site of the nickel complex in a monodentate fashion. This initial adduct formation is followed by a slow ring-closing step (first-order rate constant k_1), during which the macrocycle simultaneously changes its coordination from (planar) trans to (folded) cis. Finally, the rapid replacement in the coordination sphere of the folded macrocycle by two 1,10-phenanthroline ligands occurs to yield $[Ni(phen)_3]^{2+}$.[19]

A parallel study involving reaction of excess 2,2′-bipyridyl with $Ni(OenNtnH_4)Cl_2$ has been performed. In this case the K and k_1 values (Table III) were both slightly reduced relative to those obtained with the more rigid ligand, 1,10-phenanthroline.[20]

Previously, ligand folding has been implicated in the dissociation of flexible macrocycles from complexes containing the macrocycle coordinated in a planar form.[17,21–23] The observation of enhanced dissociation in the presence of bidentate ligands (which, on coordination, will promote folding of the macrocycle) thus provides additional indirect support for this postulate.

Acknowledgment. L.F.L. and P.A.T. thank the Australian Research Grants Scheme for support. L.F.L. acknowledges the Australian Institute for Nuclear Science and Engineering for a travel grant to visit the Lucas Heights Research Laboratory, Sydney. He also thanks Professor E. Deutsch and J. C. Sullivan for helpful discussions and Dr. K. R. Adam for assistance with the computer analysis of the rate data.

Registry No. $Ni(OenNtnH_4)Cl_2$, 66810-83-1; $Ni(OtnNtnH_4)Cl_2$, 66793-45-1; Cu, 7440-50-8; phen, 66-71-7; bpy, 366-18-7.

---

[19] The following are in accord with the proposed mechanism: (i) the adduct of 1,10-phenanthroline with a square-planar macrocyclic nickel complex has been demonstrated by X-ray diffraction to have a cis distorted-octahedral structure of the general type postulated to occur during the dissociation reaction (see: Stephens, F. S.; Vagg, R. S. *Acta Crystallogr., Sect. B* **1977**, *B33*, 3165), (ii) the formation of an intermediate involving singly N-bonded 1,10-phenanthroline to nickel has been postulated previously (see: Steinhaus, R. K.; Lee, B. I. *Inorg. Chem.* **1982**, *21*, 1829 and references therein), (iii) the ring-closing reaction involving coordination of the second nitrogen might be expected to be slow since it would be controlled by the rate with which the macrocycle changes from a planar to a folded form in the coordination sphere, and (iv) the k_1 values would be expected to be markedly dependent on macrocycle ring size (as observed), the larger value for k_1 obtained for the $OtnNtnH_4$ system being perhaps a reflection of the greater flexibility of this larger ring system aiding the folding of the macrocycle.

[20] Further kinetic runs involving $Ni(OenNtnH_4)Cl_2$ and 3,4,7,8-tetramethylphenanthroline (Me_4phen) at two concentrations (the restricted solubility of this ligand prevented a more detailed study) gave k_{obsd} values that are identical within the experimental error ($[Me_4phen] = 0.030$ M, $k_{obsd} = 0.033\ s^{-1}$; $[Me_4phen] = 0.059$ M, $k_{obsd} = 0.0480\ s^{-1}$) with those found for the corresponding 1,10-phenanthroline system. The similarity of these values suggests that "self-stacking" interactions of the type found for 1,10-phenanthroline or 2,2′-bipyridyl in aqueous solution (see: Mitchell, P. R. *J. Chem. Soc., Dalton Trans.* **1980**, 1079) or "outer-sphere stacking" interactions (see: Cayley, G. R.; Margerum, D. W. *J. Chem. Soc., Chem. Commun.* **1974**, 1002) of the type postulated to occur between free aromatic ligands and a range of nickel complexes of coordinated aromatic ligands are not significant in the present systems. The presence of substituents on the phenanthroline moiety would be expected to affect the nature of any such "stacking" whereas the normal coordination behavior might be little affected since the methyl substituents are remote from the coordination sites. Thus, if stacking of either of the above types occurred, it seems unlikely that the k_{obsd} values would remain similar as observed. Further, ^1H NMR experiments confirm that ligand self-association is insignificant under conditions that approximate those used in the present work: Mitchell, P. R., Institute of Inorganic Chemistry, University of Basel, personal communication.

[21] Diaddario, L. L.; Zimmer, L. L.; Jones, T. E.; Sokol, L. S. W. L.; Cruz, R. B.; Yee, E. L.; Ochrymowycz, L. A.; Rorabacker, D. B. *J. Am. Chem. Soc.* **1979**, *101*, 3511.

[22] Hay, R. W.; Norman, P. R. *Inorg. Chim. Acta* **1980**, *45*, L139.

[23] Busch, D. H.; Farmery, K.; Goedken, V.; Katovic, V.; Melnyk, A. C.; Sperati, C. R.; Tokel, N. In "Bioinorganic Chemistry"; Gould, R. F., Ed.; American Chemical Society: Washington, DC, 1971; ACS Mongr. No. 100.

Communications

Multiple Oxidation States of Ruthenium and Osmium Based on Dioxo/Diaquo Couples

Sir:

Recently it was shown that ruthenium(IV)–oxo complexes containing polypyridine ligands are accessible by sequential oxidation of the corresponding ruthenium(II)–aquo complexes (eq 1; py = pyridine, bpy = 2,2′-bipyridine, pH = 7).[1,2] The

$$\mathrm{(bpy)_2(py)Ru^{IV}{=}O^{2+}} \underset{(E\,=\,+0.53\ \mathrm{V})}{\underset{-e^-,-H^+}{\overset{+e^-,+H^+}{\rightleftharpoons}}} \mathrm{(bpy)_2(py)Ru^{III}{-}OH^{2+}} \underset{(E\,=\,+0.42\ \mathrm{V})}{\underset{-e^-,-H^+}{\overset{+e^-,+H^+}{\rightleftharpoons}}} \mathrm{(bpy)_2(py)Ru^{II}{-}OH_2^{2+}}$$

oxidations involve the net loss of both protons and electrons in aqueous solution over a wide pH range. The importance of the oxo/aquo redox chemistry is shown by (1) the catalytic oxidation of alcohols, aldehydes, and C—H bonds adjacent to unsaturated hydrocarbons by $(trpy)(bpy)Ru{=}O^{2+}$ (trpy is 2,2′,2″-terpyridine),[3] (2) the reversible reduction of nitrate to nitrite by $(bpy)_2(py)Ru(OH_2)^{2+}$,[4] and (3) the catalytic oxidation of water by an oxidized form of the oxo-bridged dimer of ruthenium(III) $[(bpy)_2(H_2O)RuORu(H_2O)(bpy)_2]^{4+}$.[5] In contrast to the two-electron chemistry of the monomeric aquo complexes, there is a potential four-electron chemistry associated with the diaquo systems *cis*-$(bpy)_2M(OH_2)_2^{2+}$ (M = Ru, Os). We report here that oxidation states II, III, IV, V, and VI are all accessible to the metal in the diaquo systems through a series of concomitant electron–aquo–proton losses and that the higher oxidation states appear over a remarkably narrow potential range.

Figure 1a depicts a cyclic voltammogram and Figure 1b depicts a differential pulse polarogram for *cis*-$(bpy)_2Ru(OH_2)_2^{2+}$ at pH 1.4. When combined with the results of coulometric experiments, both experiments provide evidence for a series of four sequential one-electron oxidation steps. The reversible one-electron oxidation of Ru(II) to Ru(III) has been reported.[6] It is followed by three additional one-electron oxidation steps. The Ru(III)/Ru(IV) couple, as shown by both

---

[1] All potentials are listed vs. the saturated sodium chloride calomel electrode (SSCE), in aqueous media at 25 °C. The working electrodes are glassy carbon or carbon paste.

[2] (a) Moyer, B. A.; Meyer, T. J. *J. Am. Chem. Soc.* **1978**, *100*, 3601. (b) Moyer, B. A.; Meyer, T. J. *Inorg. Chem.* **1981**, *20*, 436.

[3] Moyer, B. A.; Thompson, M. S.; Meyer, T. J. *J. Am. Chem. Soc.* **1980**, *102*, 2310.

[4] (a) Moyer, B. A.; Meyer, T. J. *J. Am. Chem. Soc.* **1979**, *101*, 1326. (b) DiGiovanni, W.; Meyer, T. J., submitted for publication.

[5] Gersten, S. W.; Samuels, G. J.; Meyer, T. J. *J. Am. Chem. Soc.* **1982**, *104*, 2049.

[6] Durham, B.; Wilson, S. R.; Hodgson, D. J.; Meyer, T. J. *J. Am. Chem. Soc.* **1980**, *102*, 600.

0020-1669/83/1322-1407$01.50/0

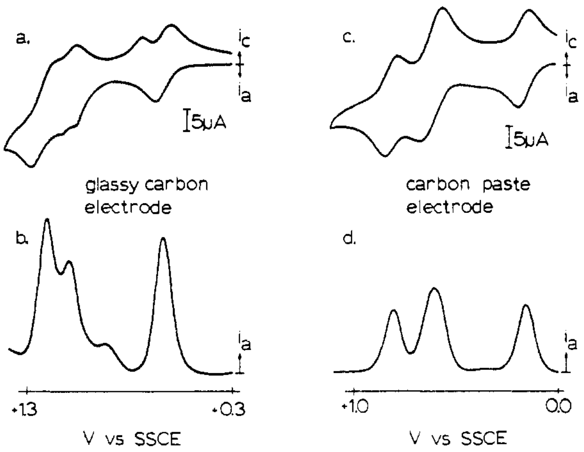

Figure 1. Cyclic voltammograms (100 mV/s) and differential-pulse polarograms (2 mV/s) of ~2 mM *cis*-$(bpy)_2M(OH_2)_2^{2+}$ (M = Ru or Os) aqueous perchloric acid solutions at pH 1.4 (μ = 0.1).

the cyclic voltammogram (E_p^a = +1.09 V, E_p^c = +0.77 V) and the differential-pulse polarogram (E_p = +0.93 V), is kinetically slow at the electrode, apparently due to complications arising from a change in proton content between the two oxidation states.[7] Similar observations have been made for $(bpy)_2(py)RuO^{2+}/(bpy)_2(py)RuOH^{2+}$ and $(trpy)(bpy)RuO^{2+}/(trpy)(bpy)RuOH^{2+}$ couples.[2,8] The Ru(III)/Ru(IV) oxidation is followed by two additional one-electron oxidations at $E_{1/2}$ = +1.10 V and $E_{1/2}$ = +1.23 V at pH 1.4.

Figure 1c shows a cyclic voltammogram and Figure 1d shows a differential pulse polarogram for *cis*-$(bpy)_2Os(OH_2)_2^{2+}$ at pH 1.4 from which evidence for three rather than four oxidation steps is obtained. The first step involves oxidation of Os(II) to Os(III) (n = 0.9 ± 0.1 by coulometry) and occurs at $E_{1/2}$ = +0.16 V. It is followed by a two-electron step in which Os(III) is oxidized to Os(V) at $E_{1/2}$ = +0.61 V and, in turn, by a one-electron step in which Os(V) is oxidized to Os(VI) at $E_{1/2}$ = +0.81 V. The numbers of electrons transferred at the waves occurring at more oxidative potentials were inferred from relative peak areas. In the range pH 2.0–5.5, the two-electron wave separates into two resolvable one-electron waves, providing evidence for both Os(IV)/Os(III) and Os(V)/Os(IV) couples.

From pH dependence measurements, $E_{1/2}$ values for each of the four redox couples based on *cis*-$(bpy)_2Ru(H_2O)_2^{2+}$ are pH dependent over the range pH 2.1–5.7. $E_{1/2}$ values decrease linearly with increasing pH (slope = −59 mV/pH unit), consistent with the loss of a single proton for each oxidation step. For *cis*-$(bpy)_2Os(H_2O)_2^{2+}$, $E_{1/2}$ values also decrease linearly with increasing pH (slope = −59 mV/pH unit) over the range pH 2.0–5.5, which is indicative of four successive one-electron, one-proton steps, in the oxidation of *cis*-$(bpy)_2Os(H_2O)_2^{2+}$. Below pH 2.0, the $E_{1/2}$ values for the Os(V)/Os(III) couple decrease linearly with increasing pH with a slope of −88 mV/pH unit, which is consistent with a couple involving three protons and two electrons.

From the pH dependence of the couples it can be inferred that the three- and four-electron-oxidation products of *cis*-$(bpy)_2Ru(OH_2)_2^{2+}$ must be $(bpy)_2Ru(O)(OH)^{2+}$ and $(bpy)_2RuO_2^{2+}$, respectively. Perchlorate salts of both can be isolated from perchloric acid solutions following the addition of 3 equiv of Ce(IV) or of an excess of Ce(IV). IR spectra in AgCl pellets show a band at 857 cm^{-1} for $(bpy)_2Ru(O)(OH)^{2+}$, which can be assigned to a ν(Ru=O) stretching vibration. For $(bpy)_2RuO_2^{2+}$, two ν(Ru=O) bands are observable, one at 860 cm^{-1} and the other at 835 cm^{-1}. The observation of two ν(Ru=O) bands is consistent with the retention of the cis geometry[9] in $(bpy)_2RuO_2^{2+}$. The pale yellow complex *cis*-$(bpy)_2OsO_2^{2+}$ can be isolated as its perchlorate salt following addition of excess Ce(IV) to solutions containing *cis*-$(bpy)_2Os(OH_2)_2^{2+}$.[10] In a Nujol mull containing the Os(VI) salt, both the ν(Os=O) antisymmetric stretch (at 878 cm^{-1}) and the ν(Os=O) symmetric stretch (at 858 cm^{-1}) are observed. The ^{1}H NMR spectrum of $(bpy)_2OsO_2^{2+}$ displayed eight peaks, which is consistent with a *cis-substituted*, diamagnetic Os(VI)–dioxo complex of C_2 symmetry. In addition, the proposed formulation of the complex is supported by the appearance of a strong parent ion peak in the mass spectrum of the salt obtained by fast atom bombardment mass spectrometry.[11]

It is important to note that a well-defined, related chemistry exists for the trans isomer *trans*-$(bpy)_2Ru(H_2O)_2^{2+}$. At pH 1.5, the Ru(III)/Ru(II) couple occurs at $E_{1/2}$ = +0.45 V and the Ru(IV)/Ru(III) couple occurs at $E_{1/2}$ = +1.01 V. Both oxidations involve the loss of one proton and one electron. Following oxidation by Ce(IV), a pale yellow perchlorate salt, [*trans*-$(bpy)_2Ru(H_2O)(O)](ClO_4)_2$, has been isolated and characterized.[12] The IR spectrum of the salt in a AgCl pellet shows a band at 848 cm^{-1}, which can be assigned to the ν(Ru=O) stretching vibration.

Based on the information presented here, it is possible to summarize the redox properties of the Ru and Os complexes with the following redox potential diagrams. The values in the diagrams are formal potentials in V vs. SSCE at 25 °C and μ = 0.10[1] (B is 2,2′-bipyridine).[13]

cis-$(bpy)_2Ru(OH_2)_2^{2+}$ at pH 4.0

$$\textit{cis}\text{-}B_2RuO_2^{2+} \xrightarrow{+1.07} \textit{cis}\text{-}B_2Ru(O)(OH)^{2+} \xrightarrow{+0.94} \textit{cis}\text{-}B_2Ru(O)(OH_2)^{2+} \xrightarrow{0.76} \textit{cis}\text{-}B_2Ru(OH)(OH_2)^{2+} \xrightarrow{+0.53} \textit{cis}\text{-}B_2Ru(OH_2)_2^{2+}$$

trans-$(bpy)_2Ru(OH_2)_2^{2+}$ at pH 1.5

$$\textit{trans}\text{-}B_2Ru(O)(OH_2)^{2+} \xrightarrow{+1.01} \textit{trans}\text{-}B_2Ru(OH)(OH_2)^{2+} \xrightarrow{+0.45} \textit{trans}\text{-}B_2Ru(OH_2)_2^{2+}$$

cis-$(bpy)_2Os(OH_2)_2^{2+}$ at pH 4.0

$$\textit{cis}\text{-}B_2Os(O)_2^{2+} \xrightarrow{+0.65} \textit{cis}\text{-}B_2Os(O)(OH)^{2+} \xrightarrow{+0.50} \textit{cis}\text{-}B_2Os(O)(OH_2)^{2+} \xrightarrow{+0.41} \textit{cis}\text{-}B_2Os(OH)(OH_2)^{2+} \xrightarrow{+0.04} \textit{cis}\text{-}B_2Os(OH_2)_2^{2+}$$

The complexes of oxidation state IV await characterization and, from the pH dependence studies, could be formulated as the dihydroxo complexes *cis*-$(bpy)_2M(OH)_2^{2+}$, rather than as the oxo complexes *cis*-$(bpy)_2M(O)(OH_2)^{2+}$, as suggested in the redox potential diagrams.

---

(7) Binstead, R. A.; Moyer, B. A.; Samuels, G. J.; Meyer, T. J. *J. Am. Chem. Soc.* **1981**, *103*, 2897.

(8) Thompson, M. S.; Takeuchi, K. J.; Pipes, D., submitted for publication.

(9) Jezowska-Trzebiatowska, B.; Hanula, J. *J. Mol. Struct.* **1973**, *19*, 109.

(10) Anal. Calcd for $[(bpy)_2OsO_2](ClO_4)_2{\cdot}H_2O$: C, 31.96; H, 2.41; n, 7.46. Found: C, 31.82; H, 1.27; N, 7.36.

(11) Cerny, R. L., private communication.

(12) Anal. Calcd for $[(bpy)_2(H_2O)Ru(O)](ClO_4)_2{\cdot}H_2O$: C, 36.16; H, 3.03; N, 8.43. Found: C, 35.77; H, 2.53; N, 8.35.

(13) Found potentials were estimated as $E_{1/2}$ values from cyclic voltammograms by $(E_{p,c} + E_{p,a})/2 = E_{1/2}$, where $E_{p,c}$ and $E_{p,a}$ are the potentials of the peak currents for the reductive and oxidative scans, respectively. Note that $E_{1/2}$ values can be taken as formal potentials with the assumption that the usually small diffusion coefficient term is negligible.

The redox chemistry observed for the diaquo complexes is remarkable both for its extent without change in coordination number and for the fact that so many couples are accessible over a narrow potential range. To put the latter point into perspective, for the diaquo systems the span in potentials from the M(VI)/M(V) to the M(III)/M(II) couples is $\Delta E_{1/2} \sim$ 0.6 V. In acetonitrile, the span in potentials for the Ru(IV)/Ru(III) $Ru(bpy)_2Cl_2^{2+/+}$ couple ($E_{1/2}$ = +1.97 V vs. the SSCE) to the Ru(III)/Ru(II) $Ru(bpy)_2Cl_2^{+/0}$ couple ($E_{1/2}$ = +0.31 V) is $\Delta E_{1/2}$ = 1.66 V. The use of water as solvent and the presence of aquo ligands are both critical features in the observation of the higher oxidation state couples. Water is necessary as a proton source or sink, given the proton demands of the couples. Loss of protons from aquo ligands on oxidation results in the relative stabilization of higher oxidation states. The primary origin of the effect appears to lie in the release of pπ electron density, which enhances $p\pi(O) \rightarrow d\pi(M)$ overlap and M–O multiple bonding in the higher oxidation state.

Initial observations suggest an extensive chemistry for the higher oxidation states of Ru and Os described here. As an example, Nijs and co-workers have reported that the photooxidation of water is catalyzed on hectorite clays by the presence of *trans*-$(bpy)_2Ru(OH_2)_2^{2+}$.[14] We find that water is oxidized to oxygen by Ce(IV) in the presence of *cis*-$(bpy)_2Ru(OH_2)_2^{2+}$ but, in contrast to the case of solutions containing the dimer $[(bpy)_2(OH_2)RuORu(OH_2)(bpy)_2]^{2+}$,[5] the oxidation of water is *not* catalytic in the presence of the monomer. In addition, the electrolytic oxidation of Cl^- to Cl_2 at pH 1 at a carbon-paste electrode is catalyzed in the presence of *cis*-$(bpy)_2Ru(OH_2)_2^{2+}$ and the active form of the catalyst system appears to be *cis*-$(bpy)_2RuO_2^{2+}$.[15]

Acknowledgment is made to the National Science Foundation for support of this research under Grant No. CHE-8002433.

Registry No. [*cis*-$(bpy)_2Ru(OH_2)_2](ClO_4)_2$, 84988-21-6; *cis*-$(bpy)_2Ru(OH)(OH_2)^{2+}$, 85027-43-6; [*cis*-$(bpy)_2Ru(O)(OH)](ClO_4)_2$, 84988-23-8; *cis*-$(bpy)_2Ru(O)_2^{2+}$, 84988-24-9; *trans*-$(bpy)_2Ru(OH_2)_2^{2+}$, 72174-10-8; *trans*-$(bpy)_2Ru(OH)(OH_2)^{2+}$, 72155-92-1; [*cis*-$(bpy)_2Os(OH_2)_2](ClO_4)_2$, 84988-26-1; *cis*-$(bpy)_2Os(OH)(OH_2)^{2+}$, 84988-27-2; *cis*-$(bpy)_2Os(O)(OH)^{2+}$, 84988-28-3; *cis*-$(bpy)_2Os(O)_2^{2+}$, 84988-29-4; [*trans*-$(bpy)_2Ru(H_2O)(O)](ClO_4)_2$, 85114-20-1; Ru, 7440-18-8; Os, 7440-04-2; Cl^-, 16887-00-6.

---

[14] Nijs, H.; Cruz, M.; Fripiat, J.; Van Damme, H. *J. Chem. Soc. Chem. Commun.* **1981**, 1026.

[15] Ellis, C. D.; Gilbert, J. A.; Murphy, W. R., Jr.; Meyer, T. J., manuscript in preparation.

Department of Chemistry
The University of North Carolina
Chapel Hill, North Carolina 27514

Kenneth J. Takeuchi
George J. Samuels
Susan W. Gersten
John A. Gilbert
Thomas J. Meyer*

Received September 22, 1982

$Ru_5(CO)_{16}(\mu\text{-}PPh_2)(\mu_5\text{-}P)$: A Low-Nuclearity Cluster with a Partially Encapsulated Phosphide

Sir:

The ability of transition-metal clusters to encapsulate atoms of the main-group elements within a polyhedral cavity is now well established.[1] Interest in the chemistry of these interstitial clusters has been stimulated by the following observations: (i) The interstitial atom may influence the molecular geometry and electronic structure of the cluster.[2] (ii) There is some evidence[3] that interstitial atoms may have a key role to play in maintaining cluster integrity under the severe conditions necessary for certain catalytic reactions. (iii) Partially exposed, multisite-bound main-group atoms may exhibit unusual chemical reactivity.[4] Much of the recent effort has focused on the carbides,[5] in large part because of the possible involvement of exposed surface carbides in Fischer–Tropsch chemistry. Only a few examples of group 5 element encapsulation in clusters are known.[6,7] Two high-nuclearity anionic rhodium clusters $[Rh_9(CO)_{21}P]^{2-}$ and $[Rh_{10}(CO)_{22}P]^{3-}$, synthesized from monomeric rhodium precursors and triphenylphosphine under extreme conditions, have been characterized.[3,8] In these anions the bare phosphorus atom is truly encapsulated, being located in the center of a capped cubic antiprism or bicapped square antiprism of rhodium atoms. Chemically, these clusters are considerably more stable to degradation under high pressures of CO and hydrogen than high-nuclearity rhodium carbonyl clusters lacking the interstitial atom. To our knowledge the only example of a semiinterstitial phosphide is in the anion $[Co_6(CO)_{14}(\mu\text{-}CO)_2P]^-$, where the phosphorus atom is bonded to all six metal atoms in an open triangulated polyhedron.[9] We describe herein the synthesis and structural characterization of a novel pentanuclear cluster $Ru_5(CO)_{16}(\mu\text{-}PPh_2)(\mu_5\text{-}P)$ (**1**) containing a partially encapsulated bare phosphorus atom. This is the lowest nuclearity cluster phosphide so far characterized[10] and the first ruthenium cluster phosphide. This study demonstrates that the phosphide ligand[11] like the carbide and nitride has the ability to exist in a partially exposed low-coordinate environment. The synthetic route to this cluster phosphide, namely, benzene elimination from a μ-hydrido, μ-diphenylphosphido cluster $Ru_3(CO)_9(H)(PPh_2)$ under moderate conditions may be a useful strategy for the generation of other interstitial or partially encapsulated phosphides.

In the formally unsaturated 46-electron cluster $Ru_3(CO)_9(\mu\text{-}PPh_2)(\mu\text{-}H)$ (**2**) the electron deficiency of one ruthenium atom is partially satisfied by a weak interaction with one P–C(Ph) bond of the phosphido bridge.[12] This interaction suggested that the phosphido bridge might be unusually re-

---

[1] Chini, P.; Longoni, G.; Albano, V. G. *Adv. Organomet. Chem.* **1976**, *14*, 285.

[2] Vidal, J. L. *Inorg. Chem.* **1981**, *20*, 243.

[3] Vidal, J. L.; Walker, W. E.; Schoening, R. C. *Inorg. Chem.* **1981**, *20*, 238.

[4] (a) Tachikawa, M.; Muetterties, E. L. *J. Am. Chem. Soc.* **1980**, *102*, 4541. (b) Holt, E. M.; Whitmire, K. H.; Shriver, D. F. *J. Organomet. Chem.* **1981**, *213*, 125. (c) Bradley, J. S.; Ansell, G. B.; Hill, E. W. *J. Am. Chem. Soc.* **1979**, *101*, 7417.

[5] Tachikawa, M.; Muetterties, E. L. *Prog. Inorg. Chem.* **1981**, *28*, 203.

[6] A few nitride clusters are known; see: (a) Martinengo, S.; Ciani, G.; Sironi, A.; Heaton, B. T.; Mason, J. *J. Am. Chem. Soc.* **1979**, *101*, 7095. (b) Tachikawa, M.; Stein, J.; Muetterties, E. L.; Teller, R. G.; Beno, M. A.; Gebert, E.; Williams, J. M. *Ibid.* **1980**, *102*, 6648. (c) Fjare, D. E.; Gladfelter, W. L. *Ibid.* **1981**, *103*, 1572.

[7] For encapsulated phosphide and arsenide clusters see ref 2, 3, and 8.

[8] Vidal, J. L. Schoening, R. C.; Pruett, R. L.; Walker, W. E. *Inorg. Chem.* **1979**, *18*, 129.

[9] Chini, P.; Ciani, G.; Martinengo, S.; Sironi, A.; Longhetti, L.; Heaton, B. T. *J. Chem. Soc., Chem. Commun.* **1979**, 188.

[10] Very recently examples of phosphorus atoms linking two dimeric iron carbonyl fragments in a spirocyclic arrangement have been described: Huttner, G.; Gerhard, M.; Bernhard, P.; Von Seyerl, J.; Zsolnai, L. *Chem. Ber.* **1982**, *6*, 2044.

[11] The term "phosphido group" has been used rather generally to describe diorganophosphide (formally R_2P^-), organophosphide (formally RP^{2-}) and phosphide (P^{3-}) ligands. For the purpose of electron counting in cluster chemistry it is more appropriate to consider these ligands as 3-electron (R_2P), 4-electron (RP), and 5-electron (P) donors when all of the valence electrons of phosphorus are used for bonding purposes. Since the metal–phosphorus bonds in complexes of these ligands are predominantly covalent, the anionic formalism has little chemical significance.

[12] MacLaughlin, S. A.; Carty, A. J.; Taylor, N. J. *Can. J. Chem.* **1982**, *60*, 87.

0020-1669/83/1322-1409$01.50/0