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Methyl Group Transfer Involving Transition-Metal Complexes by the Michaelis–Arbuzov Mechanism

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Transfer of a methyl group from $\{CpNi[P(OMe)_3]_2\}^+$ to $[Mn(CO)_5]^-$ or $[CpM(CO)_3]^-$ (M = Cr, Mo) by the Michaelis–Arbuzov reaction is described. The qualitative order of nucleophilicity of the anions is $[Mn(CO)_5]^- > [CpMo(CO)_3]^- > [CpCr(CO)_3]^-$ based on the changes in the reactant concentrations followed by ^1H NMR spectroscopy. The same reaction using Cl^-, Br^-, and I^- as nucleophiles was found to be first order in each reactant with rates at 21 °C of 0.34 (Cl^-), 0.21 (Br^-), and 0.11 $M^{-1}\,s^{-1}$ (I^-). The halide ions abstract the methyl group from $\{CpNi[P(OMe)_3]_2\}^+$ about 10^3 times faster than do the organometallic anions.

Introduction

Halide and pseudohalide ions successfully convert certain transition-metal phosphite complexes to their respective phosphonates via alkyl transfer.[1] This process is the transition-metal equivalent of the classical Michaelis–Arbuzov reaction.[2]

Metal–carbonyl anions can also display considerable nucleophilic strength.[3] We attempted to use this property to induce the Michaelis–Arbuzov (or Arbuzov) reaction in transition-metal phosphite complexes producing, in effect, the transmethylation reaction (1). A few such reactions

$$ML_n^- + L'_nM'[P(OMe)_3]^+ \rightarrow MeML_n + L'_nM'[P(O)(OMe)_2] \quad (1)$$

have been discovered previously.[4–6] For example, in the presence of $P(OMe)_3$, the disproportionation of $[CpMo(CO)_3]_2$ results in the formation of $\{CpMo(CO)_2[P(OMe)_3]_2\}^+[CpMo(CO)_3]^-$. This step is followed by what is believed to be nucleophilic attack of the anion on the cation to produce $CpMo(CO)_2[P(O)(OMe)_2][P(OMe)_3]$ and $CpMo(CO)_3Me$.[4] In another study, the mixing of $Ph_3SiMn(CO)_5$ and $P(OEt)_3$ yields as final products $EtMn(CO)_5$ and $Ph_3SiP(O)(OEt)_2$, which were proposed[5] to result from nucleophilic attack on $[Ph_3SiP(OEt)_3]^+$ by $[Mn(CO)_5]^-$. Apart from these examples, transmethylation reactions involving two metal complexes and following an ionic Arbuzov-like mechanism are largely unknown.

In this project we attempted to demethylate the relatively exposed phosphite ligands of $\{CpNi[P(OMe)_3]_2\}^+$ by adding various metal–carbonyl anion nucleophiles. Reaction 1 was successful with $[Mn(CO)_5]^-$, $[CpMo(CO)_3]^-$, and $[CpCr(CO)_3]^-$. The analogous reaction with Cl^-, Br^-, and I^- in place of the metal anions was studied to compare the reaction rates. This work is the first systematic study of nucleophilic attack of a variety of metal anions on a metal phosphite complex.

Experimental Section

$\{CpNi[P(OMe)_3]_2\}BF_4$ was prepared as described elsewhere,[7] and its purity was checked by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy. The alkali-metal salts of the metal anion nucleophiles were prepared by literature procedures.[8–13] The $[(n\text{-}Bu)_4N]X$ salts (X = Cl, Br, I) were purchased from Aldrich.

In a typical study of the general reaction, equimolar amounts (0.298 mmol) of each reactant were placed under N_2 in a voltrime tube with a septum cap. At 0 °C 2 mL of acetone-d_6 were added. Ether or THF was used for the reaction involving $[Mn(CO)_5]^-$. After the tube was shaken vigorously, the alkali-ion salt of BF_4^- precipitated. The tube was centrifuged and the supernatant divided among four NMR tubes under N_2. Each tube was placed in a separate water baths set at 30, 40, 50, and 56 °C. The products distributions were monitored periodically by ^1H NMR spectroscopy.

All the kinetic studies of the reaction of $\{CpNi[P(OMe)_3]_2\}BF_4$ with $[(n\text{-}Bu)_4N]X$ were conducted at 21 ± 0.5 °C. Procedures resemble our kinetic studies of $\{CpCo(dppe)[P(OMe)_3]\}^{2+}$ in reactions with halides.[14] In a typical experiment, the stock solutions of $[(n\text{-}Bu)_4N]I$ (45.3 mg, 0.123 mmol, 1.23×10^{-1} M) and $\{CpNi[P(OMe)_3]_2\}BF_4$ (56.4 mg, 0.123 mmol, 1.23×10^{-1} M) were prepared in 1.0 mL acetone-d_6 for each compound. The reaction of a 1:1 ratio of these two compounds was carried out by transferring 0.2 mL of each solution to a standard 5.0-mm o.d. NMR tube using a Hamilton microliter syringe. The tube was vigorously agitated and then placed in the probe of a Bruker AM-250 NMR spectrometer. Ten successive spectra were recorded during a period of 6 h. The initial concentration of $[(n\text{-}Bu)_4N]I$ (A_0) was 6.15×10^{-2} M. The initial concentration of $\{CpNi[P(OMe)_3]_2\}BF_4$ (B_0) was obtained by integrating the relative intensity of Cp of $\{CpNi[P(OMe)_3]_2\}BF_4$ and comparing them to the CH_2 intensities of $[(n\text{-}Bu)_4N]X$. The concentration of the reaction product $CpNi[P(OMe)_3][P(O)(OMe)_2]$, calculated from the integration of relative intensities of Cp at δ 5.39, was taken as x. When log $(A_0 - x)/(B_0 - x)$ was plotted vs t, the straight line indicated that the reaction is overall second-order and first-order in each of the reactants. The rate constant was calculated from the slope. That the reaction is first-order in each reactant is further confirmed by the constant value of k when the two reactants were mixed in a 2:1 and 1:2 ratio.

Results and Discussion

$\{CpNi[P(OMe)_3]_2\}^+$ has been shown to react with halide ions to produce $CpNi[P(OMe)_3][P(O)(OMe)_2]$ and CH_3X.[15,16] We chose this cation to attempt reactions with

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(1) For a review, see: Brill, T. B.; Landon, S. J. *Chem. Rev.* **1984**, *84*, 577.

(2) For reviews, see: Harvey, R. G.; DeSombre, E. R. *Top. Phosphorus Chem.* **1964**, *1*, 57. Bhattacharya, A. K.; Thyagarjan, G. *Chem. Rev.* **1981**, *81*, 415.

(3) Dessy, R. E.; Pohl, R. L.; King, R. B. *J. Am. Chem. Soc.* **1966**, *88*, 5121.

(4) Haines, R. J.; Nolte, C. R. *J. Organomet. Chem.* **1970**, *24*, 725.

(5) Ross, E. P.; Dobson, G. R. *J. Chem. Soc., Chem. Commun.* **1969**, 1229.

(6) Arabi, M. S.; Maisonnat, A.; Altali, S.; Poilblanc, R. *J. Organomet. Chem.* **1974**, *67*, 109.

(7) Salzer, A.; Werner, H. *Synth. Inorg. Met.-Org. Chem.* **1972**, *2*, 249.

(8) Edgell, W. F.; Barbetta, A. *J. Am. Chem. Soc.* **1974**, *96*, 415.

(9) Bender, R.; Braunstein, P.; Jud, J. M.; Dusausoy, Y. *Inorg. Chem.* **1983**, *23*, 3395.

(10) Pribula, C. D.; Brown, T. L. *J. Organomet. Chem.* **1974**, *71*, 415.

(11) Grismondi, T. E.; Rausch, M. D. *J. Organomet. Chem.* **1985**, *284*, 59.

(12) Hoyano, J. K.; Legzdins, P.; Malito, J. T. *Inorg. Synth.* **1978**, *18*, 126.

(13) Plotkin, J. S.; Shore, S. G. *Inorg. Chem.* **1981**, *20*, 284.

(14) Landon, S. J.; Brill, T. B. *Inorg. Chem.* **1984**, *23*, 4177; **1985**, *24*, 2863.

(15) Harder, V.; Werner, H. *Helv. Chim. Acta* **1973**, *56*, 1620.

metal anions because the phosphite ligands are relatively sterically unhindered and might be more readily dealkylated by bulky anions than other more crowded cationic phosphite complexes.

Reaction 1 was attempted with metal carbonyl anions having widely different relative nucleophilicities which are shown parenthetically:[3] $[Co(CO)_4]^-$ (1), $[CpCr(CO)_3]^-$ (4), $[CpMo(CO)_3]^-$ (67), $[Mn(CO)_5]^-$ (77), $[CpW(CO)_3]^-$ ($\sim$500), and $[CpFe(CO)_2]^-$ (7×10^7). These relative nucleophilicities were measured by their reaction with organic halides.[3] Because the transition-metal Arbuzov reaction involves phosphite complexes, it would not be surprising if the trend in nucleophilicity were somewhat different.

Among the above anions, only $[CpCr(CO)_3]^-$, $[CpMo(CO)_3]^-$, and $[Mn(CO)_5]^-$ induced dealkylation of $\{CpNi[P(OMe)_3]_2\}^+$ according to the ^1H NMR spectrum. In acetone-d_6 the reaction involving the group VI (6[22]) carbonyls is slow. About 185 min is required for 50% conversion at 40 °C. In the reaction with $[CpMo(CO)_3]^-$ two ^1H Cp signals at δ 5.85 and 4.98 are present at the outset corresponding to $\{CpNi[P(OMe)_3]_2\}^+$ and $[CpMo(CO)_3]^-$, respectively. Two new signals at 5.52 and 5.39 ppm grow with time at the expense of the signals from the reactants. These absorptions arise from $CpMo(CO)_3Me$ and $CpNi[P(OMe)_3][P(O)(OMe)_2]$, respectively. In addition, the intensity of the virtual triplet from $P(OMe)_3$ of $\{CpNi[P(OMe)_3]_2\}^+$ centered at 3.82 ppm ($^3J_{PH}$ = 12.4 Hz) diminishes while the two doublets centered at 3.70 ($^3J_{PH}$ = 12.6 Hz) and 3.43 ppm ($^3J_{PH}$ = 11.5 Hz) for $P(OMe)_3$ and $P(O)(OMe)_2^-$, respectively, of $CpNi[P(OMe)_3][P(O)(OMe)_2]$ increase. A singlet at 0.35 ppm for Me of $CpMo(CO)_3Me$ increases in intensity at the same time.

Because this reaction is essentially stopped at 0 °C and is very slow at room temperature, rate constant measurements are complicated by the fact that the metal carbonyl anions decompose to some extent during prolonged reaction times at elevated temperatures. Thus, we abandoned quantitative studies.

A reaction similar to that above occurs with $[CpCr(CO)_3]^-$, but the rate of methyl transfer is qualitatively slower reflecting the fact that $[CpCr(CO)_3]^-$ is a weaker nucleophile than $[CpMo(CO)_3]^-$. The reaction of $\{CpNi[P(OMe)_3]_2\}^+$ with $[Mn(CO)_5]^-$ cannot be carried out in acetone-d_6 because decomposition occurs. Dry ether or THF are suitable solvents. After the solution was stirred for 1 h at room temperature, the transmethylated products can be isolated following removal of the solvent. However, according to the NMR spectrum, additional unidentified products are also present as a result of side reactions. The reaction with the still stronger nucleophiles $[CpW(CO)_3]^-$ and $[CpFe(CO)_2]^-$ is even more complex. No transmethylation products were detected. Decomposition of the complexes perhaps by ligand exchange took place. These reactions were not investigated further. The weak nucleophile $[Co(CO)_4]^-$ exhibited no reaction, dealkylation or otherwise, with $\{CpNi[P(OMe)_3]_2\}^+$. There is apparently a limited range over which the transmethylation of metal complexes of this type can occur by the Arbuzov mechanism. The order of nucleophilicity for metal anions that react successfully with $\{CpNi[P(OMe)_3]_2\}^+$ is qualitatively the same as that measured for the reaction with organohalides:[3] $[Mn(CO)_5]^- > [CpMo(CO)_3]^- > [CpCr(CO)_3]^-$.

Organometallic complexes can induce the Arbuzov reaction in phosphite complexes by a radical mechanism.[1,17-21] We considered the possible role of radicals in the above reaction. First, the dimers $[CpMo(CO)_3]_2$, $[CpCr(CO)_3]_2$, and $[Mn(CO)_5]_2$ were photolyzed by UV light in the presence of $\{CpNi[P(OMe)_3]_2\}^+$ and produced no transmethylation. Thus, radicals that can form by homolytic cleavage of the metal–metal bond do not induce the reaction. Secondly, the ^1H NMR spectra taken during the reaction showed no evidence of line broadening or paramagnetic shifts under any of the conditions used. All of the metal anion reactions were performed under an N_2 atmosphere that further reduces the likelihood of forming radicals by reaction with the atmosphere.

The comparison of rates of dealkylation of $\{CpNi[P(OMe)_3]_2\}^+$ was extended beyond metal anion nucleophiles to the halide ions Cl^-, Br^-, and I^-. Fewer side reactions are possible for halide ions making a study of the kinetics somewhat more straightforward. When $\{CpNi[P(OMe)_3]_2\}BF_4$ and $[(n\text{-}Bu)_4N]X$ (X = Cl, Br, I) are mixed in acetone-d_6 at 21 °C, the reaction is quantitatively first-order in each reactant based on the concentration changes as followed by the ^1H NMR spectrum. The rate constants were found to be 0.34 (Cl^-), 0.21 (Br^-), and 0.11 $M^{-1}\ s^{-1}$ (I^-) which is the same order of nucleophilicity displayed in the demethylation of $\{CpCo(dppe)[P(OMe)_3]\}^{2+}$.[14] These rate constants are qualitatively about 10^3 larger than that for the reaction of $[CpMo(CO)_3]^-$ with $\{CpNi[P(OMe)_3]_2\}^+$.

We conclude that metal anion complexes can readily demethylate metal phosphite complexes. The reaction occurs by the ionic mechanism. However, the full range of nucleophilicity of the anions cannot be exploited because at one extreme, no reaction takes place while at the other, reactions occur that do not yield the desired products.

Registry No. $\{CpNi[P(OMe)_3]_2\}BF_4$, 39015-44-6; $[CpCr(CO)_3]^-$, 48121-47-7; $[CpMo(CO)_3]^-$, 12126-18-0; $[CpW(CO)_3]^-$, 12126-17-9; $[CpFe(CO)_2]^-$, 12107-09-4; $[Mn(CO)_5]^-$, 14971-26-7; $[Co(CO)_4]^-$, 14971-27-8; $[(n\text{-}Bu)_4N]Cl$, 1112-67-0; $[(n\text{-}Bu)_4N]Br$, 1643-19-2; $[(n\text{-}Bu)_4N]I$, 311-28-4.

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(16) Clemens, J.; Neukomm, H.; Werner, H. *Helv. Chim. Acta* **1974**, *57*, 2000.

(17) Goh, L.-Y.; D'Aniello, M. J.; Slater, S.; Muetterties, E. L.; Tavanaiepour, I.; Chang, M. I.; Fredrich, M. F.; Day, V. W. *Inorg. Chem.* **1979**, *18*, 192.

(18) Howell, J. A. S.; Rowan, A. J. *J. Chem. Soc., Dalton Trans.* **1980**, 1845.

(19) Howell, J. A. S.; Rowan, A. J.; Snell, M. S. *J. Chem. Soc., Dalton Trans.* **1981**, 325.

(20) Muetterties, E. L.; Bleeke, J. R.; Yang, Z.-Y.; Day, V. W. *J. Am. Chem. Soc.* **1982**, *104*, 2940.

(21) Wayland, B. B.; Woods, B. A. *J. Chem. Soc., Chem. Commun.* **1981**, 475.

(22) In this paper the periodic group notation in parentheses is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13–18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)