angles. This is ca. 2.5 for $V(CO)_6$ at 25 °C (Figure 4) and cannot be very much less than this for $Ir_4(CO)_{12}$ as judged by any reasonable extrapolation to $\theta = 0$ of a plot of $\log k_2 - \beta(\Delta HNP)$ against θ for data at 25 °C, β being taken as $-3.5\ V^{-1}$ (see Table IV). Extrapolation to $\Delta HNP = 0$ of ΔH_2^* for the θ-independent reactions of $V(CO)_6$ with $P(OMe)_3$ and PMe_3 gives ca. 7 kcal mol^{-1} as a measure of its intrinsic reactivity. A similar extrapolation of ΔH_2^* for reaction of $Ir_4(CO)_{12}$ with etpb (using the dependence of ΔH_2^* for $P(OPh)_3$ and P-*n*-Bu_3 on ΔHNP) leads to ca. 9 kcal mol^{-1}, which would be an upper limit if steric effects contribute to ΔH_2^* for etpb to any extent. Both $Ir_4(CO)_{12}$ and $V(CO)_6$ are very much less reactive than $(\eta^5\text{-}MeC_5H_4)M(CO)_2(NC_5H_4X)^+$, which has $\Delta H_2^* = 4.4$ kcal mol^{-1} for reaction with PPh_3[15] in spite of its high susceptibility to steric effects (see above). This high intrinsic reactivity of the Mn complex is probably due to its relatively high oxidation state as well as to its 17-electron nature.

The electronic discrimination shown at 25 °C for $Ir_4(CO)_{12}$ (β = ca. $-3.4\ V^{-1}$) is less[28] than that for $V(CO)_6$ ($\beta = -4.2\ V^{-1}$)[30] so bond formation seems to be greater for the latter. Steric effects are harder to judge. The plot in Figure 2 shows them still to be operative for $Ir_4(CO)_{12}$ even with θ as low as 101°, and the gradient gives $\gamma = -0.06\ deg^{-1}$. Figure 4 shows that steric effects for $V(CO)_6$ do not become apparent until $\theta \gtrsim 120°$, but above that γ = ca. $-0.1\ deg^{-1}$. Steric effects will depend on metal–nucleophile bond lengths in the transition states. Perhaps these are[20] longer for the 17-electron $V(CO)_6$ even though the strength of the bonds is greater as suggested by the value of β. On the other hand, as θ increases, $V(CO)_6$ may eventually offer greater steric resistance by being less flexible. $Ir_4(CO)_{12}$ may prove to be quite flexible during associative reactions (see below) so that, although steric effects are apparent even for quite small nucleophiles, sensitivity to cone angle is not as great.

It would appear from these considerations that the susceptibility of the 18-electron $Ir_4(CO)_{12}$ to nucleophilic attack is not markedly less than that of the 17-electron $V(CO)_6$, and an understanding of its high susceptibility may be reached as follows. High intrinsic reactivity is usually related[1a,31] to facile changes in the bonding of other ligands attached to the metal, and an analogous explanation can be given for $Ir_4(CO)_{12}$. In simple valence bond terms, a given Ir atom can be envisaged as being bonded to the other three by use of three of its electrons. If only one of them is used in the transition state, it can be regarded as being in a single σ orbital directed toward the middle of the tetrahedron and overlapping with three singly occupied σ orbitals from the other Ir atoms. This will lead to multicenter four-electron bonding to the other Ir atoms instead of the six-electron bonding in the unperturbed cluster. However, the singular Ir atom will now have eight nonbonding electrons and will have one vacant dsp^3-type orbital to accommodate an electron pair from the nucleophile. Thus a full Ir–P bond can be made at the expense of weakening the bonding within the Ir_4 cluster by reducing the total number of cluster bonding electrons only from 12 to 10. This weakening of the cluster bonding has been shown to be an important feature of associative reactions of other clusters[25] and implies that the intrinsic reactivity should be closely related to the strength of bonding within the metal cluster. Further, the stereochemistry around the attacked Ir atom will have changed from quasi-octahedral d^2sp^3 to roughly dsp^3, and the OC-Ir-CO angles could therefore have opened up substantially. This analysis seems to provide a reasonable explanation of the various aspects of the observed reactivity.

Summary

Associative substitution reactions of $Ir_4(CO)_{12}$ with P-donor nucleophiles have been analyzed in terms of electronic and steric effects. A general approach to quantifying the various features of such reactions of metal carbonyls has been developed. The high susceptibility of $Ir_4(CO)_{12}$ to nucleophilic attack has been demonstrated by comparison with data for reactions of other highly susceptible metal carbonyls. It can be related to its ability to form quite strong Ir–P bonds at the expense of relatively slight weakening of the bonding within the Ir_4 cluster. This is accompanied by changes of the coordination around the Ir atom that is being attacked. These result in a relatively small, but always present, steric effect. The concept of the flexibility of the coordination spheres during associative reactions of metal carbonyls is emphasized.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council, Ottawa, Canada, for support, and K.D. acknowledges the award of a SumCan undergraduate internship.

Note Added in Proof. After this paper was originally submitted, the work of Giering et al. came to our attention (Golovin, M. N.; Rahman, M. M.; Belmonte, J. E.; Giering, W. P. *Organometallics* **1985**, *4*, 1981–1991). This includes an analysis of published rate data for associative reactions that is essentially identical with that outlined here.

Registry No. $Ir_4(CO)_{12}$, 18827-81-1; P-*n*-Bu_3, 998-40-3; $P(OEt)_3$, 122-52-1; $P(OCH_2)_3CEt$, 824-11-3; $P(C_6H_{11})_3$, 2622-14-2.

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[30] A somewhat higher value was estimated in ref 15, but this did not account for any steric effects apart from that for P-*i*-Pr_3.

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Steric and Electronic Effects in Cobalt(II) Disproportionation with Phosphorus Ligands

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Received October 28, 1985

The disproportionation reaction $2Co^{2+} + 11PZ_3 \rightarrow CoL_5^+ + CoL_6^{3+}$ ($L = PZ_3$) is found to depend in a curious way upon the shape of the ligand (as well as on its steric bulk). Thus, for example $P(OMe)_3$ and $(MeO)_{ax}(\overline{POCHMe_{eq}CH_2CHMe_{eq}O})$ drive the reaction, but $P(OEt)_3$ and $(MeO)_{ax}\overline{POCH_2CMe_2CH_2O}$ do not. Secondly, the ligand must possess a minimum degree of basicity for disproportionation to occur. For example $P(OCH_2)_3CMe$ functions in this reaction, but the smaller and less basic ligands $\overline{P(OCH_2)_2CHO}$ and PF_3 do not. Thirdly, diastereomeric CoL_6^{3+} complexes of an unusual nature are detected by ^{59}Co NMR spectroscopy when L is *n*-$PrO\overline{POCH_2CH_2O}$ or *n*-$BuO\overline{POCH_2CH_2O}$. Finally, the sterically more crowded CoL_6^{3+} product prefers the larger but more basic ligand $P(OMe)_3$ while the CoL_5^+ species preferentially binds the smaller but better π acceptor $P(OCH_2)_3CEt$ when a mixture of the two ligands is employed in the disproportionation.

Introduction

The disproportionation reaction (1) in which $L = PZ_3$ has been known for over 25 years.[1] Except for the phosphite esters P-

$$2Co^{2+} + 11PZ_3 \rightarrow CoL_5^+ + CoL_6^{3+} \qquad (1)$$

$(OMe)_3$,[2] **4a**,[3] **4b**,[3] **6**,[3] **29**,[4] and **31**[5,6] and the chelating diphosphonites **35**[7] and **36**[7] (in Table I), which have been reported to drive reaction 1, the scope of this disproportionation as a function of Z has remained obscure. We show here that (a) reaction 1 is dependent in an unobvious manner upon the shape of the ligand as well as its size (cone angle), (b) there is a lower limit on the basicity of the ligand which will drive reaction 1, (c) with certain asymmetrical phosphite ester ligands, ^{59}Co NMR spectroscopic evidence can be adduced for two unusual diastereomeric configurations for the CoL_6^{3+} ion, and (d) with a mixture of ligands, the products of the disproportionation reaction tend to incorporate the more basic, albeit larger, ligand in the CoL_6^{3+} ion.

Experimental Section

UV–visible spectra were recorded on a Perkin-Elmer 320 spectrometer. Cobalt-59 (70.85 MHz) and ^{31}P (121.5 MHz) NMR spectra were recorded on a Bruker WM-300 spectrometer operating in the Fourier mode while locked on the ^2H resonance of deuterated solvents and referenced to external aqueous $K_3[Co(CN)_6]$ and 85% H_3PO_4, respectively, with positive shifts defined as being downfield.

All solvents were dried over molecular sieves before use except Et_2O which was distilled from potassium/benzophenone. $[Co(H_2O)_6](BF_4)_2$ was obtained from Alfa Products. 2,2-Dimethoxypropane, $P(OMe)_3$, $P(OEt)_3$, PCl_3, and $PPhCl_2$ were purchased from Aldrich Chemical, while $Me_2PCH_2CH_2PMe_2$ (**38**), $PEtCl_2$, $Cl_2PCH_2CH_2PCl_2$, and $PPhH_2$ were purchased from Strem Chemicals. The acyclic ligands $P(SMe)_3$,[8] $P(CH_2CH_2CN)_3$,[9] and $As(OMe)_3$,[10] the chelating systems $(MeO)_2PCH_2CH_2P(OMe)_2$[11] (**37**), *o*-$[(MeO)_2P]_2C_6H_4$[12] (**35**), and *o*-$[(EtO)_2P]_2C_6H_4$[12] (**36**), the polycyclic donors $P(OCH_2)_2CHO$[13] (**33**), $CH_2CH_2OPOCHCH_2O$[14] (**32**), $P(OCH_2)_3CMe$[15] (**29**), $P(OCH_2)_3CEt$[5] (**30**), $P(OCH)_3(CH_2)_3$[16] (**31**), and $As(OCH_2)_3CMe$[17] (**34**), and the six-membered-ring compounds $MeOPOCH_2CH_2CH_2O$[18a] (**1**), $(MeO)_{ax}POCHMe_{eq}CH_2CHMe_{eq}O$[19] (**4a**), $(MeO)_{eq}POCHMe_{eq}CH_2CHMe_{eq}O$[20] (**4b**), and $(MeO)_{ax}POCH_2CMe_2CH_2O$[19] (**5**) were prepared by literature methods. The same was true for the five-membered-ring systems $ZPOCH_2CH_2O$ (Z = MeO[21] (**6**), EtO[21] (**7**), *n*-PrO[21] (**9**), *n*-BuO[21] (**12**), *i*-BuO[21] (**13**), F[22] (**17**)), $MeOPOCHMeCH_2O$[23] (**22a,b**), and *dl*-$MeOPOCHMeCHMeO$ (**23**).[23]

$(MeO)_{ax}POCHMe_{eq}CH_2CH_2O$ (2a), $(MeO)_{eq}POCHMe_{eq}CH_2CH_2O$ (2b), (*n*-PrO)$_{ax}POCHMeCH_2CH_2O$ (3a), (*n*-PrO)$_{eq}POCHMeCH_2CH_2O$ (3b). These compounds were prepared by the route reported for the 2-alkoxy-4-methyl-1,3,2-dioxaphosphorinanes[24] with the modification that *p*-toluenesulfonic acid was used to isomerize the equatorial to the axial isomers. [^{31}P NMR (ppm) ($(CD_3)_2CO$): **3a**, 125.7; **3b**, 130.5.]

$ClPOCH_2CH_2O$ (16). This phosphorochloridite was prepared as described earlier[21] with the exception that ethylene glycol was added slowly to a solution of PCl_3 instead of adding the two reactants simultaneously.

$ZPOCH_2CH_2O$ (Z = CF_3CH_2O (8), *i*-PrO (10), PhO (11), $MeCH_2CHMeO$ (14), *t*-BuO (15), $O(CH_2CH_2)_2N$ (20)). These ligands were prepared from $ClPOCH_2CH_2O$ (**16**) and the appropriate alcohol or amine in yields of approximately 80% by an earlier method.[21] Boiling points,[21,23,25] and/or $\delta(^{31}P)$ values[23,26] ($(CD)_3CO$) agreed with those in the literature. $\delta(^{31}P)$ values for **8** (137.6), **10** (132.1), **14** (132.3), **15** (132.9), and **20** (137.9) are recorded here since they have not been previously reported.

$PhPOCH_2CH_2O$ (18). To a solution of $PPhCl_2$ (20.3 g, 113 mmol) in 500 mL of Et_2O and 40 mL of Et_3N was added dropwise over 15 min ethylene glycol (7.01 g, 113 mmol). The product was distilled in 79% yield after filtration of the precipitated $Et_3N{\cdot}HCl$. [Bp(°C)/*P* (torr): 85/1. ^{31}P NMR (ppm) ($CDCl_3$): 162 (lit.[28] 162).]

$EtPOCH_2CH_2O$ (19). To a solution of $PEtCl_2$ (9.0 g, 69 mmol) in 300 mL of Et_2O and 20 mL of Et_3N was added dropwise ethylene glycol (4.5 g, 72.5 mmol). $Et_3N{\cdot}HCl$ was filtered off, and the very air-sensitive compound was distilled in 48% yield. [Bp (°C)/*P* (torr): 40/1 (lit.[32] 53–55/18). ^{31}P NMR (ppm) ($(CD_3)_2CO$): 191.7 (lit.[32] 188.2).]

$ClPOCH_2CH_2S$. This phosphorochloridite was prepared as described previously.[27] [Bp (°C)/*P* (torr): 65/2 (lit.[27] 57/0.4).]

$MeOPOCH_2CH_2S$ (21). In 200 mL of Et_2O and 25 mL of Et_3N was dissolved $ClPOCH_2CH_2S$ (15.0 g, 102 mmol). To this solution was added MeOH (4.50 g, 140 mmol). After the precipitated $Et_3N{\cdot}HCl$ was filtered off, the product was distilled in 82% yield. [Bp (°C)/*P* (torr): 60/1. ^{31}P NMR (ppm) ($CDCl_3$): 170.3.]

***dl-meso*-$ClPOCHMeCHMeO$.** This phosphorochloridite was prepared from PCl_3 and 2,3-butanediol by a method reported earlier[23] with the modification that Et_3N was used as a base instead of *N*,*N*-dimethylaniline. [^{31}P NMR (ppm) ($(CD_3)_2CO$): 170.9, 171.8.]

***dl*-$ROPOCHMeCHMeO$ (R = Et (24), R = *n*-Pr (25), R = *i*-Pr (26)).** These phosphites were prepared by the reaction of equivalent amounts of *dl-meso*-$ClPOCHMeCHMeO$ and the appropriate alcohol in ether in the presence of Et_3N as described previously.[23] Distillation through a 2-in. Vigreaux column produced the *dl* phosphites in greater than 95% isomeric purity. [Bp (°C)/*P* (torr), ^{31}P NMR (ppm) ($(CD)_3CO$): **24**, 52.5/3.5, 140.1; **25**, 52/3, 139.0; **26**, 45/2, 139.8.]

C_6H_4-*o*-O_2PCl. This precursor was prepared by a method reported earlier.[29,30] [^{31}P NMR (ppm) (C_6D_6): 172.8.]

$CH_3OPOCMe_2CMe_2O$ (27). This phosphite was prepared by using a modification[31] of the procedure described originally by Denney and co-workers.[23]

C_6H_4-*o*-O_2POMe (28). This phosphite was prepared as reported earlier.[30] [^{31}P NMR (ppm) ($(CD_3)_2CO$): 127.7.]

Ligand Selenides. These derivatives were prepared by a method reported previously to prepare $(Se)MeOPOCH_2CH_2O$ (Se(**6**)).[18a] Because of the expected instability of the five-membered ring selenophosphates[18a] and the fact that only NMR parameters were desired for these compounds, no attempts to purify them were made [^{31}P NMR (ppm) (CD_3CN): Se(**3a**), 70.4; Se(**6**), 90.5; Se(**7**), 85.5; Se(**8**), 90.4; Se(**9**), 85.5; Se(**10**), 84.9; Se(**11**), 82.9; Se(**12**), 85.8; Se(**13**), 84.6; Se(**22a,b**), 86.9, 87.1; Se(**23**), 82.6; Se(**24**), 82.6; Se(**25**), 82.0; Se(**31**), 70.5; Se(**32**), 80.9. See Discussion for $^1J(^{31}P^{77}Se)$ coupling constants.] When an attempt was made to prepare the diselenide Se_2(**37**) in this manner, the

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^{31}P NMR of the crude product showed that the major species possessed a chemical shift of 108.7 ppm, but two selenium coupling constants were observed in nearly equal intensity (786 and 964 Hz). The monofunctional analogue $SeP(CH_3)(OCH_3)_2$ is reported to have a ^{31}P NMR chemical shift of 102.3 ppm and a phosphorus–selenium coupling constant of 861 Hz.[33] No assignment of the P–Se coupling in Se_2(**37**) was therefore made. By an earlier method,[18b] $SeP(CH_2CH_2CN)_3$ was synthesized. [^{31}P NMR (ppm) (CD_3CN): 42.6 ($^1J(^{31}P^{77}Se)$ = 739 ± 1 Hz).]

The cobalt complexes [Co(**35**)$_3$](BF$_4$)$_3$,[7,12] [Co(**36**)$_3$](BF$_4$)$_3$,[7,12] and [Co(**38**)$_3$](ClO$_4$)$_3$[34] were prepared as previously reported, and [Co(Me$_2$SO)$_6$](BF$_4$)$_2$ was prepared analogously to the route described for the perchlorate salt.[35] The remaining cobalt(III) complexes were synthesized according to eq 1 in two ways. In method A, [Co(H$_2$O)$_6$](BF$_4$)$_2$ was dehydrated with 2,2-dimethoxypropane prior to adding ligand, and in method B, ligand was combined directly with [Co(Me$_2$SO)$_6$](BF$_4$)$_2$. An example is given for each method of preparation.

Method A. This procedure parallels that described in our original report of the preparation of [Co(**29**)$_6$](ClO$_4$)$_3$ and [Co(**29**)$_5$]ClO$_4$.[5] Into a solution of [Co(H$_2$O)$_6$](BF$_4$)$_2$ (1.08 g, 3.17 mmol) in 15 mL of acetone and 15 mL of 2,2-dimethoxypropane was injected **6** (4.74 g, 31.7 mmol). The initially red solution became lemon yellow within 5 s after the addtion of **6**, and yellowish impure [Co(**6**)$_6$](BF$_4$)$_3$ precipitated from solution. Essentially pure colorless [Co(**6**)$_6$](BF$_4$)$_3$ was obtained in 82% yield after two recrystallizations from CH$_3$CN/THF. The filtrates were combined and the solvent was removed under reduced pressure. The residual yellow [Co(**6**)$_5$]BF$_4$ was redissolved in CH$_2$Cl$_2$ and precipitated in 71% yield upon addition of Et$_2$O. In addition to **6**, the ligands employed in this procedure with comparable results are P(OMe)$_3$, **1**, **2a**, **2b**, **3a**, **4a**, **4b**, **7**, **22a**,**b**, **23**, **29**, **30**, **31**, and **37**.

Method B. Into a solution of [Co(Me$_2$SO)$_6$](BF$_4$)$_2$ (1.60 g, 2.28 mmol) in 20 mL of CH$_3$CN was injected **10** (3.50 g, 23.3 mmol). The initially red solution quickly became yellow. Addition of 30 mL of THF followed by 20 mL of Et$_2$O resulted in the precipitation of impure yellowish [Co(**10**)$_6$](BF$_4$)$_3$. Two careful recrystallizations of the product by slow addition of THF to an acetonitrile solution of the impure product resulted in the precipitation of pure colorless [Co(**10**)$_6$](BF$_4$)$_3$ in 70% yield. The filtrates were combined, and the solvent was removed under reduced pressure. Attempts to crystallize [Co(**10**)$_5$]BF$_4$ failed. Other ligands that were used in this manner to give similar results are **1**, **9**, **12**, **13**, **24**, **25**, and **32**. In all cases the [Co(L)$_5$]BF$_4$ compounds prepared by reaction B could not be crystallized but could be isolated as impure yellow oils upon precipitation from CH$_2$Cl$_2$ solution by the addition of Et$_2$O.

Discussion

Syntheses. All of the Co(III) complexes discussed in subsequent sections were synthesized by reaction 1 (method A or B in the Experimental Section) except [Co(Me$_2$PCH$_2$CH$_2$PMe$_2$)$_3$](ClO$_4$)$_3$, which was prepared by an earlier method.[34] Method A incorporates Me$_2$C(OMe)$_2$ as a drying agent for the [Co(H$_2$O)$_6$](BF$_4$)$_2$ in order to minimize hydrolysis of the phosphite ester ligands.[5] During the course of the present work it was found that with certain monocyclic phosphites this method unexpectedly led to a catalytic regiospecific transesterifcation of the ligand by the methanol produced in the hydrolysis of the Me$_2$C(OMe)$_2$.[36] Thus method B in which ligand is reacted with [Co(Me$_2$SO)$_6$](BF$_4$)$_3$ was developed. The disproportionation in methods A and B occurs within seconds at room temperature.

The Co(III) complexes synthesized by both methods are stable to air over a period of hours. In neutral water these complexes are quite insoluble, but when dissolved in a 50/50 mixture of H$_2$O and MeCN, they are stable for several hours. The addition of Et$_3$N to such a solution of [Co[P(OMe)$_3$]$_6$](BF$_4$)$_3$ causes the initially colorless solution to turn to the yellow color characteristic of [Co[P(OMe)$_3$]$_5$]BF$_4$. ^{31}P NMR spectroscopy confirmed the presence of the latter complex (147 ppm), some free ligand (140 ppm), and also OP(OMe)$_3$ (2.2 ppm) arising from the reaction of oxygen (from water oxidation) and P(OMe)$_3$. Interestingly, similar treatment of [CoL$_6$](BF$_4$)$_3$ where L is P(OCH$_2$)$_3$CEt (**30**) produces ^{31}P NMR peaks only for [Co(**30**)$_5$]BF$_4$ (137 ppm) and free **30** (92 ppm). The absence of OP(OCH$_2$)$_3$CEt can be ascribed to poorer Lewis basicity of **30** compared with that of P(OMe)$_3$,[37,38] which could lower its reactivity with oxygen.

We now discuss ligand size and basicity factors, some of them unexpectedly subtle, which appear to play a role in driving reaction 1. For convenience, the structures of the monocyclic, polycyclic, and bidentate ligands that were evaluated in this study are collected in Table I, and their ability to drive reaction 1 is indicated in parentheses. The criterion used here for considering reaction 1 as being driven by a given ligand is our ability to isolate [CoL$_5$]BF$_4$ and [CoL$_6$](BF$_4$)$_3$ from the reaction mixture. It has been our experience that either the disproportionation proceeds in good yields or isolable quantities of these products are not produced.

Acyclic Ligands. It is interesting that P(OMe)$_3$ drives this reaction but P(OEt)$_3$ does not.[39] Electronically these two ligands are not very dissimilar, judging from the $^1J(^{31}P^{77}Se)$ coupling constants[40] of their selenophosphate derivatives: SeP(OMe)$_3$, 954 Hz (945 Hz[41]); SeP(OEt)$_3$, 935 Hz[41] (see Table I). The observation that the cone angle of P(OEt)$_3$ (θ = 109°) is only 2° larger than that for P(OMe)$_3$[42] could be taken to mean that the greater basicity of P(OEt)$_3$ (as implied by the lower $^{31}P^{77}Se$ coupling constant) is responsible for the lack of Co(II) disproportionation. On the other hand the reduction of cobalt(II) chloride by H$_2$O in the presence of P(OEt)$_3$ and NEt$_3$ does give the corresponding Co[P(OEt)$_3$]$_5$$^+$ species,[43] suggesting that the analogous CoL$_6$$^{3+}$ ion is unstable because of excessive phosphorus basicity or too much ligand–ligand repulsion. The former reason seems unjustified on two grounds: (a) Solution basicities of three-coordinate phosphorus are less than that of NH$_3$ and yet Co(NH$_3$)$_6$$^{3+}$ is very stable. (b) Since Co[P(OEt)$_3$]$_5$$^+$ is stable, electron release from one intermediate CoL$_n$$^{2+}$ species to another is expected to be facilitated by a more basic ligand. This is borne out by the preference of Co(III) for the more basic ligand in reaction 1 when two different ligands are employed (vide infra). Since the size of P(OEt)$_3$, as measured by the cone angle, is only marginally greater than P(OMe)$_3$, more subtle steric effects may be at play. Further evidence for the untenability of simple cone angle considerations in reaction 1 will be presented when five- and six-membered-ring phosphite ester ligands are discussed.

It could be concluded, from the failure of the very basic ligand[44] PPhH$_2$ to drive reaction 1, that unfavorable ligand packing forces in the CoL$_6$$^{3+}$ and/or the reluctance of a CoL$_n$$^{2+}$ intermediate to accept an electron, owing to excessive ligand basicity, are to blame. Some circumstantial evidence that the latter may obtain is the absence of any reports of CoL$_5$$^+$ species where L is a monodentate PR$_3$ or PPh$_3$ ligand. That steric effects are not culpable for the lack of such cations is suggested by the existence of Ni(PMe$_3$)$_5$$^{2+}$,[45] which contains a smaller (albeit a more acidic) metal ion than Co(I).

Strong evidence exists for a lower boundary on the basicity of the phosphorus ligand that can drive reaction 1. Thus the very

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(33) McFarlane, W.; Rycroft, D. S. *J. Chem. Soc., Dalton Trans.* **1973**, 2162.

(34) Ohishi, T.; Kashiwabara, K.; Fujita, J. *Chem. Lett.* **1981**, 1371.

(35) Selbin, J.; Bull, W. E.; Holmes, L. H. *J. Inorg. Nucl. Chem.* **1961**, *16*, 219.

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(39) These results parallel those realized with the reaction 2Co(SCN)$_2$ + 9L → [CoL$_5$]SCN + [*cis*-Co(NCS)$_2$L$_4$]SCN in which L = P(OMe)$_3$ but not P(OEt)$_3$ or PPh(OEt)$_2$ (Albertin, G.; Pelizzi, G.; Bordignon, E. *Inorg. Chem.* **1983**, *22*, 515).

(40) The usefulness of these values in comparing relative Lewis basicities of phosphorus compounds has been elaborated upon in previous publications (see: Socol, S. M.; Verkade, J. G. *Inorg. Chem.* **1984**, *23*, 3487 and references therein).

(41) Stec, W. J.; Okruszek, A.; Uznański, B.; Michalski, J. *Phosphorus* **1972**, *2*, 97.

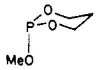
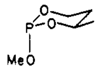
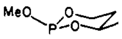
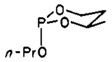
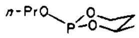
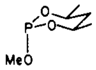
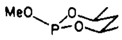
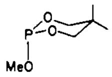
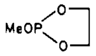
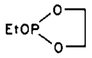
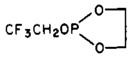
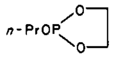
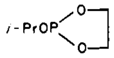
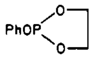
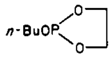
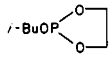
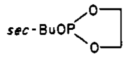
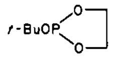
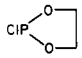
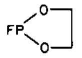
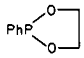
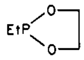
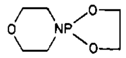
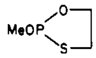
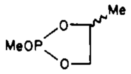
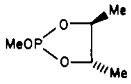
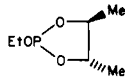
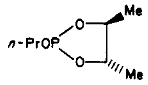
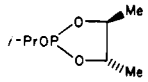
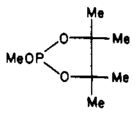
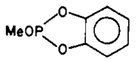
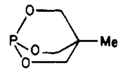
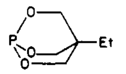
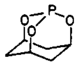
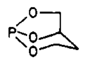
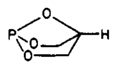
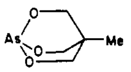
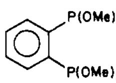
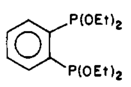
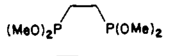
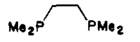
(42) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.

(43) Gosser, L. W.; Parshall, G. W. *Inorg. Chem.* **1974**, *13*, 1947.

(44) From the similarity in the $^1J(^{31}P^{77}Se)$ values of SePPh$_3$ (735.4 Hz: Pinnell, R. P.; Megerle, C. A.; Manatt, S. L.; Kroon, P. A. *J. Am. Chem. Soc.* **1973**, *95*, 977) and SePPh$_2$H (740 ± 10 Hz[33]), it can be assumed that the values for SePPhH$_2$ will still be well below that of SeP(OEt)$_3$ (935 Hz), as would be expected if PPhH$_2$ is the more basic ligand.

(45) Meier, P. F.; Merbach, A. E.; Dartiguenave, M.; Dartiguenave, Y. *Inorg. Chem.* **1979**, *18*, 610.

Table I. Ligands Used for Reaction 1 and $^{1}J(^{31}P^{77}Se)$ Values (Hz) for the Corresponding Selenium Derivatives

ligand	no.	drives reaction 1?	$^{1}J(^{31}P^{77}Se)$
$P(CH_2CH_2CN)_3$		no	739 ± 1^{a}
$PPhH_2$		no	$\sim 735^{b}$
PF_3		no	$\sim 1490^{c}$
PCl_3		no	$\sim 1065^{c}$
$P(OMe)_3$		yes	954 ± 1^{d}
$P(OEt)_3$		no	935 ± 6^{e}
$P(SMe)_3$		no	710 ± 30^{f}
$As(OMe)_3$		no	
	**1**	yes	985 ± 1^{d}
	**2a**	yes	978 ± 6^{g}
	**2b**	yes	941 ± 6^{g}
	**3a**	yes	980 ± 1^{a}
	**3b**	no	*h*
	**4a**	yes	996 ± 1^{d}
	**4b**	yes	949 ± 1^{d}
	**5**	no	961 ± 6^{g}
	**6**	yes	1008 ± 1^{a}
	**7**	yes	1000 ± 1^{a}
	**8**	no	1039 ± 1^{a}
	**9**	yes	1003 ± 1^{a}
	**10**	yes	1003 ± 1^{a}
	**11**	no	1035 ± 1^{a}
	**12**	yes	1003 ± 1^{a}
	**13**	yes	1001 ± 1^{a}
	**14**	no	*h*
	**15**	no	*h*
	**16**	no	$\sim 1130^{i}$
	**17**	no	$\sim 1160\text{–}1180^{j}$
	**18**	no	*h*
	**19**	no	*h*
	**20**	no	$\sim 970^{k}$
	**21**	no	*h*
	**22a,b**	yes	$1004, 1005^{a,l}$
	**23**	yes	998 ± 1^{a}
	**24**	yes	$996 \pm {}^{a}$
	**25**	yes	997 ± 1^{a}
	**26**	no	*h*
	**27**	no	*h*
	**28**	no	$\sim 1010^{m}$
	**29**	yes	1053^{d}
	**30**	yes	*h*
	**31**	yes	1020 ± 1^{a}
	**32**	yes	1047 ± 1^{a}
	**33**	no	1099 ± 1^{n}
	**34**	no	...
	**35**	yes	*o*
	**36**	yes	*o*
	**37**	yes	$\sim 861^{o}$
	**38**	yes	$\sim 680\text{–}700^{p,q}$

[a] This work. [b] Reference 44. [c] Reference 46. [d] Reference 18a. [e] Reference 41. [f] Using equations in ref 18a. [g] Stec. W. J. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1974**, *29B*, 109. [h] Not measured. [i] Based on the increase of 130 ± 10 Hz from the selenophosphate derivative of **28** to the corresponding chloro derivative (see citation in ref 55). [j] Based on the 150 to 170 Hz increase from the selenophosphate derivatives of **2a,b** to their corresponding axial and equatorial fluoro derivatives (Okruszek, A.; Stec, W. J. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1976**, *31B*, 351). [k] Thus the $^{1}J(^{31}P^{77}Se)$ values for **35** and **36** are likely to be close to those of $SePPh(OMe)_2$ (876 ± 4 Hz[33]) and $SePh(OEt)_2$ (850 ± 6 Hz[41]), respectively. [l] The two values correspond to the cis and trans isomers, but no coupling assignments are made. [m] Reference 56. [n] This value was measured for the derivative wherein C–H is C–Me.[18a,57] [o] See text. [p] Reference 58. [q] Expected on the basis of measured values for PMe_3 (684 ± 2 Hz[33]) and for PEt_3 (705 ± 6 Hz[41]).

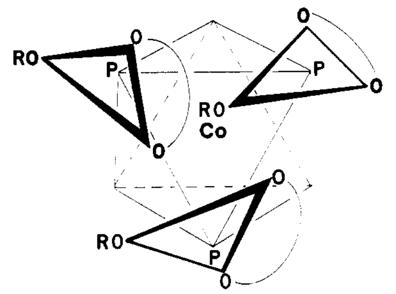


Figure 1. Schematic representation of the packing of monocyclic phosphite ester ligands around the octahedral Co^{3+} ion. The triangle in each ligand depicts the plane of the three esteratic oxygens while the curve denotes the ring carbons. The phosphorus atom is below the triangular plane.

nonbasic PF_3[6,46] and $\overline{\mathrm{P(OCH_2)_2CHO}}$,[47] which are also very small (θ = 104°[42] and < 101°,[47] respectively) fail to drive reaction 1. In view of the small increase in van der Waals radius from phosphorus to arsenic (0.05 Å), it would appear that poor basicity is probably also the dominant influence in the lack of Co(II) disproportionation with $As(OMe)_3$.

When three substituent atoms or groups larger than oxygen are present on phosphorus, cone angle considerations undoubtedly gain importance. This is implied by the inability of PCl_3 (θ = 124°[42]), $P(SMe)_3$ (θ = >124°), and $P(CH_2CH_2CN)_3$ (θ = 132°[42]) to drive reaction 1. There is considerable evidence[42,48,49] that the last ligand resembles PPh_3 in basicity more than it does PR_3 and that its π acidity approximates that of $P(OR)_3$.[48,49] Interestingly, our measurement of the $^1J(^{31}P^{77}Se)$ value of $SeP(CH_2CH_2CN)_3$ (739 ± 1 Hz) corroborates the earlier conclusion concerning the σ basicity of its parent phosphine, since this coupling value is closer to that of $SePPh_3$ (738 ± 6 Hz[41]) than it is to that of $SePEt_3$ (705 ± 6 Hz[41]) or $SeP(n\text{-}Bu)_3$ (693 ± 6 Hz[41]). On the other hand, it is well away from the much higher coupling values for $SeP(OMe)_3$ and $SeP(OEt)_3$ (Table I). These results further support earlier conclusions of ours[18a] and others[33] that ^{31}P–^{77}Se couplings are governed mainly by the Fermi contact term in the σ bond, with π-bonding influences being quite minor.

Monocylic Ligands. The importance of second-order steric forces is quite clearly revealed in the results of the investigation of reaction 1 with monocyclic phosphite esters. Of the six-membered-ring systems **1**–**5** (Table I), all drive Co^{2+} disproportionation except **3b** and **5**. That any of these ligands sustain this reaction (especially **3a** and **4b**) seems unexpected in view of their cone angles, which are expected to exceed that of $P(OEt)_3$, a ligand that (as pointed out earlier) does not drive reaction 1. It seems particularly odd that while **4a** and **4b** function in this reaction, **5** (in which the ring substitution is more distant from the donor site) does not. Examination of space-filling models reveals that monocyclic ligands such as the above six-membered ring systems experience minimal steric interactions in their CoL_6^{3+} complexes when they are oriented in one of two ways. In Figure 1 is shown an octahedron that for our purposes is viewed as a trigonal antiprism. For all six ligands to fit into this configuration, three are required to orient themselves in a head-to-tail fashion around the top face of the trigonal antiprism (two such ligands are shown schematically in Figure 1). The remaining three ligands on the bottom face must similarly arrange themselves around that bottom face (one such ligand is shown in Figure 1) except that they are permitted to do so in two ways around the S_6 axis of the trigonal antiprism, namely, in the same direction as or in the opposite direction to the three ligands bound to the top face. ^{59}Co NMR spectroscopic observations are now presented that are consistent with the presence of such diastereomers in the case of two five-membered-ring ligands **9** and **12**.

Table II. ^{59}Co NMR and Thermodynamic Data for $[Co(\mathbf{9})_6]^{3+}$ and $[Co(\mathbf{12})_6]^{3+}$

$[Co(\mathbf{9})_6]^{3+}$		$[Co(\mathbf{12})_6]^{3+}$	
$10^3/T$, K^{-1}	ln (A_d/A_u)[a]	$10^3/T$, K^{-1}	ln (A_d/A_u)[a]
3.92	−1.41	3.77	−1.75
3.70	−0.97	3.63	−1.32
3.50	−0.59	3.51	−1.19
3.38	−0.15	3.36	−0.49

	$[Co(\mathbf{9})_6]^{3+}$	$[Co(\mathbf{12})_6]^{3+}$
r^2	0.98	0.96
ΔH, kcal/mol	5	6
ΔS, cal/(mol K)	15	18

[a] Ratio of peak areas (A_d denotes downfield and A_u denotes upfield peak) measured in CH_3CN.

For the five-membered-ring ligands **9** and **12**, two ^{59}Co resonances are observed (−1008, −1160 and −993, −1172 ppm, respectively). The intensities of these peaks are temperature-dependent for each of the complexes, with the upfield peak being favored at lower temperatures. The thermodynamic parameters for the conversion of the lower energy to the higher energy species given in Table II, though precise to only ~±20%, are consistent with the interconversion of two diastereoisomers of this type. The difference in frequency of the two peaks for each complex (ca. 1 × 10^4 Hz) indicates that an isomerization rate of 7 × 10^4/s would be required to merge their resonances.

For the six-membered-ring ligands, the two diastereomeric ligand arrangements discussed in connection with Figure 1 account nicely for the inability of **5** to drive reaction 1[50] since the equatorial ring methyl group interacts sterically with the MeO group of the adjacent ligand on the same face of the trigonal antiprism. This is, of course, true for either diastereomeric configuration of the complex, and it also applies to axial binding of the phosphorus atom of **5** to the cobalt, which can be achieved from the equatorially bound conformer by a ring flip. In contrast, the equatorial ring methyls of **4a** and **4b** (which are closer to the phosphorus than in **5** and thus confer slightly larger cone angles on **4a,b**) are comfortably accommodated in either diastereomeric configuration in three locations: one methyl group from each of the three ligands on the top face of the trigonal antiprism is directed over this face, one methyl from each of the three ligands on the bottom face is positioned under that face, and the three remaining methyls from each set of ligands mesh in a staggered configuration near the "equator", which lies between the two trigonal faces.[51] Related to the suggested diastereoisomerism in our CoP_6^{3+} complexes is the observation of ^{59}Co chemical shifts associated with geometrical (and optical) isomers in $Co[(\pm)\text{-propylenediamine}]_3^{3+}$.[52]

The failure of **3b** vs. the success of **3a** to sustain reaction 1 might appear at first glance to be attributable to the larger steric re-

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(46) The generally accepted notion that PF_3 is a very poor Lewis base cannot be substantiated with a ^{31}P–^{77}Se coupling constant since $SePF_3$ is unknown. However, it has been shown that there is a linear correlation of $^1J(^{31}P^{77}Se)$ with $^1J(^{31}P^1H)$ in HPZ_3^+ species[18a] which predicts a $^1J(^{31}P^{77}Se)$ value of ca. 1490 Hz from the value of $^1J(^{31}P^1H)$ determined for HPF_3^+ (Vande Griend, L. J.; Verkade, J. G. *J. Am. Chem. Soc.* **1975**, *97*, 5958). In a similar manner $^1J(^{31}P^{77}Se)$ for $SePCl_3$ is predicted to be ca. 1065 Hz.

(47) See citation in ref 40.

(48) Cotton, F. A.; Darensbourg, D. J.; Ilsley, W. H. *Inorg. Chem.* **1981**, *20*, 578.

(49) Cotton, F. A.; Darensbourg, D. J.; Fredrich, M. F.; Ilsley, W. H.; Troup, J. M. *Inorg. Chem.* **1981**, *20*, 1869.

(50) Although the reaction of **5** with $[Co(H_2O)_6](BF_4)_2$ apparently produces $[Co(\mathbf{5})_5]^+$ as shown by a strong ^{31}P NMR shift at 149 ppm (which compares favorably with those of the analogous complexes of **4a** and **4b** (149 ppm: Yarbrough, L. W.; Verkade, J. G., unpublished results), several upfield peaks are also observed including one at −7 ppm, the value reported for the corresponding phosphate of **5**. Attempts to isolate the apparently more sterically crowded $[Co(\mathbf{5})_6]^{3+}$ failed, and no evidence for $[Co(\mathbf{5})_6]^{3+}$ could be found for this ion in the ^{59}Co NMR spectrum. Initial formation of unstable $[Co(\mathbf{5})_6]^{3+}$, which immediately oxidizes H_2O, cannot be ruled out.

(51) In the case of **2a**, **2b**, and **3a**, it is not clear from models whether to expect preferential orientation of the ring methyl groups around the "equatorial" or near the "axial" positions of the trigonal antiprism. Further work is planned for enantiomerically resolved **2a** and **2b** in reaction 1.

(52) Craighead, K. L. *J. Am. Chem. Soc.* **1973**, *95*, 4434.

quirement of **3b** when bonded axially to cobalt. However **4b**, which *must* bind in the same manner, also drives reaction 1, and it is likely that the sterically more demanding *n*-PrO group in **3b** (compared with the MeO group in **4b**) is responsible for the contrasting behaviors of these ligands in reaction 1. That coordination of these ligands proceeds with retention of configuration is suggested by the stereoretention of **4a** and **4b** in their *cis*-$Mo(CO)_4L_2$ complexes.[53,54]

The behavior of the five-membered-ring ligands **6–28** in reaction 1 parallels that of the six-membered-ring systems just discussed. Although these ligands are less basic than the six-membered-ring systems as judged by the higher ${}^{31}P{}^{77}Se$ couplings of the corresponding selenophosphates, their couplings are lower than those for the selenophosphates of the sterically less demanding and less basic bicyclic ligands **29** and **32** (Table I). Thus for unsubstituted five-membered-ring ligands having exocyclic alkoxy substituents (**6**, **7**, **9**, **10**, **12–15**) failures to drive reaction 1 (**14**, **15**) appear to stem from steric interactions. According to space-filling models, the remarkable success of ligands with large alkoxy groups such as **9**, **10**, **12**, and **13** in driving reaction 1 (in view of the failure of $P(OEt)_3$ to do so) emanates from their ability to orient and pack as shown in Figure 1, with the added feature that the large acyclic alkoxy substituent can avoid steric encumbrance by flexing radially away from the cobalt. This process can apparently be accomplished when the alkyl chain is branched at the β carbon (**13**) and at least in one instance at the α carbon (i.e., with **10** but not with **14**). Compared with that of **10**, the sizes of **8** and **11** are smaller and comparable, respectively. The weaker Lewis basicities of **8** and **11** compared with that of **10** (as measured by their ${}^{31}P{}^{77}Se$ couplings in Table I) are not as weak as those of **30** and **32**, which do drive the disproportionation reaction. It is possible, however, that below a certain threshold basicity, steric bulk becomes a more dominant factor as in **8** and **11**.

Though **17** is sterically less demanding than **6–15**, its failure to drive reaction 1 is probably associated with its very low basicity. Substitution of the MeO group in **6** with a chlorine (**16**) may also diminish the phosphorus basicity beyond its lower boundary for the five-membered-ring ligands, although the effect of a sterically larger chlorine in the place of oxygen also cannot be ruled out. Steric factors undoubtedly dominate in **18** and **19**, and they probably are dominant in **20**,[55] wherein branching occurs on the nitrogen. In **21**, the increased steric requirement of the sulfur is expected to decrease its effectiveness in driving reaction 1.

In **22a,b** through **27** we see the effect on reaction 1 of sterically encumbering the five-membered-ring with substituents. Thus, whereas **26** does not drive the reaction, **10** does. Because of the bulky ring methyl groups, even the small MeO group in **27** prevents this ligand from functioning in reaction 1. The basicity of **28** is expected to be sufficiently strong for reaction 1 (${}^{1}J({}^{31}P{}^{77}Se) \simeq 1010$ Hz[56]), so the failure of **28** to induce disproportionation is quite probably steric in origin.

Polycyclic Ligands. Ligands **29–33**, in addition to possessing smaller cone angles than $P(OMe)_3$ (e.g.: **29** and **30**, 101°;[42] **33**, <101°[47]) are also poorer Lewis bases,[37,47] as is reflected in their relatively high ${}^{1}J({}^{31}P{}^{77}Se)$ values (Table I). The basicity of **33**, as indicated by its estimated ${}^{1}J({}^{31}P{}^{77}Se)$ value of 1090 Hz,[57] is apparently below the lower boundary, however, since it does not drive reaction 1. From the range of phosphorus ligands examined in this work, it appears, that a ${}^{1}J({}^{31}P{}^{77}Se)$ value of ca. 1050 Hz is associated with the least basic ligand (**29**) that drives the disproportionation. The observation that **34** does not sustain Co^{2+} disproportionation corroborates our earlier conclusion (vide supra) that $As(OMe)_3$ does not do so owing primarily to its poor basicity, since **34** is expected to possess the smaller cone angle.

Chelating Ligands. Of the ligands **35–38**, all cause Co(II) disproportionation.[58] The observation that **35** and **36** drive reaction 1 might in large measure be ascribed to the chelate effect and a smaller cone angle for these ligands than for their acyclic analogues. The 11° decrease in cone angle from PMe_3 to **38**[59] when applied to the cone angles for $PhP(OMe)_2$ (115°[42]) and $PhP(OEt)_2$ (116°[42]) suggests that the sizes of **35** and **36** are well within the acceptable range.

Monocyclic–Bicyclic Ligand Competition. With equal concentrations of **30** and $P(OMe)_3$, a preference of Co(III) for $P(OMe)_3$ is exhibited. Examination of the ${}^{31}P$ NMR spectrum of the Co(I) product reveals peaks for coordinated **30** (137 ppm) and $P(OMe)_3$ (147 ppm) in the ratio of >9/1 in favor of **30**. Integration of the peaks in the ${}^{1}H$ NMR spectrum of the Co(III) product showed that 65% of the ligands complexed to this ion are $P(OMe)_3$. Because the Co(III) and Co(I) phosphite complexes are spin-paired high-field systems that are inert to substitution by other phosphite ligands under the conditions of reaction 1,[60] it may be supposed that electron transfer between two $CoP_6{}^{2+}$ species is most favored when the electron acceptor is statistically coordinated mainly by **30** and the donor mainly by $P(OMe)_3$. This process could then be followed by preferential elimination of one molecule of **30** from the Co(I) product. Alternatively the precursor complex could be a similar mixed-ligand complex of the type $CoP_4{}^{2+}$ or $CoP_5{}^{2+}$ that after electron transfer forms four- or five-coordinate Co(I) and Co(III) species. Such initial disproportionation products are probably spin-paired and perhaps substitution-inert, but they could undergo further phosphite coordination in accord with their ligand preferences and limiting coordination numbers. It is interesting that these ligand preferences (at whatever stage of the reaction they are expressed) apparently are not mainly steric, since the larger ligand $P(OMe)_3$ is preferred by the smaller Co(III) and the smaller ligand **30** is predominantly found on the Co(I). Rather, it appears that the more basic $P(OMe)_3$ stabilizes the more highly charged (polarizing) Co(III) and the better π acceptor **30**[61] prefers binding to the Co(I), whose lower oxidation state confers upon it better π donor properties.

Acknowledgment. We thank the National Science Foundation for generous support of this research and Mark Mason for experimental assistance.

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(53) Jacobson, R. A.; Karcher, B. A.; Montag, R. A.; Socol, S. M.; Vande Griend, L. J.; Verkade, J. G. *Phosphorus Sulfur* **1981**, *11*, 27.

(54) Vande Griend, L. J.; Verkade, J. G. *Inorg. Nucl. Chem. Lett.* **1973**, *9*, 1137.

(55) Since ${}^{1}J({}^{31}P{}^{77}Se)$ is about the same or drops at most 30 Hz from $SeP(OEt)_3$ (935 ± 6 Hz[41]) to $O(CH_2CH_2)_2N(Se)P(OEt)_2$ (920 Hz: Loginova, E. I.; Nuretdinov, I. A.; Petrov, Yu. A. *Theor. Exp. Chem. (Engl. Transl.)* **1974**, *10*, 47), the basicity of **20** is sufficiently strong to drive reaction 1 (${}^{1}J({}^{31}P{}^{77}Se) = {\sim}970$–1000 Hz) on the basis of the 1000-Hz ${}^{31}P{}^{77}Se$ coupling for **7** (Table I).

(56) The expected decrease in ${}^{1}J({}^{31}P{}^{77}Se)$ from $Cl(Se)P(O_2$-*o*-$C_6H_4)$ (1130 Hz[55]) to the MeO analogue **29** is expected to be about 120 Hz on the basis of the difference between $SeP(O$-*i*-$Bu)_2Cl$ (1030 Hz: Nuretdinov, I. A.; Nikonorova, L. K.; Grechkin, N. P.; Gainullina, R. G. *J. Gen. Chem. USSR (Engl. Transl.)* **1975**, *45*, 526) and $SeP(O$-*i*-$Pr)_3$ (912 ± 6 Hz[41])).

(57) Attempts to selenate **33** failed. However, from a linear plot of adiabatic phosphorus ionization energy vs. ${}^{1}J({}^{31}P{}^{77}Se)$ (Schiff, D. E.; Richardson, J. W.; Jacobson, R. A.; Cowley, A. H.; Lasch, J.; Verkade, J. G. *Inorg. Chem.* **1984**, *23*, 3373) the ${}^{31}P{}^{77}Se$ coupling for this compound is estimated to be ~1090 Hz, which exceeds the predicted value for $SePCl_3$,[46] the parent compound (PCl_3) of which also does not drive reaction 1.

(58) Details of the reaction of $Co(BF_4)_2$ with chelating phosphines such as **38** will be reported later (Fu, W. K.; Verkade, J. G., manuscript in preparation).

(59) Thus Tolman[42] gives cone angles of 107° for $Me_2PCH_2CH_2PMe_2$ (**38**) compared with 118° for PMe_3.

(60) The ligand dissociation constants for phosphites in $ML_5{}^{+}$ complexes are quite small (ca. 10^{-4} to 10^{-5} mol L^{-1} at room temperature: English, A. D.; Meakin, P.; Jesson, J. P. *J. Am. Chem. Soc.* **1976**, *98*, 7590). It has also been observed that substitution of $Co[P(OMe)_3]_5{}^{+}$ with $P(OCH_2)_3CEt$ to give $Co[P(OMe)_3]_2[P(OCH_2)_3CEt]_3{}^{+}$ requires refluxing methyl ethyl ketone for 24 h (Attali, S.; Poilblanc, R. *Inorg. Chim. Acta* **1972**, *6*, 475).

(61) Although the low positive charge renders this ion a poor electron pair acceptor, the Co(I) center could be envisioned to function as a good π donor (Tolman, C. A.; Yarbrough, L. W.; Verkade, J. G. *Inorg. Chem.* **1977**, *16*, 479). Alkylphosphines are, however, relatively poor π acceptors compared to phosphite esters, thus leading to poor ligand field stabilization of $[Co(PR_3)_5]^{+}$.