

considerably higher energies.<sup>35</sup> (Pure  $\chi^*$  and  $\psi^*$  excited states probably do not exist because some degree of configuration interaction is likely.) The relative energies of bands II and III are also in accord with the proposed assignments. Thus, the  $\psi^*$  and  $\chi^*$  orbitals have similar energies in the phenanthroline ligands, but calculations suggest that the  $e(xz, yz)$  orbitals occur at higher energy than  $b_1(x^2 - y^2)$  in a related  $\text{Cu}(\text{NN})_2^+$  system, where the ligand is 1,4-diazabutadiene.<sup>36</sup> Transition-state energies have also been calculated, and they reveal that the trend in orbital energies is generally a reliable indicator of excitation energies.<sup>36</sup>

The assignment of band I is more problematic. The possibility that band I is a spin-forbidden triplet CT transition can probably be ruled out because the spin-orbit coupling constant of copper is too small to account for the observed intensity. At least two other possible assignments exist for band I, however. If the assumption of  $D_{2d}$  symmetry is correct, band I must be attributed to a transition with  $x, y$  polarization. This assignment is plausible because various mechanisms exist that can impart oscillator strength to  $x, y$ -polarized transitions.<sup>7,34</sup> Indeed, perpendicularly polarized transitions have been assigned in the spectra of  $\text{W}(\text{C}-\text{O})_4(\text{NN})$ <sup>37</sup> and  $\text{Cu}(\text{dmp})\text{X}$ <sup>38</sup> systems, where X is a bridging anion. Other possibilities exist if the symmetry is lower than  $D_{2d}$ , and Crosby and co-workers have suggested that band I can be  $z$ -polarized if there is a low-symmetry distortion.<sup>39</sup> The spectra in Figure 3 may lend support to this interpretation.

**CT Spectra of  $\text{Cu}(\text{NN})_2^+$  Systems with 2,9-Di-aryl Substituents.** As can be seen in Figure 2, the low-temperature CT absorption spectrum of  $\text{Cu}(\text{dpp})_2^+$  spans an even broader range of energies than the solid-state spectrum of  $\text{Cu}(\text{dmp})_2^+$ . The CT spectrum of  $\text{Cu}(\text{tpp})_2^+$  is similar to that of  $\text{Cu}(\text{dpp})_2^+$ . Since extended Hückel calculations reveal that the presence of the phenyl substituents has little effect on the energy gap between the  $\psi^*$  and  $\chi^*$  orbitals, we attribute the spectral spread to enhanced splitting among the  $d_{x^2-y^2}$  and the  $d_{xz}$  and  $d_{yz}$  orbitals, presumably due to a low-symmetry distortion. In line with this reasoning, a related complex of a catenand ligand assumes a very distorted geometry in the solid state, where the coordination geometry is approximately trigonal pyramidal. Here the relative orientation of the ligands is probably determined, at least in part, by intramolecular interligand stacking interactions,<sup>40</sup> and these may persist in the fluid phase as well. Moreover, previous work has shown that lowering the symmetry gives rise to an intense, low-energy band in related nickel systems.<sup>44,45</sup>

In the limit of a large distortion the absorption intensity is spread over a number of transitions,<sup>7</sup> and clear resolution of transitions to the  $\chi^*$  and  $\psi^*$  orbitals is unlikely. The dnp complex also contains aromatic substituents in the 2,9-positions of the phenanthroline core; however, its CT absorption spectrum, albeit broadened, more nearly resembles that of  $\text{Cu}(\text{dmp})_2^+$  (Figure 2). This may indicate less distortion from  $D_{2d}$  symmetry.<sup>41</sup>

**Vibronic Structure.** Various CT bands in Figure 2 exhibit underlying structure. For example, band II generally consists of at least two overlapping components separated by 1000–1500  $\text{cm}^{-1}$ . In view of the magnitude of the energy separation and the splitting being essentially independent of the substituent, we attribute the structure to vibronic effects. The CT spectra of analogous  $\text{Cu}(\text{I})$  complexes of simple diazabutadiene ligands also exhibit vibrational structure, and the spacing is about 1500  $\text{cm}^{-1}$ , characteristic of

a stretching motion involving the  $\text{C}=\text{N}$  double bonds.<sup>36,42</sup> In all likelihood, the vibronic structure of the CT transitions studied herein reflects  $\text{C}=\text{N}$  stretching motion as well; however, more than one vibrational mode of the extended heteroaromatic ligands is apt to be involved.

**Emission Spectra.** Although it has been possible to identify the CT states that are involved in absorption, the assignment of the emitting state(s) is unclear because geometry changes can be expected to attend relaxation of the initially excited Franck-Condon state. This follows because a change in the formal oxidation state of the metal center attends CT excitation, and  $\text{Cu}(\text{II})$  and  $\text{Cu}(\text{I})$  centers usually assume quite different coordination geometries. As a result neither the relative energies nor the relative magnitudes of the transition probabilities necessarily correspond in the absorption and emission spectra. These complications notwithstanding, it can be noted that the magnitude of the radiative rate constant for the emitting singlet CT state of  $\text{Cu}(\text{dmp})_2^+$  is sensibly related to the molar extinction coefficient of band I in the absorption spectrum.<sup>6</sup>

At least qualitatively, the emission spectra reflect important structural effects. As can be seen from the results in Table II, only  $\text{Cu}(\text{NN})_2^+$  systems with bulky substituents in the 2,9-positions exhibit detectable luminescence in donor solvents such as methanol. We attribute this to a type of exciplex quenching that is inhibited when bulky ligands are bound to the copper center.<sup>5,8,10</sup> The correlation between the lifetime in methylene chloride and the size of the substituents in Table II suggests that even a weakly basic solvent is capable of inducing quenching. Also significant in this regard is that the above correlation is lost in a rigid matrix at 77 K, where exciplex quenching should be inhibited.<sup>43</sup>

It is intriguing to note that the  $\text{Cu}(\text{phen})_2^+$  system does not exhibit detectable luminescence even at 77 K. Since its absorption spectrum is similar to that of  $\text{Cu}(\text{dmp})_2^+$  and those of the other emitting systems, we attribute the lack of emission to efficient nonradiative decay rather than to an inefficient radiative process. Radiationless decay is enhanced if, on formation of the excited state, a large structural reorganization occurs such that the ground- and excited-state energy surfaces approach each other. This may be the case with  $\text{Cu}(\text{phen})_2^+$  because the minimal steric demands of the phen ligand would permit significant rearrangement within the coordination sphere; for example, recent studies have shown that packing forces induce a pronounced flattening distortion on the  $\text{Cu}(\text{phen})_2^+$  molecule in the solid state.<sup>29</sup> While a similar flattening occurs in complexes with bulky 2,9-substituents, these groups limit the degree of distortion.<sup>31</sup>

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#### Evidence for Differing Ion-Pair Precursor Structures in the Oxidation of Cobalt(II) Amine Derivatives by $[\text{Co}(\text{edta})]^-$

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Oxidation of racemic  $[\text{Co}(\text{en})_3]^{2+}$  by optically active  $[\Delta\text{-Co}(\text{edta})]^-$  results in formation<sup>1</sup> of an enantiomeric excess around 10% of  $[\Lambda\text{-Co}(\text{en})_3]^{3+}$ , a  $\Delta\Lambda$  interaction, in aqueous media at 25

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°C. This chiral induction is attributed to stereoselectivity in the formation of the ion-pair precursor to electron transfer since the ion pair formed between the isostructural complexes  $[\text{Co}(\text{en})_3]^{3+}$  and  $[\text{Co}(\text{edta})]^-$  also shows a  $\Delta\Lambda$  preference.<sup>2,3</sup> The electron-transfer reaction has been the subject of two detailed studies<sup>4,5</sup> in which the structures of both oxidant and reductant have been varied. Modification of the amine backbone of the oxidant<sup>4</sup> with use of the complexes  $[\Delta\text{-Co}(\text{pdta})]^-$  and  $[\Delta\text{-Co}(\text{cdta})]^-$  has little effect on the reaction kinetics or stereoselectivity, implicating the carboxylate face in a hydrogen-bonding interaction with amine protons from  $[\text{Co}(\text{en})_3]^{2+}$ . However, with  $[\text{Co}(\text{sep})]^{2+}$ ,  $[\text{Co}(\text{sen})]^{2+}$ ,  $[\text{Co}(\pm\text{-bn})_3]^{2+}$ , and  $[\text{Co}(\pm\text{-chxn})_3]^{2+}$  as reductants,<sup>5</sup> there is evidence for a change in the dominant interaction of these complexes as the steric bulk of the ligand shifts from the  $C_3$  to the  $C_2$  axis. In studies with the latter two reagents it has proved possible to show that the stereoselectivity is markedly dependent on the conformation of the five-membered chelate rings since the ligands are optically active and the conformational isomers are diastereomers, not interconvertible by simple rotations. Chelate ring conformation may be described as *lel* if the C-C bond of the five-membered ring lies parallel with the  $C_3$  axis of the complex and *ob* if the C-C bond lies oblique to this axis. Four conformational isomers are possible, designated by the trivial names *lel*<sub>3</sub>, *lel*<sub>2</sub>*ob*, *lel* *ob*<sub>2</sub>, and *ob*<sub>3</sub> where the conformation of each of the three chelate rings is indicated.<sup>6</sup> There is a trend in stereoselectivity from  $\Delta\Delta$  to  $\Delta\Lambda$  as the number of *ob* conformers increases, explicable in terms of changes in the pattern of hydrogen bonding between the reactants.<sup>5</sup>

The stereoselectivity in the oxidation of  $[\text{Co}(\text{en})_3]^{2+}$  has been shown<sup>4</sup> to have a strong solvent dependence, increasing from 10%  $\Delta\Lambda$  in water to 35%  $\Delta\Lambda$  in DMSO. One possible explanation for this result<sup>5</sup> is a change in the chelate ring conformation in  $[\text{Co}(\text{en})_3]^{2+}$  from predominantly *lel*<sub>2</sub>*ob* in water<sup>7,8</sup> to a form containing greater *ob* character in DMSO. However recent vibrational circular dichroism results<sup>9</sup> suggest the opposite to be the case with a dominant *lel*<sub>3</sub> conformation in DMSO in the presence of chloride ion. In this paper, the effect of changing solvent from water to DMSO is investigated for the oxidation of the conformationally restricted complex  $[\text{Co}(\pm\text{-chxn})_3]^{2+}$  by  $[\Delta\text{-Co}(\text{edta})]^-$ .

### Experimental Section

The reagents  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  (Baker, Analyzed),  $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  (Alfa),  $\text{CoCl}_2$  (Aldrich, anhydrous), LiCl (Aldrich, anhydrous), *rac*-(±)-1,2-diaminocyclohexane (Aldrich), 1,2-diaminoethane (Aldrich, 99+%), and DMSO (Aldrich, <0.02% water) were used as received. The complex  $\text{Na}[\Delta\text{-Co}(\text{edta})] \cdot 4\text{H}_2\text{O}$  was prepared by standard literature methods.<sup>10</sup>

Stereoselectivity experiments were run at 23 °C under an argon atmosphere to prevent aerial oxidation of the cobalt(II) complexes. In general, a 10-fold excess of the cobalt(II) reductant (ca.  $10^{-2}\text{M}$ ) over  $[\Delta\text{-Co}(\text{edta})]^-$  (ca.  $10^{-3}\text{M}$ ) was used. High amine concentrations (ca.  $10^{-1}\text{M}$ ) ensure quantitative formation of the tris complexes. The reactions are rapid and are generally over within 1–2 s. After completion, the reaction mixture was cooled to 0 °C and quenched with sufficient cold argon-purged aqueous 1 M HCl to lower the pH to 1, and after dilution ( $\times 10$ ), the cobalt(III) amine complexes were isolated on Dowex 50X2-400 ( $\text{H}^+$ ) ion-exchange resin. The resin was washed with 1 M HCl to remove cobalt(II) and water and then 2 M HCl, and finally the complexes were eluted with 5 M HCl. After solvent was removed under

**Table I.** Effects of Solvent Composition and Added LiCl on Stereoselectivity in the Reaction between  $[\Delta\text{-Co}(\text{edta})]^-$  and  $[\text{Co}(\text{en})_3]^{2+}$  at 23 °C<sup>a</sup>

% water/ DMSO (w/w)	stereo- selectivity <sup>b</sup>	% water/ DMSO (w/w)	stereo- selectivity <sup>b</sup>
<0.1 <sup>c</sup>	25 ± 1 $\Lambda$	1.0	28 ± 3 $\Lambda$
<i>f</i>	33 $\Lambda$	5.0	32 ± 3 $\Lambda$
~0.2	35 ± 1 $\Lambda$	100	10 ± 2 $\Lambda$ <sup>d,e</sup>
~0.2 (0.6 M LiCl)	34 ± 1 $\Lambda$	100 (1.0 M NaCl)	11 ± 1 $\Lambda$ <sup>e</sup>

<sup>a</sup>  $[\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}] = (0.9\text{--}1.0) \times 10^{-2}\text{M}$ ,  $[\text{en}] = (0.9\text{--}1.0) \times 10^{-1}\text{M}$ ,  $[\Delta\text{-Co}(\text{edta})]^- = (0.6\text{--}1.2) \times 10^{-3}\text{M}$ . <sup>b</sup> Quoted as percent optical purity (enantiomeric excess). <sup>c</sup>  $[\text{CoCl}_2] = (0.9\text{--}1.0) \times 10^{-2}\text{M}$ . <sup>d</sup> Reference 1. <sup>e</sup> Reference 5. <sup>f</sup> Reference 4.

**Table II.** Isomer Distributions in the Oxidations of  $[\text{Co}(\pm\text{-chxn})_3]^{2+}$  by  $[\Delta\text{-Co}(\text{edta})]^-$  in Aqueous Solution at 23 °C

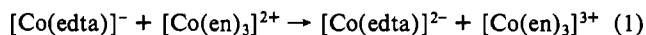
isomer	% product		
	DMSO	DMSO (0.6 M Cl <sup>-</sup> )	H <sub>2</sub> O <sup>b</sup>
<i>lel</i> <sub>3</sub>	64	92	37
<i>lel</i> <sub>2</sub> <i>ob</i>	28	6	36
<i>lel</i> <i>ob</i> <sub>2</sub>	7	<i>a</i>	19
<i>ob</i> <sub>3</sub>	1	<i>a</i>	8

<sup>a</sup> Not detected. <sup>b</sup> Reference 5.

reduced pressure, the amount of cobalt(III) complex was recorded. The stoichiometry of the reactions was determined by comparing the amount of cobalt(III) amine complex obtained with the amount of  $[\Delta\text{-Co}(\text{edta})]^-$  used in the reaction. The isomers of  $[\text{Co}(\pm\text{-chxn})_3]^{3+}$  were separated as detailed previously.<sup>5,11</sup> Stereoselectivities were determined by measuring the optical purity of the cobalt amine complexes by comparison with optically pure samples. The results are quoted as percent optical purity (enantiomeric excess).

### Results and Discussion

The available evidence suggests that the rapid reductions of  $[\text{Co}(\text{edta})]^-$  by  $[\text{Co}(\text{en})_3]^{2+}$  and its derivatives in aqueous media are outer-sphere processes.<sup>1,4,5</sup> Where detailed kinetic studies have been carried out, there is no evidence for intermediates that might be expected with an inner-sphere process.<sup>4</sup> Reaction stoichiometries are 1:1, consistent with eq 1. The same stoichiometry



prevails in DMSO solution, the reactions are rapid, and although no kinetic studies have been undertaken, outer-sphere reactions seem likely in this medium also. In Table I are shown the results of stereoselectivity studies for the oxidation of  $[\text{Co}(\text{en})_3]^{2+}$  by  $[\Delta\text{-Co}(\text{edta})]^-$  in DMSO and DMSO/water mixtures. The conditions for perchlorate as anion parallel those of Geselowitz, Hammershøi, and Taube<sup>4</sup> with very similar results. Somewhat surprisingly, the stereoselectivity appears to be unaffected by changing the anion from perchlorate to chloride. Nafie and coworkers<sup>9</sup> have indicated that the presence of chloride ion causes an increase in the *lel* character of the chelate rings by the formation of a structure in which the *lel*<sub>3</sub> conformation is maintained by chloride ions bridging amino groups on each of the  $C_2$  axes of the complex.<sup>12</sup> Either the stereoselectivity is relatively insensitive to chelate ring conformation in DMSO, contrasting with the behavior in water<sup>5</sup> or the reactivity of the reductant is modified by the proposed, strong ion-pairing interaction with chloride ion. Also of interest is the observation that small amounts of water (up to 5% w/w) added to the DMSO solution have little effect on the stereoselectivity although it appears to pass through a maximum as the percentage of water is increased, perhaps indicating that at least some water molecules are associated with intermediates in the electron-transfer process. The exact nature of this interaction is difficult to assess since small amounts of water in DMSO are difficult to estimate, but such a finding is not

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

	DMSO	DMSO (0.6 M $\text{Cl}^-$ )	$\text{H}_2\text{O}^a$
<i>lel</i> <sub>3</sub>	50% $\Delta$	43% $\Delta$	24% $\Delta$
<i>lel</i> <sub>2</sub> <i>ob</i>	72% $\Delta$	58% $\Delta$	5% $\Delta$
<i>lel ob</i> <sub>2</sub>	76% $\Delta$		7% $\Delta$
<i>ob</i> <sub>3</sub>	59% $\Delta$		16% $\Delta$

<sup>a</sup>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  $[\text{Co}((\pm)\text{-chxn})_3]^{2+}$  as reductant. The relative proportions of conformational isomers obtained in the oxidation of  $[\text{Co}((\pm)\text{-chxn})_3]^{2+}$  by  $[\Delta\text{-Co}(\text{edta})]^-$  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*<sub>3</sub> isomer at the expense primarily of *lel ob*<sub>2</sub> and *ob*<sub>3</sub>. This effect is enhanced in the presence of chloride ion such that the bulk of the product is the *lel*<sub>3</sub> isomer and *lel ob*<sub>2</sub> and *ob*<sub>3</sub> are not obtained in detectable amounts. The result that there is an increase in *lel*<sub>3</sub> character in the presence of chloride ion in DMSO solutions is in good qualitative agreement with the findings of Nafie and co-workers<sup>9</sup> from vibrational CD studies of solutions of  $[\text{Co}(\text{en})_3]^{3+}$ . 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*<sub>3</sub> isomer, the enantiomeric excess in the reaction with  $[\Delta\text{-Co}(\text{edta})]^-$  changes from 25%  $\Delta$  in aqueous solution to 50%  $\Delta$  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<sup>9</sup> are correct and the chloride ions are located specifically along the  $C_2$  axes of the reductant, then reaction of  $[\Delta\text{-Co}(\text{edta})]^-$  with  $[\text{Co}((\pm)\text{-chxn})_3 \cdot 3\text{Cl}]^-$  should involve a preferential interaction along the  $C_3$  axis where electrostatic repulsions are minimized. Previous results<sup>5</sup> suggest that this is consistent with a reduction in the magnitude of the  $\Delta\Delta$  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  $[\text{Co}(\text{en})_3]^{2+}$ . While the proportion of the *lel*<sub>3</sub> 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<sup>1,4</sup> in the oxidation of  $[\text{Co}(\text{en})_3]^{2+}$  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  $[\text{Co}(\text{edta})]^-$  and the reductant depending on the reaction medium. Geselowitz, Hammershøi, and Taube<sup>4</sup> 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  $[\Delta\text{-Co}(\text{edta})]^-$  and  $[\text{Co}((\pm)\text{-chxn})_3]^{2+}$ , the discrimination for the *lel ob*<sub>2</sub> 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;  $\text{Na}[\Delta(+)\text{-Co}(\text{edta})]$ , 111140-05-7;  $[\text{Co}(\text{en})_3]^{2+}$ , 23523-25-3;  $[\text{Co}((\pm)\text{-chxn})_3]^{2+}$ , 27910-76-5;  $\Delta\text{-}[\text{Co}(\text{chxn})_3]\text{Cl}_3$  (*lel*<sub>3</sub> isomer), 59671-81-7;  $\Delta\text{-}[\text{Co}(\text{chxn})_3]\text{Cl}_3$  (*lel*<sub>2</sub> isomer), 31537-08-3;  $\Delta\text{-}[\text{Co}(\text{chxn})_3]\text{Cl}_3$  (*lel ob* isomer), 59727-65-0;  $\Delta\text{-}[\text{Co}(\text{chxn})_3]\text{Cl}_3$  (*lel ob* isomer), 59727-62-7;  $\Delta\text{-}[\text{Co}(\text{chxn})_3]\text{Cl}_3$  (*lel ob*<sub>2</sub> isomer), 59727-66-1;  $\Delta\text{-}[\text{Co}(\text{chxn})_3]\text{Cl}_3$  (*ob*<sub>3</sub> isomer), 34369-95-4;  $\Delta\text{-}[\text{Co}(\text{en})_3]\text{Cl}_3$ , 23778-88-3;  $\text{LiCl}$ , 7447-41-8;  $\text{H}_2\text{O}$ , 7732-18-5.

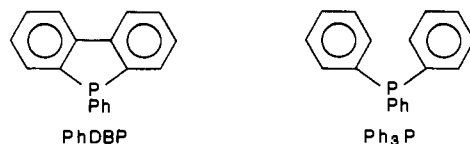
Contribution from the Guelph-Waterloo Centre for Graduate Work in Chemistry, Guelph Campus, Department of Chemistry and Biochemistry, University of Guelph, Guelph, Ontario, Canada N1G 2W1, and Department of Chemistry, University of Nevada—Reno, Reno, Nevada 89557

#### Identification by Stopped-Exchange Solution <sup>31</sup>P NMR Spectroscopy of the Stepwise Formation of $[\text{AgL}_n]\text{PF}_6$ ( $n = 1-4$ ). Comparison of Metal-Phosphorus Coupling Constants for Triphenylphosphine and 5-Phenyldibenzophosphole

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Interest in the coordination chemistry of phospholes has been steadily increasing in recent years.<sup>1</sup> 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.<sup>2,3</sup> Comparison of the donor properties of 5-phenyldibenzophosphole (PhDBP) and triphenylphosphine was first explored over 15 years



ago by two independent groups.<sup>4</sup> Our laboratories have undertaken a comprehensive study of the coordination properties of PhDBP, kindled by our interest in phospholes<sup>1</sup> and an improved synthesis<sup>5</sup> for PhDBP.

This note shows that the stepwise formation of  $[\text{L}_n\text{Ag}]^+\text{PF}_6^-$  ( $n = 1-4$ ) for  $\text{L} = \text{PhDBP}$  and  $\text{Ph}_3\text{P}$  may be readily observed in situ by stopped-exchange solution <sup>31</sup>P NMR spectroscopy. The relative ligating properties of PhDBP and  $\text{Ph}_3\text{P}$  are compared, and discussion is also extended for the first time to <sup>1</sup>J(M-P) coupling constants obtained for several well-characterized metal

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