Arbuzov-like Dealkylation Reactions of Transition-Metal–Phosphite Complexes

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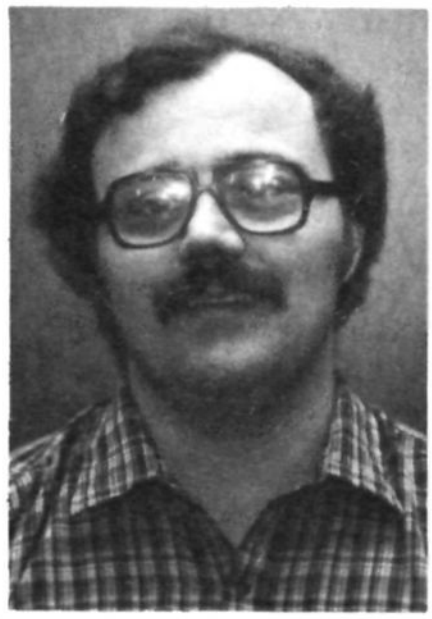
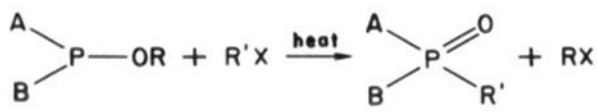


Shayne J. Landon was born in Alexandria Bay, NY, in 1954. He received his B.A. (1976) and M.A. (1979) in chemistry at the State University of New York, Plattsburgh. He completed his Ph.D. degree at the University of Delaware in August 1984 under the supervision of Professor Brill for a dissertation on the nuances of Arbuzov chemistry. He is currently a postdoctoral fellow with Prof. G. L. Geoffroy at Penn State.

I. Introduction

Alkyl phosphite Lewis bases are prevalent ligands in transition-metal chemistry. Once coordinated, these molecules are usually regarded as relatively unreactive. However, this traditional notion is being shaken by a surge of evidence that dealkylation reactions can occur involving transition-metal-bound phosphite ligands leading, ultimately, to metal–phosphonate complexes. Some of these reactions contain the essential features of the Arbuzov (or Michaelis–Arbuzov) rearrangement which is very familiar to organophosphorus chemists. In the "classical" Arbuzov reaction (1) an alkylated nucleophile, R′X, and a phosphorus(III) ester, ABP(OR), react, usually during prolonged heating and without a solvent giving an organophosphorus(V) compound with alkyl transfer. The rearrangement of a



(1)

(A, B frequently alkyl, aryl, alkoxy)

phosphite molecule to a phosphonate is also witnessed in the absence of nucleophiles and in the presence of radicals. Although the comparable reaction involving transition-metal complexes is less predictable, occurring not at all in some compounds and rapidly at room temperature in others, the variety of metal complexes engaging in the reaction is now surprisingly wide. An appreciation for the presence of this well-known reaction from main-group chemistry among transition-metal complexes springs from an awareness of the various mechanisms and an understanding of the controlling factors that are known so far. This analysis of the Arbuzov reaction involving a transition-metal center is current through the spring of 1984.

II. "Classical" Arbuzov Reaction Mechanisms

Substantial effort has been devoted to clarifying the "classical" reaction (1) which was discovered by Michaelis and Kaehne[1] and investigated by Arbuzov.[2] Reactants in (1) can be phosphinites (A, B = R) and phosphonites (A = R, B = OR) as well as phosphites (A, B = OR). When R′X = MeI and A,B = R,OR or R,R the reactivity follows the order of electron-donor ability of A,B: alkylamino > alkyl > aryl > alkoxy > aryloxy. Although many alkylating agents, R′X, induce reaction 1, alkyl halides are most frequently employed.

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When A, B = OR and X = I, the order of reactivity of R'X is R' = Me > Et > *i*-Pr.[3] R'X can be other main-group molecules; e.g., an alkyltin(IV) halide.[4]

Considerable evidence has accumulated for an *ionic mechanism* involving, as an essential feature, the intermediate "quasiphosphonium" salt in reaction 2.

$$X{-}R' + :PAB(OR) \longrightarrow [R'PAB(OR)]^+X^- \quad (2)$$

$$[R'PAB(OR)]^+ + X^- \longrightarrow R'P(O)AB + RX \quad (3)$$

Nucleophilic attack of X^- on the α-carbon of the ester (reaction 3) culminates in the exchange of alkyl groups and conversion of P(III) to P(V).[2,5] The rearrangement of P–O–C to P(=O)—C in (3) is exothermic to the extent of at least 130 kJ mol^{-1}. Although contradictory assertions have been made as to whether (2) or (3) is rate limiting,[2,6] the rate-determining step hinges largely on the nature of the reactants.[7]

The ionic dealkylation mechanism prevails if a strong nucleophile is present in the reaction. In the absence of a strong nucleophile, reaction 3 can be supplanted by an *autocatalytic mechanism*[8] (4) wherein the trivalent phosphite attacks the phosphonium intermediate producing the phosphonate and regenerating the intermediate. Self-alkylation similar to (4) is strongly

$$[ABMeP(OMe)]^+X^- + ABP(OMe) \rightarrow ABP(O)Me + [ABMeP(OMe)]^+X^- \quad (4)$$

influenced by catalytic amounts of other reagents.[9] Reaction 3 dominates with strong nucleophiles, but becomes competitive with (4) as the nucleophile becomes weaker, and finally is replaced by (4) when the nucleophile is very weak.[7]

Radicals generated by photolysis or chemical means are known to attack ABP(OR) affording Arbuzov products by a *radical mechanism* (5)[10]

$$R'\cdot + ABP(OR) \rightarrow AB\dot{P}(OR)R' \rightarrow ABP(O)R' + R\cdot \quad (5)$$

where R'· = Me_2N·, Ph·, Me·, etc. Apart from catalytic activation of the PhI bond,[11] the radical mechanism is the only path by which an arylphosphonate can be formed from an aryl halide and a phosphite.[12]

The ionic and autocatalytic mechanisms of the Arbuzov reaction generally require prolonged heating. In most cases the quasiphosphonium intermediate from (2) is sufficiently short lived so as to be undetected, much less isolated.[13,14]

III. Arbuzov Reactions Involving Transition-Metal Centers

The reaction of $P(OR)_3$ with a transition metal complex most often results in straightforward ligand substitution at the metal center. However, in some instances (6) the final product contains a phosphonato rather than the phosphito ligand. Reactions 1 and 6

$$L_nMX + P(OR)_3 \rightarrow L_nMP(O)(OR)_2 + RX \quad (6)$$

are similar in appearance but, unlike (1), (6) may occur at room temperature or with mild heating. In other instances, the phosphite ligand dealkylates to a phosphonate despite the absence of an apparent nucleophile. Upon closer examination most of these rearrangements

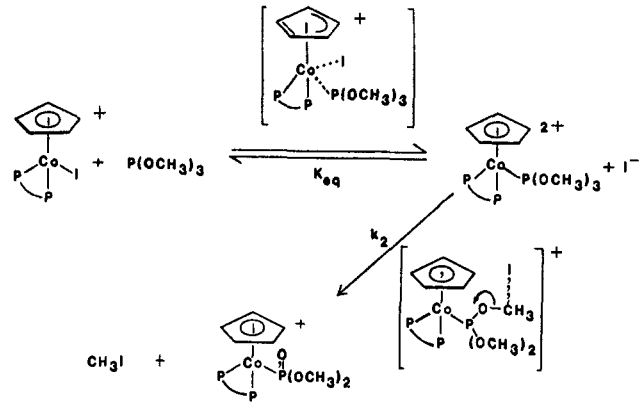


Figure 1. Ionic mechanism of the Arbuzov reaction with CpCo(dppe)I$^+$ and $P(OMe)_3$ showing possible transition states.

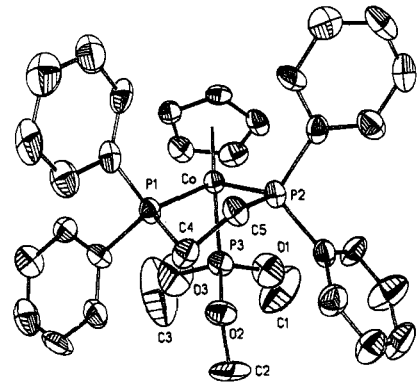


Figure 2. Structure of an intermediate "quasiphosphonium" ion of the Arbuzov reaction: $\{CpCo(dppe)[P(OMe)_3]\}^{2+}$.

can be categorized by two mechanisms.

A. The Ionic Mechanism

An Arbuzov rearrangement of an alkyl phosphite can occur in a transition metal halide complex in which a phosphite molecule first displaces the halide from the coordination sphere. The jilted halide ion then responds by attacking the coordinated phosphite. Alternatively, one may begin with the phosphito complex, add a nucleophile, and achieve the equivalent transformation. This ionic mechanism has been investigated using $[CpCo(dppe)I]^+$ and $P(OMe)_3$ as reactants.[15] ^1H and ^{31}P NMR and UV–vis spectroscopy suggest the reaction pathway shown in Figure 1. During the reaction, the ^1H NMR spectrum contains Cp signals for free and bound $P(OMe)_3$ and bound $-P(O)(OMe)_2$.[15] Two isosbestic points attest to the presence of three chromophores in solution.[16] The rate law for the disappearance of $[CpCo(dppe)I]^+$ is $-k_2K_{eq}[CpCo(dppe)I^+][P(OMe)_3]$. The lack of an expressed $[I^-]$ dependence in the reaction results from the steady-state approximation and may seem surprising. In fact, there is a small dependence of the rate on $[I^-]$ but it is close to the experimental error because the influence of $[I^-]$ is roughly counterbalancing.

The dicationic intermediate can be isolated and characterized in the absence of nucleophiles.[17] The ion shown in Figure 2 is the first structurally characterized trialkyl phosphite intermediate involved in the transition-metal Arbuzov reaction.[18] The observation and isolation of this complex is one of the features that distinguishes reaction 6 from the classical reaction 1,

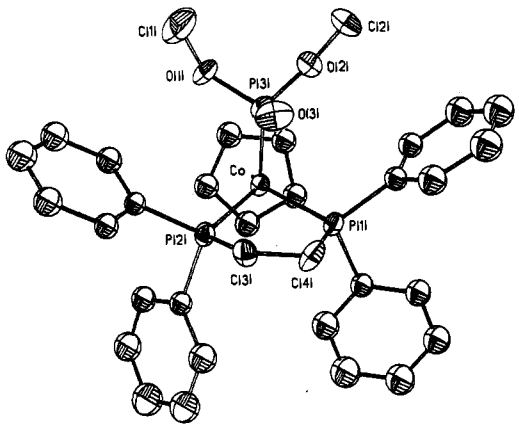


Figure 3. Structure of a phosphonate product of the Arbuzov reaction: $\{CpCo(dppe)[P(O)(OMe)_2]\}^+$.

TABLE I. Equilibrium and Rate Constant Data for the Reaction in Figure 1[a]

X	k_{obsd}[b]	K_{equil}	k_2[b]
Cl^-	0.011	0.0012	9.2
Br^-	0.24	0.027	8.7
I^-	0.76	0.13	59

[a] Temperature 20 °C; acetone-d_6. [b] L mol^{-1} s^{-1}.

and is attributable to the well-known stability of metal–phosphite complexes. The phosphonate product of the Arbuzov reaction involving this dication appears in Figure 3.

The mechanism in Figure 1 has steric and electronic contributions to each step. Bulky ligands in the reactant should diminish the equilibrium constant. Electronic effects that increase the metal–halide bond strength, diminish the residual positive charge on phosphito ligand, or reduce the strength of the nucleophile will impede the overall reaction. Steric perturbations to the equilibrium step can be created by changing the chelate ring size. The iodide and phosphite compete effectively for the coordination site when the chelate ligand is dppe and PC=CP. However, iodide is not displaced when the bulkier ligands, dppp and dppb, are present in the coordination sphere.[17] The reaction with the dppm complex, which contains the least bulky of these ditertiary phosphine chelate ligands, is complicated by the fact that dppm fails to remain fully chelated.[17] The products obtained are mentioned in section IIIC. Diminished spacial demand and the recentering of electron density toward the metal and the chelate ligand account for a 10–100-fold increase in k_{obsd} when en and pn replace dppe as the chelate ligand.[17]

The dependence of k_{obsd} on X including an empirical observation for CN^- is X = $CN^- > I^- > Br^- > Cl^-$[17] which is also the order of nucleophilicity of X in aqueous solution.[19] However, dissection of k_{obsd} into k_2 and K_{eq} (Table I) reveals that K_{eq} (reflecting the relative Co–X bond strength) as much as k_2 (reflecting the nucleophilicity of X in the dealkylation step) controls k_{obsd}.[20]

Kinetic data for the classical Arbuzov reaction are sparce. However, in keeping with the more stringent conditions needed to effect the reaction in an organophosphorus compound, k for dealkylation of $[Ph_nP(Me_3CCH_2O)_{3-n}Me]^+$ by X^- is 10^4–10^6 times smaller[21] than the equivalent step, k_2, in Table I. $\Delta H^\ddagger$ for dealkylation of $[Ph_nP(OR)_{3-n}Me]^+$ and $\{CpCo(dppe)[P(OMe)_3]\}^{2+}$ is similar, but $\Delta S^\ddagger$ is much larger in the latter (0–10 eu vs. 70–90 eu).[20] Therefore, the faster rate of dealkylation in this transition-metal system is attributable to entropy. $\Delta S^\ddagger$ is enhanced in the transition-metal system because dipositive and uninegative charged ions interact in the transition state, whereas 1+ and 1− charged ions are involved in the classical reaction. The reaction rate should be and is strongly influenced by the choice of solvent and counterion for the metal complex.[20] The rate ordering of R = Me > Et for dealkylation of $P(OR)_3$ by $[CpCo(dppe)I]^+$ mostly reflects the susceptibility of R to nucleophilic attack.[20]

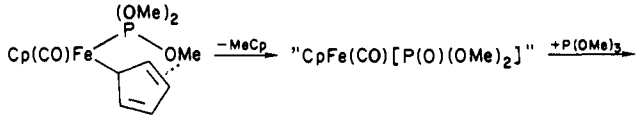
These details of the ionic mechanism frame an understanding of the facility of Arbuzov-like rearrangements in other metal complexes. Haines et al.[22] discovered $CpFe(CO)_2[P(O)AB]$ and $CpFe(CO)[P(OR)AB][P(O)AB]$ among the products of the reaction of $CpFe(CO)_2Cl$ with various phosphites, phosphonites, and phosphinites. $\{CpFe(CO)_2[P(OMe)_3]\}^+$ was identified by IR spectroscopy as an intermediate in the reaction with $P(OMe)_3$. This cation appears then to be attacked by Cl^- yielding $CpFe(CO)_2[P(O)(OMe)_2]$. On this basis, sequence 6a–8 was proposed. Reaction 8

$$CpFe(CO)_2Cl + P(OR)_3 \rightarrow \{CpFe(CO)_2[P(OR)_3]\}^+Cl^- \quad (6a)$$

$$\{CpFe(CO)_2[P(OR)_3]\}^+Cl^- \rightarrow CpFe(CO)_2[P(O)(OR)_2] + RCl \quad (7)$$

$$CpFe(CO)_2Cl + P(OR)_3 \rightarrow CpFe(CO)[P(OR)_3]Cl + CO \quad (8)$$

complicates the characterization of this system. Reactions 6 and 7 are specific to the chloride complex; the corresponding bromide and iodide complexes react only by (8). While this order of Arbuzov reactivity (X = $Cl^- > Br^-, I^-$) is opposite that of the $[CpCo(dppe)X]^+$ series, the trend originates in the strength the Fe–X bond in $CpFe(CO)_2X$ which is proposed[22] to be X = $Cl^- < Br^- < I^-$. When X = η^1-C_5H_5, a radical-chain reaction in the presence of $P(OMe)_3$[23a] produces $CpFe(CO)[P(OMe)_3](\eta^1\text{-}C_5H_5)$. Dealkylation then takes place by sequence 9 through internal nucleophilic attack by the diene on the phosphito ligand.[23b] Reaction 6 does not occur when X = η^1-C_5H_5 because $CpFe(CO)_2[P(O)(OMe)_2]$ is not formed.



$$CpFe(CO)[P(OMe)_3][P(O)(OMe)_2] \quad (9)$$

The reaction of $CpNi[P(OMe)_3]X$ (X = Cl^-, I^-) with $P(OMe)_3$ at room temperature quantitatively yields $CpNi[P(OMe)_3][P(O)(OMe)_2]$ and CH_3X within minutes.[24] The ^1H NMR spectrum of the reaction mixture below −10 °C reveals $\{CpNi[P(OMe)_3]_2\}^+$ as a thermally unstable intermediate. Halide ion attack on $\{CpNi[P(OMe)_3]_2\}^+$ produces the phosphonato ligand. $\{CpNi[P(OMe)_3]_2\}^+$ can be isolated with a very weak nucleophile such as BF_4^-.[25]

A double Arbuzov rearrangement is possible in the reaction of $CpRe(CO)_2Br_2$ with $P(OMe)_3$. In reality, $P(OMe)_3$ displaces both CO and Br^-, but no more than

one Br^- per molecule can be removed.[26] The products are $CpRe(CO)[P(OMe)_3]Br_2$, chiral $CpRe(CO)[P(OMe)_3][P(O)(OMe)_2]Br$, and MeBr. The first double Arbuzov reaction starting with a metal dihalide complex was discovered with $CpCo(CO)I_2$ and $P(OMe)_3$.[27] At room temperature a 1:3 stoichiometric ratio of these reactants generates $CpCo[P(OMe)_3][P(O)(OMe)_2]_2$ and 2MeI. This organometallic bis(phosphonate) was structurally characterized as the monohydrate,[27] but can also be obtained in the anhydrous form. The same reactants in 1:1 stoichiometry produce $CpCoI_2[P(OMe)_3]$ which appears to be an intermediate on the way to $CpCo[P(OMe)_3][P(O)(OMe)_2]_2$.

Arbuzov rearrangements also appear among inorganic coordination compounds. Dimethylglyoximato complexes of Co(III), $LCo(DH)_2Cl$, where L is a nitrogen heterocycle, yield a phosphonate complex by the proposed sequence 10–13.[28] According to the ^1H NMR

$$LCo(DH)_2Cl + P(OMe)_3 \rightarrow [P(OMe)_3]Co(DH)_2Cl + L \quad (10)$$

$$L + [P(OMe)_3]Co(DH)_2Cl \rightarrow \{[P(O)(OMe)_2]Co(DH)_2Cl\}^- + MeL^+ \quad (11)$$

$$L + [P(O)(OMe)_2]Co(DH)_2Cl^- \rightarrow [P(O)(OMe)_2]Co(DH)_2L + Cl^- \quad (12)$$

$$Cl^- + [P(OMe)_3]Co(DH)_2Cl \rightarrow \{[P(O)(OMe)_2]Co(DH)_2Cl\}^- + MeCl \quad (13)$$

spectrum, (11) occurs before (13). The trans-labilizing influence of $P(O)(OMe)_2^-$ drives (12) causing (13) to dominate in the production of the phosphonate complex. Reaction 13 was subsequently used in the form of (14) to determine the trans influence of a series of ligands, X.[29] Square-planar Pt(II) also serves as a

$$Br^- + [P(OMe)_3]Co(DH)_2X \rightarrow [P(O)(OMe)_2]Co(DH)_2X^- + MeBr \quad (14)$$

$$trans\text{-}\{PtHCl[P(Bz)_3]_2\} + P(OR)_3 \xrightarrow[50\ h]{room\ temp} trans\text{-}\{PtH[P(O)(OR)_2][P(Bz)_3]_2\} + RCl \quad (15)$$

template for the Arbuzov rearrangement (15).[30] With different reaction conditions $PtCl_4^{2-}$ and $P(OEt)_3$ in alkaline solution produce $Pt[P(OH)(OEt)_2]_2[P(O)(OEt)_2]_2$,[30b] a fact that was reported previously by others.[30c] In both cases displacement of Cl^- by $P(OR)_3$ followed by alkylation of Cl^- is believed to occur. However, hydrolysis might also be a factor in the latter reaction because it also takes place in the absence of Cl^-.[30c]

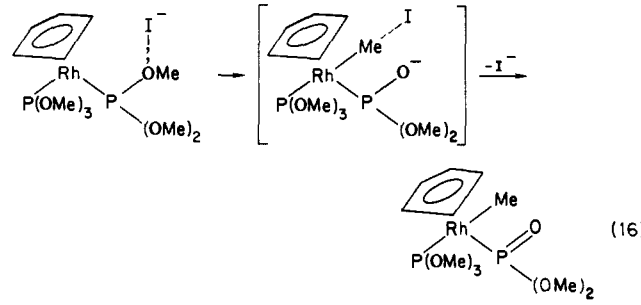
Notice in the above reactions that the pattern of the ionic mechanism is largely the same—formation of an intermediate cationic phosphite complex (equivalent to a "quasiphosphonium" species of the classical reaction) followed by nucleophilic attack on this complex to generate the phosphonate and the alkylated nucleophile. This pattern was overlooked in the titration of $[(COD)RhCl]_2$ with $P(OMe)_3$.[31] At high $[P(OMe)_3]$, one of the metal-containing products, formulated as $Rh[P(OMe)_3]_5$, was subsequently shown[32] to be $Rh[P(OMe)_3]_4[P(O)(OMe)_2]$ which resulted from nucleophilic attack of Cl^- on a coordinated phosphito ligand with liberation of MeCl. $Rh[P(OMe)_3]_4[P(O)(OMe)_2]$ also forms when $CpRh(C_2H_4)_2$ and excess $P(OMe)_3$ react[33] and was originally assumed to be $Rh_2[P(OMe)_3]_8$.[34]

Not surprisingly, the Arbuzov rearrangement can be induced with a cationic metal–phosphite complex simply by adding a nucleophile, such as a halide ion or CN^-. Werner, Klaui, and co-workers observed single, double, and triple dealkylation reactions by this route. Although these reactions are similar to the final step in Figure 1 and reactions 7 and 13, the phosphoryl oxygen atoms of the bis- and tris(phosphonate) products can chelate a variety of metals ions and H^+.

Stepwise dealkylations of $CpCo[P(OMe)_3]_3^{2+}$ by I^- and CN^- produce three organometallic products, $\{CpCo[P(OMe)_3]_{3-n}[P(O)(OMe)_2]_n\}^{+2-n}$ (n = 1–3).[35] $(Me_5C_5)Rh[P(OMe)_3]_3^{2+}$ reacts analogously with I^-. The tris(phosphonate) complexes are tripod ligands, two of which can coordinate hard metal cations to give thermally stable "supersandwich" complexes.[35,36]

A potential bidentate ligand is generated by the sequential double dealkylation of $\{(C_6H_6)OsI[P(OMe)_3]_2\}PF_6$ with NaI.[37] The product, $Na\{(C_6H_6)OsI[P(O)(OMe)_2]_2\}$, contains sodium ions associated with the phosphoryl oxygen atoms. Single and double Arbuzov rearrangements are also witnessed in $\{(CpR)Co[P(OMe)_3]_2(PMe_3)\}(PF_6)_2$ (R = various alkyl substituents) upon addition of 1 and 2 equiv, respectively, of MI (M = Li^+, Na^+, K^+).[38] The product, $\{(CpR)Co[P(O)(OMe)_2]_2(PMe_3)M\}(PF_6)$, converts to $\{(CpR)Co[P(O)(OMe)_2][P(OH)(OMe)_2](PMe_3)\}(PF_6)$ upon the addition of HCl and in turn to $(CpR)Co[P(O)(OMe)_2]_2(PMe_3)$ by neutralization with base. A phosphonate ligand can be displaced from the latter by reaction with PMe_3 and NH_4PF_6 giving $\{(CpR)Co[P(O)(OMe)_2](PMe_3)_2\}PF_6$.

The reaction of $CpRh[P(OMe)_3]_2$, a Rh(I) complex, with I^- is more complicated because of the potential for oxidative addition. Indeed, alkylation of Rh takes place by sequence 16.[39] In a further step, I^- can attack the



(16)

remaining phosphite ligand producing $CpRh(Me)[P(O)(OMe)_2]_2^-$, which crystallizes with metal cations. A racemic mixture of the product of (16) is also obtained by (17).[39]

$$CpRh[P(OMe)_3]_2 + MeI \xrightarrow{-30\ °C} \{CpRh(Me)[P(OMe)_3]_2\}I \xrightarrow{50\ °C} CpRh(Me)[P(OMe)_3][P(O)(OMe)_2] + MeI \quad (17)$$

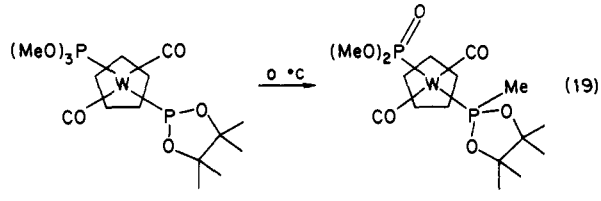
The Arbuzov reaction is stimulated in transition-metal–phosphite complexes by nucleophiles other than halogens and pseudohalogens. In fact, the original report of a probable Arbuzov reaction involving a transition-metal complex occurs in the reaction of $Ph_3SiMn(CO)_5$ with $P(OEt)_3$.[40] Although the sequence 18 is confused by further rearrangements, it was proposed to result from nucleophilic attack on $Ph_3Si[P(OEt)_3]$ by $[Mn(CO)_5]^-$. Less complicated is the reaction of $[CpMo(CO)_3]_2$ with $P(OR)_3$ (R = Me, Et, *i*-Pr,

$$Ph_3SiMn(CO)_5 + P(OEt)_3 \rightarrow \{Ph_3Si[P(OEt)_3]^+Mn(CO)_5^-\} \rightarrow EtMn(CO)_5 + Ph_3Si[P(O)(OEt)_2] \quad (18)$$

n-Bu) examined in an early study by Haines and Nolte.[41] Among the products was $CpMo(CO)_2[P(OMe)_3][P(O)(OMe)_2]$, which was believed to have formed by initial disproportionation of the dimer to the salt $\{CpMo(CO)_2[P(OMe)_3]_2\}^+[CpMo(CO)_3]^-$ followed by anion attack on the cation. In accordance, thermal decomposition of an authentic sample of this salt produced $CpMo(CO)_2[P(OMe)_3][P(O)(OMe)_2]$ and $CpMo(CO)_3Me$. $[CpMo(CO)_3]^-$ also demethylates $\{CpFe(CO)_2[P(OMe)_3]\}^+$.[41]

$Co_2(CO)_8$ and excess $P(OMe)_3$ form the unstable salt $\{Co(CO)_2[P(OMe)_3]_3\}^+[Co(CO)_4]^-$. The anion and cation react rapidly with each other to produce, ultimately, $CH_3Co(CO)_{4-n}[P(OMe)_3]_n$ (n = 0, 3).[42] Likewise $\{Co[P(OMe)_3]_5\}^+[Co(CO)_4]^-$ when refluxed in benzene produced $CH_3Co(CO)_3[P(OMe)_3]$. Phosphonate products were not isolated. Although nucleophilic attack by $[Co(CO)_4]^-$ on the cation is probably involved in the alkyl transfer,[42] there is a possibility that the reaction could occur at least partially by a radical mechanism (vide infra) involving $\cdot\{Co(CO)_{4-n}[P(OMe)_3]_n\}$. Halide ions, X^-, do not induce the Arbuzov rearrangement in $\{Co(CO)_2[P(OMe)_3]_3\}^+$ owing to the ready formation of $XCo(CO)_2[P(OMe)_3]_2$.[42]

Complexes of the type $CpM(CO)_3(EMe_2)$ (M = Mo, W; E = As, Sb) react with $P(OMe)_3$ to form $CpM(CO)_2(EMe_2)[P(OMe)_3]$.[43] Because of the nucleophilicity of E, intermolecular methyl migration occurs at room temperature with or without solvent affording $CpM(CO)_2(EMe_3)[P(O)(OMe)_2]$.[43] Analogous antimony-bridged dimers isomerize in the same manner. For a dioxaphospholane ligand in which E = P, (19) summarizes the conversion which is believed to take place by an intermolecular process.[44]



(19)

In all of the above reactions two conditions exist—a cation containing a phosphito ligand and a mobile nucleophile are present. The absence of dealkylation in other complexes where it might be expected can be traced to the lack of one of these requirements. For instance, $P(OMe)_3$ displaces CO from $[CpMo(CO)_3I]^+$ to give $\{CpMo(CO)_2[P(OMe)_3]I\}^+$.[45] No free I^- is available to attack the phosphite ligand. CpFe(dppe)I fails to react at all with $P(OMe)_3$.[17] A curious case is found in $CpRu(PPh_3)_2X$ (X = Cl^-, Br^-) which reportedly reacts with $P(OMe)_3$ to give $[CpRu(PPh_3)_2P(OMe)_3]^+$.[46] No phosphonate product was mentioned. The sensitivity of this cation toward nucleophiles would be useful to test.

B. The Radical Mechanism

The first Arbuzov rearrangement by a radical pathway involving a transition-metal complex was reported by Goh et al.[47] for the reaction of $[CpCr(CO)_3]_2$ with $P(OMe)_3$. In solvents of low polarity the symmetrically substituted dimer, $\{CpCr(CO)_2[P(OMe)_3]\}_2$, initially forms but reacts rapidly with $P(OMe)_3$, yielding, predominantly, $CpCr(CO)_2(Me)[P(OMe)_3]$ and $CpCr(CO)_2[P(OMe)_3][P(O)(OMe)_2]$. The sequence 20–22 was proposed. A slightly revised mechanism (23)–(25)

$$\{CpCr(CO)_2[P(OMe)_3]\}_2 \rightleftarrows 2CpCr(CO)_2[P(OMe)_3]\cdot \quad (20)$$

$$CpCr(CO)_2[P(OMe)_3]\cdot + P(OMe)_3 \rightarrow CpCr(CO)_2(Me)[P(OMe)_3] + P(O)(OMe)_2\cdot \quad (21)$$

$$CpCr(CO)_2[P(OMe)_3]\cdot + P(O)(OMe)_2\cdot \rightarrow CpCr(CO)_2[P(OMe)_3][P(O)(OMe)_2] \quad (22)$$

$$\{CpCr(CO)_2[P(OMe)_3]\}_2 \rightleftarrows 2CpCr(CO)_2[P(OMe)_3]\cdot \quad (23)$$

$$CpCr(CO)_2[P(OMe)_3]\cdot + P(OMe)_3 \rightarrow CpCr(CO)_2[P(OMe)_3][P(O)(OMe)_2] + Me\cdot \quad (24)$$

$$CpCr(CO)_2[P(OMe)_3]\cdot + Me\cdot \rightarrow CpCr(CO)_2(Me)[P(OMe)_3] \quad (25)$$

is also consistent and is in line with the products often encountered when radicals and alkyl phosphites react.[10] Dealkylation by the radical mechanism is supported by the observation that the same reaction by the ionic mechanism is much slower. $\{CpCr(CO)_2[P(OMe)_3]\}^+[CpCr(CO)_3]^-$, formed in the reaction of $[CpCr(CO)_3]_2$ and $P(OMe)_3$ in a high polarity solvent, only very slowly dealkylates[47] despite the fact that $[CpCr(CO)_3]^-$ is a nucleophile of respectable strength.[48] Thus, while the products of the reaction of $[CpM(CO)_3]_2$ (M = Cr, Mo) with $P(OMe)_3$ are much the same, the radical mechanism dominates when M = Cr, but the ionic mechanism appears more important when M = Mo.[41] Note that $[CpMo(CO)_3]^-$ is a slightly stronger nucleophile than $[CpCr(CO)_3]^-$.[48]

Similar studies undertaken with $[CpM(CO)_2]_2$ (M = Fe, Ru) and $P(OR)_3$ (R = Me, Et, *n*-Bu) resulted in the products of alkyl transfer,[49] $CpM(CO)_2R$ and $CpM[P(OR)_3]_2[P(O)(OMe)_2]$. Although the possibility of an ionic mechanism involving $\{CpM(CO)[P(OR)_3]_2\}^+[CpM(CO)_2]^-$ was not excluded, the radical mechanism following that of Goh et al.[47] in (20)–(22) was preferred. A mechanism analogous to (23)–(25) would also account for the products. The chance that the strong nucleophile $[CpM(CO)_2]^-$ could be present is cause for some apprehension. $[CpFe(CO)_2]^-$ is a photolysis product of $[CpFe(CO)_2]_2$.[50] $[CpFe(CO)_2]_2$ also reacts with tertiary phosphine ligands, PP, giving the disproportionated product $[CpFe(CO)PP]^+[CpFe(CO)_2]^-$.[51] To the extent that the this might occur to a small extent with $P(OR)_3$ liberating $[CpM(CO)_2]^-$ (M = Fe, Ru), the dealkylation mechanism could be affected compared to $[CpCr(CO)_3]_2$. $[CpM(CO)_2]^-$ (M = Fe, Ru) is about 10^6 times as strong a nucleophile as $[CpCr(CO)_3]^-$.[48]

The balance between the ionic and radical pathway probably can be tipped by judicious choice of the reactants and conditions. Illustrative of this is the dealkylation of $\{Co(CO)_2[P(OMe)_3]_3\}^+[Co(CO)_4]^-$ which is asserted to follow the ionic path[42] while the same reaction for $\{Co[P(OMe)_3]_5\}^+[Co(P(OMe)_3]_4]^-$ occurs by the radical path.[52] After 24 h the latter salt in THF yields $Co[P(O)(OMe)_2][P(OMe)_3]_4$, $\{Co[P(OMe)_3]_4\}\cdot$, a small quantity of $MeCo[P(OMe)_3]_4$, and $HCo[P(OMe)_3]_4$. Unlike $[Co(CO)_4]\cdot$,[53] $Co[P(OMe)_3]_4\cdot$ is a long-lived radical[52] which accumulates and efficiently

extracts methyl groups from phosphito ligands.

The Rh(II) octaethylporphyrin dimer, $[Rh(OEP)]_2$, reacts with $P(OMe)_3$ affording $Rh(OEP)[P(O)(OMe)_2]$, Rh(OEP)Me, and $MeP(O)(OMe)_2$.[54] Homolytic cleavage of the dimer is induced by $P(OMe)_3$, forming the radical monomer. Reactions 26–28 show the subsequent proposed pathway[54] to the products. This study is one of few that reports free $MeP(O)(OMe)_2$ as a product. Another route to $MeP(O)(OMe)_2$ might be the autocatalytic reaction 29.

$$Rh(OEP)[P(OMe)_3]\cdot \rightarrow Rh(OEP)[P(O)(OMe)_2] + Me\cdot \quad (26)$$

$$1/2[Rh(OEP)]_2 + Me\cdot \rightarrow Rh(OEP)Me \quad (27)$$

$$Me\cdot + P(OMe)_3 \rightarrow MeP(O)(OMe)_2 + Me\cdot \quad (28)$$

$$Rh(OEP)[P(OMe)_3]\cdot + P(OMe)_3 \rightarrow Rh(OEP)[P(OMe)_3]\cdot + MeP(O)(OMe)_2 \quad (29)$$

C. Difficult-To-Classify Examples

Several examples of methyl migration involving phosphito ligands are difficult to categorize by the mechanism. Thermolysis of $Ru[P(OMe)_3]_5$ in hexane in a sealed tube for 24 h quantitatively produces a solid product identified as $RuMe[P(O)(OMe)_3][P(OMe)_3]_4$.[55] The rearrangement is inhibited by the presence of free $P(OMe)_3$ which suggests that an equilibrium involving dissociation to $Ru[P(OMe)_3]_4$ may exist in solution.[55] However, $Ru(Me)[P(O)(OMe)_2][P(OMe)_3]_4$ also forms when neat $Ru[P(OMe)_3]_5$ is heated. It seems improbable that the rearrangement in the solid phase and in solution would follow the same mechanism. Elsewhere, other metal–phosphite complexes have been converted to metal–phosphonates by thermolysis.[56] The mechanism of this process is undoubtedly complex and could include inter- and intramolecular reactions as well as radicals. Furthermore, self-isomerization of free $P(OMe)_3$ (30) may involve autocatalysis and is enhanced by impurities.[9,57] Even during a routine melting point determination, isomerization of a metal–phosphite complex to the metal–phosphonate may take place.[55] The melting point of a phosphonate complex rather than the starting phosphite complex may instead be obtained.

$$P(OMe)_3 \xrightarrow[17.5\ h]{200\ ^\circ C} MeP(O)(OMe)_2 \quad (30)$$

$CpM(C_2H_4)_2$ (M = Rh, Ir) with excess $P(OMe)_3$ gives, as a final metal-containing product, $M[P(O)(OMe)_2][P(OMe)_3]_4$.[33] The fate of the methyl group was not established. Likewise, $Ir_4(CO)_{12}$ and $Os_3(CO)_{12}$ and $P(OMe)_3$ with H_2 and CO as companion reactants liberate CH_4 from $P(OMe)_3$.[58] In the reaction $P(OMe)_3$ is also isomerized to $MeP(O)(OMe)_2$. The details of the reaction have not been clarified although transfer of Me from $P(OMe)_3$ to the metal is a probable step.[58] Either the ionic or the radical mechanism can be imagined as responsible for alkyl migration to the metal in the reaction of $(Cp)_2Mo_2(CO)_4(Ph_2CS)$ complexes with alkyl phosphites.[59]

Although the reaction follows an ionic pathway, the Arbuzov chemistry involving $[CpCo(dppm)I]^+$ and $P(OMe)_3$ illustrates the additional complexity that arises when several ligands are able to dissociate from the coordination sphere.[60a] The initial product of the reaction is $\{CpCo(dppm)[P(OMe)_3]\}^{2+}$ which is immediately attacked by I^- to liberate $\{CpCo(dppm)[P(O)(OMe)_2]\}^+$ and MeI. The overall yield of the phosphonate complex is low because of another product identified as $\{CpCo[\mu_1\text{-dppm(O)}][P(OMe)_3]_2\}^{2+}$ is formed concurrently in much larger yield as a result of the failure of the dppm ligand to remain fully chelated. "Dangling" ditertiary phosphine ligands in complexes of this type are known to undergo ready oxidation to form a "dangling" phosphine oxide.[60b] $\{CpCo[\mu_1\text{-dppm(O)}][P(OMe)_3]_2\}^{2+}$ gradually degrades after several days in solution to form $[Ph_2P(Me)CH_2P(O)Ph_2]^+$, $HP(O)(OMe)_2$, MeOH, and an insoluble residue. Curiously, the Arbuzov chemistry is complete after several minutes with the formation of $\{CpCo(dppm)[P(O)(OMe)_2]\}^+$.

TABLE II. ^{31}P NMR Chemical Shifts[a] for Products of Arbuzov Transformations[b]

complex	X = $P(O)(OMe)_2^-$	Y = $P(OMe)_3$	ref
$CpCo(bpy)X^{2+},Y^+$	75.97[c]	118.8[e]	17
$CpCo(dppe)X^{2+},Y^+$	86.1 (m, 91.8)[d]	125.34 (t, 88)[d]	15
$CpCoX_2Y$	95.2 (134)[d]	148.9 (t, 134)[e]	27
$CoXY_4$	107.5 (6)[f]	155.9 (b)[f]	52
CpNiXY[g]	85.8 (d, 151)[e]	147.5 (m, 151)[h]	24a
$[CpRh(Me)X_2]^-$	95.7 (d)[h]		39
$CpMo(CO)_2XY$	115 (d, 36.6)[d]	188 (d, 36.6)[d]	49a
$[CpMo(CO)_2X,Y]\text{-}SbMe_2$	120[i]	187[f]	43
$[CpW(CO)_2X,\text{-}Y]_2SbMe_2$	90 (J_{WP} = 347)[d]	149 (J_{WP} = 419)[d]	43
$CpW(CO)_2X,Y\text{-}(SbMe_3)_2$	84 (J_{WP} = 317)[d]	159 (J_{WP} = 480)[d]	43
$CpW(CO)_2LX,Y$	76.1 (m)[f]	159.6 (m)[f]	44
$CpFe(CO)XY$	125.7 (d, 139.2)[d]	180.2 (139.2)[d]	49b
$CpRuXY_2$	108.5 (t, 81.3)[d]	158.4 (d, 8.13)[d]	49a

[a] Relative to external H_3PO_4; positive shifts downfield; parenthetical numbers are J_{PP} unless otherwise noted. [b] b = broad, m = multiplet, d = doublet, t = triplet, L = a dioxaphospholane. [c] CD_3OD. [d] $CDCl_3$. [e] $(CD_3)_2CO$. [f] $CD_3C_6D_5$ at 27 °C. [g] Et derivative. [h] CD_3NO_2. [i] C_6D_6.

IV. Identifying the Arbuzov Reaction

So where do we stand with respect to alkyl phosphite ligands? The above examples should quake any lingering beliefs in their innocence. On the other hand, the two predominant mechanisms form the basis for anticipating the likelihood of the dealkylation reaction. Reliable methods are needed to diagnose it.

Recognizing that an Arbuzov rearrangement has taken place in a transition-metal complex is occasionally a ticklish problem. Apart from an awareness of the reaction, there are spectroscopic flags that usually appear during the reaction or in the final products. These, coupled with other evidence such as conductivity data, often identify what has taken place. From the point of view of the metal complex, ^{31}P NMR spectroscopy is the most powerful tool for categorizing a ligand as phosphito or phosphonato. Table II reveals that δ (^{31}P) for $P(O)(OMe)_2^-$ is 40–85 ppm more shielded than $P(OMe)_3$ in analogous complexes. The range of resonances for $P(O)(OMe)_2^-$ ligands observed to date is 75–126 ppm. For comparable complexes of $P(OMe)_3$ it is 118–188 ppm. These regions partially overlap, but are unambiguous in reactions taking place by the ionic mechanism because the reaction rate is often suffi-

TABLE III. ^{1}H NMR Chemical Shifts of Me at Room Temperature (δ_{Me_4Si} = 0.00 ppm)[a,b]

complex	X = $P(O)(OMe)_2^-$	Y = $P(OMe)_3$	ref
$CpCr(CO)_2XY$	3.46 (d, 11.0);[c] 3.93 (d, 11.0)[d]	3.50 (d, 11.1);[c] 3.37 (d, 11)[d]	47
CpFe(CO)XY	3.55 (d, 11.0)[e]	3.68 (d, 12.4)[e]	49b
	3.70 (d, 11.0)[f]	3.56 (d, 11.5)[f]	23
$[CpCoXY_2]^+$	3.75 (d, 11)[g]	3.98 (vt, 12)[g]	35
$CpCoX_2Y$	3.71 (vt, 9.5, 2.0)[e]	3.84 (d, 11.2)[e]	27
$[CpCoX_3]^-$	3.64 (vq, 11)[g]		35
$[CpCo(PMe_3)_2X]^+$	3.76 (d, 11.4)[h]		38
$CpCo(PMe_3)X_2$	3.62 (vt, 10.6);[h] 3.59 (vt, 10.6)[h]		38
$[CpCo(PMe_3)XY]^+$	3.72 (d, 11.1);[h] 3.70 (d, 11.1)[h]	4.10 (d, 11.2)[h]	38
CpCoMeXY	3.55 (12)[e]	3.70 (11)[e]	67
CpCoIXY	3.70 (12)[e]	3.80 (11)[e]	67
$CpCo(dppe)X^{2+},Y^+$	2.82 (d, 11.18)[e]	3.42 (d, 11.6)[e]	15
$CpCo(bpy)X^{2+},Y^+$	3.30 (d, 11.03)[e]	3.67 (t, 10.8)[e]	17
$LCo(DH)_2X$[i]	3.34–3.51[j]		28
CpNiXY	3.34 (d, 11.7)[h]	3.68 (d, 12.6)[h]	24b
$CpMo(CO)_2XY$[k]	3.63 (d, 12.0)[e]	3.65 (d, 11.3)[e]	41
$[CpMo(CO)_2X,Y]_2SbMe_2$	3.95 (d, 10.8)[d]	3.29 (d, 12.0)[d]	43
CpRe(CO)BrXY	3.77 (d, 11)[e]	3.85 (d, 11)[e]	26
$CpRuXY_2$	3.61 (vt)[e]	3.49 (d, 10.5)[e]	49a
$[Me_5CpRhXY_2]^+$	3.63 (d)[h]	3.90 (vt)[h]	35
Me_5CpRhX_2Y	3.61 (vt)[h]	3.92 (d)[h]	35
$[Me_5CpRhX_3]^-$	3.59 (vq)[h]		35
CpRhMeXY	3.54[e]	3.66[e]	67
$[CpRhMeX_2]^-$	3.44 (vt);[h] 3.39 (vt)[h]		39
CpRhIXY	3.64[e]	3.78[e]	67

[a] Parenthetical numbers are $^3J_{PH}$ in Hz. [b] Abbreviations used: d = doublet, vt = virtual triplet, vq = virtual quartet, m = multiplet. [c] CD_3CN. [d] C_6D_6. [e] $CDCl_3$. [f] C_6H_6. [g] CD_3NO_2. [h] $(CD_3)_2CO$. [i] L = various Lewis bases, DH = dimethylglyoximato. [j] CH_2Cl_2. [k] Assignments are tentative.

ciently slow to permit detection of both the phosphito and phosphonato signals.

The ^{1}H NMR spectrum of metal complexes containing $P(OMe)_3$ and $P(O)(OMe)_2^-$ can be useful, but is frequently complicated by the similarity of the chemical shift of the Me protons. High-field spectra are usually needed. Data for typical complexes are assembled in Table III. The protons of coordinated $P(O)(OMe)_2^-$ are frequently, but not always (particularly in benzene solution), more shielded than those of coordinated $P(OMe)_3$ in a similar chemical environment. A coordination sphere containing phosphorus atoms in the ratio P_2P' often produces virtual coupling[61] in the proton signals giving rise to a second-order pattern. $^3J_{HP}$ is 9–12 Hz. Few ^{13}C chemical shifts are available[27] but they suffer from much the same problem as the ^{1}H spectra. In the case of the ionic mechanism, the alkylated nucleophile is usually evident in the ^{1}H and ^{13}C NMR spectrum.

The infrared stretching frequency of P=O in a $P(O)(OMe)_2^-$ ligand appears in the 1125–1200 cm^{-1} range. While this mode is diagnostic, its identity may be obscured by C–C and C–O modes. In general, infrared evidence of dealkylation is less sound than ^{31}P NMR evidence. Several examples of internal coordination by the phosphoryl oxygen atom have been suggested based on the P=O stretching frequency,[24a,62] but the frequencies are typical of the terminal P=O stretch.

The ligand field and electronic properties of $P(O)(OMe)_2^-$ are rather similar to those of $P(OMe)_3$. The ^{59}Co nuclear quadrupole coupling constants for the series of compounds $\{CpCo[P(OMe)_3]_{3-n}[P(O)(OMe)_2]_n\}^{+2-n}$ (n = 0–3) change smoothly and differ by less than 10%.[63] Likewise, the difference in the ^{1}H NMR chemical shift of the Me in this series is 3–6% while that of Cp, which is more sensitive to the charge on the complex, is about 12%.[35] The NQR data suggest that $P(O)(OMe)_2^-$ and $P(OMe)_3$ are electronically similar, but that $P(O)(OMe)_2^-$ is a slightly poorer electron π acceptor and/or σ donor than $P(OMe)_3$. In accordance, $CpCr(CO)_2[P(OMe)_3][P(O)(OMe)_2]$[64] and $CpCo[P(OMe)_3][P(O)(OMe)_2]_2$[27] contain metal–phosphonato bonds which are 0.05–0.09 Å longer than the metal–phosphito bond.

The most prevalent chemical activity of the phosphonato ligand observed so far has been the tendency of the phosphoryl oxygen atom to coordinate metal ions, H^+, H_2O, organometallic fragments,[35] and main-group elements.[65] The phosphonato ligand can be displaced by a strong Lewis base such as PMe_3.[38] With prolonged refluxing in MeOH, I^- slowly displaces $P(O)(OMe)_2^-$ from $\{CpCo(dppe)[P(O)(OMe)_2]\}^+$.[66]

V. Concluding Remarks

Under ordinary conditions, the likelihood of dealkylation of a metal-bound phosphito ligand is greatest if free nucleophiles and radicals are also present. The steric and electronic factors that influence the reaction by the ionic mechanism are better understood now that the details have been more firmly established. The requirements for the ionic mechanism include phosphite coordinated almost always in a cationic metal complex such that the α-carbon atoms of the phosphito ligand are susceptible to nucleophilic attack, and the availability of a nucleophile, such as a halide, pseudohalide, metal complex anion, or an organic base in solution to carry out the dealkylation. The radical mechanism requires events which to date have been initiated by phosphite-induced homolysis of a metal–metal bond. The resulting phosphite-containing radical can attack a free $P(OR)_3$ molecule or eliminate R· on the way to producing a phosphonato ligand. Thermolysis of metal–phosphite complexes is complicated and ill-defined. Unlike the ionic mechanism, thermolysis and the radical mechanism are able to produce phosphonato ligands attached to metals in a relatively low formal oxidation state.

Additional Arbuzov-like dealkylation reactions in transition-metal complexes no doubt will be found. Also, the possibility of mechanisms other than those outlined here cannot be discarded. With these thoughts in mind, this analysis will hopefully stimulate rather than close the case on transition-metal variations on the "classical" Arbuzov reaction.

Note Added in Proof. The heterolytic products from metal–metal bond cleavage[41] have been shown to result from photolysis rather than thermolysis.[68]

VI. Abbreviations

Me	CH_3
Et	CH_3CH_2
i-Pr	$CH_3(CH_3)CH$
n-Bu	$CH_3(CH_2)_3$
Ph	C_6H_5
Cp	η^5-C_5H_5
dppm	$[(C_6H_5)_2P]_2CH_2$
dppe	$[(C_6H_5)_2)P]_2(CH_2)_2$
dppp	$[(C_6H_5)_2P]_2(CH_2)_3$
dppb	$[(C_6H_5)_2P]_2(CH_2)_4$
PC=CP	$[(C_6H_5)_2P]C_2H_2$
en	$H_2N(CH_2)_2NH_2$
pn	$H_2N(CH_2)_3NH_2$
COD	1,4-cyclooctadiene
bpy	2,2′-bipyridyl
Bz	$C_6H_5CH_2$
OEP	octaethylporphyrin

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