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THE DOUBLE DEMETHYLATION PATHWAY INVOLVING CYCLOPENTADIENYLDIIODOCARBONYLCOBALT(I) AND TRIMETHYL PHOSPHITE

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Summary

The reaction steps taking place when $CpCo[P(O)(OMe)_2]_2[P(OMe)_3]$ is formed by the double Arbuzov transformation in the reaction of $CpCoI_2(CO)$ with $P(OMe)_3$ were investigated by monitoring the ^1H NMR spectrum as a function of time. The 1/1, 1/2 and 1/3 reaction stoichiometries were investigated. Concentration vs. time profiles of the reactants, intermediates and products were constructed. Four intermediates were detected. Two of the intermediates and the final product are readily isolated. It is evident that ligand substitution takes place more rapidly than does the Arbuzov-like demethylation. Only the cationic intermediates participate in the demethylation reactions.

Introduction

The first double Michaelis–Arbuzov reaction (eq. 1) starting from a metal halide complex was reported by Towle et al. [1] in 1982. At that time no detailed study

$$CpCoI_2(CO) + 3P(OMe)_3 \rightarrow CpCo[P(O)(OMe)_2]_2[P(OMe)_3] + CO + 2CH_3I \quad (1)$$

of this multistep reaction was undertaken. However, new understanding of the Arbuzov reaction in transition metal systems [2–4] stimulated our interest to reexamine this reaction. We were especially interested in the intermediate steps and the comparative rates of these steps. It was also hoped that several of the intermediate species could be isolated, as has been successful for other systems [5].

^1H NMR spectroscopy was particularly helpful because the η^5-cyclopentadienyl (Cp) signals (4.5–6.0 ppm) are diagnostic of the reactions taking place. The Cp protons of positively charged intermediates are deshielded relative to the analogous neutral complexes. For instance, in the reaction of $[CpCo(dppe)I]^+$ with $P(OMe)_3$ to yield $\{CpCo(dppe)[P(O)(OMe)_2]\}^+$ via the intermediate, $\{CpCo(dppe)[P(OMe)_3]\}^{2+}$, the Cp chemical shift for these phosphite-containing complexes changes from δ 5.57 ppm (starting monocation) to 6.06 ppm (dicationic intermediate) to 5.50

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ppm (product monocation) [2,3]. The region between 3.0–4.0 ppm is also helpful because the intensity of doublets and virtual triplets from the OMe groups can be correlated with the Cp intensity to help identify the species. The ^{31}P NMR spectra of complexes containing $P(OMe)_3$ and $P(O)(OMe)_2^-$ are also conspicuous because the chemical shift of the phosphite ligand is far downfield from that of the phosphonate ligand [4]. Also, the signal at δ 2.16 ppm from CH_3I is indicative of the occurrence of the Arbuzov-like dealkylation of a coordinated phosphite ligand. These NMR studies combined with the isolation of several complexes make it possible to establish the steps taking place in reaction 1.

Experimental

All solvents were used as obtained. $P(OMe)_3$ was distilled under nitrogen prior to use. $CpCo(CO)_2$ (Strem) was used as obtained to prepare $CpCoI_2(CO)$ by literature procedures [6,7]. Melting points were obtained in open capillary tubes. Elemental analyses were performed by Micro-Analysis, Wilmington, DE.

$CpCoI_2[P(OMe)_3]$ and $CpCo[P(O)(OMe)_2]_2[P(OMe)_3]$ were synthesized as described before [1]. The NMR spectra of these known compounds are identical to those of several of the species present in solution. $CpCoI[P(O)(OMe)_2][P(OMe)_3]$ has not been isolated previously. $P(OMe)_3$ (1.00 ml, 8.46 mmol) was added dropwise to $CpCoI_2(CO)$ (1.718 g, 4.23 mmol) in $CDCl_3$ (200 ml) at room temperature. Gas evolution was immediately apparent along with a color change to dark brown. The reaction was allowed to continue for a period of 5 h at which time the solution color was medium brown. The solvent was removed to produce a dark brown oil which may be an unresolved mixture of optical isomers. The oil was shown to be $CpCoI[P(O)(OMe)_2][P(OMe)_3]$ by NMR and elemental analysis. Found C, 28.38; H, 4.43. $C_{10}H_{20}CoO_6IP_2$ calcd.: C, 28.4; H, 4.13%.

^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker AM-250 FT spectrometer while the $^{31}P\{^1H\}$ spectra were obtained using a Bruker WM-250 FT spectrometer. The ^1H and ^{13}C chemical shifts are relative to internal TMS while the $^{31}P\{^1H\}$ chemical shifts are relative to 85% H_3PO_4 (external) with positive shifts being downfield. $CDCl_3$ was the solvent in all cases.

In a typical NMR study of the reaction sequence, a standard solution of $CpCoI_2(CO)$ (0.045 g, 0.11 mmol, 2.22×10^{-2} M) was prepared in 5.0 ml $CDCl_3$. Using a 2.0 ml Hamilton syringe, 0.5 ml of this solution was transferred to a standard 5.0 mm OD NMR tube. A reference spectrum was recorded, and the required stoichiometry of $P(OMe)_3$ was added with the Hamilton microliter syringe. The accuracy of this syringe is reported to be 0.1 μl. The tube was vigorously agitated and immediately placed in the probe of the NMR spectrometer. Successive spectra were recorded with the first spectrum being between 40 to 70 sec after the addition of $P(OMe)_3$.

The components were quantified by integrating their intensity relative to the $CD(H)Cl_3$ absorption, which served as an internal standard. The relative concentrations were then plotted with respect to time to establish the mechanistic details.

Results and discussion

By adding one, two or three equivalents of $P(OMe)_3$ to a $CDCl_3$ solution of $CpCoI_2(CO)$ and then following the evolution of the ^1H NMR signals, especially

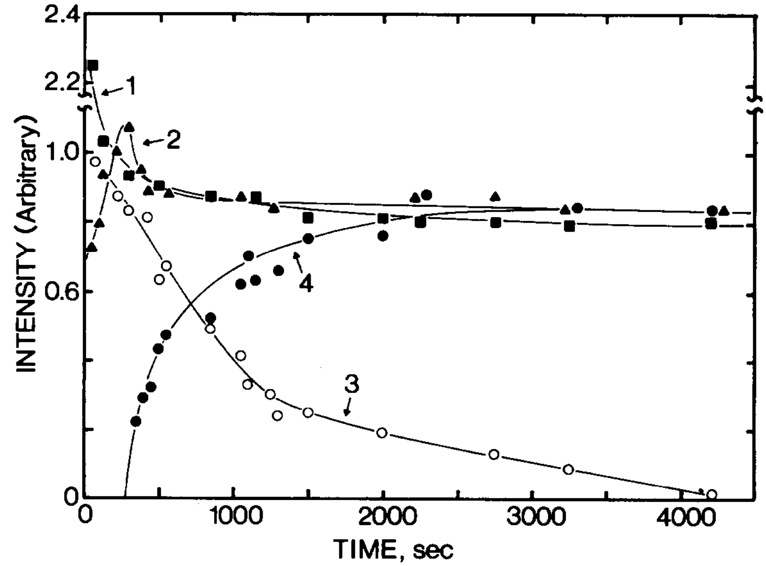


Fig. 1. The concentration versus time profile of the reactants and products when $CpCoI_2(CO)$ and $P(OMe)_3$ react in 1/1 stoichiometry in $CDCl_3$ at room temperature. The intensity of the ^1H NMR signal of the Cp ring is indicative of the concentration of the species. $CpCoI_2(CO)$ (**1**), $CpCoI_2[P(OMe)_3]$ (**2**), $\{CpCoI[P(OMe)_3]_2\}^+$ (**3**), $CpCoI[P(O)(OMe)_2][P(OMe)_3]$ (**4**).

that of Cp, it was possible to identify the intermediates and products of ligand substitution and the Arbuzov chemistry.

1/1 reaction. The time-dependence of the species in the reaction of $CpCoI_2(CO)$ with one equivalent of $P(OMe)_3$ is shown in Fig. 1. The first step of the reaction occurs rapidly at room temperature with the decrease in the intensity of the Cp signal due to $CpCoI_2(CO)$ [1] at 5.69 ppm and the appearance of a new signal at δ 5.29 ppm from the first substitution product [1] $CpCoI_2[P(OMe)_3]$ (**2**), which may form by an associative reaction [2]. This compound was separately isolated and identified. Its complete ^1H, ^{13}C and ^{31}P NMR spectra are compiled in Tables 1 and 2. The concentration of **2** increases for about 300 sec and then decreases for the next 120 sec before finally leveling off. It is a major product of the 1/1 reaction.

After the rapid initial consumption of **1**, its concentration levels off and remains in considerable quantity at the end of the reaction. This is because two additional products consume two equivalents of $P(OMe)_3$. One of these complexes is **3**, $\{CpCoI[P(OMe)_3]_2\}^+$, for which a Cp signal at δ 5.74 ppm is present. This complex was identified by the position of the Cp peak which indicates a monocation, and a virtual triplet due to the methyl protons of the two $P(OMe)_3$ ligands. The intensity of the Cp and OMe absorptions of **3** track one another with time.

Complex **3** is present in the first spectrum at 40 sec indicating that it forms rapidly from **2**, and grows in concentration for the first 200 sec until all of the $P(OMe)_3$ has been consumed. It then gradually decreases in concentration and is absent by the end of the reaction. Its reactivity toward the I^- in the solution precludes its isolation. Although not attempted, crash precipitation by a weakly nucleophic anion early in the reaction might permit its isolation. However, the

TABLE 1

^{1}H NMR DATA FOR THE PRODUCTS IN THE REACTION OF CpCoI$_2$(CO) AND P(OMe)$_3$ IN CDCl$_3$

Complex	δ (ppm)	J (Hz)
CpCoI$_2$[P(OMe)$_3$] (**2**)		
C$_5$H$_5$	5.29	
P(OMe)$_3$	3.87	10.7 (d)
{CpCoI[P(OMe)$_3$]$_2$}$^+$ (**3**)		
C$_5$H$_5$	5.74	
P(OMe)$_3$	3.96	5.5 (vt) [a]
CpCoI[P(O)(OMe)$_2$][P(OMe)$_3$] (**4**)		
C$_5$H$_5$	5.26	
P(OMe)$_3$	3.86	10.8 (d)
P(O)(OMe)$_2$	3.73	10.5 (d)
{CpCo[P(O)(OMe)$_2$][P(OMe)$_3$]$_2$}$^+$ (**5**)		
C$_5$H$_5$	5.63	
P(OMe)$_3$	3.94	7.0 (vt) [a]
P(O)(OMe)$_2$	3.78	11.9 (d)
CpCo[P(O)(OMe)$_2$]$_2$[P(OMe)$_3$] (**6**)		
C$_5$H$_5$	5.24	
P(OMe)$_3$	3.83	11.3 (d)
P(O)(OMe)$_2$	3.69	2.0 (vt) [a]

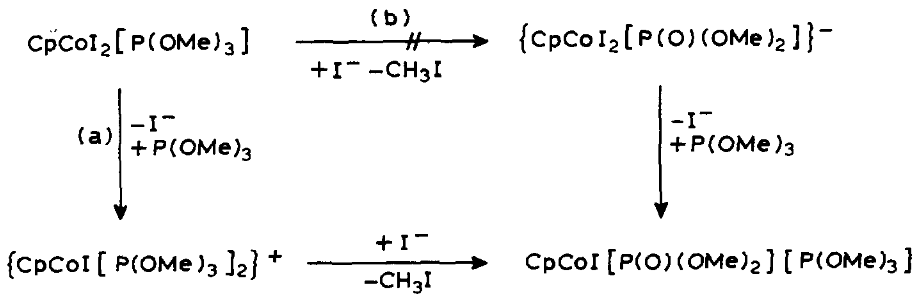
[a] Virtual triplet.

composition of **3** is reasonably certain from the NMR spectrum. The slow decrease in **3** is accompanied by the growth of a Cp signal at δ 5.26 ppm from a new complex, **4**. This complex first appears at about 350 sec and intensifies until about 1000 sec whereupon its concentration levels off. **4** becomes one of the major products which was isolated and identified as the unresolved chiral complex, CpCoI[P(O)(OMe)$_2$][P(OMe)$_3$]. Complete NMR data for **4** are given in Tables 1 and 2. **4** is produced by the Arbuzov reaction of **3** and the displaced I$^-$.

TABLE 2

^{13}C{^{1}H} AND ^{31}P{^{1}H} NMR DATA FOR THE ISOLATED SPECIES FROM THE REACTION OF CpCoI$_2$(CO) AND P(OMe)$_3$ IN CDCl$_3$

Complex	^{31}P{^{1}H}		^{13}C{^{1}H}	
	δ (ppm)	J (Hz)	δ (ppm)	J (Hz)
CpCoI$_2$[P(OMe)$_3$] (**2**)				
C$_5$H$_5$			87.19	
P(OMe)$_3$	132.5		56.55	8.2 (d)
CpCoI[P(O)(OMe)$_2$][P(OMe)$_3$] (**4**)				
C$_5$H$_5$			89.47	
P(OMe)$_3$	147.0		55.33	7.6 (d)
P(O)(OMe)$_2$	90.5	178 (d)	52.7	4.4 (d)
CpCo[P(O)(OMe)$_2$]$_2$[P(OMe)$_3$] (**6**)				
C$_5$H$_5$			90.43	
P(OMe)$_3$	149.0		54.16	7.8 (d)
P(O)(OMe)$_2$	94.5	137 (d)	51.38	4.6 (d)



SCHEME 1

The 1/1 reaction shows that the reactions in which CO and I^- are displaced from the coordination sphere by $P(OMe)_3$ are more rapid than the Arbuzov reaction [3]. This reaction also suggests that the Arbuzov reaction takes place through the cationic complex **3** (path a) rather than by path b (Scheme 1).

1/2 reaction. The 1/2 reaction further supports the conclusions of the 1/1 reaction. It shows the expected more advanced state of the described reactions. Only 40 sec after the addition of $P(OMe)_3$ to **1**, as shown in Fig. 2, the dominant complex is $\{CpCoI[P(OMe)_3]_2\}^+$ (**3**). Also present are **1** and **2** in relatively low concentration. After about 100 sec, the first Arbuzov product, **4**, begins to form while **3**

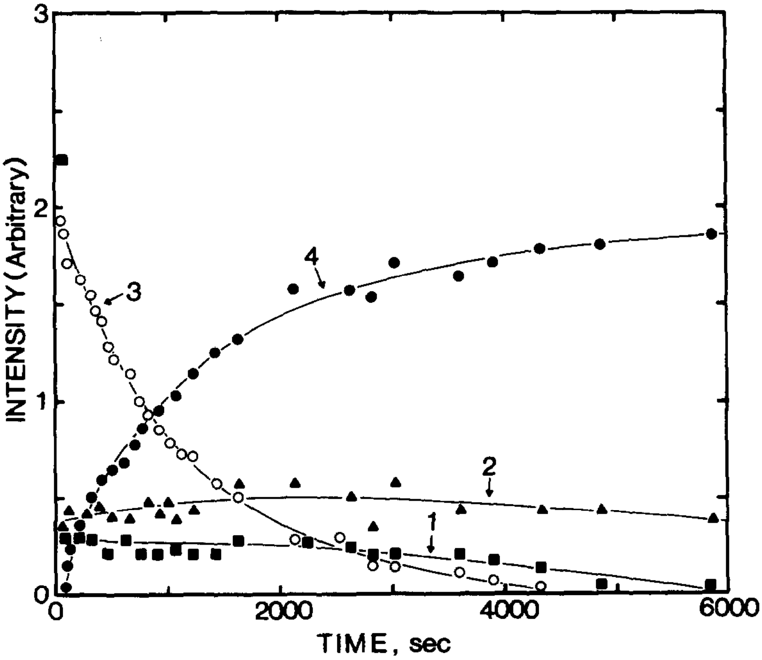


Fig. 2. The concentration versus time profile of the reactants and products when $CpCoI_2(CO)$ and $P(OMe)_3$ react in 1/2 stoichiometry in $CDCl_3$ at room temperature. The intensity of the ^1H NMR signal of the Cp ring is indicative of the concentration of the species whose formulae are given in Fig. 1.

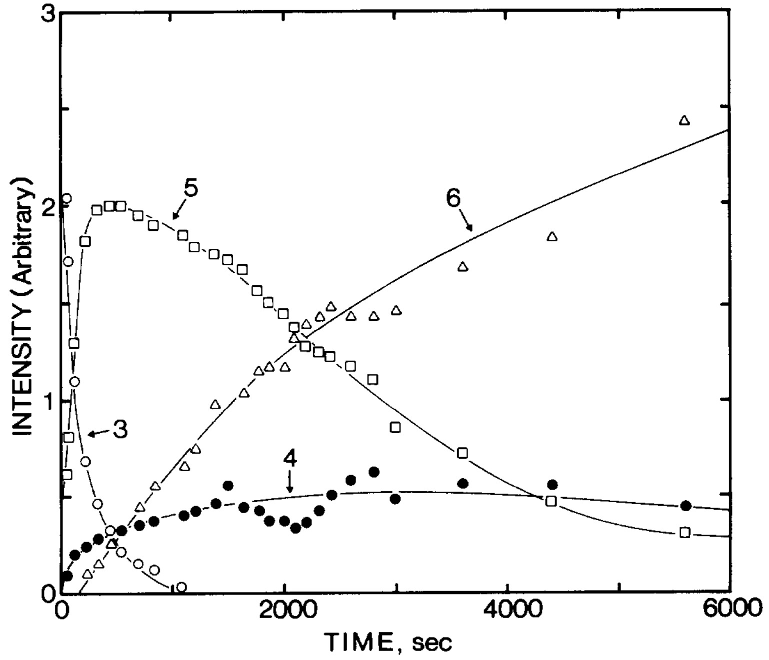


Fig. 3. The concentration versus time profile of the reactants and products when $CpCoI_2(CO)$ and $P(OMe)_3$ react in 1/3 stoichiometry in $CDCl_3$ at room temperature. The intensity of the ^1H NMR signal of the Cp ring is indicative of the concentration of the species. $\{CpCoI[P(OMe)_3]_2\}^+$ (3), $CpCoI[P(O)(OMe)_2][P(OMe)_3]$ (4), $\{CpCo[P(O)(OMe)_2][P(OMe)_3]_2\}^+$ (5), $CpCo[P(O)(OMe)_2]_2[P(OMe)_3]$ (6).

diminishes. After about 4000 sec, **3** has completely transformed to **4**. By 8000 sec, after which no further changes take place in the NMR spectrum, **1** and **2** are no longer evident and only **4** is present in the reaction. As before, the ligand substitution reactions are clearly faster than the demethylation step.

1/3 reaction. The concentration-time profile of reaction 1 when **1** and $P(OMe)_3$ are in a 1/3 ratio is shown in Fig. 3. The results for this reaction reveal additional features that are not present in the 1/1 and 1/2 reactions. At 40 sec, three species are present in solution. As in the foregoing reactions, **3** is present. However, at this concentration of $P(OMe)_3$, the reactions of **3** advance more rapidly so that **3** is consumed by 1100 sec. In its place, **4** forms, but a new complex **5** is generated in a much more dramatic manner. This complex, having a Cp signal at δ 5.63 ppm, is the monocation $\{CpCo[P(O)(OMe)_2][P(OMe)_3]_2\}^+$ whose concentration grows and then gradually diminishes. Owing to the persistence of **4** in the reaction, it may be that **4** and **5** equilibrate with one another. At 225 sec a fourth complex with a Cp signal at δ 5.24 ppm begins to appear in the spectrum. The concentration of this compound increases throughout the reaction and is the only metal complex present after 11000 sec at the completion of the reaction. This compound was isolated and separately identified as the known compound **6** [1], $CpCo[P(O)(OMe)_2]_2[P(OMe)_3]$. Its NMR spectral data are compiled in Tables 1 and 2 for comparison with the others.

In the 1/3 reaction the fast ligand exchange steps have already occurred before the first spectrum could be recorded. The first Arbuzov reaction leading to **4** takes place at a moderate rate in the presence of excess $P(OMe)_3$ (which causes more free I^- to be present in the solution) while the second Arbuzov reaction producing **6** occurs more slowly. There is no evidence of $\{CpCoI[P(O)(OMe)_2]_2\}^-$ showing that **6** only forms from the cationic species **5**.

A summary of the reaction sequence leading to the double Arbuzov reaction of $CpCoI_2(CO)$ with $P(OMe)_3$ is given by reactions 2–6.

$$CpCoI_2(CO) + P(OMe)_3 \xrightarrow{-CO} CpCoI_2[P(OMe)_3] \qquad (2)$$

$$CpCoI_2[P(OMe)_3] + P(OMe)_3 \xrightarrow{-I^-} \{CpCoI[P(OMe)_3]_2\}^+ \qquad (3)$$

$$\{CpCoI[P(OMe)_3]_2\}^+ + I^- \xrightarrow{-CH_3I} CpCoI[P(O)(OMe)_2][P(OMe)_3] \qquad (4)$$

$$CpCoI[P(O)(OMe)_2][P(OMe)_3] + P(OMe)_3 \xrightarrow{-I^-} \{CpCo[P(O)(OMe)_2][P(OMe)_3]_2\}^+ \qquad (5)$$

$$\{CpCo[P(O)(OMe)_2][P(OMe)_3]_2\}^+ + I^- \xrightarrow{-CH_3I} CpCo[P(O)(OMe)_2]_2[P(OMe)_3] \qquad (6)$$

Reactions 2, 3 and 5 are reasonably rapid while 4 and 6 occur more slowly. The Arbuzov chemistry in which the metal complexes are demethylated only takes place with the cationic intermediates. This is because the nucleophilic attack by I^- on the methoxy carbon atoms produces CH_3I and the phosphoryl group only if the carbon atom is sufficiently electrophilic [2–4]. Figures 1–3 are useful depictions of the reaction pathway because not only do they elucidate the reaction sequence, but they reveal the intermediates that are likely to be readily isolated and those whose isolation would require special protection from attacking nucleophiles and residual $P(OMe)_3$.

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