Figure 1. CD curves for: a, platycerine acetate (—), N-methyl-laurotetanine (10) (- - - -); b, pennsylpavine (—), equimolar mixture of platycerine acetate and N-methyllaurotetanine (- - - - -).

upfield shift of the C-6' bridgehead proton doublet to δ 4.21, and a still larger upfield shift of the C-11 proton signal to δ 7.60 due to the presence of acetoxyl at C-1.[9]

The absolute configurations of **1** and **2** were determined by the aromatic chirality method.[10] The strong extrema at 242(+) and 209(—) nm in the CD curve of **1** (Figure 1) are associated with the ${}^1B$ transitions of the aporphine and pavine moieties, respectively, and lead to configurational assignments as shown in **1**.[11] The sum of the individual curves for **7** and **10** (Figure 1) shows no major deviation from that obtained for **1**. Additionally, the CD curve of **2** was virtually superimposable on that of **1**.

A felicitous event was the further isolation from T. polygamum of two additional alkaloids, (+)-pennsylvanine (**8**) and (+)-pennsylvanamine (**9**),[12] belonging to the (+)-thalicarpine series in which the absolute configurations of both asymmetric centers have been established. Comparison of structures **1**, **2**, **8**, and **9** furnishes prima facie evidence that in the plant alkaloids **8** and **9** could act as the biogenetic precursors of **1** and **2**, respectively.[13]

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(12) Alkaloids **8** and **9** will be discussed in a separate paper. Whenever a phenolic function is present at C-1 of an aporphine, this species whether monomeric or dimeric tends to oxidize in a protonic solvent and turn green (see ref 2, p 205). Alkaloids **2** and **9** showed such behavior.
(13) Conclusive evidence concerning the exact biogenesis of the aporphine–pavine dimers can come only from in vivo experiments using labeled precursors.

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Stabilization of High Formal Oxidation States of the First-Row Transition Metal Series by o-Phenylenebis(dimethylphosphine)

Sir:

Primarily due to the investigations of Nyholm and his collaborators, the compound o-phenylenebis(dimethylarsine), $o\text{-}C_6H_4\{As(CH_3)_2\}_2$, diars, has proved to be one of the most versatile ligands in coordination chemistry, capable of stabilizing transition metal ions in a variety of often unusual formal oxidation states and coordina-

tion environments.[1] Much less is known about the coordination chemistry of the analogous di(tertiary phosphine), $o\text{-}C_6H_4\{P(CH_3)_2\}_2$,[2-5] diphos, mainly because the ligand is not easy to prepare in reasonable quantity. With the intention of making comparisons of arsenic and phosphorus as donor atoms to transition metal ions in a range of formal oxidation states, we have synthesized diphos in ~20% yield by a published procedure[4] and have examined some of its complexes with first-row transition metal ions of chromium through copper. These are obtained by treatment of the appropriate metal salt with the ligand in alcoholic solution, the cationic derivatives generally being isolated as their perchlorate salts.

Copper(I) forms a white diamagnetic d^{10} [Cu(diphos)$_2$]$^+$ species which is oxidized by concentrated nitric acid to the pale yellow diamagnetic square-planar d^8 [Cu(diphos)$_2$]$^{3+}$ trication. Its perchlorate salt, which behaves as a 3:1 electrolyte in acetonitrile solution[6] (Λ_M = 360 ohm^{-1} cm^2 mol^{-1}), reacts with chloride ion to generate the five-coordinate yellow dication [CuCl(diphos)$_2$]$^{2+}$; the conductivity value for this perchlorate salt (Λ_M = 286 ohm^{-1} cm^2 mol^{-1}) falls within the range for 2:1 electrolytes in acetonitrile solution.[5] The less stable diars analogs, yellow [Cu(diars)$_2$]$^{3+}$ and orange [CuCl(diars)$_2$]$^{2+}$, were obtained similarly starting from [Cu(diars)$_2$]$^+$. These appear to be the first described complexes of formal copper(III) containing tertiary phosphines and arsines. Interestingly, no copper(II) species has been observed in either of these systems.

Like copper(III), isoelectronic nickel(II) gives the diamagnetic yellow square-planar [Ni(diphos)$_2$]$^{2+}$ and orange five-coordinate [NiX(diphos)$_2$]$^+$ (X = Cl, Br) ions. Oxidation of the latter (X = Cl) with ferric chloride generates the six-coordinate green paramagnetic d^7 nickel(III) species [NiCl$_2$(diphos)$_2$]$^+$ [μ_{eff} = 1.90 BM)[7] and with concentrated nitric acid the diamagnetic deep purple formal d^6 nickel(IV) complex [NiCl$_2$(diphos)$_2$]$^{2+}$. The nickel(III) species also undergoes a reversible, one-electron electrochemical oxidation (E = +0.80 V vs. Ag|AgClO$_4$) in acetonitrile to nickel(IV); the reversibility suggests that the integrity of the complex is retained in the two oxidation states. With cobalt, six-coordinate greenish d^7 [CoCl$_2$(diphos)$_2$]^0 (μ_{eff} = 1.97 BM) and purple d^6 [CoCl$_2$(diphos)$_2$]$^+$ (diamagnetic) have been characterized. Further oxidation to a cobalt(IV) species is not observed chemically or electrochemically. Iron(II) affords light green diamagnetic d^6 [FeCl$_2$(diphos)$_2$]^0, which is oxidized by ferric chloride to the deep red low-spin d^5 iron(III) complex [FeCl$_2$(diphos)$_2$]$^+$ (μ_{eff} = 2.22 BM). This undergoes reversible, one-electron electrochemical oxidation (E =

(1) For a partial listing of diars complexes, see F. P. Dwyer and D. P. Mellor, Ed., "Chelating Agents and Metal Chelates," Academic Press, New York, N. Y., 1964, Chapter 3.
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(5) We use the abbreviation diphos by analogy with the well-established usage of diars for $o\text{-}C_6H_4\{As(CH_3)_2\}_2$, although diphos also conventionally refers to 1,2-bis(diphenylphosphino)ethane, (C$_6$H$_5$)$_2$PCH$_2$CH$_2$P(C$_6$H$_5$)$_2$.
(6) Di- and triunivalent electrolytes exhibit molar conductance values of ~200–300 and ~340–420 ohm^{-1} cm^2 mol^{-1}, respectively, in acetonitrile.
(7) All reported magnetic susceptibilities were measured by the Gouy method at room temperature. Satisfactory elemental analyses have been obtained for all compounds described herein.

+1.03 V vs. Ag|AgClO$_4$) in acetonitrile to an iron(IV) complex [FeCl$_2$(diphos)$_2$]$^{2+}$, which can be isolated as an unstable, highly oxidizing, deep purple-brown perrhenate salt (μ_{eff} = 3.65 BM) by nitric acid oxidation of [FeCl$_2$(diphos)$_2$]$^+$. The room temperature magnetic moment is close to the theoretical value of 3.6 BM for spin-paired iron(IV).[8] The lower values of 3.17 and 2.76 BM reported[9] for [FeBr$_2$(diars)$_2$](BF$_4$)$_2$ and [FeCl$_2$(diars)$_2$](BF$_4$)$_2$, respectively, are probably due to iron-(III) impurity, not tetragonal distortion as originally suggested,[9] since we find a value of 3.35 BM for [FeCl$_2$(diars)$_2$](ReO$_4$)$_2$.

The first major difference in coordinating properties of diphos and diars occurs with manganese. Diphos reacts with anhydrous manganese(II) chloride in isopropyl alcohol to give yellow crystalline high-spin MnCl$_2$(diphos)$_2$ (μ_{eff} = 6.04 BM), whereas under the same conditions diars fails to react, and only the adduct MnCl$_2 \cdot 2i$-C$_3$H$_7$OH can be recovered.[10] Oxidation of MnCl$_2$(diphos)$_2$ with (C$_6$H$_5$)$_3$C$^+$PF$_6^-$ in dichloromethane generates the orange high-spin d^4 manganese(III) salt [MnCl$_2$(diphos)$_2$]PF$_6$ (μ_{eff} = 5.09 BM), which undergoes reversible, one-electron electrochemical oxidation (E = 0.72 V vs. Ag|AgClO$_4$) in acetonitrile. The resulting high-spin manganese(IV) d^3-complex [MnCl$_2$(diphos)$_2$]$^{2+}$ can be isolated as its crystalline orange-brown perchlorate (μ_{eff} = 3.99 BM) from nitric acid oxidation of the manganese(III) complex. These compounds are to our knowledge the first reported tertiary phosphine complexes of manganese in its higher oxidation states. Chromium(III) chloride reacts with diphos to form the reddish d^3 cation, [CrCl$_2$(diphos)$_2$]$^+$ (μ_{eff} = 3.89 BM). Electrochemical reduction of this species demonstrates the presence of a strongly reducing chromium(II) species, [CrCl$_2$(diphos)$_2$]^0; there is no chemical or electrochemical indication of a chromium(IV) complex.

The six-coordinate [M^{n+}Cl$_2$(diphos)$_2$]$^{n-2}$ complexes appear to represent one of the most extensive series of isostructural complexes presently known for the first-row transition metals. Like their diars analogs, they appear to adopt a configuration in which the chlorine atoms are mutually trans. The electronic spectra of corresponding diphos and diars complexes are virtually identical in the visible spectral region except for band shifts to higher energies in the phosphine derivatives. For example, in methanol solution the d–d transition for the green d^6 trans-[CoCl$_2$(diars)$_2$]$^+$ ion at 16,390 cm^{-1}

(ϵ 85) is shifted in the purple trans-[CoCl$_2$(diphos)$_2$]$^+$ ion to 17,790 cm^{-1} (ϵ 78). This feature reflects the expected[11] stronger ligand field of the diphosphine compared with the diarsine. In general, the diphos complexes are chemically more robust in solution than their diars analogs, a feature which is most apparent in the manganese system.

The marked similarity in the coordinating abilities of diphos and diars is further demonstrated electrochemically by the observation that the six-coordinate species, [M^{n+}Cl$_2$L$_2$]$^{n-2}$ (L = diphos, diars), undergo reversible one-electron redox reactions in acetonitrile solution by cyclic voltammetry. Electrochemically irreversible redox reactions are observed whenever there is a change in the coordination environment of the metal, e.g., in the reduction of a six-coordinate d^7 species to a five-coordinate d^8 species. The basic trend of the redox potentials appears to reflect the high relative stability of the low spin d^6 (Fe^{II}, Co^{III}, Ni^{IV}) electron configuration and suggests that the electrons are added to or removed from orbitals which do not reside predominantly on the ligands but which have considerable metal character.[12] Interestingly, the redox potentials for corresponding diphos and diars complexes are generally very similar.[13] Details will be reported in a subsequent communication.

Our results suggest that o-phenylenebis(dimethylphosphine) forms complexes in a wider range of formal oxidation states than either its arsenic analog or the more flexible bidentate ligand 1,2-bis(dimethylphosphino)ethane,[14] presumably as a consequence of the combined effects of the strong σ-donor dimethylphosphino groups and the rigid o-phenylene backbone. We are investigating these aspects and extending to other transition metals the chemistry of this most versatile di(tertiary phosphine).

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Book Reviews

Cannabis and Its Derivatives. Edited by W. D. M. Paton (University of Oxford) and J. Crown (Institute for Study of Drug Dependence). Oxford University Press, London. 1973. xii + 198 pp. £4.00.
Marijuana. Edited by R. Mechoulam (Hebrew University). Academic Press, New York, N. Y. 1973. xiv + 409 pp. $24.50.
It is most timely that these two books on Cannabis sativa and

its active ingredients are available. After years of neglect, scientific research in this area has finally again become fashionable—no doubt because of the impact cannabis abuse has had, especially in Western societies. The lay person or politician will find no easy answers to the questions of long term harm vs. benefit or legalization vs. severe restriction of pot. However, much new data are summarized in somewhat different formats in these two books.