double decomposition of Ph_4AsCl and **4** in aqueous methanol (80%) afforded a crystalline complex of the expected composition: Ph_4AsOsA_3 (**7**). Like **4**, **7** dissolves in organic solvents. However, in $CDCl_3$ **7** displays three equally intense methyl signals (δ = 2.15, 2.39, and 2.47). In acetonitrile the molar conductance of **7** (Λ_M = 67 mho cm^2 M^{-1}) is substantially less than that of **4**. On addition of $NaPh_4B$ to a solution of **7** in ethanol (or methanol), white $[Ph_4As][Ph_4B]$ is quantitatively precipitated and from the solution **4** can be isolated in high yield. The interconversion of **4** and **7** is summarized in eq 1.

$$4 \underset{NaPh_4B}{\overset{Ph_4AsCl}{\rightleftarrows}} 7 \tag{1}$$

The ^1H NMR spectrum of **7** is consistent with a meridional geometry of the OsA_3^- fragment, but this assignment would also mean that the highly facile transformations of eq 1 are attended by isomerization of the osmium(II) coordination sphere. Such stereochemical lability is highly incompatible with a low-spin 5d^6 configuration. It is far more likely that in chloroform solution **7** exists as *fac*-OsA_3^- covalently bonded to Ph_4As^+ via an oximato bridge of type Os–N–O–As.[22] In the adduct thus formed, the original C_3 axis of "free" *fac*-OsA_3^- is no longer retained and the observation of three ^1H methyl signals falls in place. The existence of trigonal-bipyramidal oximato–arsoranes of type Me_4As—O—N=CMeR (R = H, Me) provides strong support for the above proposal regarding the nature of **7**.[23] The observed electrical

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(10) Chakravarty, A. R.; Chakravorty, A. *Inorg. Chem.* **1981**, *20*, 3138–3143.

(11) Chakravarty, A. R.; Chakravorty, A.; Cotton, F. A.; Falvello, L. R.; Ghosh, B. K.; Tomas, M. *Inorg. Chem.* **1983**, *22*, 1892–1896.

(12) Wolfang, S.; Strekas, T. C.; Gafney, H. D.; Krause, R. A.; Krause, K. *Inorg. Chem.* **1984**, *23*, 2650–2655 and references therein. Reveco, P.; Schmehl, R. H.; Cherry, W. R.; Fronczek, F. R.; Selbin, J. *Inorg. Chem.* **1985**, *24*, 4078–4082. Benson, E. P.; Legg, J. I. *Inorg. Chem.* **1981**, *20*, 2504–2507.

(13) Bennett, M. A.; Bruce, M. I.; Matheson, T. W. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: New York, 1982; Vol. 4, pp 691–820.

(14) Arylazo oximes as a class (ArN=NC(=NOH)R, where Ar = aryl and R = alkyl, aryl) are versatile chelating agents.[4,10,11,15,16]

(15) Bandyopadhyay, D.; Bandyopadhyay, P.; Chakravorty, A.; Cotton, F. A.; Falvello, L. R. *Inorg. Chem.* **1984**, *23*, 1785–1787.

(16) Pal, S.; Bandyopadhyay, D.; Datta, D.; Chakravorty, A. *J. Chem. Soc., Dalton Trans.* **1985**, 159–162. Dickman, M. H.; Doedens, R. J. *Inorg. Chem.* **1980**, *19*, 3112–3116.

(17) Pal, S.; Melton, T.; Mukherjee, R. N.; Chakravarty, A. R.; Tomas, M.; Falvello, L. R.; Chakravorty, A. *Inorg. Chem.* **1985**, *24*, 1250–1257.

(18) Pal, S.; Mukherjee, R. N.; Tomas, M.; Falvello, L. R.; Chakravorty, A. *Inorg. Chem.* **1986**, *25*, 200–207.

(19) Raghavendra, B. S. R.; Gupta, S.; Chakravorty, A. *Transition Met. Chem.* (*Weinheim, Ger.*) **1979**, *4*, 42–45.

(20) Geary, W. J. *Coord. Chem. Rev.* **1971**, *7*, 81–122.

(21) Kalia, K. C.; Chakravorty, A. *Inorg. Chem.* **1969**, *8*, 2586–2590.

(22) We are very thankful to a reviewer for this suggestion.

Table I. Characterization Data

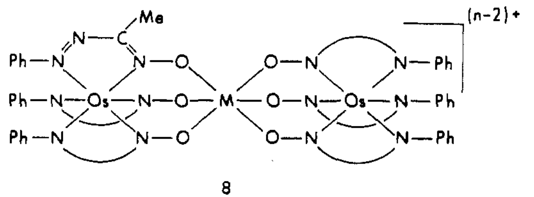
			EPR spectra[c]		electrochemistry[d-f] $E°_{298}$, V (ΔE_p, mV)	
compd	M_r[a]	μ_{eff},[b] μ_B	phase	*g*	M(III)/M(II)	ligand redn
5a	1375 (1378)	*g*		*h*		−0.53 (70), −0.67 (70)
5b	1392 (1408)	5.82	powder glass[i]	6.276, 1.997 6.276, 1.979	0.56 (80)	−0.49 (80), −0.67 (70)
5c	*j*	5.94	powder glass[i]	6.665, 5.443, 4.187 6.888, 5.420, 4.239	−0.01 (80)	−0.37 (60), −0.59 (90)
5d	1419 (1412)	5.15		*h*	0.76 (130)[k]	−0.52 (60), −0.68 (70)
5e	1410 (1412)	3.12		*h*		−0.51 (70), −0.68 (60)

[a] Molecular weight; calculated values are in parentheses. [b] In the solid state at 298 K. [c] At 77 K [d] Unless otherwise stated, the solvent is acetonitrile 0.1 M in supporting electrolyte, TEAP, and the solute concentration is 10^{-3} M. [e] Working electrode, platinum; reference electrode, SCE. [f] Cyclic voltammetric scan rate 50 mV s^{-1}. $E°_{298}$ is taken as the average of peak potentials, and ΔE_p is peak-to-peak separation. [g] Diamagnetic. [h] EPR inactive. [i] In acetonitrile–toluene (1:1). [j] Not measured because of ionic nature. [k] In dichloromethane.

conductance of **7** in acetonitrile and the conversion **7** → **4** (eq 1) in alcoholic media imply that **7** undergoes partial dissociation into OsA_3^- and Ph_4As^+ in polar solvents. The following facts are also compatible with this. The electrochemical behavior of **7** in acetonitrile is closely akin ($E°_{298}$: osmium(III)–osmium(II) couple, 0.44 V; ligand reduction, −1.10 V) to that of **4** (vide infra). When Mg^{2+} is added to a solution of **4** in ethanol, the color sharply changes from green to greenish brown due to formation of **5a**. Such a sharp color change does not occur in the case of **7**. However, on removal of the solvent under vacuum **5a** is found to be present in the residue.

Interestingly the Ph_4As^+ salt of *fac*-FeA_3^- shows only one methyl signal in $CDCl_3$ solution even at low temperature,[17] suggesting that oximato–arsorane formation is less favorable here. This may be due to the poorer donor character of the oximato oxygen of FeA_3^- as compared to that of OsA_3^-. This gradation of donor character is fully compatible with other results (vide infra).

C. Trinuclear Species. a. Formulation. In acetonitrile solution all type **5** complexes are nonelectrolytic except **5c**, which behaves as a 1:1 electrolyte (Λ_M = 120 mho cm^2 M^{-1}). The osmometric molecular weights of the nonelectrolytic complexes in chloroform solution agree excellently with the trinuclear formulation (Table I). Magnetic, spectral, and electrochemical properties reported below clearly reveal that the gross structure (shown schematically in **8**) of $[(OsA_3)_2M]^{(n-2)+}$ is the same as that of the X-ray-characterized iron analogues. We have failed to obtain X-ray-quality single crystals of **5**. Quite generally crystals are difficult to grow for the $[(FeA_3)_2M]^{(n-2)+}$ species as well. In two cases where positive results were obtained, the refinement of the diffraction data did not proceed too well (R_w > 0.09).[17,18] In **8** each OsA_3^- unit acts as a tridentate O_3 ligand spanning one face of the MO_6 octahedron. Complex **5c** shows a strong IR stretch at 425 cm^{-1} assignable to $\nu_{Fe^{III}O}$ of the FeO_6 core. Except for small shifts in frequencies there is a 1:1 correspondence in the IR spectra of **5c** and $[(FeA_3)_2Fe]ClO_4{\cdot}H_2O$ in the region 400–2000 cm^{-1}.



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b. Magnetism and Magnetic Resonance Spectra. Complex **5a** is diamagnetic and displays a sharp single methyl ^1H resonance in $CDCl_3$ at δ 2.97. The downfield shift from the signal in **4** is in agreement with the stronger inductive effect of Mg^{2+} compared to that of Na^+. The single resonance is compatible with the effective equivalence of the two *fac*-OsA_3 units.

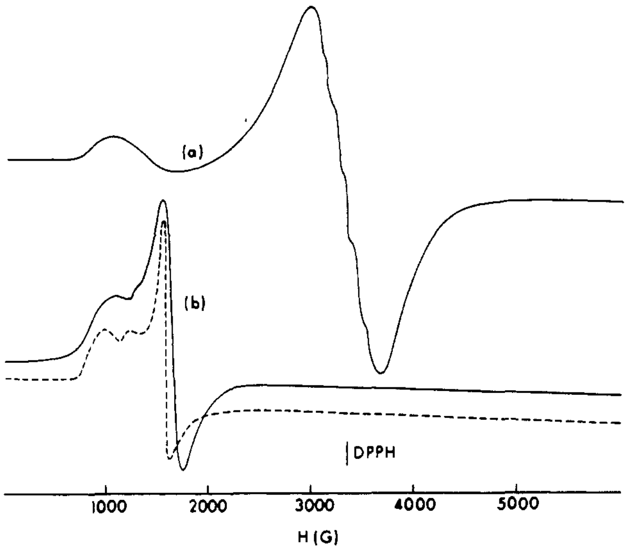

Figure 1. EPR spectra (X-band) at 77 K: (a) $Mn(OsA_3)_2$ (**5b**) in a 1:1 acetonitrile-toluene glass; (b) $Fe(OsA_3)_2ClO_4$ (**5c**) in polycrystalline form (—) and in a 1:1 acetonitrile–toluene glass (- - -).

Complexes **5b–e** are paramagnetic, and their moments correspond to the high-spin nature of the MO_6 octahedra: $S = {}^5/_2$, ${}^5/_2$, ${}^3/_2$, and 1, respectively (Table I). In the cases of $S = {}^5/_2$ species (**5b, c**), distortions of the MO_6 sphere from O_h symmetry were examined with the help of EPR spectra run in the X-band on polycrystalline samples as well as on frozen 1:1 acetonitrile–toluene solutions at 77 K. Data are in Figure 1 and Table I. Polycrystalline spectra at room temperature are essentially the same as those at 77 K.

The magnetic levels of $S = {}^5/_2$ ions in distorted octahedral situations consist of three Kramers doublets, and the zero-field parameters are *D* and *E* ($\lambda = E/D$).[24,25] In the case of **5b**, two resonances are observed: $g_\parallel \approx 6.28$ and $g_\perp \approx 1.99$. It represents a model case[24] of small λ with $D \geq 0.2$ cm^{-1}. The ^{55}Mn hyperfine structure (average $A_\perp$ = 92 G) is clearly discernible in the $g_\perp$ resonance. For **5c**, the most dominant spectral feature is the strong signal at $g \approx 4.2$. This is characteristic of near-perfect rhombicity: $\lambda \simeq {}^1/_3$ ($D > 0.2$ cm^{-1}). The weaker resonances (Table I) at lower fields could at least in part be due to deviations from ideal rhombicity ($\lambda = {}^1/_3$). Complex **5c** incorporating the trivalent ion (Fe^{3+}) has larger rhombic distortion than **5b**, which has a bivalent ion (Mn^{2+}) at the center.

c. Electrochemical Characterization. The electroactivities of **4** and **5** were examined in acetonitrile or dichloromethane solution

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(23) Eberwein, B.; Otto, R.; Weidlein, J. *Z. Anorg. Allg. Chem.* **1977**, *431*, 95–104.

(24) Dowsing, R. D.; Gibson, J. F. *J. Chem. Phys.* **1969**, *50*, 294–303.

(25) Peisach, J.; Blumberg, W. E.; Lode, E. T.; Coon, M. J. *J. Biol. Chem.* **1971**, *246*, 5877–5881. Wickman, H. H.; Klein, M. P.; Shirley, D. A. *J. Chem. Phys.* **1965**, *42*, 2113–2117.

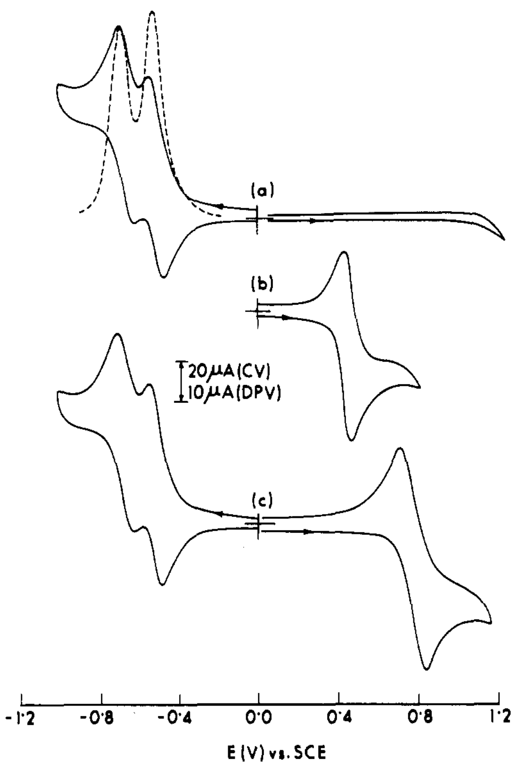

Figure 2. (a) Cyclic voltammogram (CV) (—) and differential pulse voltammogram (DPV) (---) of $Ni(OsA_3)_2$ (**5e**). (b) CV of *fac*-$NaOsA_3{\cdot}3H_2O$ (**4**). (c) CV of $Co(OsA_3)_2$ (**5d**). In (a) and (c) the solvents are acetonitrile and dichloromethane for scans at potentials negative and positive to SCE; in (b) the solvent is acetonitrile. In all cases the working electrode is platinum, the temperature is 298 K, and the supporting electrolyte is TEAP. The scan rate for CV is 50 mV s^{-1} and for DPV is 10 mV s^{-1}. The modulation amplitude for DPV is 25 mV. The solute concentration is $\sim 10^{-3}$ M.

at a platinum electrode with use of voltammetric techniques. Data are presented in Figure 2 and Table I; all potentials are referenced to the saturated calomel electrode (SCE). The major electrochemical features are as follows.

Complex **4** displays a characteristic cyclic voltammetric response having $E°_{298} = 0.44$ V in acetonitrile. Constant-potential coulometry (coulomb count found for 8.01 mg of **4** is 0.98 C; calculated 1.02 C) at 0.65 V established the 1e nature of the response, which is reversible (peak-to-peak separation $\Delta E_p = 60$ mV). The response is assigned to the couple of eq 2.

$$Os^{III}A_3 + e^- \rightleftharpoons Os^{II}A_3^- \qquad (2)$$

The $E°_{298}$ value of couple 2 is 150 mV more positive than that of the FeA_3–FeA_3^- couple.[17] The lower oxidation state of the metal is effectively better stabilized for osmium. This is an uncommon situation. Among low-spin species the usual trend of $E°_{298}$ is Fe > Os. Good examples are $E°_{298}$ (OsB_3^{3+}–OsB_3^{2+}) = 0.81 V,[26] $E°_{298}$(FeB_3^{3+}–FB_3^{2+}) = 1.06 V[27] and $E°_{298}$ (OsC_3^{3+}–OsC_3^{2+}) = 1.74 V,[9] $E°_{298}$(FeC_3^{3+}–FeC_3^{2+}) = 1.84 V[28] (B = 2.2′-bipyridine and C = 2-(phenylazo)pyridine).

While stronger binding (see below, in the discussion of couples 4 and 5 for complex **5**) of Na^+ to OsA_3^- compared to that for Na^+ to FeA_3^- may be one of the factors, we believe that there is an important reason which can bring about this uncommon situation ($E°_{298}(Os) > E°_{298}(Fe)$) and that is the strong ligand field binding as in the case of hexacyano complexes.[29] Here the enthalpy terms associated with ligand field stabilization and complex formation are large enough to offset the opposing (Os < Fe) contributions of the ionization potential and pairing energy terms.[30] That A^- has a ligand field and bonding strength comparable to that of CN^- is strongly suggested by the low-spin nature[31] of MnA_3^- ($S = {}^1/_2$).

Binding of M^{n+} cations to OsA_3^- as in **5** may be expected to shift the osmium(III)–osmium(II) response (couple 2) to high potentials. The observed effect is indeed dramatic, and the response is not observable at all upto 1 V in **5a**, **e**. Above this potential several irreversible responses due to ligand oxidation are observed. In **5b–d** the central metal atom (M) is itself electroactive below 1 V and the cyclic response due to the $M^{III}O_6$–$M^{II}O_6$ couple (eq 3) is observable.

$$[(Os^{II}A_3)_2M^{III}]^+ + e^- \rightleftharpoons [(Os^{II}A_3)_2M^{II}] \qquad (3)$$

Finally, all complexes of type **5** afford a pair of cyclic voltammetric responses on the negative side (−0.3 to −0.7 V; ΔE_p = 60–90 mV) of the SCE due to successive ligand reductions (eq 4 and 5). This pair is diagnostic of trinucleation, and the associated

$$(OsA_3)_2M + e^- \rightleftharpoons (OsA_2A^{\bullet -})(OsA_3)M \qquad (4)$$

$$(OsA_2A^{\bullet -})(OsA_3)M + e^- \rightleftharpoons (OsA_2A^{\bullet -})_2M \qquad (5)$$

electron transfers are believed to involve primarily the azo functions of the ligands.[18] Complex **4** shows a single one-electron ligand reduction couple ($E°_{298} = -1.05$ V; $\Delta E_p = 60$ mV). A number of ill-defined irreversible responses occur below this potential, but these were not examined carefully.

Since the +2 state of the metal is effectively better stabilized (vide supra) in OsA_3^- than in FeA_3^-, ligand reduction might have been expected to occur at a *lower* potential in **5** than in $[(FeA_3)_2M]$. In practice, however, the formal potentials of the couples of eq 4 and 5 are substantially *higher* (by ~300 mV) than those of the corresponding couples[17,18] of $[(FeA_3)_2M]$. We believe that the stronger binding of the M^{n+} center in osmium complexes is an important factor. In this context it is significant that the methyl chemical shift in **5a** is downfield from that of $(FeA_3)_2Mg$ (δ 2.87).[31] Further, the $Fe^{III}O$ stretch of **5c** (425 cm^{-1}) is higher than that[17] of $[(FeA_3)_2Fe]ClO_4{\cdot}H_2O$ (400 cm^{-1}).

D. Concluding Remarks. It is demonstrated that osmium(II) forms a facial anionic tris chelate with A^-. The facile formation of $[(OsA_3)_2M]^{(n-2)+}$ from OsA_3^- and M^{n+} enlarges the scope of the trinucleation reaction so far known only for FeA_3^-.

We have been unsuccessful in obtaining RuA_3^- and trinuclear derivatives thereof. From the reaction of $RuCl_3{\cdot}3H_2O$ with HA only species of types **2** and **3** can be isolated.[10,11] We considered the possibility that the reaction of **3** with HA in the presence of a base (NEt_3, K_2CO_3, and MeONa were tried) may afford RuA_3^- via dehydrohalogenation. In practice, however, only partial deprotonation and isomerization occur, affording the green anion *trans*-$RuX_2(HA)(A)^-$, which is identical with the species generated by one-electron electrochemical (+0.2 V) or chemical reduction of **2**. Other methods were also examined. For example we tried reactions of HA with (i) tris(acetylacetonato)ruthenium(III) in ethyl benzoate and (ii) $K_2RuCl_5{\cdot}H_2O$ in boiling aqeuous ethanol in the presence of base (K_2CO_3). In reaction i a blue-violet species is formed. Although it has not been fully characterized, it is certainly not a tris chelate. In reaction ii *trans*-$RuCl_2(HA)(A)^-$ is formed. Our search for the elusive RuA_3^- continues.

Experimental Section

Materials. Arylazo oximes were prepared by using the reported method.[32] Osmium tetraoxide received from Arora-Matthey, Calcutta, India, was reacted with concentrated HBr to afford $(NH_4)_2OsBr_6$.[33] Hydrated metal perchlorates were prepared by treatment of the corresponding metal carbonates or hydroxides with 70% aqueous perchloric

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(26) Kober, E. M.; Sullivan, B. P.; Dressick, W. J.; Caspar, J. V.; Meyer, T. J. *J. Am. Chem. Soc.* **1980**, *102*, 7383–7385.

(27) Weiner, M. A.; Basu, A. *Inorg. Chem.* **1980**, *19*, 2797–2800.

(28) Goswami, S.; Bandyopadhyay, P.; Chakravorty, A., unpublished results.

(29) Sharpe, A. G. *The Chemistry of Cyano Complexes of the Transition Metals*; *Academic*: New York, 1976; Chapter VII, pp 99–158.

(30) Buckingham, D. A.; Sargeson, A. M. In *Chelating Agents and Metal Chelates*; Dwyer, F. P., Mellor, D. P., Eds.; Academic: New York, 1964; Chapter 6, pp 261–264. (The sign convention for $E°_{298}$ in this work is opposite to the present convention as used by us.)

(31) Pal, S.; Chakravorty, A., unpublished results.

(32) Bamberger, E.; Pemsel, W. *Ber. Dtsch. Chem. Ges.* **1903**, *36*, 85. Kalia, K. C.; Chakravorty, A. *J. Org. Chem.* **1970**, *35*, 2231–2234.

(33) Dwyer, F. P.; Hogarth, J. W. *Inorg. Synth.* **1957**, *5*, 204–209.

acid followed by crystallization. (*Caution*! *Perchlorates may explode on heating*.) The purification of acetonitrile and dichloromethane and preparation of tetraethylammonium perchlorate (TEAP) for electrochemical work were done as described earlier.[18] All other chemicals and organic solvents used for synthetic experiments and for spectroscopy and other measurements were of analytical grade available commercially.

Measurements. Infrared spectra (KBr disk, 4000–400 cm^{-1}) were obtained with a Perkin-Elmer 783 spectrophotometer. ^1H NMR spectra were collected in $CDCl_3$ on a Bruker 270-MHz spectrometer. Magnetic susceptibilities were measured with a PAR vibrating-sample magnetometer (Model 155) fitted with a Walker Scientific magnet (Model L75 FBAL). Solution electrical conductivity measurements were made by using a Philips (Calcutta, India) PR 9500 conductivity bridge with a solute concentration of $\sim 10^{-3}$ M. Molecular weights were determined in chloroform solution by using a Knauer vapor pressure osmometer with benzil as calibrant. X-Band EPR spectra were recorded with a Varian E-109C spectrometer fitted with a quartz Dewar for measurements at 77 K (liquid dinitrogen). The spectra were calibrated with the help of DPPH ($g = 2.0037$). Electrochemical measurements were done with the help of a PAR Model 370-4 electrochemistry system incorporating a Model 174A polarographic analyzer, a Model 175 universal programmer, a Model RE0074 X-Y recorder, a Model 173 potentiostat, a Model 179 digital coulometer, and a Model 377A cell system. The three-electrode measurements were carried out with use of a planar Beckman Model 39273 platinum-inlay working electrode, a platinum-wire auxiliary electrode, and an aqueous saturated calomel reference electrode (SCE). For coulometry a platinum-wire-gauze working electrode was used. All experiments were done at 298 ± 1 K under a dinitrogen atmosphere, and the reported potentials are uncorrected for junction contribution. Microanalytical data (C, H, N) were obtained with use of a Perkin-Elmer Model 240C elemental analyzer.

Preparation of Complexes. *fac*-Sodium Tris((phenylazo)acetaldoximato)osmate(II) Trihydrate, $NaOsA_3\cdot 3H_2O$ (4). Dinitrogen was passed for 15 min through a solution containing HA (0.70 g, 4.29 mmol) and NaOH (0.18 g, 4.50 mmol) in methanol–water (40 mL, 1:1) kept under reflux. Following this, $(NH_4)_2OsBr_6$ (0.302 g, 0.429 mmol) dissolved in methanol–water (60 mL, 1:1) in a separate container was added dropwise to the above solution. The whole solution was then kept under reflux for a further period of 4 h, during which time the brown solution turned green. The solvent was then evaporated completely under reduced pressure. The residue was extracted with Acid-free dichloromethane. When the solvent was evaporated on a steam bath, a green gummy mass resulted. This was dried over anhydrous $CaCl_2$. The dried mass was dissolved in acetonitrile and was subjected to chromatography on a neutral alumina (BDH) column (30 × 1 cm). At first a red-brown solution was eluted with acetonitrile. Finally the green band was eluted with acetonitrile–methanol (3:1). On slow evaporation of the eluant a gummy mass was obtained. This was recrystallized from acetonitrile–water (4:1), affording the required complex in 60% yield. Anal. Calcd for $NaOsC_{24}H_{30}N_9O_6$ (**4**): C, 38.24; H, 4.01; N, 16.72. Found: C, 38.44; H, 4.01; N, 16.81.

Bis[tris((phenylazo)acetaldoximato)osmato(II)]magnesium(II), $[(OsA_3)_2Mg]$ (5a). To a solution containing **4** (0.10 g, 0.13 mmol) in ethanol (15 mL) was added $Mg(ClO_4)_2\cdot 6H_2O$ (0.025 g, 0.08 mmol). The green color of the solution immediately changed to greenish brown. The mixture was stirred magnetically at room temperature (298 K) for 4 h. The reaction solution was then evaporated completely under reduced pressure. The resulting mass was washed thoroughly with water and finally with a little hexane. The crystalline solid was dried in vacuo over P_4O_{10}. The yield was 85%. Anal. Calcd for $MgOs_2C_{48}H_{48}N_{18}O_6$ (**5a**): C, 41.84; H, 3.51; N, 18.30. Found: C, 41.81; H, 3.61; N, 18.42.

The other type **5** complexes were prepared similarly. Anal. Calcd for $MnOs_2C_{48}H_{48}N_{18}O_6$ (**5b**): C, 40.93; H, 3.43; N, 17.90. Found: C, 40.93; H, 3.48; N, 17.82. Calcd for $FeOs_2C_{48}H_{48}N_{18}O_{10}Cl$ (**5c**): C, 38.21; H, 3.21; N, 16.71. Found: C, 38.12; H, 3.25; N, 16.80. Calcd for $CoOs_2C_{48}H_{48}N_{18}O_6$ (**5d**): C, 40.82; H, 3.42; N, 17.85. Found: C, 40.92; H, 3.32; N, 17.80. Calcd for $NiOs_2C_{48}H_{48}N_{18}O_6$ (**5e**): C, 40.82; H, 3.43; N, 17.85. Found: C, 40.91; H, 3.46; N, 17.95.

Extrusion of M^{n+} from 5. Details are given for a representative case (**5a**). To a solution of **5a** (0.10 g, 0.07 mmol) in acetone (50 mL) was added dropwise an aqueous solution (15 mL) of sodium hydroxide (0.016 g, 0.40 mmol). The mixture was stirred for $^1/_2$ h at room temperature (298 K), when it rapidly turned green. The solution was filtered from precipitated $Mg(OH)_2$ through a fine frit, and the filtrate was evaporated under reduced pressure. The resulting mass was recrystallized from acetonitrile–water (4:1), affording **4** in near-quantitative yield.

Tetraphenylarsonium Tris((phenylazo)acetaldoximato)osmate(II), Ph_4AsOsA_3 (7). Complex **4** (0.20 g, 0.26 mmol) was dissolved in methanol (16 mL). To this was added Ph_4AsCl (0.11 g, 0.26 mmol) dissolved in H_2O (4 mL). The mixture was stirred magnetically at room temperature (298 K) for 5 h. The solution was slowly evaporated. The precipitated complex was filtered and washed throughly with water and finally with petroleum ether (boiling range 60–80 °C). The shining dark crystalline compound was thus obtained. It was dried in vacuo over P_4O_{10}. The yield was 80% (of sodium salt). Anal. Calcd for $AsOsC_{48}H_{44}N_9O_3$ (**7**): C, 54.39; H, 4.18; N, 11.89. Found: C, 54.49; H, 4.22; N, 11.94.

Reaction of 7 with $NaPh_4B$. Ph_4AsOsA_3 (100 mg, 0.094 mmol) was dissolved in absolute ethanol. To this was added $NaPh_4B$ (32 mg, 0.094 mmol), and the mixture was stirred magnetically for a few minutes at room temperature. Precipitated $[Ph_4As][Ph_4B]$ was filtered off by using a fine frit. The green filtrate was evaporated under reduced pressure to afford $NaOsA_3\cdot 3H_2O$ (yield 95%).

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Supplementary Material Available: A figure showing the ^1H methyl NMR spectra of **4**, **5a**, and **7** (1 page). Ordering information is given on any current masthead page.