

for metal clusters containing, e.g., more than 13 metal atoms. Our rules are no exception. Nevertheless, we include in Table I a 17- and a 20-vertex polyhedra of high symmetry. The 17-vertex bicapped (O^2) face-sharing bi(pentagonal prism) (69, Chart XXIV), with 20 faces and $X = 4$, is expected to have 244 electrons. The observed value in the $[\text{Pt}_{19}(\text{CO})_{22}]^{4-}$ tetraanion,⁸⁷ with two encapsulated platinum in the pentagonal-prismatic holes, is 238e, six electrons below the predicted value, again a characteristic of platinum carbonyl clusters.

The 20-vertex pentagonal dodecahedron (70), with 12 pentagonal faces and $X = 0$ (3-connected, rule 1; cf. Chart I in the preceding paper), is predicted to have an electron count of 300e. This polyhedral structure is yet unknown in metal cluster chemistry though the corresponding polyhedron in organic chemistry—the dodecahedrane⁹¹ $\text{C}_{20}\text{H}_{20}$ —has been synthesized recently.

A new approach to electron counting for high nuclearity metal clusters has been developed by Teo.⁹²

Conclusion

It is shown in this paper that the topological electron-counting theory, developed in the preceding paper, can be applied to a wide variety of transition-metal or post-transition-metal clusters. This theory encompasses polyhedra that follow, as well as those that violate, the effective atomic number and/or the skeletal electron pair rule. As is evident from Table I, the agreement between the predicted and the

observed electron counts (N) is generally very good. The only major exceptions are the platinum carbonyl or gold phosphine clusters of high nuclearity, which often have electron counts of four or six electrons under the predicted value. For example, the series of $[\text{Pt}_3(\text{CO})_6]_m^{2-}$ clusters, which have structures formed by stacking m nearly eclipsed platinum triangles (polyhedra 11, 32, 58, 68), all have electron counts of $42m + 2$, four electrons below the expected value of $42m + 6$.⁹³ Another example is the $[\text{Pt}_{19}(\text{CO})_{22}]^{4-}$ tetraanion, which has 238 electrons (six electrons short) rather than the expected value of 244e. A similar situation is also found for gold phosphine clusters. For example, the $[\text{Au}_{13}\text{Cl}_2(\text{PMe}_2\text{Ph})_{10}]^{3+}$ trication⁸¹ is 8e below the expected electron count of 170e for an icosahedral cluster. This phenomenon may be related to the fact that platinum or gold has a tendency to form 16e rather than 18e complexes.

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Contribution from the Department of Chemistry,
University of Delaware, Newark, Delaware 19716

Steric and Electronic Control of the Arbuzov Reaction in Transition-Metal Halides: A ^1H and ^{31}P NMR Study of the Reaction of $[\text{CpCo}(\text{L}\text{L})\text{X}]^+$ Complexes ($\text{L}\text{L} = \text{N}, \text{P}, \text{As}$ Chelate Ligands; $\text{X}^- = \text{Cl}^-, \text{Br}^-, \text{I}^-, \text{CN}^-$) with $\text{P}(\text{OCH}_3)_3$

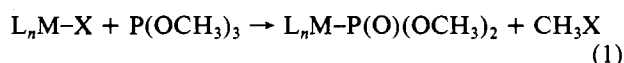
SHAYNE J. LANDON and THOMAS B. BRILL*

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Synthesis of a series of complexes, $[\text{CpCo}(\text{L}\text{L})\text{X}]^+$ ($\text{L}\text{L} = \text{N}, \text{P}, \text{As}$ chelate ligands; $\text{X}^- = \text{Cl}^-, \text{Br}^-, \text{I}^-, \text{CN}^-$), was undertaken with the goal of characterizing the Michaelis-Arbuzov reaction between these complexes and $\text{P}(\text{OCH}_3)_3$. ^1H and ^{31}P NMR results provide support for the previously postulated two-step mechanism involving an initial equilibrium reaction $[\text{CpCo}(\text{L}\text{L})\text{X}]^+ + \text{P}(\text{OCH}_3)_3 \rightleftharpoons \{\text{CpCo}(\text{L}\text{L})[\text{P}(\text{OCH}_3)_3]\}^{2+} + \text{X}^-$ followed by alkylation of X^- to produce an organo-metal-phosphonate complex, $\{\text{CpCo}(\text{L}\text{L})[\text{P}(\text{OCH}_3)_3]\}^{2+} + \text{X}^- \rightarrow \{\text{CpCo}(\text{L}\text{L})[\text{P}(\text{O})(\text{OCH}_3)_2]\}^+ + \text{CH}_3\text{X}$. Several of the intermediate phosphite dications were synthesized and characterized. They enable the above reactions to be qualitatively separated. The initial reaction was quenched by sterically bulky chelate ligands. The rate of the overall reaction parallels the electron donor power of the attacking nucleophile ($\text{CN}^- > \text{I}^- > \text{Br}^- > \text{Cl}^-$) and also depends on the donor atoms of LL ($\text{N} > \text{P}$). Chelate dissociation occurs when $\text{L}\text{L} = \text{As}$. The results for $[\text{CpCo}(\text{L}\text{L})\text{X}]^+$ and other transition metal-halide complexes are discussed in terms of why the Arbuzov reaction takes place in some of these complexes but not with others.

Introduction

Some transition-metal complexes possessing a substitutionally labile nucleophilic ligand are known to react with alkyl phosphites and yield a final product containing a coordinated phosphonate ligand rather than coordinated phosphite.¹⁻⁸



Equation 1 is formally analogous to the Michaelis-Arbuzov reaction (hereinafter referred to as the Arbuzov reaction)

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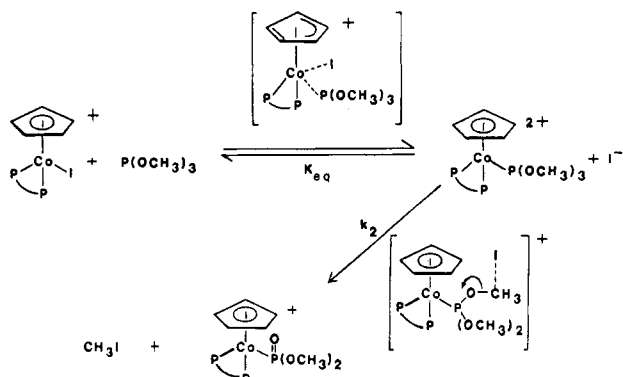
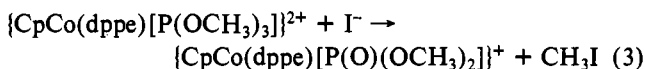
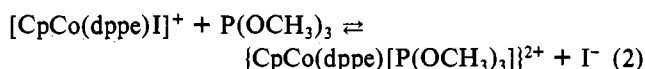


Figure 1. Proposed mechanism of the Arbuzov rearrangement involving $[\text{CpCo}(\text{dppe})\text{I}]^+$ and $\text{P}(\text{OCH}_3)_3$ showing structural details. The species in brackets are possible transition states. k_2 is the rate-determining step,⁶ but the overall rate k_{obsd} equals $K_{\text{eq}}k_2$.

wherein an alkyl halide and an alkyl phosphite react to form a phosphonate with alkyl transfer.⁹

The mechanism of the Arbuzov reaction involving $[\text{CpCo}(\text{dppe})\text{I}]^+$ was recently shown by ¹H and ³¹P NMR spectroscopy to follow the two-step sequence summarized by eq 2 and 3.^{6,10}



- (8) Reaction of transition-metal complexes with $\text{P}(\text{OCH}_3)_3$ is known in several instances to produce metal-phosphonate bonds via various other types of methyl migration. (a) $\text{Ru}[\text{P}(\text{OCH}_3)_3]_2$ reacts at 120 °C with $\text{P}(\text{OCH}_3)_3$ to give $\text{Ru}[\text{P}(\text{OCH}_3)_3]_4(\text{CH}_3)[\text{P}(\text{O})(\text{OCH}_3)_2]$: Pomeroy, R. K.; Alex, R. F. *J. Chem. Soc., Chem. Commun.* **1980**, 1114. Alex, R. F.; Pomeroy, R. K. *Organometallics* **1982**, *1*, 453. (b) The reaction of $\{\text{CpCr}(\text{CO})_2[\text{P}(\text{OCH}_3)_3]\}_2$ gives $\text{CpCr}(\text{CO})_2(\text{CH}_3)[\text{P}(\text{OCH}_3)_3]$ and $\text{CpCr}[\text{P}(\text{O})(\text{OCH}_3)_2][\text{CO}][\text{P}(\text{OCH}_3)_3]$: Goh, L.-Y.; D'aniello, M. J., Jr.; Slater, S.; Muettterties, E. L.; Tavaniapour, I.; Chang, M. I.; Frederich, M. F.; Day, V. W. *Inorg. Chem.* **1979**, *18*, 192. Day, V. W.; Tavaniapour, I.; Abdel-Meguid, S. S.; Kirner, J. F.; Goh, L.-Y.; Muettterties, E. L. *Ibid.* **1982**, *21*, 657. (c) $\text{P}(\text{OCH}_3)_3$ and $[\text{CpRu}(\text{CO})_2]$ forms phosphonate products: Howell, J. A. S.; Rowan, A. J. *J. Chem. Soc., Dalton Trans.* **1980**, 1845. (d) $[\text{CpMo}(\text{CO})_2]$ and $\text{P}(\text{OCH}_3)_3$ form $\text{CpMo}(\text{CO})_2[\text{P}(\text{O})(\text{OCH}_3)_2][\text{P}(\text{OCH}_3)_3]$ and $\text{CpMo}(\text{CO})_2(\text{CH}_3)$: Haines, R. J.; Nolte, C. R. *J. Organomet. Chem.* **1970**, *24*, 725. (e) Elimination of CH_3I from $[\text{CpRh}(\text{CH}_3)[\text{P}(\text{OCH}_3)_3]_2\text{I}]$ by heating produces $\text{CpRh}(\text{CH}_3)[\text{P}(\text{O})(\text{OCH}_3)_2][\text{P}(\text{OCH}_3)_3]$: Werner, H.; Neukomm, H.; Kläui, W. *Helv. Chim. Acta* **1977**, *60*, 326. (f) $\text{P}(\text{OCH}_3)_3$ and $\text{CpMo}(\text{CO})_2[\text{As}(\text{CH}_3)_2]$ yield $\text{CpMo}(\text{CO})_2[\text{P}(\text{O})(\text{OCH}_3)_2][\text{As}(\text{CH}_3)_3]$: Malisch, W.; Janta, R. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 211. (g) $\{\text{Co}(\text{CO})_2[\text{P}(\text{OCH}_3)_3]\}[\text{Co}(\text{CO})_4]$ rearranges to $\text{CH}_3\text{CoCo}(\text{CO})_2[\text{P}(\text{OCH}_3)_3]$: Arabi, M. S.; Maisonnat, A.; Attali, S.; Poiblan, R. *J. Organomet. Chem.* **1974**, *67*, 109. (h) $(\text{C}_6\text{H}_5)_3\text{SiMn}(\text{CO})_5$ and triisopropyl phosphite react to form $(\text{C}_6\text{H}_5)_3\text{SiP}(\text{O})(i\text{-OC}_3\text{H}_7)_2$ and $(i\text{-C}_3\text{H}_7)_2\text{Mn}(\text{CO})_2$: Ross, E. P.; Dobson, G. R. *J. Chem. Soc., Chem. Commun.* **1969**, 1229. (i) $[\text{octaethylporphyrin}]\text{Rh}_2$ reacts with $\text{P}(\text{OCH}_3)_3$ to produce $\text{Rh}(\text{OEt})[\text{P}(\text{O})(\text{OCH}_3)_2]$ and $\text{Rh}(\text{OEt})(\text{CH}_3)$: Wayland, B. B.; Woods, B. A. *J. Chem. Soc., Chem. Commun.* **1981**, 475. (j) Refluxing $[\text{CpFe}(\text{CO})_2]_2$ in xylene with 4 equiv of $\text{P}(\text{OCH}_3)_3$ yields $\text{CpFe}(\text{CO})[\text{P}(\text{OCH}_3)_3][\text{P}(\text{O})(\text{OCH}_3)_2]$ and $\text{CpFe}(\text{CO})(\text{COCH}_3)[\text{P}(\text{OCH}_3)_3]$: Howell, J. A. S.; Rowan, A. J.; Snell, M. S. *J. Chem. Soc., Dalton Trans.* **1981**, 325. (k) Reaction of CoCl_2 , $\text{P}(\text{OCH}_3)_3$, and Na/Hg yields $\text{Co}[\text{P}(\text{O})(\text{OCH}_3)_2][\text{P}(\text{OCH}_3)_3]_4$: Muettterties, E. L.; Bluke, J. R.; Yang, Z. Y.; Day, V. W. *J. Am. Chem. Soc.* **1982**, *104*, 2940. (l) $\text{IrCl}[\text{P}(\text{OCH}_3)_3]_3$ with Na(ether) or Na/Hg reacts to produce $\text{Ir}(\text{P}(\text{O})(\text{OCH}_3)_2)[\text{P}(\text{OCH}_3)_3]_4$: Hitchcock, P. B.; Klein, S. I.; Nixon, J. F. *J. Organomet. Chem.* **1983**, *241*, C9.

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- (10) Abbreviations: $\eta^2\text{-C}_2\text{H}_4$, Cp; bis(diphenylphosphino)methane, dppm; 1,2-bis(diphenylphosphino)ethane, dppe; 1,3-bis(diphenylphosphino)propane, dppp; 1,4-bis(diphenylphosphino)butane, dppb; 1,2-bis(diphenylphosphino)ethylene, PC=CP; 1,2-bis(diphenylarsino)ethane, dpae; 2,2'-bipyridyl, bpy; ethylenediamine, en; 1,3-propanediamine, pn; a bidentate chelate ligand, L L.

According to this mechanism, the occurrence of the overall reaction will depend upon the equilibrium constant of eq 2 and the concert of bond breaking and bond formation in the rate-determining step, eq 3. Indeed, the Arbuzov reaction is observed with some organo transition metal-halide complexes, but not with others. The reasons must lie in the influence of other ligands in the coordination sphere, the nucleophiles, and the metal on the rate of each step. These factors have not been systematically explored.

Figure 1 more specifically summarizes the pertinent details of the mechanism from a structural standpoint. The equilibrium, eq 2, probably involves an associative transition state in which the 18e configuration of the metal is maintained by ring slippage.⁶ The electron donor power of the nucleophile should play a role in the rate of eq 3 as well as eq 2.

In this paper a study of the steric and electronic variables in a closely related series of transition-metal complexes, $[\text{CpCo}(\text{L})\text{X}]^+$ (L = chelate; X = nucleophile), was conducted in order to unravel the controlling features. The dicationic intermediate complex was synthesized so that eq 2 and 3 can be qualitatively separated. Steric control of eq 2 was probed by altering the size of the bis(tertiary phosphine) chelate ring. Electronic control of eq 3 was probed by varying the donor atoms of the chelate through N, P, and As. Comparisons of the rate of the overall reaction as a function of the strength of the nucleophile were made for $[\text{CpCo}(\text{dppe})\text{X}]^+$ ($\text{X} = \text{Cl}^-, \text{Br}^-, \text{I}^-, \text{CN}^-$) and after the addition of NH_4X salts to $\{\text{CpCo}(\text{dppe})[\text{P}(\text{OCH}_3)_3]\}^{2+}$. The results support the mechanism in Figure 1 and provide the basis for understanding the conditions that favor the Arbuzov reaction in transition metal-halide complexes.

Experimental Section

Synthesis. General Procedures. $\text{CpCo}(\text{CO})_2$ (Strem) and the bidentate amine, phosphine, and arsine ligands were used as received. $\text{P}(\text{OCH}_3)_3$ (Strem) was distilled prior to use. Methylene chloride, chloroform, benzene, and acetonitrile were purified by standard methods.¹¹ Methanol was refluxed over Mg/I_2 and distilled in an N_2 atmosphere. Unless otherwise stated, all reaction leading to metal complexes were conducted in the open air. $\text{CpCoI}_2(\text{CO})$,^{12,13} $[\text{CpCo}(\text{en})\text{I}]\text{I}$,¹² $[\text{CpCo}(\text{PC}=\text{CP})\text{I}]\text{I}$,¹⁵ $[\text{CpCo}(\text{bpy})\text{I}]\text{I}$,¹³ $[\text{CpCo}(\text{bpy})(\text{CH}_3\text{CN})](\text{BF}_4)_2$,¹⁴ and $[\text{CpCo}(\text{dppe})\text{I}]\text{I}$ ^{6,15} were prepared according to published procedures.

$[\text{CpCo}(\text{dppp})\text{I}]\text{I}$. $\text{CpCoI}_2(\text{CO})$ (0.5514 g, 1.35 mmol) in C_6H_6 (75 mL) and 1,3-bis(diphenylphosphino)propane (0.5594 g, 1.35 mmol) in C_6H_6 (25 mL) were stirred at 20 °C for 3 h. $[\text{CpCo}(\text{dppp})\text{I}]\text{I}$ gradually precipitated. The brown solid was filtered and washed with diethyl ether (2 × 50 mL) and pentane (2 × 50 mL): 0.9574 g (89% yield); mp 181-83 °C dec; $\Delta_M = 121 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$. Anal. Calcd for $\text{C}_{32}\text{H}_{31}\text{CoI}_2\text{P}_3$: C, 48.63; H, 3.95. Found: C, 47.83; H, 3.91.

$[\text{CpCo}(\text{dppb})\text{I}]\text{I}$. $\text{CpCoI}_2(\text{CO})$ (1.0602 g, 2.61 mmol) and 1,4-bis(diphenylphosphino)butane (1.1180 g, 2.61 mmol) were stirred in CH_2Cl_2 at 20 °C for 3 h. Removal of the solvent at 25 °C resulted in a dark brown solid that was chromatographed on silica gel by using CH_2Cl_2 . The major brown band was isolated, producing brown crystals: 1.7030 g (81% yield); mp 187-189 °C; $\Delta_M = 123 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$. Anal. Calcd for $\text{C}_{33}\text{H}_{33}\text{CoI}_2\text{P}_2$: C, 49.28; H, 4.10; Co, 7.33; P, 7.70. Found: C, 48.83; H, 3.97; Co, 7.28; P, 7.62.

$[\text{CpCo}(\text{dpae})\text{I}]\text{I}$. Dropwise addition of a C_6H_6 solution (15 mL) of 1,2-bis(diphenylarsino)ethane (1.200 g, 2.46 mmol) to $\text{CpCoI}_2(\text{CO})$ (1.00 g, 2.46 mmol) in C_6H_6 (100 mL) produced a green solution from which a brown product precipitated after 3 h. The product was washed with C_6H_6 until the washings were clear (ca. 150 mL) followed by diethyl ether (2 × 50 mL) and pentane (2 × 50 mL): 0.8404 g (75% yield); mp 186-89 °C dec; $\Delta_M = 125 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$. Anal. Calcd for $\text{C}_{31}\text{H}_{29}\text{CoI}_2\text{As}_2$: C, 43.09; H, 3.35; Co, 6.82. Found: C,

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43.07; H, 3.10; Co, 6.73. Concentration of the green benzene filtrate produced 0.3135 g of a green solid, mp 168 °C dec. The general insolubility of the material made spectroscopic characterization difficult. The ¹H NMR spectrum reveals that C₆H₅, η⁵-C₅H₅, and (CH₃)₂ protons are present.

[CpCo(dppe)(CH₃CN)](BF₄)₂. An acetonitrile solution of [CpCo(dppe)I]I (3.4398 g, 4.43 mmol) was added dropwise to a suspension of AgBF₄ (1.7268 g, 8.87 mmol) in CH₃CN (50 mL) under an N₂ atmosphere. Although precipitation and a color change to orange-red occurred immediately, the solution was stirred for 3 h. After filtration through Celite, the solvent was removed under reduced pressure (25 °C), affording a dark orange solid: 2.8973 g (88% yield); Λ_M = 226 Ω⁻¹ cm² mol⁻¹; IR (KBr) ν(C≡N) 2395 (w), 2295 cm⁻¹ (w). Anal. Calcd for C₃₃H₃₂NCoP₂B₂F₈: C, 54.57; H, 4.03; P, 8.22. Found: C, 54.20; H, 4.43; P, 8.12. [CpCo(dppp)(CH₃CN)](BF₄)₂ and [CpCo(dppb)(CH₃CN)](BF₄)₂ were prepared in a similar manner from the corresponding iodide salts. Their identities were confirmed by ¹H and ³¹P NMR spectroscopy.

[CpCo(dppe)[P(OCH₃)₃](BF₄)₂. P(OCH₃)₃ (0.0897 g, 0.72 mmol, 0.085 mL) was added dropwise to an acetonitrile solution (50 mL) of [CpCo(dppe)(CH₃CN)](BF₄)₂ (0.5336 g, 0.72 mmol). The orange-red solution immediately turned yellow. After 3 h, the solvent was removed under reduced pressure (25 °C), yielding a yellow solid. Recrystallization from an acetone/ether solution (60/40 (v/v)) gives yellow crystals: 0.4353 g (75% yield); mp 217–19 °C dec; Λ_M = 237 Ω⁻¹ cm² mol⁻¹. Anal. Calcd for C₃₄H₃₈CoO₃P₃B₂F₈: C, 49.86; H, 4.63; Co, 7.18; P, 11.3. Found: C, 49.93; H, 4.64; Co, 7.13; P, 11.16.

[CpCo(dppe)X]BF₄ (X = Cl⁻, Br⁻). To a CH₃OH solution (100 mL) of [CpCo(dppe)(CH₃CN)](BF₄)₂ (1.200 g, 1.63 mmol) was added an excess of NH₄Cl or NH₄Br in CH₃OH. The orange-red solution gradually turned brown within 30 min. The reaction was stirred for 3 h followed by solvent removal under reduced pressure (25 °C). The resulting brown solid was extracted with several portions of CHCl₃. The combined CHCl₃ fractions were filtered through Celite and evaporated, yielding a dark brown solid. For [CpCo(dppe)Br]BF₄: 70% yield; mp 120–123 °C dec; Λ_M = 123 Ω⁻¹ cm² mol⁻¹. Anal. Calcd for C₃₁H₂₉CoBrP₂BF₄: C, 54.03; H, 4.21. Found: C, 52.69; H, 4.30. For [CpCo(dppe)Cl]BF₄: 88% yield; mp 126–127 °C dec; Λ_M = 124 Ω⁻¹ cm² mol⁻¹. Anal. Calcd for C₃₁H₂₉CoClP₂BF₄: C, 56.72; H, 4.53. Found: C, 55.09; H, 4.53.

[CpCo(dppe)CN]I. [CpCo(dppe)I]I (0.9129 g, 1.22 mmol) was reacted with KCN (0.080 g, 1.22 mmol) in 100 mL of CH₃OH. The solution slowly turned orange-brown and then yellow over a period of 1 h. The solvent was removed under reduced pressure (40 °C) and the resulting yellow solid extracted with acetone: 0.7352 g (89% yield); mp 103–105 °C dec; Λ_M = 121 Ω⁻¹ cm² mol⁻¹; IR (KBr) ν(C≡N) 2068 cm⁻¹ (m). Anal. Calcd for C₃₂H₂₉CoNIP₂: C, 62.66; H, 4.77. Found: C, 62.51; H, 4.72. The I⁻ anion may be exchanged for BF₄⁻ by the addition of AgBF₄.

[CpCo(pn)I]B(C₆H₅)₄. CpCoI₂(CO) (2.000 g, 4.90 mmol) and 1,3-propylenediamine (0.3653 g, 4.90 mmol, 0.41 mL) were reacted in CH₂Cl₂. Addition of the amine resulted in vigorous gas evolution and formation of a precipitate. After 1 h, filtration yielded the dark brown [CpCo(pn)I]I complex, which was dissolved in distilled H₂O (50 mL). Addition of NaB(C₆H₅)₄ (0.6603 g, 1.93 mmol) with cooling in ice for 30 min gave a violet solid, which was washed with H₂O (100 mL) and chromatographed on silica gel with acetone. The purple solid was washed with diethyl ether (100 mL) and dried under vacuum (50 °C) for 24 h: 2.6870 g (80% yield); mp 139–141 °C dec; Λ_M = 127 Ω⁻¹ cm² mol⁻¹. Anal. Calcd for C₃₂H₃₄N₂CoIB: C, 61.03; H, 5.88. Found: C, 61.57; H, 5.84. [CpCo(en)I]B(C₆H₅)₄ was prepared in a similar fashion starting with [CpCo(en)I]I.

[CpCo(bpy)[P(OCH₃)₃](BF₄)₂. [CpCo(bpy)(CH₃CN)](BF₄)₂ was generated in situ by the reaction of [CpCo(bpy)I]I (1.700 g, 3.20 mmol) and AgBF₄ (1.200 g, 6.4 mmol) in CH₃CN (100 mL). The AgI was removed by filtration through Celite and the resulting red solution treated dropwise with P(OCH₃)₃ (0.400 g, 3.2 mmol). A yellow solution immediately formed. Removal of the solvent under reduced pressure (25 °C) gave an orange-red solid: 1.14 g (95% yield); mp 183 °C dec; Λ_M = 215 Ω⁻¹ cm² mol⁻¹. Anal. Calcd for C₁₈H₂₂CoN₂O₃PB₂F₈: C, 37.41; H, 3.84. Found: C, 37.43; H, 3.82.

Arbuzov Reactions. Reaction of [CpCo(dppe)X]BF₄ (X = Cl⁻, Br⁻, I⁻, CN⁻) with P(OCH₃)₃. P(OCH₃)₃ (0.0249 g, 0.20 mmol, 0.23 mL) was added dropwise to a CHCl₃ solution (50 mL) of [CpCo(dppe)-X]BF₄ (X = Cl⁻, Br⁻, I⁻, CN⁻) (0.20 mmol). An initial color change from brown to dark orange took place followed by a gradual de-

colorization to yellow within 2 h. The solvent was removed, producing yellow {CpCo(dppe)[P(O)(OCH₃)₂]}BF₄: 80–89% yield; mp 158–160 °C dec. This product was identical with that obtained previously.⁶

Reaction of [CpCo(bpy)I] with P(OCH₃)₃. To a CH₃OH solution of [CpCo(bpy)I]I (0.8370 g, 1.5 mmol) was added P(OCH₃)₃ (0.1857 g, 3.0 mmol). The color immediately turned from purple to orange-brown. After 3 h, the solvent was removed and the resulting solid chromatographed on silica gel by using CH₃CN. The major orange-red band was collected and the solvent removed in vacuo (30 °C), affording orange-red {CpCo(bpy)[P(O)(OCH₃)₂]}I: 0.5979 g (78% yield); mp 179–180 °C dec; Λ_M = 118 Ω⁻¹ cm² mol⁻¹. Anal. Calcd for C₁₇H₁₉CoN₂O₃PI: C, 39.54; H, 3.91. Found: C, 39.66; H, 4.13.

Reaction of [CpCo(en)I]B(C₆H₅)₄ with P(OCH₃)₃. A CH₃OH solution (75 mL) of [CpCo(en)I]B(C₆H₅)₄ (0.500 g, 0.75 mmol) was reacted with P(OCH₃)₃ (0.0919 g, 0.75 mmol, 0.08 mL). The originally purple solution immediately changed to orange-brown. The solvent was removed under vacuum (35 °C), producing brown solid {CpCo(en)[P(O)(OCH₃)₂]}B(C₆H₅)₄: 0.3665 g (82% yield); mp 137 °C dec; Λ_M = 123 Ω⁻¹ cm² mol⁻¹. Anal. Calcd for C₃₃H₃₇CoN₂O₃PB: C, 64.95; H, 6.11. Found: C, 64.69; H, 6.15. The reaction of [CpCo(pn)I]B(C₆H₅)₄ with P(OCH₃)₃ was conducted in the same way.

Reaction of [CpCo(dpae)I] with P(OCH₃)₃. A CH₂Cl₂ solution of [CpCo(dpae)I]I (0.5525 g, 0.64 mmol) was reacted with P(OCH₃)₃ (0.2378 g, 1.92 mmol, 0.23 mL). The initially brown solution immediately became bright yellow. After the mixture was stirred for 1 h, the solvent was removed, giving a yellow solid that was chromatographed on silica with CH₂Cl₂. However, continued elution with CH₂Cl₂ did not remove the yellow band. Acetone was used, and the only organometallic product was a yellow solid: 0.3235 g (53% yield); mp 143 °C. ¹H NMR in CDCl₃ revealed the product to be {CpCo[P(O)(OCH₃)₂]}[P(OCH₃)₃]. The CH₂Cl₂ solution upon concentration gave 0.3100 g (85% recovery) of dpae, which was identified by its NMR spectrum and melting point.

Reaction of [CpCo(dppe)[P(OCH₃)₃](BF₄)₂ with Nucleophiles. A methanol solution (20 mL) of [CpCo(dppe)[P(OCH₃)₃](BF₄)₂ (0.200 g, 0.24 mmol) was reacted with NH₄Br (0.023 g, 0.24 mmol). A dark brown solution formed immediately that gradually became yellow within 1 h. Removal of the solvent under reduced pressure (35 °C) gave a yellow solid that was {CpCo(dppe)[P(O)(OCH₃)₂]}BF₄: 0.1710 g (98% yield). Reactions conducted similarly, in which NH₄Cl, NH₄Cl, and KCN were added stoichiometrically in place of NH₄Br, also resulted in the Arbuzov transformation. {CpCo(bpy)[P(OCH₃)₃](BF₄)₂ rapidly converts to {CpCo(bpy)[P(O)(OCH₃)₂]}BF₄ upon addition of these ammonium salts.

Spectra and Characterization. The ¹H and ³¹P{¹H} spectra were recorded on a Bruker WM-250 FT spectrometer. The ¹H chemical shifts are referenced to internal Me₄Si (δ 0.0). The ³¹P shifts are relative to 85% H₃PO₄ (external), with positive chemical shifts being upfield. The IR spectra were recorded in KBr dispersions by using a Perkin-Elmer 180 spectrometer. Conductivities were measured in CH₃CN solutions (ca. 1.0 × 10⁻³ M) with use of a standard cell thermostated at 25 °C. Melting points were obtained in open capillary tubes and are not corrected. Analyses were performed by Microanalysis, Wilmington, DE.

Results and Discussion

Organometal-Halide Reactants. A general synthetic route to the cyclopentadienylcobalt-halide reactants in which the chelate ligand L⁻L is varied is summarized by eq 4.^{12,13} For



the purpose of the work in this paper, the halide anion was exchanged for a weak nucleophile by the addition of AgBF₄, AgPF₆, or NaB(C₆H₅)₄. [CpCo(L⁻L)I]I in eq 4 precipitates directly when L⁻L = en and bpy if CH₂Cl₂ is the solvent.¹² C₆H₆ was reported to be a suitable solvent in eq 4 with bis-(tertiary phosphine) chelates.¹⁵ We find this to be true for dppe, PC=CP, and dppp, but in our hands, C₆H₆ could not be used for dppb. [CpCo(dppb)I]⁺ was instead prepared in a CHCl₃ solution. Equation 4 where L⁻L is dpae yields a brown precipitate and a green solution in C₆H₆. The insoluble product is the desired chelate complex. The green solution

Table I. ^1H and ^{31}P NMR Data^a

complex	^1H chem shift, ppm			^{31}P chem shift, ppm	
	$\eta^5\text{-C}_5\text{H}_5^b$	$(\text{CH}_2)_2$	other	chelate	$\text{P}(\text{OCH}_3)_3$ or $\text{P}(\text{O})(\text{OCH}_3)_2^c$
$[\text{CpCo}(\text{dppe})\text{I}]\text{I}^c$	5.57	3.27-3.35 (b m)		80.91	
$[\text{CpCo}(\text{PC}=\text{CP})\text{I}]\text{B}(\text{C}_6\text{H}_5)_4^d$	5.86	2.75 (b m)		81.05	
$[\text{CpCo}(\text{dppp})\text{I}]\text{I}^d$	5.49	2.91, 3.92 (m)		28.47	
$[\text{CpCo}(\text{dppb})\text{I}]\text{I}^d$	5.30	1.82, 2.61, 3.48 (b m)		35.34	
$[\text{CpCo}(\text{dpae})\text{I}]\text{I}^d$	5.61	2.60-3.01 (b m)			
$[\text{CpCo}(\text{dppe})\text{Br}]\text{BF}_4^d$	5.43	2.87-3.07 (b m)		95.62	
$[\text{CpCo}(\text{dppe})\text{Cl}]\text{BF}_4^e$	5.50	2.83		81.88	
$[\text{CpCo}(\text{dppe})\text{CN}]\text{I}^c$	5.67	3.09-3.17 (b m)		84.53	
$[\text{CpCo}(\text{dppe})(\text{CH}_3\text{CN})](\text{BF}_4)_2^d$	6.15	3.28 (b m)	$\text{CH}_3\text{CN} = 1.89$	80.57	
$[\text{CpCo}(\text{dppp})(\text{CH}_3\text{CN})](\text{BF}_4)_2^d$	6.18	2.93, 3.41 (b m)	$\text{CH}_3\text{CN} = 1.79$	28.15	
$[\text{CpCo}(\text{dppb})(\text{CH}_3\text{CN})](\text{BF}_4)_2^d$	6.22	2.10, 2.78, 3.55 (b m)	$\text{CH}_3\text{CN} = 1.82$	34.29	
$\{\text{CpCo}(\text{dppe})[\text{P}(\text{OCH}_3)_3]\}(\text{BF}_4)_2$	6.05 ^d	3.02 (b m) [#]	$\text{P}(\text{OCH}_3)_3 = 3.29$ ($d, {}^2J_{\text{HP}} = 11.18$ Hz) ^c	78.02 ($d, {}^2J_{\text{PP}} = 90.2$ Hz) ^e	125.8 (b)
$\{\text{CpCo}(\text{dppe})[\text{P}(\text{O})(\text{OCH}_3)_2]\}(\text{BF}_4)_2^c$	5.50	2.69 (b), 3.72-3.80 (m)	$\text{P}(\text{O})(\text{OCH}_3)_2 = 2.82$ ($d, {}^3J_{\text{HP}} = 11.18$ Hz)	83.2	86.1 (${}^2J_{\text{PP}} = 91.8$ Hz)
$\{\text{CpCo}(\text{PC}=\text{CP})[\text{P}(\text{O})(\text{OCH}_3)_2]\}(\text{BF}_4)_2^d$	5.49	3.30-3.34 (b m)	$\text{P}(\text{O})(\text{OCH}_3)_2 = 2.92$ ($d, {}^3J_{\text{HP}} = 10.9$ Hz)	84.35 ^h	86.9 ^h
$[\text{CpCo}(\text{en})\text{I}]\text{B}(\text{C}_6\text{H}_5)_4^d$	5.52	2.50-2.70 (b m)			
$[\text{CpCo}(\text{pn})\text{I}]\text{B}(\text{C}_6\text{H}_5)_4^d$	5.61	2.60-3.01 (b m)			
$[\text{CpCo}(\text{bpy})\text{I}]\text{I}^f$	6.01		$\text{bpy} = 7.87$ (d), 8.32 (d), 8.49 (d), 9.89 (d)		
$\{\text{CpCo}(\text{bpy})[\text{P}(\text{OCH}_3)_3]\}(\text{BF}_4)_2^f$	6.08		$\text{bpy} = 7.74$ (t), 8.32 (t), 8.46 (d), 9.06 (d); $\text{P}(\text{OCH}_3)_3 = 3.67$ ($t, {}^3J_{\text{HP}} = 10.8$ Hz)		118.8
$\{\text{CpCo}(\text{bpy})[\text{P}(\text{O})(\text{OCH}_3)_2]\}(\text{BF}_4)_2^f$	5.57		$\text{bpy} = 7.60$ (t), 8.20 (t), 8.37 (d); 8.96 (d); $\text{P}(\text{O})(\text{OCH}_3)_2 = 3.30$ (${}^3J_{\text{HP}} = 11.03$ Hz)		75.97
$\{\text{CpCo}(\text{en})[\text{P}(\text{O})(\text{OCH}_3)_2]\}(\text{BF}_4)_2^d$	5.58		$\text{P}(\text{O})(\text{OCH}_3)_2 = 2.93$ (${}^3J_{\text{HP}} = 11.58$ Hz)		78.85

^a Phenyl ring and anion data not shown. ^b Singlet. ^c CDCl_3 . ^d Acetone- d_6 . ^e CD_3CN . ^f CD_3OD . ^g A second multiplet was obscured by a solvent peak. ^h Broad due to overlapping second-order spectra.

appears to contain a neutral product, either $\text{CpCoI}_2(\text{dpae})$, in which the dpae ligand is monodentate, or the bridged complex $\text{CpCoI}_2(\text{dpae})_2\text{CoCp}$. It is noteworthy that $\text{CpCoI}_2[\text{As}(\text{C}_6\text{H}_5)_3]$ forms a green solution in benzene.¹⁶ Because $\text{CpCoCl}_2(\text{CO})$ and $\text{CpCoBr}_2(\text{CO})$ are thermally unstable,¹² eq 4 was not used in the synthesis of $[\text{CpCo}(\text{dppe})\text{Cl}]\text{I}^+$ and $[\text{CpCo}(\text{dppe})\text{Br}]\text{I}^+$. These complexes were prepared by reaction of $[\text{CpCo}(\text{dppe})(\text{CH}_3\text{CN})]^{2+}$ with the corresponding ammonium halides.

There is precedent for ligand displacement within the same series of metal complexes, leading to three types of products:¹⁷ monosubstituted bis(tertiary phosphine) products, chelates, and dinuclear complexes. With this concern in mind, all of the products of eq 4 were characterized, aside from elemental analysis, in terms of their molecular weight. First, their conductivities in CH_3CN fall in the range of 118-125 $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$, which is indicative of 1:1 electrolytes¹⁸ and, therefore, chelation. Second, their ^{31}P NMR spectra contain a single line, ruling out monosubstituted products. Third, the chemical shifts of the phosphines upon coordination (Table I) exhibit variations characteristic of chelation.^{19,20} Five-membered chelate rings produce large downfield shifts compared to the four-, six-, and seven-membered homologues.¹⁹ Values of $\delta(^{31}\text{P})$ for $\text{Pt}(\text{CH}_3)_2(\text{P}^i\text{P})$ complexes containing chelated bis(tertiary phosphines)²¹ follow the same pattern (Figure 2) as those for $[\text{CpCo}(\text{P}^i\text{P})\text{I}]\text{I}^+$ salts of the same phosphines, although the magnitudes differ. Thus, the conductivity, the analyses, and the ^{31}P NMR spectra all support the monomeric formulation

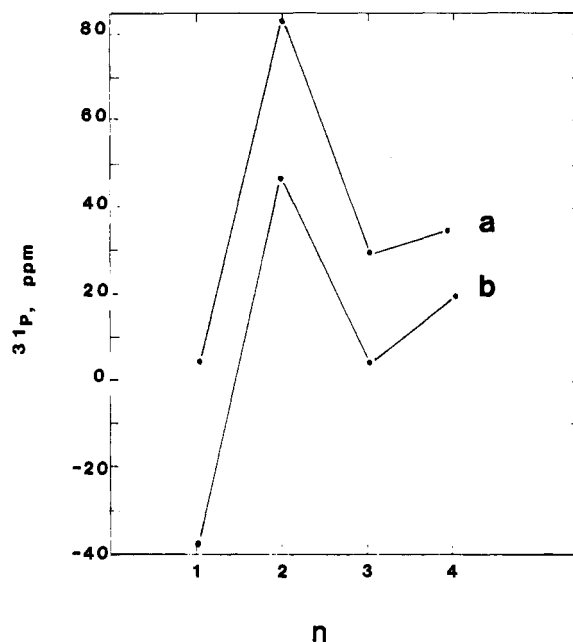


Figure 2. Correlation of the ^{31}P chemical shifts as a function of the ring size for (a) $[\text{CpCo}(\text{L}^i\text{L})\text{I}]\text{I}^+$ and (b) $\text{Pt}(\text{CH}_3)_2(\text{L}^i\text{L})$ complexes where L^iL^i is a chelate ligand from the series $(\text{C}_6\text{H}_5)_2\text{P}(\text{CH}_2)_n\text{P}(\text{C}_6\text{H}_5)_2$.

of $[\text{CpCo}(\text{L}^i\text{L})\text{X}]\text{I}^+$ for the complexes in this study.

The Intermediate Dications. The dicationic phosphite complex $\{\text{CpCo}(\text{dppe})[\text{P}(\text{OCH}_3)_3]\}^{2+}$ was observed as a transient species when $[\text{CpCo}(\text{dppe})\text{I}]\text{I}^+$ and $\text{P}(\text{OCH}_3)_3$ react to produce $\{[\text{CpCo}(\text{dppe})[\text{P}(\text{O})(\text{OCH}_3)_2]]\}^+$ and CH_3I .⁶ The complex was not isolated, owing to its instability in the presence of nucleophiles. However, the formation of this phosphite complex appears to be necessary for the Arbuzov reaction. The

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complex can be considered as a "quasi-phosphonium ion" of the type postulated in the classical Arbuzov reaction of organophosphorus compounds, but these species are rarely observed.⁹

In this paper, some of the dicationic phosphite intermediates were synthesized via a route that involves no strong nucleophiles (eq 5 and 6). Equation 5 produces orange crystalline $[\text{CpCo}(\widehat{\text{L}}\widehat{\text{L}})\text{I}]\text{I} + 2\text{AgBF}_4 + \text{CH}_3\text{CN}$ (excess) \rightarrow $[\text{CpCo}(\widehat{\text{L}}\widehat{\text{L}})(\text{CH}_3\text{CN})](\text{BF}_4)_2 + 2\text{AgI}$ (5)

$[\text{CpCo}(\widehat{\text{L}}\widehat{\text{L}})(\text{CH}_3\text{CN})](\text{BF}_4)_2 + \text{P}(\text{OCH}_3)_3 \rightarrow$
 $[\text{CpCo}(\widehat{\text{L}}\widehat{\text{L}})\text{P}(\text{OCH}_3)_3](\text{BF}_4)_2 + \text{CH}_3\text{CN}$ (6)

air-stable products from which the CH_3CN ligand may be displaced at room temperature by a variety of ligands. The reaction with $\text{P}(\text{OCH}_3)_3$ (eq 6) is of interest in this work. The products of eq 6 are yellow air-stable crystalline solids having high reactivity in solution toward nucleophiles. The ^1H and ^{31}P NMR spectra of $[\text{CpCo}(\text{dppe})\text{P}(\text{OCH}_3)_3]^{2+}$ prepared in this fashion are identical with those found previously for this species as a kinetic intermediate.⁶ $[\text{CpCo}(\text{bpy})\text{P}(\text{OCH}_3)_3](\text{BF}_4)_2$ was also prepared. On the other hand, $[\text{CpCo}(\text{dppp})(\text{CH}_3\text{CN})]^{2+}$ and $[\text{CpCo}(\text{dppb})(\text{CH}_3\text{CN})]^{2+}$ do not react with $\text{P}(\text{OCH}_3)_3$, even after prolonged heating at 40 °C. The main difference between the complexes that react with $\text{P}(\text{OCH}_3)_3$ and those that do not is the size of the bis-(tertiary phosphine) chelate. A PMP angle of 82° is typical of the five-membered chelates.²² The six- and seven-membered chelate rings require 90–97°.²³ The increased bite angle apparently reduces the space available at the reaction site so that the sterically more demanding $\text{P}(\text{OCH}_3)_3$ ligand cannot displace the less demanding CH_3CN ligand. However, ring size is not the sole criterion in eq 6 because $[\text{CpCo}(\text{pn})(\text{CH}_3\text{CN})]^{2+}$ rapidly reacts with $\text{P}(\text{OCH}_3)_3$, despite having a six-membered chelate ring in the coordination sphere. Phosphorus being larger than nitrogen and phenyl rings bound to the phosphorus atoms create much more steric crowding for the phosphine chelates than for the amines.

The stoichiometric reaction of $[\text{CpCo}(\text{dpae})(\text{CH}_3\text{CN})]^{2+}$ with $\text{P}(\text{OCH}_3)_3$ gives products resulting from the cleavage of the Co–As bonds, in addition to $[\text{CpCo}(\text{dpae})\text{P}(\text{OCH}_3)_3]^{2+}$. Excess $\text{P}(\text{OCH}_3)_3$ completely removes the dpae ligand from the coordination sphere. The final product appears to be $[\text{CpCo}[\text{P}(\text{OCH}_3)_3]_3]^{2+}$. For these reasons, one expects that the Arbuzov chemistry of $[\text{CpCo}(\text{dpae})\text{I}]^+$ will be complex.

The ^1H NMR signal of Cp in the dications in acetone-*d*₆ chloroform-*d* solutions (Table I) is above 6.0 ppm. Although the chemical shift is solvent dependent, the signals for the dications are always downfield from the monocations in Table I. The position of the line proved to be a reasonably reliable indication of the charge on individual complexes in a reaction solution.

Knowledge of the ability of certain complexes to form the required dicationic metal–phosphite complex greatly enhances the understanding of the Arbuzov chemistry in the following section.

Reaction of $[\text{CpCo}(\widehat{\text{L}}\widehat{\text{L}})\text{I}]^+$ with $\text{P}(\text{OCH}_3)_3$. A comparison was made of the Arbuzov reaction for $[\text{CpCo}(\widehat{\text{L}}\widehat{\text{L}})\text{I}]^+$ complexes, where $\widehat{\text{L}}\widehat{\text{L}} = \text{N}, \text{P}$, and As donor chelate ligands with various ring sizes. In the presence of $\text{P}(\text{OCH}_3)_3$, the $[\text{CpCo}(\widehat{\text{N}}\widehat{\text{N}})\text{I}]^+$ complexes where $\widehat{\text{N}}\widehat{\text{N}} =$ ethylenediamine, propylenediamine, and bipyridyl smoothly convert in a matter of seconds at room temperature to the corresponding phosphonate complex $[\text{CpCo}(\widehat{\text{N}}\widehat{\text{N}})\text{P}(\text{O})(\text{OCH}_3)_2]^{2+}$ and CH_3I . Note that five- and six-membered chelate rings are represented

in this series. The reaction rate is similar for both ring sizes but is too rapid for study by the conventional NMR methods used for this work. However, the ^1H NMR spectrum does reveal that the reaction proceeds through the dicationic phosphite complex and follows the mechanism shown in Figure 1. The intermediate complex was synthesized in the case of $\{\text{CpCo}(\text{bpy})[\text{P}(\text{OCH}_3)_3]\}^{2+}$.

The Arbuzov reaction occurs smoothly in minutes at room temperature with $[\text{CpCo}(\widehat{\text{P}}\widehat{\text{P}})\text{I}]^+$ complexes where $\widehat{\text{P}}\widehat{\text{P}} =$ dppe and $\text{PC}=\text{CP}$. The chelate ring is five-membered, and the reaction rate is very similar for both ligands. The mechanism is that shown in Figure 1, according to the ^1H and ^{31}P NMR spectra. When eq 5 and 6 are employed, the phosphite intermediate species can be isolated. On the other hand, $[\text{CpCo}(\text{dppp})\text{I}]^+$ and $[\text{CpCo}(\text{dppb})\text{I}]^+$, which possess six- and seven-membered chelates, do not react with $\text{P}(\text{OCH}_3)_3$ even with prolonged and gentle heating. The absence of the Arbuzov reaction in complexes with higher membered chelate rings is attributable to their inability to form the dicationic phosphite intermediate species (vide supra). Steric blockage of the equilibrium reaction is consistent with eq 2 having an associative transition state.

$[\text{CpCo}(\widehat{\text{As}}\widehat{\text{As}})\text{I}]^+$, where $\widehat{\text{As}}\widehat{\text{As}} =$ dpae, reacts with $\text{P}(\text{OCH}_3)_3$ to yield a complex mixture of products. As noted above, $\text{P}(\text{OCH}_3)_3$ is able to displace dpae from the coordination sphere. Similarly, excess $\text{P}(\text{OCH}_3)_3$ in a solution of $[\text{CpCo}(\text{dpae})\text{I}]\text{I}$ results in the formation of $\text{CpCo}[\text{P}(\text{O})(\text{OCH}_3)_2]_2[\text{P}(\text{OCH}_3)_3]^{5,24}$ as a result of a double Arbuzov transformation. These reactions complicate the system but point out the need in these studies of having a metal–chelate interaction that is more favored than two Co– $\text{P}(\text{OCH}_3)_3$ bonds. There are no signals in the ^1H NMR spectrum of the reaction mixture that can be assigned to $[\text{CpCo}(\text{dpae})\text{P}(\text{O})(\text{OCH}_3)_2]^{2+}$, although a short-lived Cp signal at 6.20 ppm may result from $[\text{CpCo}(\text{dpae})\text{P}(\text{OCH}_3)_3]^{2+}$.

The phosphonate complexes, $[\text{CpCo}(\widehat{\text{L}}\widehat{\text{L}})\text{P}(\text{O})(\text{OCH}_3)_2]^{2+}$, from these reactions were characterized by ^1H and ^{31}P NMR spectroscopy and were isolated in some cases. Conductivity measurements indicate that all are 1:1 electrolytes. Their ^{31}P chemical shifts in Table I lie in the range of 70–88 ppm and are readily distinguishable from the corresponding phosphite complexes that resonate in the 115–130 ppm range. The ^1H NMR signal of the Cp ring of the phosphonate complex is slightly shielded with respect to the corresponding halide reactant.

Reaction of $[\text{CpCo}(\text{dppe})\text{X}]^+$ ($\text{X}^- = \text{Cl}^-, \text{Br}^-, \text{I}^-, \text{CN}^-$) with $\text{P}(\text{OCH}_3)_3$. In the preceding two sections, some of the steric and electronic controls of the Arbuzov reaction by the chelate ligand were explored. However, the rate-determining step is the attack of the nucleophile on the carbon atom of the coordinated phosphite ligand. The nucleophilic strength of the species to be alkylated must play a predominant role in the rate of the reaction. This effect was elucidated at room temperature for the series of complexes $[\text{CpCo}(\text{dppe})\text{X}]^+$ ($\text{X}^- = \text{Cl}^-, \text{Br}^-, \text{I}^-, \text{CN}^-$) upon addition of $\text{P}(\text{OCH}_3)_3$. Of course, the ease by which $\text{P}(\text{OCH}_3)_3$ is able to displace X^- from the coordination sphere in eq 2 is a factor in the rate. However, because eq 2 is found to be fast at room temperature compared to eq 3, the overall rate of eq 2 and 3 is also controlled by the transmethylation step, eq 3. The relative reaction rates were ascertained by the color change and the rate of appearance of products in the ^1H NMR spectrum. The order is $\text{CN}^- > \text{I}^- > \text{Br}^- > \text{Cl}^-$, which is also the order of the electron donor strength of these ions.²⁵ CN^- reacts completely in several minutes, while Cl^- and Br^- require several hours. This result further supports the mechanism in Figure 1 by verifying that

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the rate of the Arbuzov reaction has an electronic component in the rate-determining step. Rate constant measurements for these reactions are in progress and will be reported elsewhere.²⁶

As a complement to these studies, experiments were conducted in which NH_4^+ salts of Cl^- , Br^- , and I^- were added in CH_3CN or CH_3OH solution to $\{\text{CpCo}(\text{dppe})[\text{P}(\text{OCH}_3)_3]\}^{2+}$ and $\{\text{CpCo}(\text{bpy})[\text{P}(\text{OCH}_3)_3]\}^{2+}$. For $\{\text{CpCo}(\text{dppe})[\text{P}(\text{OCH}_3)_3]\}^{2+}$ an instantaneous color change from orange to brown occurs due to rapid equilibration of $\text{P}(\text{OCH}_3)_3$ and X^- in the coordination sphere by eq 2. The brown solution gradually decolorizes owing to the attack of X^- on the coordinated phosphite ligand to produce $\{\text{CpCo}(\text{dppe})[\text{P}(\text{O})(\text{OCH}_3)_2]\}^+$ and CH_3X . These results were confirmed by ^1H NMR and UV-vis spectra of the reaction mixture. Arbuzov chemistry has been produced before by the addition of nucleophiles to phosphite complexes.²⁷⁻²⁹

Conclusions

The experiments conducted in this work illustrate some of the major steric and electronic factors that control the occurrence and rate of the Arbuzov reaction with transition metal-halide complexes. Two steps describe the reaction mechanism. The first is the rapid equilibrium of the halide and phosphite in the coordination sphere of the metal atom. The second and rate-determining step is nucleophilic attack of the halide on the coordinated phosphite ligand. The preequilibrium step is probably associative on the basis of the fact that complexes in which space is available in the coordination sphere react, while those that are crowded do not.

Electronic control of the rate-determining step by the chelate ring is evident when nitrogen and phosphorus donor chelates are compared. Because nitrogen is more electronegative than phosphorus, a shift in electron density from the phosphite ligand toward the chelate might occur making the phosphite methyl groups making more susceptible to attack by a nu-

cleophile. In accordance, the conversion of $[\text{CpCo}(\text{N}\text{N})\text{I}]^+$ complexes to $\{\text{CpCo}(\text{N}\text{N})[\text{P}(\text{O})(\text{OCH}_3)_2]\}^+$ takes place in seconds at room temperature whereas $[\text{CpCo}(\text{P}\text{P})\text{I}]^+$ analogues require minutes under the same conditions.

The electron donor strength of the nucleophile plays a role in the rate-determining step as is shown by the fact that $[\text{CpCo}(\text{dppe})\text{X}]^+$ reacts with $\text{P}(\text{OCH}_3)_3$ to produce $\{\text{CpCo}(\text{dppe})[\text{P}(\text{O})(\text{OCH}_3)_2]\}^+$ with a rate of $\text{X}^- = \text{CN}^- > \text{I}^- > \text{Br}^- > \text{Cl}^-$. This order parallels the electron donor power of X^- and the leaving group tendency of X^- . In all of these compounds the initial equilibrium step yielding $\{\text{CpCo}(\text{dppe})[\text{P}(\text{O})(\text{OCH}_3)_2]\}^{2+}$ occurs rapidly.

Phosphonate products formed by reaction with $\text{P}(\text{OCH}_3)_3$ have also been observed in $\text{CpFe}(\text{CO})_2\text{X}^1$ and $\text{CpNi}[\text{P}(\text{OCH}_3)_3]\text{X}^2$ ($\text{X}^- = \text{Cl}^-$, Br^-), $\text{CpRe}(\text{CO})_2\text{Br}_2$,⁴ and $\text{CpCoI}_2(\text{CO})$.⁵ All of these complexes appear to form an intermediate phosphite complex, which subsequently reacts with the displaced halide. On the other hand, the transformation is not mentioned with other transition metal-halide complexes such as $\text{CpRu}[\text{P}(\text{C}_6\text{H}_5)_3]_2\text{X}^{30}$ ($\text{X}^- = \text{Cl}^-$, Br^-) and $[\text{CpMo}(\text{CO})_3\text{I}]^+$.³¹ In these latter complexes only the monophosphite complex forms. $\text{CpFe}(\text{dppe})\text{I}$, which is isoelectronic with $[\text{CpCo}(\text{dppe})\text{I}]^+$, fails to react at all with $\text{P}(\text{OCH}_3)_3$ in refluxing CH_2Cl_2 after 3 h.³² Nucleophilic attack on complexes in which the metal has a relatively low oxidation state does not react or require more stringent conditions²⁸ probably because smaller residual positive charge resides on the methyl groups of the coordinated phosphite.

In summary, the progress of the transition-metal Arbuzov reaction may be altered by steric blocking in eq 2 or strengthening the $\text{M}-\text{X}$ bond. If eq 2 occurs, the rate of eq 3 may be diminished by (a) reducing the residual positive charge on the carbon atoms of phosphite through placement of electron donor ligands in the metal coordination sphere, or by use of metals in lower oxidation states, and (b) having only weak nucleophiles present in the reaction.

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