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Comparative Study of Tertiary Phosphine and Arsine Coordination to the Transition Metals. Stabilization of High Formal Oxidation States by *o*-Phenylene-Based Chelate Ligands

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o-Phenylenebis(dimethylphosphine), *o*-$C_6H_4[P(CH_3)_2]_2$ (diphos), resembles its much studied arsenic analogue (diars) in its ability to stabilize high formal oxidation states of the transition elements. The first trivalent copper and silver complexes of a tertiary phosphine or arsine, planar $[ML_2]^{3+}$ and square-pyramidal $[MClL_2]^{2+}$ (M = Cu, Ag; L = diphos, diars), have been isolated. diphos resembles diars in forming octahedral, spin-paired, tri- and tetravalent nickel and iron complexes, *trans*-$[MCl_2L_2]^{n+}$ (M = Ni, Fe; n = 1, 2), but differs from it in forming octahedral manganese(II), -(III), and -(IV) complexes, *trans*-$[MnCl_2L_2]^{n+}$ (n = 0–2), which are the first well-characterized tertiary phosphine complexes of manganese in its normal and higher oxidation states. These and other diphos complexes of general formula $[M^{m+}X_nL_2]^{m-n}$ (M = first-, second-, or third-row transition metal; X = Cl, Br; m = 1–4; n = 0–2) have been characterized by room-temperature magnetic susceptibility measurements, electronic and far-ir spectra, conductivities, and cyclic voltammetry. diars generally forms more labile complexes than diphos but appears to stabilize five- and six-coordination in d^8 complexes more readily than diphos. The ligand field splitting parameter Dq^{xy} of 2850 cm^{-1} estimated for diphos on cobalt(III) is higher than that of most neutral donors. Many of the six-coordinate d^3–d^7 systems undergo reversible redox reactions, the potentials of which are generally only slightly affected (<100 mV) by interchange of diphos with diars, or of chloride with bromide, implying that the two group 5 ligands are about equal in their ability to stabilize high oxidation states such as nickel(IV) and iron(IV) toward reduction. In the d^8 series the redox potentials are usually irreversible, but the trends suggest that diphos stabilizes the d^8 configuration more effectively than diars. Electron-transfer processes in complexes of diphos and diars are believed to be primarily metal based, so that the ligands are "innocent".

The pioneering studies of Nyholm and co-workers since 1950 have shown *o*-phenylenebis(dimethylarsine), *o*-$C_6H_4[As(CH_3)_2]_2$ (diars), to be a most versatile ligand which is capable of stabilizing a range of common and uncommon oxidation states and stereochemistries for almost all of the transition elements.[1] We[2] recently noted that the analogous di(tertiary phosphine) *o*-$C_6H_4[P(CH_3)_2]_2$(diphos)[3-6] stabilizes high oxidation states of the first-row transition elements even more readily than diars and that many of the resulting complexes undergo reversible one-electron-transfer reactions. The latter behavior is reminiscent of the family of "suspect" or "noninnocent" ligands exemplified by the delocalized sulfur chelates, the 1,2-dithiolenes,[7] which undergo primarily ligand-based one-electron-transfer reactions. In 1968 it was suggested[8] on the basis of ESR data that the cation $[NiCl_2(diars)_2]^+$ is better regarded as a nickel(II) complex of a radical cation, although later[9] the unpaired electron was said to be in a metal $3d_{z^2}$ orbital, possibly strongly delocalized over all six donor atoms.[10] Other papers have dealt with the degree of σ and π bonding in diars complexes of five-coordinate nickel(II)[11] and of octahedral trivalent metals.[12-15]

In an effort to compare metal–phosphorus and metal–arsenic bonding in normal and high formal oxidation state complexes and to shed light on the possible "noninnocent" behavior of diphos and diars, we have made a detailed comparison of four-, five-, and six-coordinate complexes of the general type $[M^{m+}X_nL_2]^{m-n}$ (X = Cl, Br; L = diphos, diars; m = 1–4; n = 0–2), the results of which are reported here.

Experimental Section

Preparation of Compounds. diars was prepared by the published procedure, method 1.[16]

***o*-Phenylenebis(dimethylphosphine), *o*-$C_6H_4[P(CH_3)_2]_2$ (diphos).** Dioxane was refluxed over sodium metal for 20 h and distilled under an atmosphere of nitrogen. A mixture of 50.0 g of tetramethyldiphosphine disulfide[17] (269 mmol) and 40.5 g of sodium metal (1.76 mol) was added to 400 ml of the freshly distilled dioxane in a 1-l. round-bottom flask fitted with a mechanical stirrer. The reaction mixture was rapidly stirred at reflux under nitrogen for 20 h, affording a gray slurry. About one-third of the *o*-dichlorobenzene, 41.7 g total (284 mmol), was added to the stirred slurry which was cooled to 8–9 °C (just above the melting point of the solvent) with a large water bath. The mixture was allowed to warm to room temperature, and the addition was repeated twice with the remaining *o*-dichlorobenzene. The resulting brown mixture was treated with 40 ml of deoxygenated methanol, and the dioxane was removed in vacuo without heating. Deoxygenated water, 200 ml, was added to the residue, and the oily organic layer which gradually separated was transferred under an atmosphere of nitrogen to another flask and distilled in vacuo. The first low-boiling fraction distilling at ca. 35 °C at 0.05 mmHg was predominantly dimethylphenylphosphine (^1H NMR identification), the next fraction boiling at 60–70 °C was the desired diphos, 9.34 g (47.2 mmol, 17.5%) which was stored in a refrigerator under nitrogen. The colorless, oily, foul-smelling liquid generally contained small amounts of impurities which could not be readily removed by vacuum distillation. ^1H NMR (C_6D_6): τ 8.8 (t, $^2J + {}^5J$ = 4.4 Hz, P–CH_3). $^1H\{^{31}P\}$ NMR (C_6D_6): τ 8.8 (s). Several lower intensity impurity resonances were observed in the region τ 8.4–9.2; some of these were not coupled to ^{31}P and may be due to dioxane cleavage products. A low-resolution mass spectrum of the ligand gave a parent peak at 198 (mol wt 198.19) and exhibited fragment ions corresponding to successive losses of methyl groups.

All reactions involving the free diphos and diars ligands were conducted under an atmosphere of nitrogen. Analytical data for new compounds are given in Table I. Spectral and other properties are summarized in Tables II–IX.

Bis[*o*-phenylenebis(dimethylphosphine)]copper(I) Perchlorate, $[Cu(diphos)_2]ClO_4$. To a deoxygenated methanol solution containing 0.54 g of diphos (2.7 mmol) was added 0.44 g (1.3 mmol) of $[Cu(NCCH_3)_4]ClO_4$ (prepared by refluxing $Cu(ClO_4)_2{\cdot}6H_2O$ with Cu filings in acetonitrile), and the mixture refluxed for 10 min. The solvent was allowed to boil off under a nitrogen stream until a white solid began to separate. The mixture was allowed to cool with stirring and then was further cooled in an ice bath and filtered. The white crystalline powder was washed once with 1-propanol and air-dried, affording 0.31 g (41%) of $[Cu(diphos)_2]ClO_4$. The diars complex[18] was similarly prepared.

Bis[*o*-phenylenebis(dimethylarsine)]copper(III) Triperchlorate, $[Cu(diars)_2](ClO_4)_3$, and Its diphos Analogue. A suspension of 0.30 g of $[Cu(diars)_2]ClO_4$ in 5 ml of 70% aqueous perchloric acid was cooled in an ice bath and treated with ca. 15 drops of cooled concentrated nitric acid from a pipet while being rapidly stirred. The resulting bright yellow precipitate was filtered, washed successively with cold water and 1-propanol, and air-dried. The microcrystalline $[Cu(diars)_2](ClO_4)_3$, 0.295 g (78%), was refrigerated to prevent decomposition.

The corresponding $[Cu(diphos)_2](ClO_4)_3$ was similarly obtained

Table I. Analytical Data for diphos and New diars Complexes

	% calcd				% found			
Complex	C	H	M	X	C	H	M	X
$[Cu(diphos)_2]ClO_4$	42.94	5.77	11.36		42.73	5.46	11.25	
$[Cu(diphos)_2](ClO_4)_3$	31.68	4.25	8.38	14.03	31.31	4.54	8.47	13.35
$[Cu(diars)_2](ClO_4)_3$	25.72	3.45	6.80	11.39	25.06	3.98	6.10	10.21
$[CuCl(diphos)_2](ClO_4)_2$	34.60	4.65	9.15	15.32	34.10	5.11	8.74	15.70
$[CuCl(diars)_2](ClO_4)_2$	27.61	3.71	7.30	12.22	27.93	4.10	7.09	12.62
$[Ag(diphos)_2]ClO_4$	39.79	5.34	17.87		39.38	5.03	17.74	
$[Ag(diphos)_2](ClO_4)_3$	29.93	4.02			28.39[a]	4.27		
$[Ag(diars)_2](ClO_4)_3$	24.55	3.30	11.03		23.56[a]	3.55	10.55	
$[Au(diphos)_2](ClO_4)_3$	26.94	3.62	22.09		26.72	3.94	21.64	
$[Au(diars)_2](ClO_4)_3$	22.50	3.02	18.45		22.38	3.31	18.10	
$[AuCl(diphos)_2](ClO_4)_2$	29.02	3.90	23.80	12.85	28.81	4.00	23.62	12.80
$[AuCl(diars)_2](ClO_4)_2$	23.94	3.21	19.63	10.60	23.28	3.24	18.91	10.84
$[AuCl_2(diphos)_2]Cl$	34.33	4.61	28.15	15.20	34.16	4.45	27.74	14.69
$[AuCl_2(diars)_2]Cl$	27.44	3.68	22.50	12.15	27.31	4.23	22.08	12.13
$[Ni(diphos)_2](ClO_4)_2$	36.73	4.93	8.98		36.83	5.12	9.05	
$[NiCl(diphos)_2]ClO_4$	40.72	5.47	9.95	12.02	40.48	5.57	9.93	11.84
$[NiCl_2(diphos)_2]ClO_4$	38.41	5.16	9.39	17.01	38.60	5.43	9.59	17.17
$[NiBr_2(diphos)_2]ClO_4$	33.63	4.52		27.33	34.00	4.53		27.20
$[NiCl_2(diphos)_2](ClO_4)_2$	33.14	4.45			32.47	4.39		
$[Pd(diphos)_2](ClO_4)_2$	34.23	4.60			34.00	4.59		
$[PdCl_2(diphos)_2](ClO_4)_2$	31.09	4.18	13.77	18.36	30.25	4.56	13.69	18.04
$[Pt(diphos)_2](ClO_4)_2$	30.39	4.08	24.68		30.15	4.19	24.41	
$[PtCl_2(diphos)_2](ClO_4)_2$	27.89	3.75	22.65	16.47	27.82	3.99	22.58	16.67
$CoCl_2(diphos)_2$	45.65	6.13	11.20	13.48	45.52	6.30	11.00	13.20
$[CoCl_2(diphos)_2]ClO_4$	38.39	5.16	9.42	17.00	39.02	5.28	9.69	17.47
$[CoBr_2(diphos)_2]ClO_4$	33.62	4.51			33.82	4.38		
$[RhCl_2(diphos)_2]ClO_4$	35.87	4.82		15.88	35.68	4.96		15.90
$[IrCl_2(diphos)_2]ClO_4$	31.65	4.25		14.01	31.45	4.47		13.90
$[IrCl_2(diars)_2]ClO_4$	25.70	3.45			26.11	4.39		
$FeCl_2(diphos)_2$	45.92	6.17	10.68	13.55	45.30	6.35	10.69	13.29
$[FeCl_2(diphos)_2]ClO_4$	38.58	5.18	8.97		38.71	5.26	9.70	
$[FeBr_2(diphos)_2]BF_4$	34.37	4.62		22.87	34.35	4.33		22.18
$[FeCl_2(diphos)_2](ReO_4)_2$	23.47	3.15	5.46[b]	6.93	25.10[a]	3.54	5.40	7.36
$[FeCl_2(diars)_2](ReO_4)_2$	20.03	2.69	4.66[b]	5.91	21.07[a]	2.94	4.80	5.72
$RuCl_2(diphos)_2$	42.27	5.68			41.86	5.68		
$[RuCl_2(diphos)_2]ClO_4$	35.97	4.83		15.93	36.05	5.18		16.13
$OsCl_2(diphos)_2$	36.54	4.91			36.80	4.97		
$[OsCl_2(diphos)_2]ClO_4$	31.74	4.26		14.05	31.55	3.96		14.13
$MnCl_2(diphos)_2$	46.00	6.18	10.52	13.58	46.16	6.33	11.07	14.05
$[MnCl_2(diphos)_2]PF_6$	36.00	4.84	8.23	10.63	35.73	5.18	8.14	10.41
$[MnBr_2(diphos)_2]ClO_4$	33.81	4.54			34.02	4.88		
$[MnCl_2(diphos)_2](ClO_4)_2$	33.31	4.47	7.62		32.33	4.39	7.92	
$[ReCl_2(diphos)_2]ClO_4$	31.90	4.28		14.13	32.14	4.73		14.32
$[ReCl_2(diars)_2]ClO_4$	25.87	3.47		11.45	26.09	4.02		11.79
$[CrCl_2(diphos)_2]ClO_4$	38.82	5.21	8.40	17.19	38.61	5.56	8.23	16.84
$[CrBr_2(diphos)_2]ClO_4$	33.95	4.56			34.45	4.75		

[a] The instabilities at the strongly oxidizing Ag(III) and Fe(IV) complexes made purification impractical and the analytical figures reflect this. [b] Fe analysis.

as very pale yellow crystals. These complexes may be recrystallized by dissolving at room temperature in the minimum quantity of concentrated nitric acid, adding concentrated perchloric acid, and refrigerating.

Caution! Extreme care must be taken to avoid scratching or grinding these explosive perchlorate salts.

Bis[*o*-phenylenebis(dimethylarsine)]chlorocopper(III) Diperchlorate, $[CuCl(diars)_2](ClO_4)_2$, and Its diphos Analogue. $[Cu(diars)_2](ClO_4)_3$, 0.135 g, was dissolved in the minimum quantity of concentrated nitric acid (ca. 1 ml) at room temperature. The resulting yellow solution was cooled in an ice bath and concentrated hydrochloric acid was added dropwise with stirring until no further deepening of the color took place (ca. 0.25 ml). Cooled dilute aqueous perchloric acid (ca. 4 ml) was added dropwise to this deep red solution producing an orange precipitate which was filtered, washed with water, and air-dried; the yield was 0.087 g (71%) of $[CuCl(diars)_2](ClO_4)_2$. The corresponding, similarly prepared, bright yellow $[CuCl(diphos)_2](ClO_4)_2$ was much more stable in solution than its diars analogue; this complex could be crystallized from cold, concentrated HCl by the addition of $HClO_4$ and refrigerating, whereas the diars complex rapidly decomposed in this medium.

Bis[*o*-phenylenebis(dimethylphosphine)]silver(I) Perchlorate, $[Ag(diphos)_2]ClO_4$, Bis[*o*-phenylenebis(dimethylphosphine)]silver(III) Triperchlorate, $[Ag(diphos)_2](ClO_4)_3$, and Their diars Analogues. These were obtained similarly to the corresponding copper compounds starting from $[AgL_2]ClO_4$ salts.[19] The filtered $[Ag(diars)_2](ClO_4)_3$ was washed only with 1-propanol, as it decomposed on contact with water. Both complexes decomposed in the presence of aqueous chloride ion. Chloride ion adducts were observed only with the Ag^{III}–diphos system in aprotic solvents (e.g., acetonitrile with $(C_2H_5)_4NCl$) but these were not isolated due to their instability (see text). The $[AgL_2](ClO_4)_3$ salts were refrigerated to prevent decomposition.

Bis[*o*-phenylenebis(dimethylphosphine)]chlorogold(III) Diperchlorate, $[AuCl(diphos)_2](ClO_4)_2$, and Its diars Analogue. A stirred solution of 0.35 g (1.77 mmol) of diphos in methanol (20 ml) was treated dropwise at room temperature with a methanol solution (ca. 10 ml) containing 0.34 g (0.85 mmol) of $NaAuCl_4 \cdot 2H_2O$. The resulting clear, pale yellow solution was refluxed for 5 min, 2 ml of 70% $HClO_4$ was added, and the mixture was refluxed another 5 min and allowed to cool. The white, crystalline precipitate of crude $[AuCl(diphos)_2](ClO_4)_2$ was filtered and washed successively with 1-propanol and water. After drying in air, the yield was 0.345 g (49%). The material was purified by dissolving in the minimum quantity of concentrated HCl, adding 70% $HClO_4$, and refrigerating. The resulting precipitate was filtered, washed with 1-propanol, and dried in vacuo to give a pure white, crystalline powder. Subsequent reactions and physical measurements were carried out on this purified material. The corresponding complex $[AuCl(diars)_2](ClO_4)_2$ was prepared and

Table II. Conductance Data for d^8 ML_2 Complexes[a]

Compd	Solvent	Λ_M, $cm^2\ \Omega^{-1}\ mol^{-1}$ L = diphos	L = diars
$[CuL_2](ClO_4)_3$	CH_3CN	360	*b*
$[CuClL_2](ClO_4)_2$	CH_3CN	286	*b*
$[AgL_2](ClO_4)_3$	CH_3CN	350	*b*
$[AuL_2](ClO_4)_3$	CH_3CN	338	292
$[AuClL_2](ClO_4)_2$	CH_3CN	271	297
$[AuCl_2L_2]Cl$	CH_3CN	127	134
	CH_3OH	115	94
	H_2O	355	248
$NiCl_2L_2$	CH_3CN	127	133
	CH_3OH	75	82
	H_2O	178	153
$PdCl_2L_2$	CH_3CN	135	138
	CH_3OH	126	117
$PtCl_2L_2$	CH_3CN	152	146
	CH_3OH	157	149

[a] Obtained on freshly prepared ~5 × 10^{-4} M solutions at room temperature. Molar conductance values (all in $cm^2\ \Omega^{-1}\ mol^{-1}$) for 1:1 electrolytes are ~120–160 in CH_3CN, ~80–115 in CH_3OH, and ca. 100 in H_2O; for 2:1 electrolytes, ~220–300 in CH_3CN, 160–200 in CH_3OH, and ~230–260 in H_2O; for 3:1 electrolytes, ~340–420 in CH_3CN and ~400–430 in H_2O. These data fromW. J. Geary, *Coord. Chem. Rev.*, 7, 81 (1971), and T. Moeller, "Inorganic Chemistry", Wiley, New York, N.Y., 1952, Chapter 7, p 232. [b] Solutions decomposed before measurements could be taken.

Table III. Electrochemical Data for the Copper and Nickel Group $[ML_2]^{m+}$ Complexes[a]

$$\begin{array}{lcl}
d^8 & & d^{10} \\
[NiL_2]^{2+} & \xrightarrow{(-1.16),\ (-0.90)} & Ni\ (0)^b \\
[PdL_2]^{2+} & \xrightarrow{(-1.50),\ (-1.16)} & Pd\ (0) \\
[PtL_2]^{2+} & \xrightarrow{(-1.66),\ (-1.44)} & Pt\ (0) \\
[CuL_2]^{3+} & \xrightarrow{(+0.11),\ (+0.32)} & [CuL_2]^+ \\
[AgL_2]^{3+} & \xrightarrow{(-0.03),\ (+0.26)} & [AgL_2]^+ \\
[AuL_2]^{3+} & \xrightarrow{(-0.45),\ (-0.17)} & [AuL_2]^+
\end{array}$$

[a] Reduction potentials (V vs. $Ag/AgClO_4$ in CH_3CN) are designated atop arrows: the first for L = diphos, the second for L = diars. All couples are irreversible, indicated by potentials in parentheses. Addition of chloride ion to the d^8 complexes results in a 100–350-mV cathodic shift of the reduction potentials; e.g., the Au(III) → Au(I) potentials are (−0.80 V) and (−0.55 V) for L = diphos and diars, respectively, in the presence of a large excess of $(C_2H_5)_4NCl$. [b] Reduced nickel group complexes are presumed to be of the $[ML_2]^0$ type.

purified by the same procedure. Crystallization from $HCl–HClO_4$ gave initially white crystals which apparently lost solvent on washing and vacuum drying to form a pale yellow powder. ^1H NMR (CD_3CN): τ 7.41 (s, $As–CH_3$).

Bis[*o*-phenylenebis(dimethylphosphine)]gold(III) Triperchlorate, $[Au(diphos)_2](ClO_4)_3$, and Its diars Analogue. The purified $[AuCl(diphos)_2](ClO_4)_2$ salt, 0.132 g, was dissolved in the minimum amount of concentrated HNO_3 at room temperature and flushed with nitrogen to remove nitrous fumes. Concentrated $HClO_4$, ca. 3 ml, was added and the mixture allowed to cool in a refrigerator. Pure white, crystalline $[Au(diphos)_2](ClO_4)_3$, 0.104 g (75%), was obtained after filtering and washing with 1-propanol. The analogous pure white $[Au(diars)_2](ClO_4)_3$[20] was prepared similarly.

Bis[*o*-phenylenebis(dimethylphosphine)]dichlorogold(III) Chloride, $[AuCl_2(diphos)_2]Cl$, and Its diars Analogue. A solution of 0.053 g of purified $[AuCl(diphos)_2](ClO_4)_2$ in the minimum quantity of hot acetonitrile was treated with an excess of dry $(C_2H_5)_4NCl$. Pale yellow crystals of $[AuCl_2(diphos)_2]Cl$ which separated on continued heating were filtered and washed with dry acetonitrile; yield 0.016 g (36%). To obtain pure $[AuCl_2(diars)_2]Cl$, 0.120 g of purified $[AuCl(diars)_2](ClO_4)_2$ was dissolved in acetonitrile and cooled in ice, and excess $(C_2H_5)_4NCl$ in CH_3CN was added dropwise to give a yellow precipitate. The mixture was stored in the refrigerator for 20 h, filtered, and washed with acetonitrile to afford 0.070 g (67%) of bright yellow microcrystalline $[AuCl_2(diars)_2]Cl$.

Bis[*o*-phenylenebis(dimethylphosphine)]nickel(II) Diperchlorate, $[Ni(diphos)_2](ClO_4)_2$, Bis[*o*-phenylenebis(dimethylphosphine)]chloronickel(II) Perchlorate, $[NiCl(diphos)_2]ClO_4$, Bis[*o*-phenylenebis(dimethylphosphine)]dichloronickel(II), $NiCl_2(diphos)_2$, and Their diars Analogues. $[Ni(diphos)_2](ClO_4)_2$ was obtained in high yield by refluxing $Ni(ClO_4)_2 \cdot 6H_2O$ with 2 equiv of diphos in ethanol. Bright yellow crystals of the complex were filtered and washed with ethanol and then with water. The complex could be crystallized from an acetonitrile/1-propanol mixture. Orange, crystalline $[Ni(diars)_2](ClO_4)_2$[21] was obtained similarly. The complex $[NiCl(diphos)_2]ClO_4$ was conveniently obtained as bright orange crystals by treatment of solid $[Ni(diphos)_2](ClO_4)_2$ with concentrated hydrochloric acid at room temperature. The deep red $[NiCl(diars)_2]ClO_4$[21] was obtained by adding a few drops of concentrated HCl to a refluxing suspension of the diperchlorate salt in ethanol. ^1H NMR (CD_3CN): τ 8.09 (s, $As–CH_3$). The dichloro complexes $NiCl_2L_2$ were prepared quantitatively from the corresponding diperchlorates in acetonitrile solution by the addition of excess $(C_2H_5)_4NCl$. The insoluble, crystalline, orange $NiCl_2(diphos)_2$ and brown $NiCl_2(diars)_2$[22] were filtered, washed with acetone, and dried in vacuo.

Bis[*o*-phenylenebis(dimethylphosphine)]dichloro- and -dibromonickel(III) Perchlorates, $[NiX_2(diphos)_2]ClO_4$ (X = Cl, Br), and Their diars Analogues. A mixture of 0.314 g (0.48 mmol) of $[Ni(diphos)_2](ClO_4)_2$ and 0.165 g (0.61 mmol) of $FeCl_3 \cdot 6H_2O$ was refluxed in 20 ml of methanol containing 6 ml of water and 2 ml of concentrated HCl and then treated dropwise with ca. 2 ml of 70% $HClO_4$. On cooling of the mixture in a refrigerator, pale grass green crystals of $[NiCl_2(diphos)_2]ClO_4$ separated. These were washed with water and air-dried; yield 0.273 g, 92%. The same procedure was used to prepare light brown $[NiCl_2(diars)_2]ClO_4$.[22] The corresponding dibromo complexes were obtained by refluxing the chloro salts in methanol with an excess of lithium bromide. Dilute $HClO_4$ was added, the methanol was boiled off until crystals began to form, and the mixtures were allowed to cool, affording nearly quantitative yields of reddish brown $[NiBr_2(diphos)_2]ClO_4$ and orange $[NiBr_2(diars)_2]ClO_4$.

Bis[*o*-phenylenebis(dimethylphosphine)]dichloronickel(IV) Diperchlorate, $[NiCl_2(diphos)_2](ClO_4)_2$, and Its diars Analogue. The nickel(III) salt $[NiCl_2L_2]ClO_4$ was dissolved in the minimum quantity of cold (0 °C) concentrated nitric acid, forming an intensely colored solution. Cold, dilute $HClO_4$ was then added dropwise until the crystalline complex, deep blue $[NiCl_2(diars)_2](ClO_4)_2$[23] or deep violet $[NiCl_2(diphos)_2](ClO_4)_2$, precipitated. Another procedure for preparing crystalline nickel(IV) complexes is chlorine oxidation of the nickel(II) species. Dry chlorine was bubbled through a suspension of 0.10 g of $[Ni(diars)_2](ClO_4)_2$ in carbon tetrachloride until the solid turned dark (~2 min). The mixture was stirred for 5 min and filtered, and the intense blue crystals were washed with water. The yield of $[NiCl_2(diars)_2](ClO_4)_2$ was 0.085 g (79%). Deep maroon crystals of $[NiCl_2(diphos)_2](ClO_4)_2$ were similarly obtained.

Bis[*o*-phenylenebis(dimethylphosphine)]palladium(II) or -platinum(II) Diperchlorate, $[M(diphos)_2](ClO_4)_2$, Bis[*o*-phenylenebis(dimethylphosphine)]chloropalladium(II) or -platinum(II) Perchlorate, $[MCl(diphos)_2]ClO_4$, Bis[*o*-phenylenebis(dimethylphosphine)]dichloropalladium(II) or -platinum(II), $MCl_2(diphos)_2$ (M = Pd, Pt), and Their diars Analogues. Disodium tetrachloropalladate trihydrate, 0.50 g (1.43 mmol), in a small quantity of water was added to a methanol solution (ca. 50 ml) containing 0.73 g (3.69 mmol) of diphos. The initial orange-tinged precipitate dissolved on refluxing to form a pale yellow solution. The addition of 2 ml of 70% $HClO_4$ gave a pale yellow precipitate which was filtered, washed with water, and crystallized from hot methanol containing 2 ml of concentrated HCl to give 0.441 g (48%) of crude $[PdCl(diphos)_2]ClO_4$ as pale yellow plates. This material was converted to the diperchlorate salt by dissolving in hot water, adding a few drops of perchloric acid, and cooling, whereupon white crystals of $[Pd(diphos)_2](ClO_4)_2$ separated. Pale yellow crystalline $PdCl_2(diphos)_2$ precipitated from acetonitrile solutions of either of the perchlorate salts by treatment with an excess of $(C_2H_5)_4NCl$. The corresponding diars complexes,[24] yellow $[PdCl(diars)_2]ClO_4$ and $PdCl_2(diars)_2$ and white $[Pd(diars)_2](ClO_4)_2$, were similarly obtained. The analogous platinum(II) systems were prepared from $Na_2PtCl_4 \cdot 4H_2O$ using the same procedure in aqueous methanol containing a small amount of hydrochloric acid; the crude perchlorate salts were purified as the diperchlorates white [Pt(di-

Table IV. Electrochemical Data for the Cobalt and Nickel Group $[\mathrm{M}^{m+}\mathrm{X}_n\mathrm{L}_2]^{m-n}$ Complexes[a]

Chloro Complexes

d^6 d^7 d^8

$$[\mathrm{CoCl_2L_2}]^+ \xleftrightarrow{-0.66,\,-0.58} [\mathrm{CoCl_2L_2}]^0 \xrightarrow{(\sim-1.4),\,(\sim-1.4)} \mathrm{Co(I)}$$

$$[\mathrm{RhCl_2L_2}]^+ \xrightarrow{\qquad(-1.14),\,(-1.08)\qquad} \mathrm{Rh(I)}$$

$$[\mathrm{IrCl_2L_2}]^+ \xrightarrow{\qquad(-1.76),\,(-1.64)\qquad} \mathrm{Ir(I)}$$

$$[\mathrm{NiCl_2L_2}]^{2+} \xleftrightarrow{+0.80,\,+0.84} [\mathrm{NiCl_2L_2}]^+ \xrightarrow{(-0.11),^b\,(-0.26)^b} [\mathrm{NiClL_2}]^+$$

$$[\mathrm{PdCl_2L_2}]^{2+} \xrightarrow{\qquad(+0.34),\,(\sim+0.32)^c\qquad} [\mathrm{PdClL_2}]^+$$

$$[\mathrm{PtCl_2L_2}]^{2+} \xrightarrow{\qquad(-0.04),\,(-0.06)\qquad} [\mathrm{PtClL_2}]^+$$

Bromo Complexes

d^6 d^7 d^8

$$[\mathrm{CoBr_2L_2}]^+ \xleftrightarrow{-0.51,\,-0.46} [\mathrm{CoBr_2L_2}]^0$$

$$[\mathrm{NiBr_2L_2}]^{2+} \xleftrightarrow{+0.77,\,+0.80} [\mathrm{NiBr_2L_2}]^+ \xrightarrow{(+0.03),^b\,(-0.11)^b} [\mathrm{NiBrL_2}]^+$$

[a] Reduction potentials (V *vs.* Ag/AgClO$_4$ in CH$_3$CN) in the order L = diphos, L = diars are designated atop arrows. Parentheses indicate irreversible couples; ~ represents highly irreversible couples. Reduced cobalt group complexes are presumed to be of the $[\mathrm{ML_2}]^+$ type. [b] Carried out in the presence of excess halide ion; see ref 63 and Figure 1. [c] Pd(IV) species decomposed in the electrolyte medium; reduction potential estimated from oxidation potential.

Table V. Electrochemical Data for the Chromium, Manganese, and Iron Group $[\mathrm{M}^{m+}\mathrm{Cl_2L_2}]^{m-2}$ Complexes[a]

Chloro Complexes

d^3 d^4 d^5 d^6

$$[\mathrm{CrCl_2L_2}]^+ \xleftrightarrow{-0.99,\,(-0.75)^b} [\mathrm{CrCl_2L_2}]^0$$

$$[\mathrm{MnCl_2L_2}]^{2+} \xleftrightarrow{+0.78,\,\ldots} [\mathrm{MnCl_2L_2}]^+ \xrightarrow{(\sim-0.6),\,\ldots} [\mathrm{MnCl_2L_2}]^{0\,c}$$

$$\mathrm{Re(IV)}^c \xleftarrow{(+0.97),^d\,(+0.96)^d} [\mathrm{ReCl_2L_2}]^+ \xleftrightarrow{-0.65,\,-0.71} [\mathrm{ReCl_2L_2}]^0 \xleftrightarrow{-1.82,\,-1.84} [\mathrm{ReCl_2L_2}]^-$$

$$[\mathrm{FeCl_2L_2}]^{2+} \xleftrightarrow{+1.09,\,+1.07} [\mathrm{FeCl_2L_2}]^+ \xleftrightarrow{-0.24,\,(-0.15)^b} [\mathrm{FeCl_2L_2}]^{0\,e}$$

$$\mathrm{Ru(IV)}^c \xleftarrow{(1.24),^d\,(1.28)^d} [\mathrm{RuCl_2L_2}]^+ \xleftrightarrow{+0.20,\,+0.17} [\mathrm{RuCl_2L_2}]^0$$

$$[\mathrm{OsCl_2L_2}]^{2+} \xleftrightarrow{+1.12,^f\,+1.13} [\mathrm{OsCl_2L_2}]^+ \xleftrightarrow{-0.09,\,-0.15} [\mathrm{OsCl_2L_2}]^0$$

Bromo Complexes

d^3 d^4 d^5 d^6

$$[\mathrm{CrBr_2L_2}]^+ \xleftrightarrow{-0.97,\,(-0.76)^b} [\mathrm{CrBr_2L_2}]^0$$

$$[\mathrm{MnBr_2L_2}]^{2+} \xleftrightarrow{+0.72,\,\ldots} [\mathrm{MnBr_2L_2}]^+ \xrightarrow{(\sim0.4),\,\ldots} [\mathrm{MnBr_2L_2}]^0$$

$$[\mathrm{FeBr_2L_2}]^{2+} \xleftrightarrow{+1.04,\,+1.02} [\mathrm{FeBr_2L_2}]^+ \xleftrightarrow{-0.21,\,(-0.14)^b} [\mathrm{FeBr_2L_2}]^0$$

[a] Reduction potentials (V *vs.* Ag/AgClO$_4$ in CH$_3$CN) in the order L = diphos, L = diars are designated atop arrows. Parentheses indicate irreversible couples; ~ represents highly irreversible couples. [b] Electrode coated. [c] Decomposes in the electrolyte medium. [d] Oxidation potentials reported. [e] The $[\mathrm{FeCl_2(diphos)_2}]^0$ complex undergoes an irreversible one-electron reduction to an Fe(I) species at *ca.* −1.23 V. [f] Run at −30 °C; irreversible couple at 23 °C.

Table VI. Electronic Spectral Data for the Copper Group d^8 ML$_2$ Complexes[a]

Complex	M	Soln (CH$_3$CN) color and λ, nm ($\epsilon_{\max}$)		Solid-state (Nujol mull) color and λ, nm	
		L = diphos	L = diars	L = diphos	L = diars
$[\mathrm{ML_2}]^{3+}$	Cu	Pale yellow CT <380	*b*	Pale yellow 325	Yellow 353
	Ag	Pale yellow CT <380	*b*	Pale yellow 322	Yellow 340
	Au	Colorless CT <320	Colorless CT <360		
$[\mathrm{MClL_2}]^{2+\,c}$	Cu	*b*	*b*	Yellow 384	Orange 417
	Ag	Yellow sh 420 (550)	*b*	*d*	*d*
	Au	Colorless sh 325 (550)	Pale yellow sh 370 (430)		
$[\mathrm{MCl_2L_2}]^{+\,c}$	Cu	*b*	*b*	Red-orange[d]	*d*
	Ag	Red-orange 482 (>120)[e]	*b*	*d*	*d*
	Au	Pale yellow 354 (330)	Yellow 413 (270)		

[a] Solutions run at room temperature on perchlorate salts; sh = shoulder; CT = higher energy charge transfer and intraligand transitions and are not reported in these data. [b] Compound decomposes in the solvent. [c] From ML$_2$$^{3+}$ solutions by adding requisite amounts of Cl$^-$ ion as (C$_2$H$_5$)$_4$NCl; these spectra are identical with those of the pure $[\mathrm{MClL_2}](\mathrm{ClO_4})_2$ and $[\mathrm{MCl_2L_2}]\mathrm{Cl}$ salts, where available. [d] Not isolated as solids. [e] Rapidly decomposing during measurement.

Table VII. Electronic Spectral Data for the Nickel Group d^8 ML_2 Complexes[a]

Complex	M	Soln (H_2O) color and λ, nm (ϵ_{max})		Soln (CH_3CN) color and λ, nm (ϵ_{max})		Solid-state (Nujol mull) color and λ, nm (rel absorbance)	
		L = diphos	L = diars	L = diphos	L = diars	L = diphos	L = diars
$[ML_2]^{2+}$	Ni	Pale yellow	Pale orange	Yellow	Orange	Yellow	Yellow-orange
		370 (600)	441 (630)[b]	374 (1200)	442 (1200)	sh 350 (0.75)	415 (0.73)
		323 (3000)	324 (3250)	310 (2150)			380 (0.71)
	Pd	Colorless	Colorless	Colorless	Colorless	325 (1.8)	323 (1.90)
		CT <280	CT <300	CT <280	CT <300		
	Pt	Colorless	Colorless	Colorless	Colorless		
		298 (800)	sh 293 (850)	296 (820)	sh 290 (1000)		
$[MClL_2]^{+}$ [c]	Ni	Orange	Red	Orange	Red	Orange	Red-brown
		381 (1000)	452 (970)	395 (1150)	477 (1100)	sh 490 (0.37)	
		320 (4300)	319 (4700)	323 (3100)	sh 320 (3700)	400 (1.00)	473 (0.3)
						357 (1.45)	345 (0.42)
	Pd	Colorless	Colorless	Pale yellow	Yellow		
		d	*d*	341 (430)	393 (350)		
	Pt	Colorless	Colorless	Colorless	Pale yellow		
		d	*d*		sh 330 (800)		
				302 (9200)	298 (10 000)		
$[MCl_2L_2]^0$	Ni					Orange	Red-brown
						sh 480 (0.35)	
						sh 400 (0.90)	471 (0.50)
						360 (1.61)	352 (0.87)
	Pd					Pale yellow	Yellow
						sh 360	401
	Pt					Colorless	Pale yellow
							sh 320 (0.75)
						295	295 (0.85)

[a] Solutions run at room temperature on perchlorate salts unless otherwise stated; sh = shoulder; CT = higher energy charge transfer and intraligand transitions, usually not reported in these data. [b] BF_4^- salt. [c] From ML_2^{2+} solutions containing ~3×10^{-2} M LiCl in water or 4×10^{-3} M $(C_2H_5)_4NCl$ in CH_3CN; these spectra are identical with those run on the pure $[MClL_2]ClO_4$ salts. [d] No change from ML_2^{2+} spectrum.

Table VIII. Magnetic Susceptibility Data on Paramagnetic *trans*-MX_2L_2 Complexes

Electron config	Compd	Temp, K	$10^6\chi_M$, cgsu	μ_{eff}, μ_B
d^7	$CoCl_2(diphos)_2$	299	1 610	1.97
	$[NiCl_2(diphos)_2]ClO_4$	299	1 493	1.90
d^5	$MnCl_2(diphos)_2$	296	15 330	6.04
	$[FeCl_2(diphos)_2]ClO_4$	298	2 056	2.22
				(2.20)[a]
	$[RuCl_2(diphos)_2]^+$			(2.20)[a]
	$[OsCl_2(diphos)_2]^+$			(1.94)[a]
d^4	$[MnCl_2(diphos)_2]ClO_4$	296	3 621	3.10
	$[MnBr_2(diphos)_2]ClO_4$	296	3 727	3.14
	$[ReCl_2(diphos)_2]ClO_4$	298	1 899	2.14
	$[ReCl_2(diars)_2]ClO_4$	298	1 764	2.06
	$[FeCl_2(diphos)_2](ReO_4)_2$	297	5 562	3.65
	$[FeCl_2(diars)_2](ReO_4)_2$	297	4 781	3.38
d^3	$[CrCl_2(diphos)_2]ClO_4$	296	6 348	3.89
	$[MnCl_2(diphos)_2](ClO_4)_2$	297	6 646	3.99

[a] Values in parentheses are the average *g* values, *g*, from the ESR spectra of glasses at 100 K[49].

phos)$_2$]$(ClO_4)_2$ and $[Pt(diars)_2](ClO_4)_2$.[21] White $PtCl_2(diphos)_2$ and pale yellow $PtCl_2(diars)_2$[21] were obtained from acetonitrile.

Bis[*o*-phenylenebis(dimethylphosphine)]dichloropalladium(IV) and -platinum(IV) Diperchlorates, $[MCl_2(diphos)_2](ClO_4)_2$, and Their diars Analogues. These were prepared by dissolving the $[ML_2](ClO_4)_2$ or MCl_2L_2 salts in the minimum quantity of cold (0 °C) concentrated nitric acid in the presence of a few drops of concentrated HCl and slowly adding cold dilute $HClO_4$ until the crystalline complexes precipitated. $[PdCl(diphos)_2]ClO_4$, 0.160 g, was converted to bright yellow $[PdCl_2(diphos)_2](ClO_4)_2$, 0.160 g, in 83% yield. The orange $[PdCl_2(diars)_2](ClO_4)_2$,[21] pale yellow $[PtCl_2(diars)_2](ClO_4)_2$,[21] and white $[PtCl_2(diphos)_2](ClO_4)_2$ were similarly isolated.

Bis[*o*-phenylenebis(dimethylphosphine)]dichlorocobalt(II), $CoCl_2(diphos)_2$, Bis[*o*-phenylenebis(dimethylphosphine)]dichloro- and -dibromocobalt(III) Perchlorates, $[CoX_2(diphos)_2]ClO_4$ (X = Cl, Br), and Their diars Analogues. A mixture of 0.40 g (1.68 mmol) of $CoCl_2 \cdot 6H_2O$ and 0.66 g (3.33 mmol) of diphos was refluxed in ca. 30 ml of methanol. Greenish crystals of $CoCl_2(diphos)_2$, 0.248 g (28%), separated on cooling, were filtered in a Schlenk apparatus, and were washed with deoxygenated 1-propanol. The filtrate was treated with ca. 1 ml of concentrated HCl and 1 ml of 70% $HClO_4$ and stirred in the air. Light purple $[CoCl_2(diphos)_2]ClO_4$ separated, 0.575 g (55%), and was recrystallized from CH_3CN/1-propanol by slow evaporation. ^1H NMR (CD_3CN): τ 2.00 (1, m, aromatic H), 8.06 (3, m, P–CH_3). The Co–diars systems[25] were obtained similarly. The green bromocobalt(III) complexes were prepared by refluxing the chloro derivatives with a large excess of lithium bromide in methanol.

Bis[*o*-phenylenebis(dimethylphosphine)]dichlororhodium(III) Perchlorate, $[RhCl_2(diphos)_2]ClO_4$, and Its diars Analogue. Trisodium hexachlororhodate(III), 0.40 g (1.04 mmol), was refluxed in ca. 40 ml of 2-propanol containing 5 ml of water with 0.40 g (2.02 mmol) of diphos. The resulting yellow solution was evaporated to dryness in vacuo, the residue extracted with boiling water (ca. 15 ml) and filtered, and the filtrate treated with concentrated HCl (5 ml). On cooling, white, crystalline *trans*-$[RhCl_2(diphos)_2]Cl$ separated and was converted to the pale yellow perchlorate salt (0.030 g, 4.4%). ^1H NMR (CD_3CN): τ 2.04 (1, m, aromatic H), 8.02 (3, m, P–CH_3). The formation of substantial amounts of the unisolated cis isomer under these conditions may account for the low yield of this trans rhodium(III) complex. The analogous yellow *trans*-$[RhCl_2(diars)_2]^+$ complex was prepared in 37% yield by the published procedure[26] and was precipitated as the crystalline perchlorate directly by treatment of the reaction solution with $HClO_4$.

Bis[*o*-phenylenebis(dimethylarsine)]dichloroiridium(III) Perchlorate, $[IrCl_2(diars)_2]ClO_4$. Bis(cyclooctene)chloroiridium(I) (0.27 g, 0.60 mmol) was refluxed with 0.43 g (1.50 mmol) of diars for 1 min in ca. 30 ml of methanol. The pale yellow solution was cooled in ice and dry chlorine was bubbled in under a blanket of nitrogen until the solution turned nearly colorless. After removal of the solvent in vacuo, the residue was extracted with boiling water and filtered. On cooling, pale yellow *trans*-$[IrCl_2(diars)_2]Cl$ crystallized from the filtrate. This material was converted to the perchlorate salt *trans*-$[IrCl_2(diars)_2]ClO_4$[27] and crystallized from CH_3CN/1-propanol as pale yellow plates (0.22 g, 39%). ^1H NMR (CD_3CN): τ 2.07 (1, m, aromatic H), 8.07 (3, s, As–CH_3).

Bis[*o*-phenylenebis(dimethylphosphine)]dichloroiridium(III) Perchlorate, $[IrCl_2(diphos)_2]ClO_4$. The reaction of 0.46 g (1.03 mmol) of bis(cyclooctene)chloroiridium(I) with 0.44 g (2.22 mmol) of diphos in methanol at room temperature gave a deep red-orange solution.

This was cooled to 0 °C and treated with dry chlorine as above and the solvent was removed in vacuo. The residue was taken up in boiling aqueous methanol, and the cooled solution was treated with decolorizing charcoal and filtered through filter paper. The solvent was removed in vacuo and the pale yellow residue was washed with hot toluene and dissolved in hot methanol/water. The methanol was removed from the filtered solution with a rotary evaporator and the remaining aqueous portion (ca. 10 ml) treated with concentrated HCl. The resulting precipitate of the crude trans iridium(III) chloride salt was recrystallized from a small volume of hot aqueous solution containing HCl as pale yellow needles, which were converted by means of $HClO_4$ to white *trans*-$[IrCl_2(diphos)_2]ClO_4$ (0.190 g, 24%). ^1H NMR (CD_3CN): τ 2.05 (1, m, aromatic H), 8.01 (3, m, P–CH_3).

Bis[*o*-phenylenebis(dimethylphosphine)]dichloroiron(II), $FeCl_2(diphos)_2$, Bis[*o*-phenylenebis(dimethylphosphine)]dichloro- and -dibromoiron(III) Perchlorate or Perrhenate, $[FeX_2(diphos)_2]YO_4$ (X = Cl, Br; Y = Cl, Re), and Their diars Analogues. A hot 2-propanol solution (ca. 30 ml) of 0.20 g of $FeCl_2{\cdot}4H_2O$ (1.01 mmol) was treated with 0.32 g (1.62 mmol) of diphos. After refluxing for 20 min, the mixture was cooled in ice and the pale green, crystalline $FeCl_2(diphos)_2$, 0.18 g (42%), filtered in a Schlenk apparatus and washed with deoxygenated 2-propanol. The iron(II) complex was readily oxidized with 1 equiv of hydrated ferric chloride in aqueous acetone or in methanol. The resulting deep red $[FeCl_2(diphos)_2]^+$ complex was isolated as the purple-red perchlorate or perrhenate salts (by means of $HReO_4$) in 75% yield. The corresponding bright yellow $FeCl_2(diars)_2$ and red $[FeCl_2(diars)_2]ClO_4$[28] were similarly obtained. Bromo derivatives were obtained by refluxing the chloro complexes in methanol with hydrobromic acid (L = diars) or with lithium bromide (L = diphos).

Bis[*o*-phenylenebis(dimethylphosphine)]dichloroiron(IV) Diperrhenate, $[FeCl_2(diphos)_2](ReO_4)_2$, and Its diars Analogue. The very unstable iron(IV) cations were best handled as their nonexplosive perrhenate salts. To a slurry of 0.194 g (0.25 mmol) of $[FeCl_2(diphos)_2]ReO_4$ and 1.35 g (2.8 mmol, excess) of Re_2O_7 dissolved in 1.5 ml of water in a 10 ml flask was added concentrated nitric acid slowly with stirring at room temperature. The mixture darkened and nearly black crystals were formed. These were filtered, washed quickly with cold water, and air-dried. The yield of purple-brown, crystalline $[FeCl_2(diphos)_2](ReO_4)_2$ was 0.230 g (92%). The corresponding $[FeCl_2(diars)_2](ReO_4)_2$ was prepared by exactly the same procedure and isolated as a deep green-black microcrystalline powder (79%), which appeared to be purer than the reported hygroscopic fluoroborate salt.[29] Both complexes were stored in a refrigerator.

Bis[*o*-phenylenebis(dimethylphosphine)]dichlororuthenium(II), $RuCl_2(diphos)_2$, Bis[*o*-phenylenebis(dimethylphosphine)]dichlororuthenium(III) Perchlorate, $[RuCl_2(diphos)_2]ClO_4$, and Their diars Analogues. Commercial "$RuCl_3{\cdot}3H_2O$", 0.20 g (0.76 mmol), was reduced in 30 ml of methanol with hydrogen at 2 atm pressure and a trace of Adams catalyst. After being decanted from the catalyst, the deep blue solution was treated with diphos (0.30 g, 1.52 mmol) and the mixture was refluxed for 5 h. The pale precipitate which formed was filtered and washed with methanol and acetone to give 0.113 g of crude off-white $RuCl_2(diphos)_2$ (26%). All of this material was stirred in 5 ml of methanol to which concentrated HNO_3, 4 ml, was slowly added. The mixture formed a dark green solution, which was then cooled in an ice bath and treated dropwise with 70% $HClO_4$ until precipitation began. Deep green crystals of $[RuCl_2(diphos)_2]ClO_4$ (0.104 g, 78%) were filtered and washed with water. A pale yellow, microcrystalline precipitate of pure $RuCl_2(diphos)_2$ was obtained in ca. 50% yield by chromous (from $CrCl_3$/HCl/Zn in methanol) reduction of the ruthenium(III) complex dissolved in methanol. Crude $RuCl_2(diars)_2$[30] (0.087 g, 0.117 mmol) was oxidized to ruthenium(III) with trityl tetrafluoroborate (0.10 g, 0.303 mmol) in hot acetonitrile (a procedure which was unsuccessful with the diphos complex). The resulting green solution was treated with a few drops of 45% HBF_4 and water was slowly added until green, crystalline $[RuCl_2(diars)_2]BF_4$, 0.081 g (83%), separated. The pure Ru^{II}–diars complex was prepared similarly to the diphos compound as a pale yellow microcrystalline powder.

Bis[*o*-phenylenebis(dimethylphosphine)]dichloroosmium(II), $OsCl_2(diphos)_2$, Bis[*o*-phenylenebis(dimethylphosphine)]dichloroosmium(III) Perchlorate, $[OsCl_2(diphos)_2]ClO_4$, and Their diars Analogues. To 0.53 g of diphos (2.68 mmol) in 25 ml of ethanol was added a slurry of 0.40 g (0.91 mmol) of $(NH_4)_2OsCl_6$ in 20 ml of dilute HCl. The mixture was refluxed under nitrogen for 20 h and cooled, and the pale orange powder, 0.115 g, was filtered off. This crude osmium(II) complex was oxidized in CH_2Cl_2 by adding HCl-acidified methanol containing a slight excess of 30% H_2O_2. Solvents were removed in vacuo from the resulting deep red mixture, and the solid was extracted with a small quantity of hot water. The filtered red aqueous solution was treated with concentrated HCl to precipitate the crude osmium(III) chloride salt which was converted to the purple-red *trans*-$[OsCl_2(diphos)_2]ClO_4$ salt, 0.060 g (9%). The formation of cis isomers may account for the low yield. The analogous diars complex was prepared by trityl tetrafluoroborate oxidation of the crude $OsCl_2(diars)_2$[31] in dichloromethane. This mixture was evaporated to dryness in vacuo, the residue extracted with methanol, and the resulting red solution treated with a small amount of $HClO_4$. Upon reduction of the volume of the solvent, dull red crystals of *trans*-$[OsCl_2(diars)_2]ClO_4$ separated in 22% yield. The pure osmium(II) complexes, pale yellow $OsCl_2(diphos)_2$ and $OsCl_2(diars)_2$,[31] were prepared in ca. 50% yield from the crystalline osmium(III) derivatives by chromous reduction in methanol.

Unstable osmium(IV) complexes were generated in concentrated nitric acid. The deep blue-green $[OsCl_2(diars)_2]^{2+}$ ion is moderately stable in HNO_3 and has been isolated as the diperchlorate salt.[31] The deep blue $[OsCl_2(diphos)_2]^{2+}$ ion, on the other hand, rapidly decomposed in HNO_3 at room temperature to unknown products. These complexes were not isolated in this study.

Bis[*o*-phenylenebis(dimethylphosphine)]dichloro- and -dibromomanganese(II), $MnX_2(diphos)_2$ (X = Cl, Br). Manganous chloride was dehydrated in vacuo by heating the hydrate in a tube with a flame. To a deoxygenated 2-propanol solution (ca. 50 ml) of 0.24 g of $MnCl_2$ (1.91 mmol) was added 0.83 g of diphos (4.19 mmol) to give a pale yellow solution. As the solution was stirred, a yellow solid gradually precipitated over a few hours. The mixture was cooled in an ice bath, and the solid was filtered under nitrogen through a Schlenk apparatus and washed successively with cold deoxygenated 2-propanol and toluene. The yellow crystalline $MnCl_2(diphos)_2$, 0.445 g (45%), was stable to the air but was stored under nitrogen in a refrigerator. The odor of free diphosphine could be detected from the crystalline solid and solutions of the complex smelled strongly of free ligand, indicative of extensive dissociation. The pale yellow bromo complex, $MnBr_2(diphos)_2$, was similarly prepared from anhydrous $MnBr_2$; this derivative was less soluble than its chloro analogue.

Bis[*o*-phenylenebis(dimethylphosphine)]dichloro- and -dibromomanganese(III) Perchlorates, $[MnX_2(diphos)_2]ClO_4$, and Bis[*o*-phenylenebis(dimethylphosphine)]dichloromanganese(IV) Diperchlorate, $[MnCl_2(diphos)_2](ClO_4)_2$. Trityl hexafluorophosphate, $(C_6H_5)_3C^+PF_6^-$ (0.194 g, 0.50 mmol), was dissolved in 40 ml of dichloromethane and the solution was stirred while 0.258 g (0.49 mmol) of solid $MnCl_2(diphos)_2$ was added. The resulting orange suspension was stirred for 20 h under nitrogen. Filtering and washing with toluene afforded 0.224 g (68%) of orange, crystalline $[MnCl_2(diphos)_2]PF_6$. Purification was effected by dissolving this material in the minimum quantity of dry acetonitrile at room temperature and salting out the perchlorate salt by stirring with excess solid anhydrous $LiClO_4$. The resulting orange crystalline solid was filtered and washed with 1-propanol to remove $LiClO_4$. Solutions of the manganese(III) complex in protic solvents decompose fairly rapidly; acetonitrile was found to be one of the best solvents for the perchlorate salt. The corresponding bromo derivative was similarly prepared from 0.15 g of $MnBr_2(diphos)_2$ and 0.11 g of trityl hexafluorophosphate in dichloromethane as above. The resulting deep orange mixture was evaporated to dryness at room temperature in vacuo, and the residue extracted with a small quantity of dry acetonitrile. This filtered solution was then treated with an excess of $LiClO_4$, whereupon a red-orange, crystalline precipitate of $[MnBr_2(diphos)_2]ClO_4$ formed on stirring at room temperature. The complex was filtered and washed with 1-propanol; yield 0.073 g (42%).

The manganese(IV) derivative was prepared from $[MnCl_2(diphos)_2]ClO_4$ by the concentrated nitric acid oxidation procedure employed for the nickel systems. The orange-brown, crystalline $[MnCl_2(diphos)_2](ClO_4)_2$ was washed with water, air-dried, and stored in a refrigerator.

Bis[*o*-phenylenebis(dimethylphosphine)]dichlororhenium(III) Perchlorate, $[ReCl_2(diphos)_2]ClO_4$, and Its diars Analogue. Rhenium heptoxide (0.20 g, 0.42 mmol) was refluxed for 5 min in 30 ml of ethanol containing ca. 1.5 ml (60 drops) of concentrated HCl and ca. 0.75 ml (30 drops) of 50% hypophosphorous acid. diphos (0.50 g, 2.53 mmol) was added and the resulting dark yellow-green solution

Table IX. Electronic Spectra of Hexacoordinate *trans*-MX_2L_2 Complexes[a]

Electron config	Metal oxidn state	Compd	Solvent	Color and band max, nm (ε or rel absorbance)	
				L = diphos	L = diars
d^7	M^{II}	$CoCl_2L_2$	Nujol mull	Pale green	Yellow
				560 (0.18)[b]	655 (0.02)[b]
				sh 360 (1.15)	sh 380 (0.70)
	M^{III}	$[NiCl_2L_2]BF_4$	CH_3CN	Green	Yellow-brown
				677 (41)	754 (50)
		$[NiBr_2L_2]ClO_4$	CH_3CN	Red-brown	Deep orange
				706 (47)	771 (43)
				460 (1120)	419 (7700)
d^6	M^{II}	$FeCl_2L_2$	Nujol mull	Pale green	Yellow
				655 (0.16)	710 (0.14)
				385 (1.05)	sh 380 (0.98)
		$RuCl_2L_2$	$CHCl_3$	Pale yellow	Pale yellow
				403 (65)	447 (70)
				319 (1030)	318 (1150)
		$OsCl_2L_2$	Nujol mull	Pale yellow	Pale yellow
				sh 375 (0.50)	384 (0.37)
				335 (0.65)	341 (0.43)
	M^{III}	$[CoCl_2L_2]ClO_4$	CH_3OH	Purple-green[c]	Green
				562 (78)	610 (85)
				373 (3850)	387 (5400)
		$[CoBr_2L_2]ClO_4$	CH_3CN	Green	Yellow-green
				596 (75)	637 (104)
		$[RhCl_2L_2]ClO_4$	CH_3CN	Pale yellow	Yellow
				381 (230)	406 (250)
		$[IrCl_2L_2]ClO_4$	CH_3CN	Very pale yellow	Pale yellow
				383 (12)	407 (12)
				326 (115)	344 (130)
	M^{IV}	$[NiCl_2L_2](ClO_4)_2$	Nujol mull	Deep violet	Deep blue
				565 (0.65)	605 (0.65)
				375 (1.0)	410 (1.1)
		$[PdCl_2L_2](ClO_4)_2$	$HCl-H_2O$[d]	Yellow-orange	Orange
				415 (4500)	443 (4300)
		$[PtCl_2L_2](ClO_4)_2$	$HCl-H_2O$[d]	Colorless	Pale yellow
				313 (4500)	330 (6100)
d^5	M^{II}	$MnCl_2L_2$	Nujol mull	Yellow	
				404	
		$MnBr_2L_2$	Nujol mull	Yellow	
				437	
	M^{III}	$[FeCl_2L_2]BF_4$	CH_3CN	Red	Red
				561 (1900)	556 (2000)
				sh 505 (300)	sh 505 (300)
				351 (4200)	370 (6600)
		$[FeBr_2L_2]ClO_4$	CH_3CN	Deep green[e]	Deep green
				611 (1260)	606 (4430)
					sh 550 (400)
				384 (1030)	408 (4230)
		$[RuCl_2L_2]ClO_4$	CH_3CN	Deep green	Deep green
				687 (1720)	663 (1800)
				sh 580 (260)	sh 576 (350)
		$[OsCl_2L_2]ClO_4$	CH_3CN	Red	Red
				559 (2260)	537 (1880)
				476 (380)	469 (480)
					sh 393 (260)
d^4	M^{III}	$[MnCl_2L_2]ClO_4$	CH_3CN	Orange	
				519 (72)	
		$[MnBr_2L_2]ClO_4$	CH_3CN	Red-orange	
				548 (74)	
		$[ReCl_2L_2]ClO_4$	CH_3CN	Yellow	Yellow
				427 (2260)	413 (2470)
				394 (3440)	383 (3980)
	M^{IV}	$[FeCl_2L_2](ReO_4)_2$	*f*	Deep red	Green-black[c]
		$[OsCl_2L_2]^{2+}$	*f*	Deep blue	Deep blue-green
d^3	M^{III}	$[CrCl_2L_2]ClO_4$	CH_3CN	Red-green[c]	Green
				562 (53)	595 (79)
					sh 470
				423 (1250)	423 (1300)
				386 (800)	390 (870)
		$[CrBr_2L_2]ClO_4$	CH_3CN	Green	Green
				578 (49)	617 (75)
				432 (1140)	439 (1250)
				sh 402 (750)	406 (680)
	M^{IV}	$[MnCl_2L_2](ClO_4)_2$	Nujol mull	Red-brown	
				sh 504 (0.38)	
				471 (0.45)	
				415 (0.49)	

Table IX (*Footnotes*)

[a] Solutions run at room temperature; sh = shoulder; higher energy charge transfer and intraligand transitions not recorded. [b] Very broad absorptions, λ_{max} not definite; some oxidation to Co^{III} may have occurred. [c] Dichroic. [d] Concentrated aqueous HCl is the only solvent in which these compounds dissolve without decomposition; band maxima were identical with those in a Nujol mull for the Pd systems. [e] BF_4^- salt. [f] Spectra of these unstable compounds not obtained; colors of Os complexes observed in concentrated HNO_3 solutions.

Table X. X-Ray Crystal Structure Determinations

Electron config	Complex	Structure	M-X, Å	M-P(As), Å	Ref
d^8	$[CuCl(diphos)_2](ClO_4)_2$	Square pyramidal	Cu-Cl = 2.461 (1) Cu-$OClO_3$ = 2.889 (4)	Cu-P(av) = 2.263	36
d^7	$[NiCl_2(diars)_2]Cl$	Trans octahedral	Ni-Cl = 2.425 (3)	Ni-As(av) = 2.342	43
d^6	$[CoCl_2(diars)_2]Cl$	Trans octahedral	Co-Cl = 2.256 (3)	Co-As(av) = 2.334	43, 44
	$[CoCl_2(diphos)_2]ClO_4$	Trans octahedral	Co-Cl(av) = 2.253	Co-P(av) = 2.251	36
d^5	$[MnCl_2(diphos)_2]^0$	Trans octahedral	Mn-Cl = 2.502 (1)	Mn-P(av) = 2.625	53
d^4	$[MnCl_2(diphos)_2]ClO_4$	Trans octahedral	Mn-Cl = 2.239 (2)	Mn-P(av) = 2.344	53
d^3	$[MnCl_2(diphos)_2][H(NO_3)_2]_2$	Trans octahedral	Mn-Cl = 2.195 (1)	Mn-P(av) = 2.428	53

was refluxed for 1 h. After evaporation of the deep yellow solution to small volume, ca. 150 ml of concentrated HCl was added, and the mixture was set aside. The yellow precipitate of $[ReCl_2(diphos)_2]Cl$ which formed was filtered, dissolved in methanol, and converted to the perchlorate salt with dilute $HClO_4$. This crude perchlorate salt was crystallized from ethanol containing a few drops of 70% $HClO_4$ by slow evaporation. The bright yellow crystals of $[ReCl_2(diphos)_2]ClO_4$, (0.084 g, 13%) had a subtle greenish tinge.

The bright yellow $[ReCl_2(diars)_2]ClO_4$[32] was similarly prepared from Re_2O_7 and diars in a 1:6 molar ratio. The crystalline perchlorate salt could be precipitated directly from the yellow reaction solution with perchloric acid; the yield was 61% based on Re_2O_7.

Bis[*o*-phenylenebis(dimethylphosphine)]dichloro- and -dibromochromium(III) Perchlorates, $[CrX_2(diphos)_2]ClO_4$ (X = Cl, Br), and Their diars Analogues. Chromic trichloride hexahydrate, 2.0 g, was heated on a steam bath with concentrated hydrochloric acid to near dryness. The purple residue was treated with 8 ml of 70% $HClO_4$ and evaporated further to a syrup. This was dissolved in 2-propanol to a total volume of 100 ml. A portion of this solution, 16.8 ml (1.26 mmol of Cr), was treated with 0.5 g of diphos (2.53 mmol) in 2-propanol and heated at reflux for 30 min. The resulting reddish solution deposited a yellow, semicrystalline material upon cooling, which upon recrystallization from methanol containing a trace of $HClO_4$ yielded 0.25 g (32%) of dichroic red-khaki green $[CrCl_2(diphos)_2]ClO_4$. The corresponding green bromo derivative, $[CrBr_2(diphos)_2]ClO_4$, was similarly prepared from a chromic solution prepared as follows: 2.5 g of $Cr(ClO_4)_3 \cdot 6H_2O$ was heated to near dryness on a steam bath with concentrated hydrobromic acid; the residue was treated with 5 ml of 70% $HClO_4$, and the solution was reheated for 10 min, cooled, and diluted to 100 ml with 2-propanol. The green diars complexes,[33] $[CrX_2(diars)_2]ClO_4$, X = Cl, Br, were prepared from the same chromic solutions; the crystalline salts precipitated from the reaction mixture after ca. 30 min of refluxing.

Physical Measurements. Conductivities were determined on a Philips GM4144 conductivity bridge. Electrochemical data were obtained by cyclic voltammetry on a PAR Model 170 electrochemistry system equipped with a three-electrode geometry. Acetonitrile was the solvent employed with 0.10 M tetraethylammonium perchlorate (TEAP) as supporting electrolyte; potentials were measured at a stationary platinum electrode vs. a $Ag/AgClO_4$ (0.01 M in CH_3CN containing 0.10 M TEAP) electrode as reference. The metal complex concentration was (0.5–1.0) × 10^{-3} M and the sweep rate ca. 100 mV/s. Electronic spectra were measured on Cary Models 14 and 118 recording spectrophotometers. Magnetic susceptibilities were measured by the Gouy and Faraday methods on a Newport Instruments single-temperature Gouy balance, using solid $[Ni(en)_3]S_2O_3$ as the calibrant; all magnetic moments quoted in the text refer to room temperature (298 ± 2 K). Far-infrared spectra of Nujol mulls were measured on a Perkin-Elmer 225 grating infrared spectrometer. The proton NMR spectra were recorded on a Varian HA-100 spectrometer and the ESR spectra on a Varian Model V-4502 X-band spectrometer. The mass spectrum of the diphosphine ligand was recorded on an AEI MS902 instrument at 70 eV.

Results

Ligand Synthesis. diphos is most conveniently synthesized by the method of Clark et al.[5] which starts from tetramethyldiphosphine disulfide

$$\begin{tikzcd}{[(CH_3)_2PS]_2 + 6Na} \arrow[r, "dioxane"] & {2NaP(CH_3)_2 + 2Na_2S} \arrow[d, "o\text{-}C_6H_4Cl_2"] \\ & {o\text{-}C_6H_4[P(CH_3)_2]_2}\end{tikzcd}$$

The yield of impure product is ca. 20%, considerably less than the 40–50% yield of diars which is obtained from sodium dimethylarsenide and *o*-dichlorobenzene in tetrahydrofuran.[16] The latter solvent cannot be used in the preparation of diphos owing to its ready cleavage by $NaP(CH_3)_2$; even dioxane is cleaved to some extent under the reaction conditions as indicated by the ^1H NMR spectrum of impure diphos (see Experimental Section). Use of liquid ammonia in place of dioxane, or of *o*-bromoiodobenzene in place of *o*-dichlorobenzene, failed to give significant amounts of diphos. It is of interest that the methyl resonance of diphos appears as a sharp 1:2:1 triplet, not as the expected doublet, indicating that $|^2J(PH) - {}^5J(PH)|^2 < 2J(PP')\Delta\nu_{1/2}$,[34] where $\Delta\nu_{1/2}$ is the resolving power of the instrument. Similar behavior is observed with tetramethyldiphosphine.[35]

Complexes. diphos complexes are obtained by the same well-established procedures used for diars complexes,[1] i.e., treatment of the appropriate metal salts with the ligand in alcoholic solution. Cationic derivatives have usually been isolated as perchlorates or occasionally as the potentially safer perrhenates. Invariably the complexes isolated under these conditions contain two diphos ligands per metal ion; mono- or tris-ligand complexes are not observed. We discuss the complexes by metal triad, starting with the copper group.

Copper, Silver, Gold. Copper(I) with diars and diphos forms colorless, diamagnetic d^{10} $[ML_2]^+$ species[18] which are oxidized by concentrated nitric acid to diamagnetic, planar d^8 $[CuL_2]^{3+}$ cations, isolated as the pale yellow (L = diphos) or bright yellow (L = diars) perchlorate salts. The trications react with chloride ion in the oxidizing medium to generate the five-coordinate, yellow (L = diphos) and orange (L = diars) cations $[CuClL_2]^{2+}$. The molar conductivities for the more stable diphos complexes (Table II) support these formulations. A single-crystal x-ray study of $[CuCl(diphos)_2](ClO_4)_2$[36] shows the copper atom to have an approximately square-pyramidal ligand arrangement with a long ionic perchlorate contact in the sixth coordination position. Relevant bond distances are recorded in Table X.

Both the diars complexes of copper(III) are much less chemically stable than their diphos counterparts; dissolution in acetonitrile results in decomposition within a few seconds, whereas the diphos analogues are stable in this solvent for nearly 1 min. Attempts to prepare six-coordinate $[CuCl_2L_2]^+$ complexes were unsuccessful; excess chloride ion in organic solvents caused immediate decomposition. However, treatment of solid $[CuCl(diphos)_2](ClO_4)_2$ with a dilute dichloromethane solution of tetramethylammonium chloride at −80 °C caused a deep red-orange color to form on the crystal surface, which rapidly disappeared at higher temperatures. We ascribe this color to the $[CuCl_2(diphos)_2]^+$ ion, by analogy with the silver and gold systems described below. The electronic spectra of the d^8 copper(III) species are presented in Table VI. These systems are the first described complexes of formal Cu(III) containing tertiary phosphines and arsines as ligands. Formal d^9 copper(II) species were not observed electrochemically or chemically; no apparent reaction occurred on mixing equimolar amounts of $[CuL_2]^+$ and $[CuL_2]^{3+}$ in acetonitrile solution.

Like copper(I), silver(I) forms tetrahedral d^{10} $[AgL_2]^+$ complexes[19] which can be oxidized with concentrated nitric acid to the diamagnetic square-planar $[AgL_2]^{3+}$ ions, containing formal silver(III). Bright yellow $[Ag(diars)_2](ClO_4)_3$ is very unstable and decomposes on contact with water, chloride ion, and many organic solvents. Pale yellow $[Ag(diphos)_2](ClO_4)_3$, on the other hand, is relatively stable to water but decomposes in the presence of aqueous chloride ion, even in concentrated nitric acid solution; solutions in dry acetonitrile are stable over a period of hours at room temperature. The molar conductivity (Table II) supports the tricationic formulation for the diphos complex. Chloride ion adducts were observed only in the diphos system in acetonitrile solution. Bright yellow and orange species formulated respectively as the five-coordinate $[AgCl(diphos)_2]^{2+}$ and six-coordinate $[AgCl_2(diphos)_2]^+$ ions were identified by their electronic spectra, which resemble those of the analogous gold(III) compounds (Table VI). The adducts could not be isolated as they decomposed within minutes in solutions. These complexes are the first reported trivalent silver systems with tertiary phosphine or arsine ligands. As with copper, no d^9 silver(II) species were observed chemically or electrochemically.

The chemistry of the $[Au(diars)_2]^{3+}$ system has been examined in detail by Harris and Nyholm,[20] who prepared the iodide ion adducts. We have prepared the new chloride ion adducts for comparison with the analogous diphos system. The reaction of sodium tetrachloroaurate(III) with diphos or diars[20] in ethanol affords diamagnetic, five-coordinate trivalent gold species, $[AuClL_2]^{2+}$, the perchlorate salts of which behave as 2:1 electrolytes in acetonitrile (Table II). The ^1H NMR spectrum of $[AuCl(diars)_2](ClO_4)_2$ in CD_3CN at room temperature shows only a sharp singlet resonance for the $As-CH_3$ protons, whereas for a static square-pyramidal structure two such resonances, arising from inequivalent methyl groups on each arsenic atom, might have been expected. This suggests that chloride ion exchange is rapid on the NMR time scale. (An alternative fluxional four-coordinate structure in solution with a chloride ion and one bidentate and one monodentate ligand cannot be discounted in this type of complex.) Removal of the coordinated chloride ion with concentrated nitric acid generates the $[AuL_2]^{3+}$ species which are isolated as their perchlorate salts. Whereas $[Au(diphos)_2](ClO_4)_3$ behaves as a nearly 3:1 electrolyte in acetonitrile solution, the corresponding diars complex is a 2:1 electrolyte in this solvent and presumably exists as the five-coordinate $[Au(ClO_4)(diars)_2]^{2+}$ ion.

The six-coordinate, pale yellow $[AuCl_2(diphos)_2]Cl$ and bright yellow $[AuCl_2(diars)_2]Cl$ precipitate on addition of excess tetraethylammonium chloride to acetonitrile solutions containing the $[AuL_2]^{3+}$ or $[AuClL_2]^{2+}$ complexes. The molar conductivities of these salts (Table II) show that they are 1:1 electrolytes (six-coordinate cations) in acetonitrile and methanol but are extensively dissociated in water. They probably have a tetragonally distorted octahedral structure similar to that found for $[AuI_2(diars)_2]I$ in the solid state.[37] Electronic spectral data for the individual complexes are presented in Table VI. The lower reduction potentials for the trivalent gold systems (Table III) relative to their copper(III) and silver(III) analogues accounts in part for their greater stabilities in solution.

Nickel, Palladium, Platinum. The coordination chemistry of diphos with nickel in its higher oxidation states is substantially the same as found by Nyholm for diars.[21-23] Nickel(II) forms the diamagnetic, yellow, square-planar $[Ni(diphos)_2]^{2+}$ and the orange, five-coordinate (in solution) $[NiCl(diphos)_2]^+$ and orange, six-coordinate (solid state) $NiCl_2(diphos)_2$. Unlike the case for the diars analogues, aqueous solutions containing these nickel(II) diphos species do not smell of free ligand. Electronic spectra for the d^8 $[NiL_2]^{2+}$ complexes of diars and diphos and their chloride ion adducts in aqueous and acetonitrile solutions and in the solid state are given in Table VII. Ligand arrangements in these nickel(II) systems are expected to be similar to those described for the copper(III) complexes. In the solid state, $NiI_2(diars)_2$ has been shown[38] to be essentially square planar with axial iodide ions at nearly ionic distances. The $[NiClL_2]ClO_4$ salts may have a related solid-state structure with bridging halide ions, as indicated from x-ray diffraction studies[39] and from similarities in the mull spectra of these and the corresponding $NiCl_2L_2$ complexes. As with $[AuCl(diars)_2](ClO_4)_2$, the ^1H NMR spectrum of $[NiCl(diars)_2]ClO_4$ in CD_3CN at room temperature shows a singlet $As-CH_3$ resonance, suggesting that in this case too chloride ion exchange is rapid on the NMR time scale.

Table III records the redox potentials in acetonitrile solution for the irreversible two-electron reduction of the square-planar $[NiL_2]^{2+}$ ions to the corresponding tetrahedral $[NiL_2]^0$ species; the nickel(0) complex with L = diars has been isolated.[40] The Ni^{II}–diphos and –diars complexes in the presence of excess chloride ion also undergo an irreversible one-electron electrochemical oxidation to the six-coordinate $[NiCl_2L_2]^+$ ions (Table IV) containing formal nickel(III); ferric chloride in methanol generates these species chemically. The green $[NiCl_2(diphos)_2]^+$ ion has a magnetic moment of 1.90 μ_B (Table VIII) in agreement with a low-spin d^7 electron configuration. ESR spectra of solutions of $[NiCl_2(diphos)_2]^+$ in acetonitrile and ethanol at room temperature show more or less resolved hyperfine splittings arising from interaction of the unpaired electron with both chlorine and phosphorus nuclei.[41] These observations are qualitatively similar to those made with the analogous diars comples.[9,10] The low value of $\nu(M-Cl)$ for *trans*-$[NiCl_2(diphos)_2]ClO_4$ (d^7) is also a feature of the diars analogue[42] (Table XI). This suggests that the diphos complex will resemble $[NiCl_2(diars)_2]Cl$[8,43] in having relatively long Ni–Cl bond lengths (Table X).

Both nickel(III) complexes undergo reversible, one-electron electrochemical oxidations in acetonitrile to the formal d^6 nickel(IV) complexes, $[NiCl_2L_2]^{2+}$. The reversibility of these redox reactions implies that the basic stereochemical integrity of the complexes is retained in the two oxidation states. Chemically, nitric acid effects this oxidation, and the diamagnetic, deep purple $[NiCl_2(diphos)_2]^{2+}$ ion is isolated as the perchlorate salt. Electrochemical and electronic spectral data for the nickel(III) and nickel(IV) chloro and related bromo complexes are presented in Tables IV and IX, respectively. Figure 1 depicts a cyclic voltammogram of the $[NiCl_2(diphos)_2]^+$ complex.

The diphos complexes of palladium and platinum are analogous to those of diars.[21] Molar conductivities and electronic spectra of the d^8 $[M(diphos)_2]^{2+}$ species (M = Pd, Pt) and their chloride ion adducts are presented in Tables II and VII, together with those of the corresponding diars complexes. The uncharged $MCl_2(diphos)_2$ complexes are

Table XI. ν(M–Cl) Frequencies (cm^{-1}) in *trans*-MCl_2L_2 Complexes

Electron config	M^{III}	ν(M–Cl) [MCl_2-(diphos)$_2$]-ClO_4	 [MCl_2-(diars)$_2$]-ClO_4[a]
d^7	Ni	258	260
d^6	Co	395	388
d^5	Fe	376	373
d^4	Mn	374[b]	
d^3	Cr	373	375

Electron config	M^{II}	ν(M–Cl) [MCl_2-(diphos)$_2$]^0	 [MCl_2-(diars)$_2$]^0 [a]
d^7	Co	N.o.[c]	N.o.[c]
d^6	Fe	349	348
d^5	Mn	319[d]	

[a] Data from ref 42. [b] ν(Mn–Cl) 381 cm^{-1} in PF_6^- salt. [c] Not observed down to 200 cm^{-1}. [d] Assignment tentative owing to overlapping ligand bands.

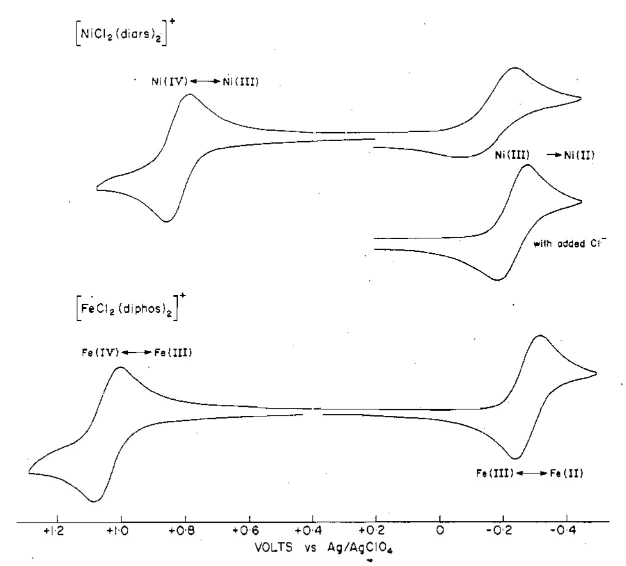

Figure 1. Representative cyclic voltammograms of some nickel and iron complexes in acetonitrile: top, [$NiCl_2$(diars)$_2$]$^+$ without and with added Cl$^-$;[63] bottom, [$FeCl_2$(diphos)$_2$]$^+$. Sweep rates were 100 mV/s using a stationary platinum electrode.

presumably tetragonally distorted octahedral in the solid state on the basis of x-ray crystal structures of related diars systems,[38] but the salts ionize to varying extents depending on the polarity of the solvent (Table II).

The two-electron electrochemical reduction of the palladium(II) and platinum(II) [ML_2]$^{2+}$ complexes in acetonitrile solution generates the corresponding [ML_2]^0 species (Table III), of which Pd(diars)$_2$ has been previously described.[40] Electrochemical oxidation of the [ML_2]$^{2+}$ complexes does not occur unless halide ion is present, whereupon a two-electron step to produce the d^6 metal(IV) complexes [MCl_2L_2]$^{2+}$ takes place; the reduction potentials for these latter reactions are presented in Table IV. The [MCl_2(diphos)$_2$]$^{2+}$ complexes (M = Pd, Pt) are obtained chemically by nitric acid oxidation of the metal(II) complexes in the presence of chloride ion. The yellow [$PdCl_2$(diphos)$_2$]$^{2+}$ ion is considerably more stable in solution than its diars analogue. Electronic spectral data are given in Table IX. Unlike nickel, no formal d^7 metal(III) oxidation states were observed in these second- and third-row complexes of diars and diphos.

Cobalt, Rhodium, Iridium. The coordination chemistry of diphos with cobalt is substantially the same as found with diars.[25] Cobalt(II) chloride forms sparingly soluble, greenish $CoCl_2$(diphos)$_2$, which has a magnetic moment $\mu_{eff} = 1.97\ \mu_B$ (Table VIII) in the range expected for a low-spin d^7 electron configuration. Aerial oxidation of this complex produces the purple, diamagnetic d^6 [$CoCl_2$(diphos)$_2$]$^+$ ion. An x-ray diffraction study[36] of the perchlorate salt has established a trans configuration for the cation (Figure 2), the structure being very similar to that of the corresponding [$CoCl_2$(diars)$_2$]$^+$ complex.[43,44] Relevant structural parameters are listed in Table X. Electronic spectral data for these and some bromo complexes are given in Table IX.

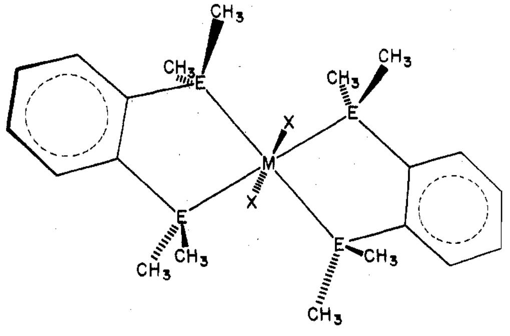

Figure 2. Structure of *trans*-dihalogenobis(ligand)(transition metal) complexes (ligand = diphos or diars).

The electrochemical reversibility of the [CoX_2L_2]$^{0,+}$ redox couples (X = Cl, Br) in acetonitrile indicates that the ligand disposition about the metal is retained in the two oxidation states and establishes a trans, six-coordinate stereochemistry for the cobalt(II) systems in that solvent. The failure to observe a band due to ν(Co–Cl) for either of the d^7 $CoCl_2L_2$ systems down to 200 cm^{-1} in the solid state suggests that these complexes are best viewed as tetragonally distorted octahedral, like their isoelectronic nickel(III) counterparts.[42] At lower potentials, highly irreversible couples (Table IV) are observed, corresponding to reduction to cobalt(I) species, presumably of the type [CoL_2]$^+$. No oxidation chemically or electrochemically to a cobalt(IV) species is observed.

diphos reacts with rhodium(III) chloride to form the pale yellow, diamagnetic *trans*-[$RhCl_2$(diphos)$_2$]$^+$ species, analogous to the diars complex.[26] The low yield obtained for the trans diphos complex may be due to the formation of a substantial amount of the unisolated cis isomer under the reaction conditions employed. The related ligand 1,2-bis(dimethylphosphino)ethane, dmpe, also gives a mixture of *cis*- and *trans*-[$RhCl_2$(dmpe)$_2$]$^+$ complexes by this procedure.[45] The corresponding d^6 iridium(III) complexes are prepared by chlorination of the [IrL_2]$^+$ species generated in situ from [IrCl(cyclooctene)$_2$]$_2$ and L in methanol. Far-infrared,[27,42] electronic spectral (Table IX), and ^1H NMR data establish the trans configuration for these six-coordinate rhodium(III) and iridium(III) systems. Electrochemically, the [MCl_2L_2]$^+$ complexes undergo an irreversible two-electron reduction to metal(I) species, presumably of the form [ML_2]$^+$, which have been described previously for L = diars[46,47] (Table IV). Surprisingly, in view of the existence of monodentate tertiary phosphine–iridium(IV) complexes of the type $IrCl_4(PR_3)_2$,[48] there was no chemical or electrochemical indication of Rh(IV) or Ir(IV) species in our systems.

Iron, Ruthenium, Osmium. As with diars,[28,29] (diphos)$_2$ complexes have been characterized in which iron has the formal oxidation states II, III, and IV. Iron(II) chloride forms pale green, diamagnetic d^6 $FeCl_2$(diphos)$_2$, which is oxidized by ferric chloride to the deep red, paramagnetic iron(III) complex [$FeCl_2$(diphos)$_2$]$^+$, isolated as its perchlorate salt; the magnetic moment, $\mu_{eff} = 2.22\ \mu_B$, is in the range expected for a low-spin d^5 electronic configuration (Table VIII). At 110 K this species and its diars analogue show three g-value ESR spectra[49] indicative of rhombic ligand fields. The electronic spectra in the visible region of the Fe(III) and isoelectronic Ru(III) and Os(III) diars and diphos complexes (Table IX) (vide infra) are characterized by a single intense charge-transfer absorption band, suggesting that the chlorine atoms are trans.[50] The appearance of only one ν(M–Cl) band in the ir spectra of a number of these compounds[42] (Table XI) supports this assignment.

Two reversible, one-electron redox couples are observed (Figure 1) in the $[FeX_2(diphos)_2]^{n+}$ systems (X = Cl, Br) corresponding to Fe(II)–Fe(III) and Fe(III)–Fe(IV) interconversions (Table V). The new formal iron(IV) complex $[FeCl_2(diphos)_2]^{2+}$ is prepared by nitric acid oxidation of the iron(III) species and isolated as the deep purple-brown perrhenate salt, $\mu_{eff} = 3.65\ \mu_B$. The room-temperature magnetic moment of this complex is close to the theoretical value of 3.6 μ_B for low-spin d^4 Fe(IV).[51] The lower values of 3.17 and 2.76 μ_B reported[29] for the diars derivatives $[FeX_2(diars)_2](BF_4)_2$, where X = Br and Cl, respectively, are probably due to iron(III) impurity, not tetragonal distortion (elongation) as originally suggested;[29] since we find a value of 3.38 μ_B for $[FeCl_2(diars)_2](ReO_4)_2$ (Table VIII). However, Mössbauer studies[52] indicate that there is a strong axial compression of the ligand field in the Fe^{IV}–diars complexes.

Ruthenium and osmium form the diamagnetic, divalent $MCl_2(diphos)_2$ and paramagnetic, trivalent $[MCl_2(diphos)_2]^+$ complexes, analogous to the diars systems.[30,31] Electronic spectral data for these systems are compared with those of the diars derivatives in Table IX. As with the iron(III) species, three g-value ESR spectra are observed for the low-spin d^5 ruthenium(III) and osmium(III) complexes.[49] Average g values, $\bar{g}$, are given in Table VIII.

Reversible one-electron M(II)–M(III) redox couples are observed for the ruthenium and osmium $[MCl_2L_2]^{0,+}$ systems (Table V). The $[RuCl_2L_2]^+$ derivatives, unlike the iron systems, undergo irreversible one-electron oxidation reactions to formal ruthenium(IV) complexes which apparently decompose rapidly in the electrolyte medium. The strongly oxidizing nature of these ruthenium(IV) species, demonstrated by their very high potentials (Table V), probably precludes their isolation from other solvent systems.[30] With the corresponding $[OsCl_2L_2]^+$ systems, the Os(III)–Os(IV) redox couple is reversible at room temperature for L = diars but irreversible (cf. Ru(IV)) for L = diphos except at lower temperatures, <ca. -30 °C. This feature is in accord with the relative chemical stabilities of the two $[OsCl_2L_2]^{2+}$ complexes: while nitric acid oxidation of the osmium(III) complex in the case of diars forms deep blue-green solutions from which $[OsCl_2(diars)_2]^{2+}$ salts can be isolated,[31] in the case of diphos, transient deep blue Os(IV) solutions are produced which decolorize rapidly to unknown materials. This is the only clear case in which diars stabilizes a higher oxidation state complex more effectively than diphos.

Manganese, Rhenium. diphos reacts with anhydrous manganese(II) chloride in 2-propanol to form a yellow solution from which yellow $MnCl_2(diphos)_2$, $\mu_{eff} = 6.04\ \mu_B$, separates on cooling. This compound appears to be the first described tertiary phosphine complex of high-spin manganese(II), and an x-ray diffraction study has shown it to have the trans structure (Figure 2).[53] The unusually long Mn–Cl and Mn–P bond lengths shown in Table VIII are in accord with the ionic character expected for the stable high-spin d^5 electronic configuration. Chemically, the diphos complex is stable in dry air, but it appears to dissociate in solution, as judged by the odor of free phosphine and, in some cases (e.g., water), by the disappearance of the yellow color. The manganese(II) species can, however, be oxidized in dichloromethane solution with trityl salts to form the stable, orange, low-spin d^4 manganese(III) ion, isolated as the perchlorate salt $[MnCl_2(diphos)_2]ClO_4$, $\mu_{eff} = 3.10\ \mu_B$.[54] In acetonitrile this complex shows an electrochemically irreversible Mn(II)–Mn(III) redox couple due to rapid dissociation of the reduced species in the polar solvent. In addition, a reversible one-electron oxidation to a formal manganese(IV) complex is observed; chemically this oxidation is effected by concentrated nitric acid to form the high-spin d^3 $[MnCl_2(diphos)_2]^{2+}$ ion, which is isolated as the orange-brown diperchlorate, $\mu_{eff} = 3.99\ \mu_B$. The chemical properties of the corresponding bromo derivatives, pale yellow $MnBr_2(diphos)_2$ and red-orange $[MnBr_2(diphos)_2]ClO_4$, are very similar to those of the chloro complexes; electrochemical and spectral data are compared in Tables V and IX. These diphos complexes represent to our knowledge the first reported tertiary phosphine complexes of manganese in its higher oxidation states; the manganese(III) derivatives are among the very few low-spin complexes for this d^4 ion.

The trans arrangement (Figure 2) of the chloride ligands in the manganese(III) and -(IV) complexes $[MnCl_2(diphos)_2]ClO_4$ and $[MnCl_2(diphos)_2][H(NO_3)_2]_2$, respectively, has been established by x-ray diffraction studies.[53] Relevant structural parameters are listed in Table X. The decrease in the Mn–Cl bond lengths with increasing oxidation state (II to IV) suggests that the metal–halogen interaction is an important feature in the stabilization of the higher oxidation states in this series of complexes. Indeed, in the manganese(IV) structure the close approach of the axial chlorine atoms to the metal results in repulsion of the equatorial phosphorus ligands to a greater distance than found in the manganese(III) complex.

In contrast with the case of diphos, there is no reaction between diars and anhydrous manganese(II) chloride or bromide in 2-propanol; the solutions remain colorless and only the alcoholates, $MnX_2(2\text{-}C_3H_7OH)$, separate on cooling. Likewise, we have been unable to reproduce Nyholm and Sutton's observation[55] that diars reacts with anhydrous manganese(II) halides in dioxane solution to produce $MnX_2(diars)_2$. Rather than forming a solution in dioxane, $MnCl_2$ dehydrated as described in the Experimental Section was found to produce highly insoluble polymeric white $MnCl_2(dioxane)$,[56] even in the presence of excess diars; a similar adduct is formed in tetrahydrofuran. Partially hydrated $MnCl_2$ does, however, dissolve in these ether solvents and after prolonged contact with diars deposits small quantities of an uncharacterized white material which does not react with trityl salts. Recently, it has been shown[57] that in the presence of traces of water, manganese(II) halides and tertiary phosphines or arsines react to give phosphine- or arsine-oxide complexes of manganese(II). Claims[57,58] that $MnX_2(diars)_2$ can be prepared under conditions normally leading to oxidized-ligand complexes thus seem inconsistent, and further investigation appears warranted; the colorless,[59] hygroscopic compounds formulated as $MnX_2(diars)_2$[55,58] bear little resemblance to the yellow, air-stable diphos complexes.[71]

Rhenium forms with diphos the paramagnetic yellow $[ReCl_2(diphos)_2]^+$ species, analogous to the diars complex.[32] Like the manganese(III) analogue, these systems have magnetic moments (Table VIII) in the range for spin-paired d^4 Re(III). The electronic spectra of the diphos and diars complexes are dominated by intense charge-transfer absorptions (Table IX). Electrochemically these complexes may be reversibly reduced to the six-coordinate divalent species $ReCl_2L_2$ which has been isolated in the case of diars[32] (Table V). Unexpectedly, a further reversible one-electron reduction to the formal rhenium(I) complexes $[ReCl_2L_2]^-$ is observed. Although not isolated due to their strongly reducing nature, these electrochemically generated rhenium(I) species represent the first anionic diars and diphos complexes of this formulation, illustrating the special stability of the low-spin d^6 electronic configuration. Irreversible one-electron oxidations of the $[ReCl_2L_2]^+$ systems to formal rhenium(IV) species of unknown formulation are also observed.

Chromium. Chromium(III) chloride reacts with diphos to form the green–red dichroic d^3 cation $[CrCl_2(diphos)_2]^+$, $\mu_{eff} = 3.89\ \mu_B$. This complex is considerably more stable in protic solvents than the corresponding green diars species.[33] The electronic spectral data for these complexes and the dibromo derivatives are compared in Table IX. Electrochemically, the chromium(III) complexes of diphos undergo reversible one-electron reductions (Table V) to strongly reducing chromium(II) species, $CrX_2(diphos)_2$ (X = Cl, Br), while the corresponding diars compound (X = Cl) exhibits an irreversible reduction owing to coating of the electrode surface. The recently reported chromium(II) complexes of diars formulated as $CrX_2(diars)_2$[60] are low-spin, which is reasonable in view of the low-spin behavior of our isoelectronic manganese(III) complexes, $[MnX_2(diphos)_2]^+$. There is no chemical or electrochemical indication of a chromium(IV) complex of diphos or diars.

Discussion

The range of d^8 complexes formed by *o*-phenylene-based group 5 donor ligands has been extended to include trivalent copper and silver. These are much less stable than their trivalent gold counterparts, and there is only spectroscopic evidence for the chloride ion adducts of $[Ag(diphos)_2]^{3+}$, but all complexes in the series are probably isostructural. The d^8 systems display a marked tendency to increase their coordination number from 4 in planar $[ML_2]^{m+}$ (M = Cu, Ag, Au, $m = 3$; M = Ni, Pd, Pt, $m = 2$) to 5 (distorted square pyramidal) in $[MClL_2]^{(m-1)+}$ and 6 (tetragonally distorted octahedral) in $[MCl_2L_2]^{(m-2)+}$ species. This feature is evident from equivalent conductivities of 10^{-4} M solutions of representative complexes in various solvents (Table II); as expected, ion pairing is most effective in aprotic solvents such as acetonitrile. The lability of the ligands added to the fifth and sixth coordination positions is evidenced by the NMR equivalence of the diars methyl resonances (see Results) and is perhaps a reflection of the essentially electrostatic nature of the interaction. Our data are consistent with known trends for d^8 complexes,[61,62] i.e., (1) arsenic promotes the higher coordination numbers more readily than phosphorus, perhaps because its greater distance from the metal atom permits closer approach of the additional ligands, and (2) the tendency to add ligands is in the order Ni >> Pd > Pt. A similar ordering could not be established for the copper triad owing to the instability of the copper(III) and silver(III) complexes.

An outstanding feature of diphos and diars is their ability to form a series of *trans*-dihalogenobis(bidentate) $[M^{m+}X_2L_2]^{m-2}$ complexes with all the d-block transition elements, from the chromium to copper groups; in several of these systems the metal varies its formal oxidation state but the stereochemistry of the complex remains essentially unchanged. The electrochemistry of these complexes potentially provides some information about electronic differences between phosphorus and arsenic, as well as between isoelectronic metal ions of a triad. Tables III–V give the half-peak reduction potentials relative to $Ag/AgClO_4$ (10^{-2} M in acetonitrile) for 15 metal $[M^{m+}Cl_nL_2]^{m-n}$ systems and in some cases for the analogous bromides, determined by cyclic voltammetry. Electrochemically irreversible redox reactions are observed in the diphos and diars complexes whenever there is a change in the coordination environment of the metal, e.g., d^8 (square planar, solvated) → d^{10} (tetrahedral) and d^7 (hexacoordinate) → d^8 (five-coordinate). Conversely, many of the six-coordinate d^3–d^7 systems undergo reversible one-electron redox reactions in which the stereochemistry is retained.

Significant differences in the reduction potentials of corresponding diphos and diars complexes are observed only with the irreversible electron transfers which occur between the d^8 configuration and d^7 and d^{10} species. Although the measured reduction potentials for these irreversible couples are not strictly comparable in an electrochemical sense, relative differences between the potentials in a given triad may be meaningful for rough comparative purposes. They do, in fact, appear to reflect the relative *chemical* stabilities of the oxidized species toward reduction. In the $[ML_2]^{m+}$ $d^8 \rightarrow d^{10}$ conversions, the d^8 oxidation states are apparently stabilized toward reduction by up to ca. 300 mV with L = diphos relative to L = diars, as seen from the lower potentials for the diphos complexes. Thus, $[Cu(diphos)_2]^{3+}$ should be more difficult to reduce to Cu(I) than $[Cu(diars)_2]^{3+}$, and $[Ni(diars)_2]^{2+}$ is expected to reduce to Ni(0) more readily than $[Ni(diphos)_2]^{2+}$. Potentials for the d^7 $[NiX_2L_2]^+ \rightarrow d^8$ $[NiXL_2]^+$ redox couples[63] also demonstrate this greater tendency for the diphos systems to achieve the d^8 configuration relative to their diars counterparts, the Ni(III) → Ni(II) electron transfers occurring at higher potentials (ca. 150 mV) with L = diphos than with L = diars. Varying the axial substituents X = Cl, Br in these nickel(III) systems affects these potentials to the same extent as changing the equatorial ligands: the $[NiBr_2L_2]^+$ complexes reduce more readily than their $[NiCl_2L_2]^+$ counterparts by ca. 150 mV.

In general, however, interchanging diphos with diars or chloride with bromide has very little effect on the reduction potentials (<100 mV) of the electrochemically reversible, six-coordinate $[M^{m+}X_2L_2]^{m-2}$ interconversions. This is particularly evident in redox reactions involving the M(IV) species, implying that this high oxidation state is more or less equally stabilized to reduction by phosphorus as by arsenic and by chloride as by bromide. This feature is unexpected considering the differences in ligand field strengths. Of the various metal systems in this category which were examined, notable variations in the potentials are exhibited only with the reversible d^6 $[CoX_2L_2]^+ \rightarrow d^7$ $[CoX_2L_2]^0$ redox couples when the axial ligands (X = Cl, Br) are changed. Here, the bromocobalt(III) derivatives reduce ca. 150 mV more easily than the chloro systems, though this trend is not followed with the isoelectronic nickel(IV)–nickel(III) couples. The smaller potential variations observed with the remaining metal systems do not exhibit any consistent trends, although the diphos complexes tend to attain a d^6 electron configuration somewhat more readily than their diars analogues.

The reduction potentials in Tables III and IV show that the order of increasing ease of reduction of the copper group M(III) ions is Cu(III) > Ag(III) > Au(III) and for the nickel group M(IV) ions is Ni(IV) > Pd(IV) > Pt(IV). Interestingly, the ordering is different for the iron group M(IV) ions, Ru(IV) > Os(IV) > Fe(IV), where the first-row element most easily attains the high oxidation state (Table V). The formation of stable d^7 species in the first-row cobalt and nickel systems contrasts with their second- and third-row counterparts.

As noted in the introduction, the reversible redox behavior of many of the six-coordinate $[trans\text{-}M^{m+}X_2L_2]^{m-2}$ systems presents the problem of the extent to which electrons reside in metal d orbitals or in ligand molecular orbitals. The chemical and electrochemical features of the diphos and diars systems bear little resemblance to those of "noninnocent" ligands such as the dithiolenes. With the former, there is a trend (Figure 3) in the redox potentials which reflects the high relative stabilities of the filled (d^6) and half-filled (d^3) t_2 subshells, similar to that found with the metal dithiocarbamates.[64] In further contrast with the dithiolenes,

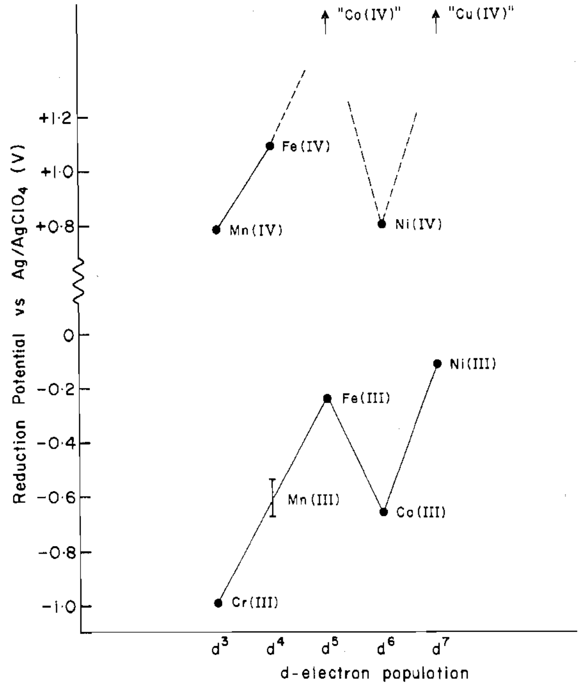

Figure 3. Dependence of the reduction potentials of the first-row $[\mathrm{M}^{m+}\mathrm{Cl}_2(\mathrm{diphos})_2]^{m-2}$ complexes on the d-electron population, showing the relative resistance of the filled (d^6) and half-filled (d^3) subshells toward reduction.

"improbable" metal oxidation states, particularly of the second- and third-row metals, are not observed in the diphos and diars systems, e.g., d^9 Ag(II) or Au(II) (or even Cu(II)), d^7 Pd(III), Pt(III), Rh(II), or Ir(II), or d^5 Co(IV), Rh(IV), or Ir(IV). These features strongly suggest that electron-transfer processes in the diphos and diars complexes primarily involve changes in oxidation state of the metal. The question of the degree of delocalization in diphos and diars complexes can only be answered ultimately from ESR studies. Analysis of the presently available data,[9–12] a formidable task in itself, suggests that only rather low total unpaired spin densities reside on all ligand donor atoms, with the predominant spin localized on the paramagnetic metal atom.[9,12] The most detailed treatment,[10] in which the unpaired electron is said to be "thoroughly delocalized over the [donor] system", appears to have overestimated the extent of the delocalization.[65] The qualitative ESR results we have obtained with d^7 and d^5 systems also support the predominantly metal-based character of the unpaired electron in these complexes. Finally, the observed[53] invariance of bond lengths within a coordinated diphos in the redox series $[\mathrm{MnCl_2(diphos)_2}]^{n+}$ (n = 0–2) is in marked contrast with the behavior of metal dithiolene systems[7] and suggests strongly that electron addition or removal takes place at the metal atom and not on the ligand.

In general, the electronic spectra of diphos and diars complexes in the visible region (Table IX) exhibit typical d–d transitions and closely resemble spectra of related amine systems, suggesting that delocalization effects are not large. Higher energy ligand field bands, which are often observable in the nitrogen donor systems, are effectively obscured in the phosphine and arsine spectra due to the onset of intense charge-transfer and/or intraligand transitions from about 25 000 cm^{-1}. It has therefore not been possible to evaluate ligand field parameters for diphos and diars in the tetragonal systems described in this study. A rough spectrochemical ordering of these and the reference ligand ethylenediamine can, however, be based on the energy of the first spin-allowed d–d transition of tetragonal ($\sim D_{4h}$) d^3 and d^6 complexes of the type *trans*-$[\mathrm{MX_2L_2}]^{n+}$.[66] Table XII presents these data for a series of Co(III), Rh(III), Ir(III), Ru(II), and Cr(III) complexes.

Table XII. Electronic Spectral Data for Trans Tetragonal Dihalometal Complexes in $\mathrm{CH_3CN}$

Complex type	L	Band max,[a] μm^{-1}	Ref
$[\mathrm{CoCl_2L_2}]^+$	diphos	178	*b*
	diars	164	*b*
	en	164	*b*
$[\mathrm{CoBr_2L_2}]^+$	diphos	168	*b*
	diars	157	*b*
	en	154	*b*
$[\mathrm{RhCl_2L_2}]^+$	diphos	262	*b*
	diars	246	*b*
	en	246	*c*
$[\mathrm{IrCl_2L_2}]^+$	diphos	307	*b*
	diars	291	*b*
	en	290	*d*
$[\mathrm{CrCl_2L_2}]^+$	diphos	178	*b*
	diars	168	*b*
	en	176	*b*
$[\mathrm{CrBr_2L_2}]^+$	diphos	173	*b*
	diars	162	*b*
	en	167	*b*

[a] Energy of the first spin-allowed d–d transition.[66] [b] This work; $\mathrm{ClO_4}^-$ or $\mathrm{BF_4}^-$ salts measured in $\mathrm{CH_3CN}$ solution. Chromium-ethylenediamine (en) complexes were prepared from *trans*-$[\mathrm{CrF_2(en)_2}]^+$ salts by treatment with the appropriate hydrohalic acid: J. W. Baughn, O. J. Stvan, and V. E. Magnuson, *Inorg. Chem.*, 7, 736 (1968). [c] S. A. Johnson and F. Basolo, *ibid.*, 1, 925 (1962). [d] R. A. Bauer and F. Basolo, *ibid.*, 8, 2231 (1969).

Spectrochemical series derived from the five metal systems vary somewhat as a consequence of the different electronic and/or steric requirements of the particular metal ions. For example, the position of diars relative to ethylenediamine in the series is higher for Co(III) than for Cr(III), a feature attributed[67] to the greater capacity of the spin-paired t_2^6 configuration to π back-donate to arsenic. In all cases, however, the highest ligand fields are induced by diphos. With an estimated ligand field splitting parameter Dq^{xy} = 2850 cm^{-1},[68] diphos appears to possess one of the strongest fields on cobalt(III) of most uncharged donors, including both diars (2600 cm^{-1}) and the macrocyclic tetraamines.[69] Unfortunately, due to the limited spectroscopic data available, differences in the coordinating capacities of diphos and diars compared with nitrogen donors are not clearly accounted for, e.g., the ability of diphos and diars to induce spin pairing with many first-row metal ions. It is likely that nephelauxetic and interelectronic repulsion parameters would be more informative in this regard and attempts to obtain such data have been made.[13]

The fact that Dq for diphos is higher than that for diars follows the usual trend for tertiary phosphines and arsines[67] and can probably be correlated with the greater strength of metal–phosphine bonding. This is manifested in the greater lability of the diars complexes relative to their diphos counterparts; for example, solutions of certain diars complexes in aqueous or alcoholic media smell of the free ligand, whereas this is not observed for the diphos counterparts. Other examples of the same phenomenon are the failure to isolate Mn–diars complexes and the greater tendency toward irreversibility in redox couples involving diars complexes (e.g., Fe(II) and Cr(II)). The only exception to the trend appears to be osmium(IV) (see Results), but in this case the mode of decomposition is unknown.

The *trans*-dihalogenobis(bidentate) configuration (Figure 2) is clearly the most stable, at least for the kinetically labile metal ions. The trans halogen atoms probably play an important role in reducing the effective charge on the metal atom in the higher oxidation states, perhaps by π donation,[52] as well as in lowering the overall charge on the complex. We consider that a combination of two important factors contributes to the high ligand field strengths and to the ability of diphos and diars to stabilize high oxidation states of the transition elements: (1) the small size (cone angle)[70] and strong σ-donor power of the P(CH$_3$)$_2$ and As(CH$_3$)$_2$ groups and (2) the rigidity of the *o*-phenylene backbone, which stabilizes the complexes toward ligand dissociation relative to monodentate P and As donors and more flexible bidentate counterparts. Electrochemical and electronic spectral data of related complexes which serve to emphasize the importance of the second factor will be presented in a separate paper.[49]

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Registry No. [Cu(diphos)$_2$]ClO$_4$, 60489-16-9; [Cu(diphos)$_2$](ClO$_4$)$_3$, 53030-20-9; [Cu(diars)$_2$](ClO$_4$)$_3$, 60489-18-1; [CuCl(diphos)$_2$](ClO$_4$)$_2$, 60536-60-9; [CuCl(diars)$_2$](ClO$_4$)$_2$, 60489-20-5; [Ag(diphos)$_2$]ClO$_4$, 60489-22-7; [Ag(diphos)$_2$](ClO$_4$)$_3$, 60489-24-9; [Ag(diars)$_2$](ClO$_4$)$_3$, 60499-26-5; [Au(diphos)$_2$](ClO$_4$)$_3$, 60489-26-1; [Au(diars)$_2$](ClO$_4$)$_3$, 60489-28-3; [AuCl(diphos)$_2$](ClO$_4$)$_2$, 60489-30-7; [AuCl(diars)$_2$](ClO$_4$)$_2$, 60489-32-9; [AuCl$_2$(diphos)$_2$]Cl, 60489-33-0; [AuCl$_2$(diars)$_2$]Cl, 60489-34-1; [Ni(diphos)$_2$](ClO$_4$)$_2$, 60489-35-2; [NiCl(diphos)$_2$]ClO$_4$, 60488-87-1; [NiCl$_2$(diphos)$_2$]ClO$_4$, 60536-62-1; [NiBr$_2$(diphos)$_2$]ClO$_4$, 60489-37-4; [NiCl$_2$(diphos)$_2$](ClO$_4$)$_2$, 60562-08-5; [Pd(diphos)$_2$](ClO$_4$)$_2$, 60489-39-6; [PdCl$_2$(diphos)$_2$](ClO$_4$)$_2$, 60489-41-0; [Pt(diphos)$_2$](ClO$_4$)$_2$, 60489-43-2; [PtCl$_2$(diphos)$_2$](ClO$_4$)$_2$, 60489-45-4; CoCl$_2$(diphos)$_2$, 60536-63-2; [CoCl$_2$(diphos)$_2$]ClO$_4$, 60489-46-5; [CoBr$_2$(diphos)$_2$]ClO$_4$, 60489-48-7; [RhCl$_2$(diphos)$_2$]ClO$_4$, 60489-50-1; [IrCl$_2$(diphos)$_2$]ClO$_4$, 60489-52-3; [IrCl$_2$(diars)$_2$]ClO$_4$, 14127-31-2; FeCl$_2$(diphos)$_2$, 60536-64-3; [FeCl$_2$(diphos)$_2$]ClO$_4$, 60536-66-5; [FeBr$_2$(diphos)$_2$]BF$_4$, 60489-54-5; [FeCl$_2$(diphos)$_2$](ReO$_4$)$_2$, 60536-68-7; [FeCl$_2$(diars)$_2$](ReO$_4$)$_2$, 60499-27-6; RuCl$_2$(diphos)$_2$, 60489-55-6; [RuCl$_2$(diphos)$_2$]ClO$_4$, 60489-57-8; OsCl$_2$(diphos)$_2$, 60489-58-9; [OsCl$_2$(diphos)$_2$]ClO$_4$, 60489-60-3; MnCl$_2$(diphos)$_2$, 60536-69-8; [MnCl$_2$(diphos)$_2$]PF$_6$, 60536-71-2; [MnBr$_2$(diphos)$_2$]ClO$_4$, 60489-62-5; [MnCl$_2$(diphos)$_2$](ClO$_4$)$_2$, 60536-73-4; [ReCl$_2$(diphos)$_2$]ClO$_4$, 60489-64-7; [ReCl$_2$(diars)$_2$]ClO$_4$, 14127-35-6; [CrCl$_2$(diphos)$_2$]ClO$_4$, 60536-75-6; [CrBr$_2$(diphos)$_2$]ClO$_4$, 60489-66-9; NiCl$_2$(diphos)$_2$, 60489-67-0; NiCl$_2$(diars)$_2$, 14127-28-7; PdCl$_2$(diphos)$_2$, 60499-28-7; PdCl$_2$(diars)$_2$, 60489-68-1; PtCl$_2$(diphos)$_2$, 60489-69-2; PtCl$_2$(diars)$_2$, 14319-71-2; diphos, 7237-07-2; tetramethyldiphosphine disulfide, 3676-97-9; *o*-dichlorobenzene, 95-50-1; [Cu(NCCH$_3$)$_4$]ClO$_4$, 14057-91-1; [Cu(diars)$_2$]ClO$_4$, 60489-71-6; NaAuCl$_4$, 15189-51-2; trisodium hexachlororhodate(III), 14972-70-4; bis(cyclooctene)chloroiridium(I), 12246-51-4; (NH$_4$)$_2$OsCl$_6$, 12125-08-5; [CoCl$_2$(en)$_2$]$^+$, 14403-91-9; [CoBr$_2$(en)$_2$]$^+$, 15379-04-1; [CrCl$_2$(en)$_2$]$^+$, 14403-88-4; [CrBr$_2$(en)$_2$]$^+$, 33882-25-6; CoCl$_2$(diars)$_2$, 14127-25-4; [NiCl$_2$(diars)$_2$]BF$_4$, 60489-72-7; [NiBr$_2$(diars)$_2$]ClO$_4$, 60489-74-9; FeCl$_2$(diars)$_2$, 14127-26-5; RuCl$_2$(diars)$_2$, 14170-32-2; OsCl$_2$(diars)$_2$, 14516-58-6; [CoCl$_2$(diars)$_2$]ClO$_4$, 17083-97-5; [CoBr$_2$(diars)$_2$]ClO$_4$, 21148-21-0; [RhCl$_2$(diars)$_2$]ClO$_4$, 14127-36-7; [NiCl$_2$(diars)$_2$](ClO$_4$)$_2$, 51417-96-0; [PdCl$_2$(diars)$_2$](ClO$_4$)$_2$, 60489-76-1; [PtCl$_2$(diars)$_2$](ClO$_4$)$_2$, 60489-77-2; MnBr$_2$(diphos)$_2$, 60489-78-3; [FeCl$_2$(diars)$_2$]BF$_4$, 37817-55-3; [FeBr$_2$(diars)$_2$]ClO$_4$, 36421-93-9; [RuCl$_2$(diars)$_2$]ClO$_4$, 14319-72-3; [OsCl$_2$(diars)$_2$]ClO$_4$, 14127-34-5; [OsCl$_2$(diars)$_2$]$^{2+}$, 60489-79-4; [CrCl$_2$(diars)$_2$]ClO$_4$, 14127-30-1; [CrBr$_2$(diars)$_2$]ClO$_4$, 60536-77-8; CoBr$_2$(diphos)$_2$, 60536-78-9; CoBr$_2$(diars)$_2$, 60536-79-0; [Ni(diars)$_2$]$^{2+}$, 60489-80-7; [Pd(diars)$_2$]$^{2+}$, 47384-75-8; [Pt(diars)$_2$]$^{2+}$, 19210-41-4; [Cu(diars)$_2$]$^+$, 60489-70-5; [Ag(diars)$_2$]$^+$, 60489-81-8; [Au(diars)$_2$]$^+$, 60489-82-9; [Au(diphos)$_2$]$^+$, 60489-83-0; [NiBr$_2$(diphos)$_2$]$^{2+}$, 60489-84-1; [NiBr$_2$(diars)$_2$]$^{2+}$, 51446-93-6; [NiCl(diars)$_2$]$^+$, 18918-73-5; [PdCl(diphos)$_2$]ClO$_4$, 60489-86-3; [PdCl(diars)$_2$]$^+$, 18947-49-4; [PtCl(diphos)$_2$]$^+$, 60489-87-4; [PtCl(diars)$_2$]$^+$, 16560-63-7; [NiBr(diphos)$_2$]$^+$, 53030-24-3; [NiBr(diars)$_2$]$^+$, 18918-71-3; [MnBr$_2$(diphos)$_2$]$^{2+}$, 60489-88-5; CrCl$_2$(diphos)$_2$, 60536-80-3; CrCl$_2$(diars)$_2$, 60536-81-4; [OsCl$_2$(diphos)$_2$]$^{2+}$, 60489-89-6; CrBr$_2$(diphos)$_2$, 60489-90-9; CrBr$_2$(diars)$_2$, 60536-82-5; [FeBr$_2$(diphos)$_2$]$^{2+}$, 60489-91-0; [FeBr$_2$(diars)$_2$]$^{2+}$, 54512-26-4; ReCl$_2$(diphos)$_2$, 60489-92-1; ReCl$_2$(diars)$_2$, 14325-13-4; [ReCl$_2$(diphos)$_2$]$^-$, 60489-93-2; [ReCl$_2$(diars)$_2$]$^-$, 60489-94-3; FeBr$_2$(diphos)$_2$, 60489-95-4; FeBr$_2$(diars)$_2$, 21148-19-6; [AgCl(diphos)$_2$]$^{2+}$, 60489-96-5; [AgCl$_2$(diphos)$_2$]$^+$, 60489-97-6.

References and Notes

(1) The coordination chemistry of diars is reviewed by E. C. Alyea in "Transition Metal Complexes of Phosphorus, Arsenic, and Antimony Ligands", C. A. McAuliffe, Ed., Macmillan, London, 1973.
(2) L. F. Warren and M. A. Bennett, *J. Am. Chem. Soc.*, **96**, 3340 (1974).
(3) F. A. Hart, *J. Chem. Soc.*, 3324 (1960).
(4) J. Chatt and F. A. Hart, *J. Chem. Soc.*, 1378 (1960).
(5) R. J. H. Clark, R. H. U. Negrotti, and R. S. Nyholm, *Chem. Commun.*, 486 (1966).
(6) The abbreviation diphos is adopted by analogy with the well-established usage of diars for *o*-C$_6$H$_4$[As(CH$_3$)$_2$]$_2$, even though diphos commonly refers to 1,2-bis(diphenylphosphino)ethane, (C$_6$H$_5$)$_2$PCH$_2$CH$_2$P(C$_6$H$_5$)$_2$. We suggest that the more recent designation dppe be reserved for this ligand.
(7) J. A. McCleverty, *Prog. Inorg. Chem.*, **10**, 49 (1968).
(8) P. Kreisman, R. E. Marsh, J. Preer, and H. B. Gray, *J. Am. Chem. Soc.*, **90**, 1067 (1968).
(9) P. T. Manoharan and M. Rogers, *J. Chem. Phys.*, **53**, 1682 (1970).
(10) P. K. Bernstein and H. B. Gray, *Inorg. Chem.*, **11**, 3035 (1972).
(11) J. R. Preer and H. B. Gray, *J. Am. Chem. Soc.*, **92**, 7306 (1970).
(12) R. D. Feltham, W. Silverthorn, and G. McPherson, *Inorg. Chem.*, **8**, 344 (1967).
(13) R. D. Feltham and W. Silverthorn, *Inorg. Chem.*, **7**, 1154 (1968).
(14) R. D. Feltham and W. Silverthorn, *Inorg. Chem.*, **9**, 1207 (1970).
(15) R. D. Feltham, W. Silverthorn, H. Wickman, and W. Weslowski, *Inorg. Chem.*, **11**, 676 (1972).
(16) R. D. Feltham, A. Kasenally, and R. S. Nyholm, *J. Organomet. Chem.*, **7**, 285 (1967).
(17) H. Niebergall and B. Langenfeld, *Chem. Ber.*, **95**, 64 (1962).
(18) A. Kabesh and R. S. Nyholm, *J. Chem. Soc.*, 38 (1951).
(19) J. Lewis, R. S. Nyholm, and D. J. Phillips, *J. Chem. Soc.*, 2177 (1962).
(20) C. M. Harris and R. S. Nyholm, *J. Chem. Soc.*, 63 (1957).
(21) C. M. Harris, R. S. Nyholm, and D. J. Phillips, *J. Chem. Soc.*, 4379 (1960).
(22) R. S. Nyholm, *J. Chem. Soc.*, 2061 (1950).
(23) R. S. Nyholm, *J. Chem. Soc.*, 2902 (1951).
(24) C. M. Harris and R. S. Nyholm, *J. Chem. Soc.*, 4375 (1956).
(25) R. S. Nyholm, *J. Chem. Soc.*, 2071 (1950).
(26) R. S. Nyholm, *J. Chem. Soc.*, 857 (1950).
(27) L. Volponi, B. Zarli, and C. Colombini, *Gazz. Chim. Ital.*, **98**, 413 (1968); *Chem. Abstr.*, **69**, 15469 (1968).
(28) R. S. Nyholm, *J. Chem. Soc.*, 851 (1950).
(29) (a) R. S. Nyholm and R. V. Parish, *Chem. Ind.* (*London*), 470 (1956); (b) G. S. F. Hazeldean, R. S. Nyholm, and R. V. Parish, *J. Chem. Soc. A*, 162 (1966).
(30) R. S. Nyholm and G. J. Sutton, *J. Chem. Soc.*, 567 (1958).
(31) R. S. Nyholm and G. J. Sutton, *J. Chem. Soc.*, 572 (1958).
(32) N. F. Curtis, J. E. Fergusson, and R. S. Nyholm, *Chem. Ind.* (*London*), 625 (1958).
(33) R. S. Nyholm and G. J. Sutton, *J. Chem. Soc.*, 560 (1958).
(34) R. K. Harris, *Can. J. Chem.*, **42**, 2275 (1964).
(35) R. K. Harris and R. G. Hayter, *Can. J. Chem.*, **42**, 2282 (1964).
(36) D. Taylor and G. B. Robertson, private communication.
(37) V. F. Duckworth and N. C. Stephenson, *Inorg. Chem.*, **8**, 1661 (1969).
(38) N. C. Stephenson, *Acta Crystallogr.*, **17**, 592, 1517 (1964); *J. Inorg. Nucl. Chem.*, **24**, 791, 797 (1962).
(39) N. C. Stephenson, unpublished observation cited in ref 42.
(40) J. Chatt, F. A. Hart, and H. R. Watson, *J. Chem. Soc.*, 2537 (1962).
(41) At least nine hyperfine lines were observed in these spectra, which were dependent upon both solvent and counterion employed; interpretation of the ESR data is beyond the scope of this paper.
(42) J. Lewis, R. S. Nyholm, and G. A. Rodley, *J. Chem. Soc.*, 1483 (1965).
(43) P. Bernstein, G. A. Rodley, R. Marsh, and H. B. Gray, *Inorg. Chem.*, **11**, 3040 (1972).
(44) P. J. Pauling, D. W. Porter, and G. B. Robertson, *J. Chem. Soc. A*, 2728 (1970).
(45) S. A. Butter and J. Chatt, *J. Chem. Soc. A*, 1411 (1970).
(46) J. T. Mague, *Inorg. Chem.*, **11**, 2558 (1972).
(47) F. Canziani, U. Zartorelli, and F. Zingales, *Rend. Ist. Lomb. Accad. Sci. Lett. A*, **101**, 227 (1967); *Chem. Abstr.*, **68**, 839475 (1968).
(48) J. Chatt, G. J. Leigh, D. M. P. Mingos, and R. J. Paske, *J. Chem. Soc. A*, 2636 (1968).
(49) L. F. Warren and M. A. Bennett, in preparation.
(50) E. Verdonck and L. G. Vanquickenborne, *Inorg. Chem.*, **13**, 762 (1974).
(51) B. N. Figgis and J. Lewis, *Prog. Inorg. Chem.*, **6**, 164 (1964).
(52) E. A. Paez, D. L. Weaver, and W. T. Oosterhuis, *J. Chem. Phys.*, **57**, 3709 (1972).
(53) J. M. Rosalky, Ph.D Thesis, Australian National University, 1975.
(54) Our initial report[2] of *high*-spin behavior for [MnCl$_2$(diphos)$_2$]PF$_6$ (μ_{eff} = 5.09 μ_{B}) is incorrect; the high magnetic moment was probably due to manganese(II) impurities.
(55) R. S. Nyholm and G. J. Sutton, *J. Chem. Soc.*, 564 (1958).
(56) G. W. A. Fowles, D. A. Rice, and R. A. Walton, *J. Chem. Soc.*, 1842 (1968).

(57) Unpublished observation cited in S. Casey, W. Levason, and C. A. McAuliffe, *J. Chem. Soc., Dalton Trans.*, 886 (1974).
(58) W. Levason and C. A. McAuliffe, *J. Inorg. Nucl. Chem.*, **37**, 340 (1975).
(59) The pale yellow color reported for the complex formulated as $MnI_2(diars)_2$ in ref 55 may be due to traces of the brown $CoI_2(diars)_2$ complex from the *purple* MnX_2 dioxane solutions observed by these authors. The purple color suggests that there were cobalt impurities in the manganese starting materials: J. J. Foster and N. S. Gill, *J. Chem. Soc. A*, 2625 (1968).
(60) F. Mani, P. Stoppioni, and L. Sacconi, *J. Chem. Soc., Dalton Trans.*, 461 (1975).
(61) A. D. Westland, *J. Chem. Soc.*, 3060 (1965).
(62) W. Levason and C. A. McAuliffe, *Inorg. Chim. Acta*, **11**, 33 (1974); *J. Chem. Soc., Dalton Trans.*, 2238 (1974), and references therein.
(63) The $Ni^{III} \rightarrow Ni^{II}$ redox couples can be made to appear reversible with cyclic voltammetry by incorporating slow potential-scan rates with an excess of X^- ion present. The measured potentials probably correspond to the $[NiX_2L_2]^+ \rightleftarrows [NiX_2L_2]$ conversion involving formally six-coordinate nickel(II).
(64) R. Chant, A. R. Hendrickson, R. L. Martin, and N. M. Rohde, *Aust. J. Chem.*, **26**, 2533 (1973).
(65) The isotropic hyperfine splittings A_{iso}^{Cl} and A_{iso}^{As} found for $[NiCl_2(diars)_2]^+$ in ref 10, taken with the atomic data given in Tables A3.1 and A3.2 by P. B. Ayscough, "Electron Spin Resonance in Chemistry", Methuen, London, 1967, show that only about 1.4–2% of the total unpaired electron density resides on the four As atoms taken together and about 2–4.6% on the two Cl atoms.
(66) Specifically, the ${}^1E \leftarrow {}^1A_1$ transition in tetragonal Co(III) (R. A. D. Wentworth and T. S. Piper, *Inorg. Chem.*, **4**, 709 (1965)) and the ${}^4E \leftarrow {}^4B_1$ transition in tetragonal Cr(III) (ref 13).
(67) M. A. Bennett, R. J. H. Clark, and A. D. J. Goodwin, *Inorg. Chem.*, **6**, 1625 (1967).
(68) Calculated for the Co^{III} complexes based on ref 66 using $Dq^z(Cl^-) = 1460\ cm^{-1}$ and $Dq^z(Br^-) = 1277\ cm^{-1}$ as standard values.
(69) S. C. Jackels, K. Farmery, E. K. Barefield, N. J. Rose, and D. H. Busch, *Inorg. Chem.*, **11**, 2893 (1972); L. Y. Martin, L. J. De Hayes, L. J. Zompa, and D. H. Busch, *J. Am. Chem. Soc.*, **96**, 4046 (1974).
(70) C. A. Tolman, W. C. Seidel, and L. W. Gosser, *J. Am. Chem. Soc.*, **96**, 53 (1974), and references therein.
(71) **Note Added in Proof.** See now M. H. Jones, W. Levason, C. A. McAuliffe, and M. J. Parrott, *J. Chem. Soc., Dalton Trans.*, 1642 (1976).

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Intramolecular Rearrangement in (η-Diene)tricarbonyliron and -ruthenium Compounds. A Carbon-13 Nuclear Magnetic Resonance Study

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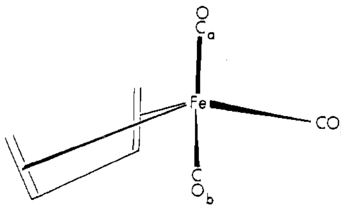
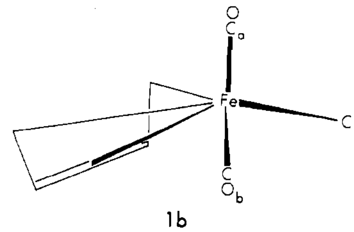
The fluxional behavior of a series of (η-diene)tricarbonyliron and (η-diene)tricarbonylruthenium complexes studied by variable-temperature ^{13}C NMR spectroscopy is reported. The difference in the rates of rearrangement between conjugated and nonconjugated dienes is noted. The increased activation barrier for carbonyl scrambling in (η-1,3-diene)tricarbonyliron complexes is attributed to the mixing in of "six-coordinate character" into these formally five-coordinate molecules. The dependence of the rearrangement energetics on the electronic structure of the conjugated diene is fully consistent with the above postulate. Possible mechanisms which are consistent with the permutational nature of the exchange are detailed and the apparent differences between conjugated and nonconjugated dienes are discussed. The variations in the averaged ^{13}C chemical shifts of the carbonyl groups can be satisfactorily accounted for by a metal→carbonyl π-back-bonding model. However, the individual carbonyl resonances observed in the low-temperature spectra are at odds with force constant calculations. This apparent discrepency is commented upon.

Introduction

The study of intramolecular rearrangement in five-coordinate d^8 transition metal complexes has attracted a great deal of attention since the first unambiguous demonstration of the phenomenon in $(CF_3)Co(CO)_3PF_3$ by Udovich and Clark.[1] The studies, besides establishing the generality of the phenomenon,[2,3] have also provided important mechanistic insights into the nature of the dynamic process.[4,5] It is then interesting to observe that $Fe(CO)_5$[5a] and some of its derivatives (η-norbornadiene)tricarbonyliron,[6a] [bis(dimethylphosphino)ethane]tricarbonyliron,[6b] [bis(diphenylphosphino)methane]tricarbonyliron,[6c] $(R_3P)Fe(CO)_4$,[6a,d,e] $(py)Fe(CO)_4$,[6f] and $(CHO)Fe(CO)_4^-$ [6g] are conspicuous because of their low activation barriers for rearrangement and the consequent observation of time-averaged spectra even at the lowest accessible temperatures. Indeed, until recently, only in (1–4-η-cyclooctatetraene)tricarbonyliron,[7] (η-butadiene)$Fe(CO)_{3-x}(PF_3)_x$,[8] and (η-1,3-cyclohexadiene)$Fe(CO)_{3-x}(PF_3)_x$[9] has intramolecular rearrangement in an iron-containing five-coordinate molecule been demonstrated. Although the above complexes all contained a conjugated diene ligand, the importance of this structural unit on the activation barrier for rearrangement seemed to have been overlooked. Indeed, two previous reports[10] on the ^{13}C NMR of (η-butadiene)tricarbonyliron were concerned only with the question of whether **1a** or **1b** was a better representation of the bonding for the molecule in solution. No attempt was made to rationalize the observation of a single sharp resonance for the three carbonyl groups, which is clearly inconsistent with either **1a** or **1b** and the known tetragonal-pyramidal geometry of the complex[11] in the solid state. Nor was there a variable-temperature study initiated to verify whether the single line was due to accidental coincidence or nonrigid behavior.



1a



1b

We[12] and others[13] have recently reported a variable-temperature ^{13}C NMR study of **1** showing that in fact intramolecular rearrangement was responsible for the single ^{13}CO line observed at room temperature. In an attempt to un-