Table III. Electron-Transfer Stereoselectivity in the Oxidation of $[Co((\pm)\text{-}chxn)_3]^{2+}$ by $[\Delta\text{-}Co(edta)]^-$ in DMSO and Aqueous Solutions at 23 °C

	DMSO	DMSO (0.6 M Cl^-)	H_2O[a]
lel$_3$	50% Λ	43% Λ	24% Δ
lel$_2$*ob*	72% Λ	58% Λ	5% Δ
lel ob$_2$	76% Λ		7% Λ
ob$_3$	59% Λ		16% Λ

[a] Reference 5.

unexpected in view of the strong hydrogen-bonding ability of both oxidant and reductant.

Much greater insight into the effects of solvent and added chloride ion is obtained with use of the conformationally restricted complex $[Co((\pm)\text{-}chxn)_3]^{2+}$ as reductant. The relative proportions of conformational isomers obtained in the oxidation of $[Co((\pm)\text{-}chxn)_3]^{2+}$ by $[\Delta\text{-}Co(edta)]^-$ in both DMSO and water are shown in Table II. Results from the nonaqueous solvent show a marked increase in the proportion of the *lel*$_3$ isomer at the expense primarily of *lel ob*$_2$ and *ob*$_3$. This effect is enhanced in the presence of chloride ion such that the bulk of the product is the *lel*$_3$ isomer and *lel ob*$_2$ and *ob*$_3$ are not obtained in detectable amounts. The result that there is an increase in *lel*$_3$ character in the presence of chloride ion in DMSO solutions is in good qualitative agreement with the findings of Nafie and co-workers[9] from vibrational CD studies of solutions of $[Co(en)_3]^{3+}$. Clearly these solvent- and anion-dependent conformational changes are relatively general and are found even with the more bulky 1,2-diaminocyclohexane ligand.

The stereoselectivities observed for the different conformational isomers are shown in Table III. The results from the DMSO experiments differ markedly from those obtained previously for aqueous solution. In particular, for the *lel*$_3$ isomer, the enantiomeric excess in the reaction with $[\Delta\text{-}Co(edta)]^-$ changes from 25% Δ in aqueous solution to 50% Λ in DMSO. Not only are the stereoselectivities much larger in the aprotic solvent but also in some instances they differ in the absolute sense and do not show the well-defined trend with chelate ring conformation observed in aqueous solution. The presence of chloride ion in DMSO solution appears to reduce the stereoselectivity for each of the conformational isomers by between 15% and 20%. If Nafie's suggestions[9] are correct and the chloride ions are located specifically along the C_2 axes of the reductant, then reaction of $[\Delta\text{-}Co(edta)]^-$ with $[Co((\pm)\text{-}chxn)_3\cdot 3Cl]^-$ should involve a preferential interaction along the C_3 axis where electrostatic repulsions are minimized. Previous results[5] suggest that this is consistent with a reduction in the magnitude of the ΔΛ enantiomeric excess, but clearly, such explanations based on observations for aqueous systems are oversimplified. A simpler explanation may be that the presence of chloride ion decreases the electrostatic attraction between the complexes. The balance between the changes in conformational isomer selectivity and stereoselectivity on the addition of chloride ion coupled with the reduced dependence of the stereoselectivity on chelate ring conformation in DMSO provides an explanation for the absence of a substantial chloride ion dependence in the oxidation of conformationally labile $[Co(en)_3]^{2+}$. While the proportion of the *lel*$_3$ isomer may be enhanced, the stereoselectivity is modified by the presence of the added anion, counteracting this change.

These results dispel any notion that the increased stereoselectivity observed by Geselowitz and co-workers[1,4] in the oxidation of $[Co(en)_3]^{2+}$ on going from aqueous solution to DMSO is due solely to a change in chelate ring conformation. Clearly, there are substantial differences in the mode of interaction between $[Co(edta)]^-$ and the reductant depending on the reaction medium. Geselowitz, Hammershøi, and Taube[4] assert that hydrogen-bonding solvents interfere with the hydrogen bonding between the reactants, causing reduced stereoselectivity. This may be an understatement. In strongly hydrogen-bonding aqueous media, it is likely that the ion pair incorporates a great deal of solvent structure and is perhaps best described in terms of a solvent-separated ion pair. Although there is some evidence for a role for trace amounts of water in the interaction in DMSO, the larger stereoselectivity suggests a more intimate contact between the reactants. The lack of a strong dependence on chelate ring conformation also points to a reduced involvement of hydrogen-bonding structure.

Finally, the study indicates that substantial stereoselectivity can result in outer-sphere electron-transfer reactions and, further, that this stereoselectivity can be manipulated by careful choice of solvent and added electrolyte. For the reaction between $[\Delta\text{-}Co(edta)]^-$ and $[Co((\pm)\text{-}chxn)_3]^{2+}$, the discrimination for the *lel ob*$_2$ isomer represents a factor of 7 in the electron-transfer rate constant, while the reaction in the presence of chloride ion shows enhanced isomer selectivity. These results give some hope that with greater understanding of the processes and interactions involved in the induction of chirality in electron-transfer reactions, substantially higher selectivities might be attained.

Acknowledgment. The generous support of the National Science Foundation (Grant No. CHE84-06113) is gratefully acknowledged.

Registry No. DMSO, 67-68-5; $Na[\Delta\text{-}(+)_{546}\text{-}Co(edta)]$, 111140-05-7; $[Co(en)_3]^{2+}$, 23523-25-3; $[Co((\pm)\text{-}chxn)_3]^{2+}$, 27910-76-5; $\Lambda\text{-}[Co(chxn)_3]Cl_3$ (*lel*$_3$ isomer), 59671-81-7; $\Delta\text{-}[Co(chxn)_3]Cl_3$ (*lel*$_3$ isomer), 31537-08-3; $\Lambda\text{-}[Co(chxn)_3]Cl_3$ (*lel*$_2$*ob* isomer), 59727-65-0; $\Delta\text{-}[Co(chxn)_3]Cl_3$ (*lel*$_2$*ob* isomer), 59727-62-7; $\Lambda\text{-}[Co(chxn)_3]Cl_3$ (*lel ob*$_2$ isomer), 59727-66-1; $\Lambda\text{-}[Co(chxn)_3]Cl_3$ (*ob*$_3$ isomer), 34369-95-4; $\Lambda\text{-}[Co(en)_3]Cl_3$, 23778-88-3; LiCl, 7447-41-8; H_2O, 7732-18-5.

Contribution from the Guelph-Waterloo Centre for Graduate Work in Chemistry, Guelph Campus, Department of Chemistry and Biochemistry, University of Guelph, Guelph, Ontario, Canada N1G 2W1, and Department of Chemistry, University of Nevada—Reno, Reno, Nevada 89557

Identification by Stopped-Exchange Solution ^{31}P NMR Spectroscopy of the Stepwise Formation of $[AgL_n]PF_6$ (n = 1–4). Comparison of Metal–Phosphorus Coupling Constants for Triphenylphosphine and 5-Phenyldibenzophosphole

Elmer C. Alyea,*[†] John Malito,[†] and John H. Nelson*[‡]

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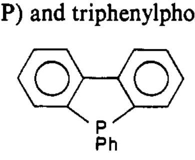
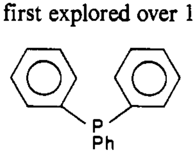
Interest in the coordination chemistry of phospholes has been steadily increasing in recent years.[1] A useful approach for an evaluation of the donor properties of a given phosphole involves the direct comparison of the coordination chemistries of the phosphole and its closest acyclic phosphine analogue.[2,3] Comparison of the donor properties of 5-phenyldibenzophosphole (PhDBP) and triphenylphosphine was first explored over 15 years ago by two independent groups.[4] Our laboratories have undertaken a comprehensive study of the coordination properties of PhDBP, kindled by our interest in phospholes[1] and an improved synthesis[5] for PhDBP.



PhDBP



Ph_3P

This note shows that the stepwise formation of $[L_nAg]^+PF_6^-$ (n = 1–4) for L = PhDBP and Ph_3P may be readily observed in situ by stopped-exchange solution ^{31}P NMR spectroscopy. The relative ligating properties of PhDBP and Ph_3P are compared, and discussion is also extended for the first time to $^1J(M\text{–}P)$ coupling constants obtained for several well-characterized metal

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[†] University of Guelph.

[‡] University of Nevada—Reno.

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Table I. ^{31}P NMR Chemical Shifts and ^{107}Ag–^{31}P Spin–Spin Couplings (Hz) for [L_nAg]PF_6[a]

	$\delta_{^{31}P}$ (^1J(Ag–P))			
L	$n = 1$	$n = 2$	$n = 3$	$n = 4$
PhDBP	3.0 (730)	4.9 (510)	2.7 (316)	−1.9 (223[b])
Ph_3P	15.8 (755)	15.3 (507)	11.5 (319)	5.6[c] (224[c])

[a] The septet pattern observed for the PF_6^- anion at −144.8 ppm (716 Hz) is excluded from the table and Figure 1. The free ligands resonate at −11.3 ppm (PhDBP) and −5.8 ppm (Ph_3P) under the same conditions. Coupling to ^{109}Ag, which is equal to 1.15 times that to ^{107}Ag, is not tabulated. [b] For isolated [(PhDBP)$_4$Ag]NO_3: mp 280–282 °C; $\Lambda_M(CH_3NO_2)$ = 80.4 mho; J = 225 Hz. [c] Values of δ 7.5 and J = 222 Hz at 178 K have been reported.[12]

complexes of these two ligands.

Experimental Section

The preparation of PhDBP is reported elsewhere.[5] The ^{31}P NMR spectra for the [L_nAg]$^+PF_6^-$ species (n = 1–4; L = PhDBP and PPh_3) reported herein were recorded on a Bruker AM-250 spectrometer operating at 101.26 MHz in the FT mode at 193 K to ensure stopped-exchange conditions. Some resultant spectra for L = PhDBP and Ph_3P are shown as composites in parts a and b, respectively, of Figure 1. Each spectrum represents a minimum of 400 transients at a data point resolution of 2.4 Hz. The chemical shifts (positive shifts are downfield of 85% H_3PO_4 at 0.0 ppm) and coupling constants are given in Table I. The spectra were recorded after adding $^1/_2$-equiv (1 equiv = 0.10 mmol) increments of ligand to saturated $AgPF_6$–CH_2Cl_2 solutions to the point where the free ligand resonance appeared in the spectrum. The stoichiometric mole ratios shown in the spectra were determined by comparison to spectra obtained for some separate additions of either ligand to $AgPF_6$ solutions of known concentration. It was found that either free ligand was only observed when the L/$AgPF_6$ mole ratio exceeded 4.0. Incremental additions of PhDBP and Ph_3P to 0.1 mmol CH_2Cl_2 solutions of $AgPF_6$ were also performed at 223 K to corroborate the spectral assignments at 196 K and to give evidence about ligand exchange.

Results and Discussion

The solution ^{31}P NMR spectra for silver(I) phosphine complexes are typically characterized by a diagnostic doublet of doublets type pattern for each phosphorus environment.[6] This pattern results from the coupling of the phosphorus to each of the spin $I = {}^1/_2$ silver isotopes (^{107}Ag, 51.8% natural abundance; ^{109}Ag, 48.2% natural abundance). For complexes containing chelating[7,8] or bulky phosphine ligands[9,10] $^1J(^{107,109}Ag–^{31}P)$ is observable at ambient temperature. The higher kinetic lability of smaller monodentate phosphine,[6] phosphite,[11] and aminophosphine[12] ligands, however, leads to a rapid ligand exchange on the NMR time scale and necessitates lower temperatures (typically less than 203 K) for resolution of silver–phosphorus coupling. In this study at 193 K, the appearance of distinct doublets of doublets for each chemical species (Figure 1), coupled with the knowledge of the ligand to metal ratio present in solution, makes the assignments unambiguous. Spectra for the additions of less than 1 equiv of either ligand are not shown because they are virtually identical with those shown for 1 equiv; the broad resonances observed for 1 equiv or less of added PhDBP reflect the greater exchange rate of the phosphole as compared to that of Ph_3P.

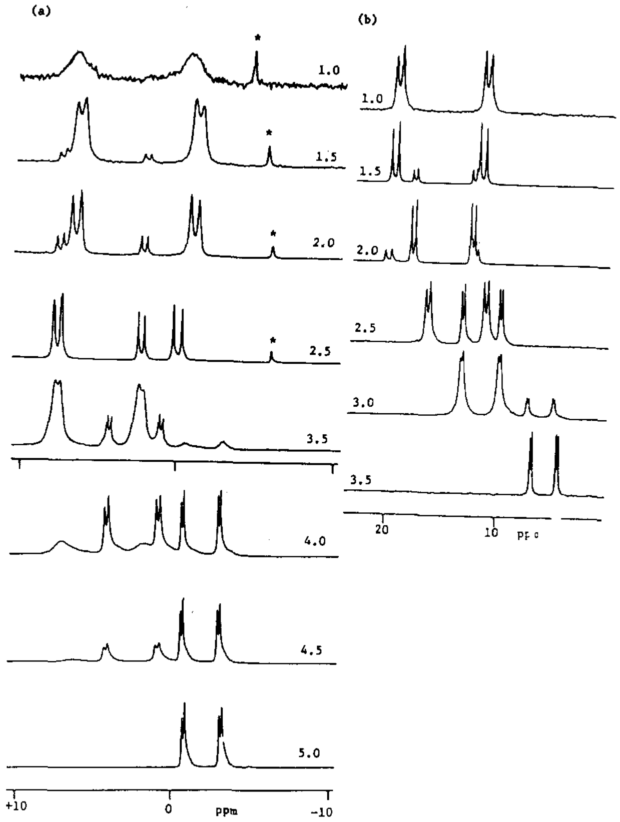

Figure 1. ^{31}P NMR spectra in dichloromethane solutions at 193 K for the stepwise addition of equivalents (shown on spectra) of (a) PhDBP or (b) Ph_3P to a saturated solution of $AgPF_6$. The impurity peak (*) is due to the left component of a triplet arising from a PF_6^- hydrolysis product present in the commerical $AgPF_6$ sample.

The general trend of decreasing phosphorus chemical shift with increasing coordination number is consistent with the expectation that shielding of the phosphorus approaches that of the uncoordinated ligand when the C–P–C angles can increase the least. It also suggests that the average silver–phosphorus bond strength decreases with increasing coordination number. The similarity in the $\delta_{^{31}P}$ values for the PPh_3AgPF_6 and [$(PPh_3)_2Ag$]$^+PF_6^-$ complexes and the reversal observed for the PhDBP analogues suggest that the C–P–C angles are already maximized for the [$(R_3P)_2Ag$]$^+PF_6^-$ species. The chemical shifts for the R_3PAgPF_6 complexes of either PhDBP or Ph_3P are also compatible with each silver atom being two-coordinate due to interaction with the PF_6^- anion. Although such semicoordination of anions such as PF_6^- and BF_4^- is relatively rare,[13] it is not surprising in this instance, as previously noted[11] for some 1:1 complexes of $AgBF_4$ with certain phosphites.

The magnitude of the coupling constants is characteristic of the number of coordinated ligands, decreasing substantially with increasing coordination number. The recent structural characterization[14] of [$(Ph_3P)_nAg$]$^+NO_3^-$ (n = 2–4), together with their solid-state CPMAS ^{31}P NMR data (J = 470, 310, and 190 Hz for n = 2, 3, and 4, respectively), firmly establishes the inverse correlation of coordination number with the magnitude of the coupling constant. Apparently, weak coordination of the anion causes a slight decrease in J for the nitrate complexes as compared to the PF_6^- species.[6,8,11-14]

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Table II. Spin-Spin Coupling Constants for Representative PhDBP and Ph_3P Complexes

compd[a]	$^1J(^nM-^{31}P)$, Hz	temp, K
$(PhDBP)_2HgI_2$	2217	243
$(Ph_3P)_2HgI_2$[b]	3073	230
	2951	243
$(PhDBP)_2Hg(SCN)_2$	3001	223
$(Ph_3P)_2Hg(SCN)_2$[b]	3716	230
$(PhDBP)_2PtCl_2$	3489	299
$(Ph_3P)_2PtCl_2$[c]	3676	299
$(PhDBP)Mo(CO)_5$	132	298
$(Ph_3P)Mo(CO)_5$[d]	139	298
$(PhDBP)W(CO)_5$	231	298
$(Ph_3P)W(CO)_5$[e]	245	298

[a] Measured in CH_2Cl_2 solution. Satisfactory elemental analyses were obtained for the new PhDBP complexes; details of their syntheses will be reported elsewhere. [b] Reference 18. [c] Goel, R. G. *Inorg. Nucl. Chem. Lett.* **1979**, *15*, 437. [d] Reference 21. [e] Keiter, R. L.; Vander Velde, D. G. *J. Organomet. Chem.* **1983**, *258*, 234.

The significantly larger coupling constant observed for the PPh_3AgPF_6 complex indicates that PPh_3 forms a stronger bond to the silver atom than does PhDBP when only PF_6 is a competing ligand. On the other hand, the nearly identical coupling constants for each pair of $[(R_3P)_nAg]^+PF_6^-$ (n = 2-4) complexes suggest that PhDBP and Ph_3P have very similar donor strengths. Together, these observations imply that the lower basicity of PhDBP ($pK_a = 0.5$)[15] as compared to that of Ph_3P ($pK_a = 2.73$)[16] is somewhat compensated for by a greater π-acceptor ability for PhDBP. This is supported by the coupling constant data given in Table II for other metal complexes of PhDBP and Ph_3P. By way of comparison, we have also observed the ^{31}P NMR spectra for the species R_3PAgPF_6 and $[(R_3P)_2Ag]^+PF_6^-$: R_3P = $(p\text{-}ClC_6H_4)_3P$ ($pK_a = 1.03$)[17] and $(p\text{-}CH_3OC_6H_4)_3P$ ($pK_a = 4.57$).[17] The coupling constants of 505 and 506 Hz for these two $[(R_3P)_2Ag]^+PF_6^-$ species differ very little from those observed for the PhDBP and Ph_3P analogues. The coupling constants of 757 and 767 Hz for these R_3PAgPF_6 complexes are close to the value observed for PPh_3AgPF_6.

It is clear from the data in Figure 1 that the low-coordination-number species persist at relatively higher ligand to metal ratios for PhDBP than for Ph_3P. For example, the R_3PAgPF_6 species is still present when the relative L:M ratio is greater than 2.0 for PhDBP. In contrast, the $[(R_3P)_4Ag]^+PF_6^-$ complex is already present at a L:M ratio of 3.0 for PPh_3. At the same equivalents added of 2.5 equiv, it is seen that $[(Ph_3P)_2Ag]^+PF_6^-$ and $[(Ph_3P)_3Ag]^+PF_6^-$ are present in nearly equal concentrations, whereas only the 1:1 and 1:2 species are present in the solution containing added PhDBP. In addition, the ^{31}P coordination chemical shifts $\Delta\delta_{^{31}P} = \delta_{^{31}P}(\text{complex}) - \delta_{^{31}P}(\text{ligand})$ (a reasonable measure of metal-phosphorus bond strength) are uniformly larger for the Ph_3P complexes than for their DPB analogues. Hence, the higher coordination number species have a greater thermodynamic stability for Ph_3P than for PhDBP. This is surprising as PhDBP is sterically smaller than Ph_3P. It is interesting to note that the $[(R_3P)_2Ag]^+PF_6^-$ species for both ligands are fairly stable. They do not disproportionate to higher and lower coordination number species even upon an increase to room temperature. This is perhaps related to the C-P-C bond angle maximization mentioned above for the $[(R_3P)_2Ag]^+PF_6^-$ species.

Evidence for the faster exchange rate of the PhDBP complexes has already been alluded to in the above discussion. In addition, we note that the line widths of the ^{31}P resonances for the Ph_3P complexes are narrower than those of the PhDBP analogues. Also, there are never more than two species present in solution for the Ph_3P system, whereas three species are simultaneously present for at least three L:M ratios for the PhDBP system. The ease of formation of $[Ag(PhDBP)_4]^+PF_6^-$ at 223 K (vide infra), even with a deficiency of added PhDBP, similarly is consistent with faster exchange for the phosphole ligand. Thus, in general, the PhDBP complexes are kinetically more labile than the Ph_3P complexes.

The stepwise additions of either ligand to $AgPF_6$ solutions at the higher temperature of 223 K again show the presence of four species in each case. Faster exchange is especially evident for both $[AgL_3]^+PF_6^-$ species, and the coupling is not resolved for the broad doublets observed at 2.3 and 11.1 ppm for L = PhDBP and Ph_3P, respectively. For the Ph_3P additions, the broad resonance ($\Delta\nu_{1/2}$ = 470 Hz) at 7 ppm for a 3.5:1 ratio of Ph_3P to $AgPF_6$, which signifies an exchange between $Ag(PPh_3)_3^+$ and $Ag(PPh_3)_4^+$ cations, changes to a doublet at 5.5 ppm due to $Ag(PPh_3)_4^+$ itself with the addition of another 0.5 equiv of Ph_3P. In contrast, the presence of a resolved doublet of doublets for $[Ag(PhDBP)_4]^+PF_6^-$ at -1.3 ppm is already dominant at a 2.0:1 ratio of PhDBP to $AgPF_6$; above a ratio of 2.5:1, only $[Ag(PhDBP)_4]^+PF_6^-$ is observable until excess PhDBP (4.25:1 ratio) gives a peak at -12 ppm. Clearly, PhDBP has a much greater tendency than Ph_3P to form the higher coordination number species at 223 K.

A correlation between anion electronegativity and $J(^{199}Hg-^{31}P)$ is expected for mercury(II) phosphine complexes,[18,19] which is consistent with no π-bonding being involved in the mercury-phosphorus bond.[20] The lower $^1J(^{199}Hg-^{31}P)$ values for the mercury(II) complexes of PhDBP thus directly reflect the lower σ-donor ability of PhDBP as compared to that of Ph_3P. If the metal can particpate in π-bonding, as is expected for Pt(II), Mo(0), and W(0), then the coupling constants are similar but remain smaller for PhDBP than for Ph_3P. This is due to the much better π-acceptor ability of PhDBP and the synergistic relation between the σ and π metal-ligand interactions. In corroboration of this property of PhDBP, the ^{95}Mo NMR chemical shift for $(PhDBP)Mo(CO)_5$, -1795 ppm, is considerably upfield from that previously reported for $Ph_3PMo(CO)_5$, -1743 ppm.[21]

Several series of metal complexes are under current investigation in order to compare the coordination chemistry of PhDBP and Ph_3P in greater detail. The results of these studies will be reported in future publications.

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Contribution from the Department of Chemistry
and MSU Shared Laser Laboratory, Michigan State University,
East Lansing, Michigan 48824

Iron Porphyrin π Cation Radicals: Solution Resonance Raman Spectra of $(OEP^{\bullet+})Fe^{III}(X)(X')$

Asaad Salehi, W. Anthony Oertling, Gerald T. Babcock,*
and Chi K. Chang*

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Heme catalysis in peroxidases, catalases, and cytochromes P450 proceeds through high-valent intermediates, some of which are