Inorg. Chem. **1981**, *20*, 467-470

which we have not been able to determine experimentally, the formation constants $\beta_{1,6,3}$ and $\beta_{3,12,6}$ cannot be deduced from our experimental data. However, the present measurements may conveniently be described by $^*\beta_{3,12,6}$, the constant of equilibrium 10 written with the species of lower nuclearity as reagent.

Values of $^*\beta_{3,12,6}$ can be obtained from $\log F_{3,12} + 3 \log a = \log K_{al}{}^6\beta_{3,12,6}\beta_{1,6,3}{}^{-3} = \log {}^*\beta_{3,12,6}$. Using the data of Table II, we find $\log {}^*\beta_{3,12,6} = -6.37 \pm 0.08$.

It was desirable to compare the whole set of emf data directly with model curves as such a comparison enables us to evaluate the magnitude of the uncertainty of the equilibrium constant. As a check of the consistency of the graphical results, the data were finally treated with the generalized least-squares program LETAGROP.[9] The graphical approach consisting of comparing the data recalculated in the form $y(x)$, $y = (6 - Z)/3$ and $x = \log (Bd^{-3}a^{1.5})$, with the normalized $Y(X)$ function

$$Y = 2v^2/(1 + 3v^2) \qquad (11)$$

$$X = x + \tfrac{1}{2} \log {}^*\beta_{3,12,6} = \log v + \log (1 + 3v) \qquad (12)$$

Equations 11 and 12 were easily derived by introducing in the expression of $y(x)$ the new variable

$$v^2 = {}^*\beta_{3,12,6}c^2d^{-6}a^3 \qquad (13)$$

In position of best fit, shown in Figure 2, we calculated from the difference $X - x$

$$\log {}^*\beta_{3,12,6} = -6.40 \pm 0.08$$

For the numerical treatment, we used the most recent version, ETITR, of LETAGROP.[9] The calculations consisted of the minimization of the sum $\sum(H - H_{\text{calcd}})^2$, where H_{calcd} is the value of H calculated with a particular $^*\beta_{3,12,6}$. The minimum sum was found with $\log {}^*\beta_{3,12,6} = -6.43 \pm 0.03$, which is seen to agree well with the graphical evaluation. The uncertainty of the LETAGROP constant is 3 times the standard deviation. Of 146 experimental points considered, 76 have shown negative and 70 positive deviations from the calculated H. The average positive deviation $\delta H/H$ amounts to 0.21%; the negative to 0.26%. The sign and the magnitude of the deviations do not exhibit any systematic trend with B and d. Since the average deviation of H is just above its experimental accuracy, ±0.1%, we may conclude that the data can be quite satisfactorily explained with equilibrium 10.

Structure and Bonding of the Uranyl Carbonate Complexes

The stoichiometry of the uranyl carbonate complexes formed in the solutions studied are $UO_2(CO_3)_3{}^{4-}$ and $(UO_2)_3(CO_3)_6{}^{6-}$. Through a ^{13}C NMR investigation of solutions containing these complexes as dominating species, we were able to get some idea of the bonding of the carbonate ligand.

The mononuclear complex has one single ^{13}C resonance peak indicating equivalence between the three coordinated ligands. In the solid state, the $UO_2(CO_3)_3{}^{4-}$ group consists of three bidentate ligands coordinated in a plane perpendicular to the UO_2 axis.[11] The NMR data are consistent with this model. Quantitative information about the solution structure may be obtained by an X-ray diffraction study of concentrated $UO_2(CO_3)_3{}^{4-}$ solutions, the results of such a study will be published in the near future.

The trinuclear complex gives two separate ^{13}C NMR peaks with the ratio 1:2 between the integrated intensities. The smaller peak has approximately the same chemical shift as the carbonate groups in the mononuclear complex, while the other is displaced 70 Hz toward higher frequency. The NMR data indicate the presence of both bridging and terminal carbonato groups. The terminal carbonate groups are probably chelating.

More detailed structure information will be presented in a forthcoming X-ray structure investigation of the complex in solution. In this study, we also hope to obtain evidence for the location of coordinated water molecules.

There is no evidence for exchange broadening, neither between the two sites in the trinuclear complex nor between the mono- and trinuclear complexes. A more detailed NMR study will be presented in a following publication.

Acknowledgment. The investigation was financially supported by the Swedish Natural Science Research Council and by PRAV (the Swedish National Council for Radioactive Waste). The financial support from the Italian CNR (the National Research Council) to Francesco Salvatore is gratefully acknowledged.

Registry No. $UO_2(CO_3)_3{}^{4-}$, 17872-00-3; $(UO_2)_3(CO_3)_6{}^{6-}$, 75311-41-0.

Supplementary Material Available: A listing of primary experimental data in the form of $Z(\log d)$ at various B and a levels (3 pages). Ordering information is given on any current masthead page.

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Mechanism of Dissociation of Alkynes from Some Platinum-Alkyne Complexes

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Five-coordinate platinum-alkyne complexes [PtXMe(RC≡CR)(2,2′-bpy)] (bpy = 2,2′-bipyridine) have been prepared and characterized. An investigation of the kinetics and mechanism of thermal dissociation of alkyne from these complexes has been made. When X = Cl and R = CO_2Me, the rate of reaction is very strongly accelerated in more polar solvents and is retarded by added chloride, and a mechanism involving preliminary ionization of chloride is proposed. However, when X = Cl or I and R = CF_3, the rate is essentially independent of solvent polarity and is not retarded by added halide, and a nonpolar intermediate is proposed in this case.

Introduction

During investigations of the reactions of alkyl(2,2′-bipyridine)platinum(II) complexes with alkenes and alkynes,[2-5] it was found that solutions of [PtClMe($MeO_2CC≡CCO_2Me$)(bpy)] underwent dissociation of alkyne much more

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Table I. Melting Points and Spectroscopic Data for Complexes [PtXMe(bpy)(RC≡CR)]

complex X	complex R	mp, °C	ν(C≡C),[a] cm^{-1}	δ(MePt)[b]	^2J(PtH),[b] Hz
Cl	CO_2Me	166-169	1815	0.35	72
I	CO_2Me	160	1818	0.58	68
Cl	CF_3	208-213	1865	0.59	70
I	CF_3	195	1868	0.64	68

[a] Nujol mull. [b] Solvent $CDCl_3$.

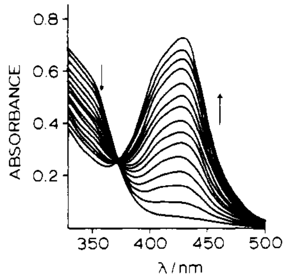
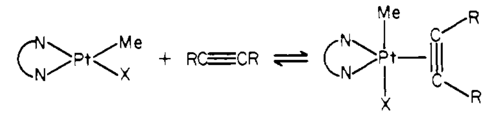


Figure 1. Changes in the UV-visible spectrum during decomposition of [PtClMe($MeO_2CC{\equiv}CCO_2Me$)(bpy)] in acetone at 40 °C.

rapidly in acetone solution than in benzene, suggesting a polar intermediate or transition state. Since polar species such as $[PtMe(alkyne)L_2]^+$ have been suggested as intermediates in insertion of alkynes into methylplatinum bonds,[6] it was decided to study the mechanism of alkyne dissociation and to determine the nature of any polar intermediates. A preliminary account of some of this work has been published.[7]

Results

The platinum-alkyne complexes (I) were prepared by reaction of [PtXMe(bpy)] (bpy = 2,2′-bipyridine, X = Cl or I) with the corresponding alkyne RC≡CR (R = CF_3 or CO_2Me). Electron-withdrawing groups on the alkyne were necessary to give stable complexes. The complexes are colorless or very pale yellow whereas the compounds [PtXMe(bpy)] are yellow or orange when X = Cl or I, respectively.[2] The compounds were characterized by elemental analysis and by the infrared and NMR spectra (Table I). Several five-coordinate platinum-alkyne complexes are now known, and comparison of the spectroscopic data with those for complexes fully characterized by X-ray structure determinations[8,9] allows structure I (eq 1) to be deduced with confidence ($\widehat{NN}$ = bpy).



(1)

Ia: R = CO_2Me, X = Cl
Ib: R = CO_2Me, X = I
Ic: R = CF_3, X = Cl
Id: R = CF_3, X = I

When R = CO_2Me, the complexes decomposed to the starting materials in acetone solution, the reaction being essentially quantitative in the absence of added alkyne. The rate of reaction was monitored by recording the UV-visible spectrum as a function of time. Figure 1 illustrates the growth of the metal to ligand charge-transfer band[2] at 400-500 nm due to square-planar [PtXMe(bpy)] as the reaction proceeds.

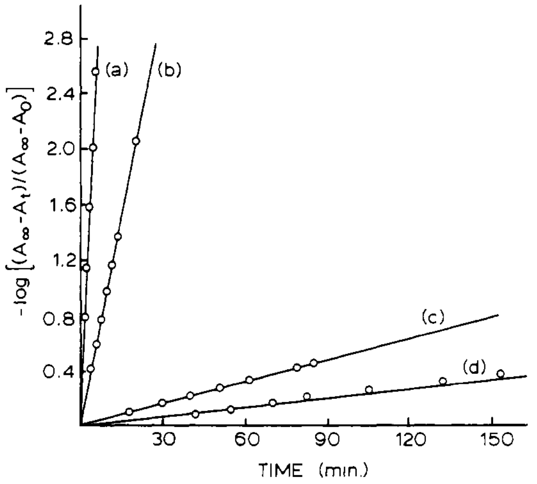


Figure 2. First-order plots for the decomposition of [PtClMe($MeO_2CC{\equiv}CCO_2Me$)(bpy)] at 40 °C: (a) solvent MeCN, (b) solvent acetone, (c) solvent tetrahydrofuran, (d) solvent benzene.

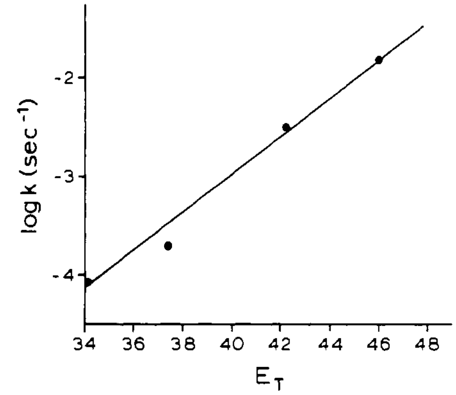


Figure 3. Graph of log k_{obsd}, where k_{obsd} is the first-order rate constant for decomposition of complex Ia at 40 °C, vs. the Reichardt E_T parameter of solvent polarity.

Table II. Solvent Effects on the First-Order Rate Constants for Decomposition of [PtXMe(bpy)(RC≡CR)] at 40 °C

		10^5k, s^{-1}		
solvent	E_T	X = Cl, R = CO_2Me	X = I, R = CO_2Me	X = I, R = CF_3
mesitylene				21.2
benzene	34.1	8.0	200[a]	22.3
tetrahydrofuran	37.4	19.5	230[a]	
acetone	42.2	31.8	630[a]	23.2
methyl cyanide	46.0	1520		7.7

[a] From ref 5.

Table III. Effect of Added Chloride on the First-Order Rate Constant, k, for Decomposition of [PtClMe(bpy)($MeO_2CC{\equiv}CCO_2Me$)] in Acetone at 40 °C

10^4[LiCl], M	0	2.06	10.2	51.5	103.0
10^4k, s^{-1}	31.8	8.45	5.18	3.45	2.98

This decomposition reaction followed good first-order kinetics, and some graphs of $-\log[(A_\infty - A)/(A_\infty - A_0)]$ vs. t are given in Figure 2. The resulting rate constants k_{obsd} at 40 °C in solvents benzene, tetrahydrofuran, acetone, and methyl cyanide together with the values of the Reichardt E_T parameters of solvent polarity[10] are given in Table II. The

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Table IV. Temperature Dependence of the First-Order Rate Constants for the Decomposition of [PtXMe(RC≡CR)(bpy)]

X = Cl, R = CO_2Me[a]		X = Cl, R = CF_3[b]		X = I, R = CF_3[c]	
T, °C	10^3k, s^{-1}	T, °C	10^3k, s^{-1}	T, °C	10^3k, s^{-1}
30.5	1.23	75	1.04	40	0.212
35.5	1.95	83	1.70	50	0.883
40.0	3.18	90	3.52	60	1.85
42.0	3.80			70	5.58
45.0	4.20				
50.0	9.5				

[a] E_a = 84 kJ mol^{-1}, $\Delta S^{\ddagger} = -25$ J K^{-1} mol^{-1}, solvent acetone.
[b] E_a = 89 kJ mol^{-1}, $\Delta S^{\ddagger} = -30$ J K^{-1} mol^{-1}, solvent mesitylene.
[c] E_a = 91 kJ mol^{-1}, $\Delta S^{\ddagger} = -43$ J K^{-1} mol^{-1}, solvent mesitylene.

increase in reaction rate with solvent polarity is impressive. A graph of the values of log k_{obsd} vs. the E_T values of the solvents was linear with a slope of 0.19 (Figure 3), strongly suggesting an ionic intermediate in the reaction.[10,11]

The reaction rate was strongly retarded by added chloride in acetone solution (Table III). Reactions were carried out with lithium chloride (10^{-2}–10^{-3} M) in acetone, and concentrations of free chloride were calculated after one allows for ion pairing by using the known equilibrium constant.[12] At high chloride concentrations a plateau is reached, suggesting that there is a component of the reaction which is independent of chloride concentration. A good fit was obtained by using the expression k_{obsd} (s^{-1}) = $2.03 \times 10^{-4} + 1/(5.52 \times 10^7[Cl^-] + 335)$.

The temperature dependence of the overall rate constant k_{obsd} in acetone solution was studied (Table IV), and the Arrhenius parameters were calculated to be E_a = 84 kJ mol^{-1} and $\Delta S^{\ddagger} = -25$ J K^{-1} mol^{-1}.

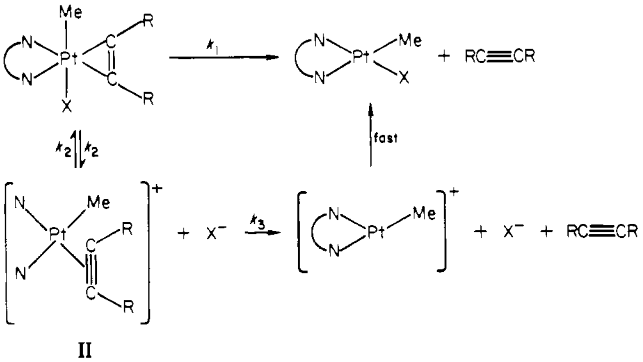
The kinetics of decomposition of the complexes [PtXMe(bpy)($CF_3C{\equiv}CCF_3$)] were also studied. When X = Cl, decomposition was slow at 40 °C in all solvents, but when X = I, reasonable reaction rates were observed (Table II). It will be seen that the reaction rate was almost constant for reactions in mesitylene, benzene, and acetone, and reaction was *slowest* in the most polar solvent methyl cyanide. This is in complete contrast to the behavior of Ia described earlier and is hardly consistent with an ionic intermediate in this case. Qualitative experiments showed a similar lack of dependence of rate on solvent polarity for decomposition of Ic, but the rates were inconveniently slow for detailed investigation. The rate of decomposition of Id was independent of iodide concentration in acetone solution at 40 °C at concentrations of sodium iodide up to 2 × 10^{-3} M and was also unaffected by added 2,2′-bipyridine.

From the temperature dependence of the rate constants for decomposition of [PtXMe(bpy)($CF_3C{\equiv}CCF_3$)] in mesitylene (Table IV), the Arrhenius parameters were calculated to be E_a = 91 kJ mol^{-1}, $\Delta S^{\ddagger} = -43$ J K^{-1} mol^{-1} for X = Cl and E_a = 89 kJ mol^{-1} and $\Delta S^{\ddagger} = -30$ J K^{-1} mol^{-1} for X = I.

Discussion

For the decomposition of complex Ia it is clear that the major part of the dissociation of alkyne occurs from a cationic species, formed by preliminary ionization of chloride, and the proposed mechanism is shown in Scheme I (X = Cl, R = CO_2Me). If the stationary-state approximation is made for concentrations of reaction intermediates then $-d(Ia)/dt = k_{obsd}[Ia]$, where $k_{obsd} = k_1 + k_2k_3/(k_3 + k_{-2}[Cl^-])$. Hence from the retardation by added chloride in acetone at 40 °C, we obtain $k_1 = 2.03 \times 10^{-4}$ s^{-1}, $k_2 = 2.98 \times 10^{-3}$ s^{-1}, and $k_{-2}/k_3 = 16.4 \times 10^4$ L mol^{-1}. Thus in the absence of added chloride about 94% of reaction occurs by the k_2 path and 6% by the k_1 path (Scheme I). It is possible that the k_1 path could also involve ionization of chloride to give a tight ion pair, which dissociates alkyne to form the final product, but, since we have no evidence on this point, the reaction is written as a simple dissociation. It is also possible that the k_3 step involves displacement of alkyne by solvent, rather than simple dissociation of alkyne from II.

Scheme I[a]



[a] The reverse reaction is negligible under the experimental conditions and is ignored.

From the lack of solvent dependence on the rate of reaction and the observation that the rate is not retarded by added halide, it seems clear that the decomposition of Ic and Id does not occur by way of an ionic intermediate. The rate was also unaffected by added 2,2′-bipyridine, and we therefore conclude that the alkyne is lost in a simple dissociation step. The negative entropies of activation observed are somewhat surprising for a dissociative mechanism and indicate an ordered transition state. In related complexes the Pt–C_4F_6 bond energy has been found to be 270 ± 20 kJ mol^{-1}.[13] The activation energies for dissociation of C_4F_6 from Ic and Id are about 90 kJ mol^{-1}, or only one-third of the Pt–C_4F_6 bond energy. This is presumably because in a concerted mechanism of decomposition the C≡C bond increases in strength as the Pt–C_4F_6 bond is broken. It has been estimated that the C≡C bond is about 200 kJ mol^{-1} stronger in the free acetylene than in the coordinated acetylene in complexes of this type.[13]

It now remains only to comment on the different mechanisms of decomposition of Ia and Ib compared with Ic and Id. As mentioned above, the platinum–alkyne bond in complexes I is strong due to effective back-bonding from platinum to vacant π^* orbitals of the alkynes in the electron-rich five-coordinate complexes.[13] If halide dissociation occurs readily giving the cationic species II, the back-bonding will decrease greatly, the platinum–alkyne bond will be weakened, and hence the alkyne will dissociate or be displaced more easily than from I. Clearly, halide dissociation occurs more readily for Ia and Ib than for Ic and Id. In all cases the Pt–X bond in I will be weak and polar due to the high trans influence of the methyl group in the trans position, and it is possible that dissociation of X^- from Ia and Ib may be further aided by intramolecular coordination of a carbonyl group of the carboxylic ester substituents. Halide dissociation from some five-coordinate platinum–ethylene and platinum–alkyne complexes has been observed recently[14] and thus may be a generally facile process. The present work shows that this reaction is very strongly

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accelerated in polar solvents for Ia and Ib, and this solvent effect may well prove to be a useful criterion for identifying preliminary ionization effects in organometallic reaction mechanisms.

Experimental Section

[PtClMe(bpy)] was prepared by the literature method.[2]

[PtClMe($MeO_2CC{\equiv}CCO_2Me$)(bpy)]. $MeO_2CC{\equiv}CCO_2Me$ (0.15 mL) was added to [PtClMe(bpy)] (0.18 g) in dry acetone (50 mL), and the mixture was stirred for 1 h. The white precipitate was filtered off, washed thoroughly with ether, and dried under vacuum. The yield was 0.13 g. Anal. Calcd for $C_{17}H_{17}ClN_2O_4Pt$: C, 37.5; H, 3.1; Pt, 35.9. Found: C, 37.1; H, 3.0; Pt, 35.7.

[PtClMe($CF_3C{\equiv}CCF_3$)(bpy)]. Hexafluorobut-2-yne (5 mmol) was condensed into a Carius tube containing [PtClMe(bpy)] (0.19 g) in acetone (10 mL), the solution was cooled by liquid nitrogen, and the tube was then sealed and allowed to warm to room temperature. The tube was shaken at room temperature for 12 h and then opened, and the white precipitate was filtered off, washed with ether, and recrystallized from CH_2Cl_2. The yield was 0.19 g. Anal. Calcd for $C_{15}H_{11}F_6ClN_2Pt$: C, 25.6; H, 2.2; N, 5.4; F, 22.1. Found: C, 25.4; H, 2.0; N, 5.3; F, 20.9.

PtIMe($CF_3C{\equiv}CCF_3$)(bpy)] was prepared similarly from [PtIMe(bpy)]. The yield was 71%. Anal. Calcd for $C_{15}H_{11}F_6IN_2Pt$: C, 21.8; H, 1.8; F, 18.8. Found: C, 21.4; H, 1.6; F, 18.4.

Kinetic Studies. Changes in UV–visible spectra were recorded as reaction proceeded with solutions of the alkyne complexes (10^{-4} M) in 1-cm quartz cuvettes held in the thermostated electrically heated cell compartment of a Unicam SP 8000 spectrophotometer. Solutions were made up immediately prior to the kinetic run.

Registry No. Ia, 75764-67-9; Ib, 75764-68-0; Ic, 75764-69-1; Id, 75764-70-4; PtClMe(bpy), 50726-77-7; PtIMe(bpy), 71674-45-8.

Contribution from The Research School of Chemistry, Australian National University, Canberra, ACT 2600, Australia, and the Chemistry Department, Faculty of Military Studies, University of New South Wales, Duntroon, ACT 2600, Australia

Labile (Trifluoromethanesulfonato)cobalt(III) Amine Complexes

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Facile synthetic routes to cobalt(III) amine complexes of the labile unidentate trifluoromethanesulfonate anion ($CF_3SO_3^-$), namely, $Co(NH_3)_5(OSO_2CF_3)^{2+}$, *cis*-$Co(en)_2(OSO_2CF_3)_2^+$, and *fac*-$Co(dien)(OSO_2CF_3)_3$, are reported. The use of these complexes as synthetic precursors for a range of complexes involving direct solvolysis or reactions in poorly coordinating solvents such as sulfolane or acetone is described. For example, in the pentaamminecobalt(III) system, syntheses of $Co(NH_3)_5L^{n+}$ (L = OH_2, NH_3, $OHCH_3$, $OHCH_2CH_3$, $OHCH(CH_3)_2$, $NCCH_3$, $OP(OCH_3)_3$, $OCH{\cdot}N(CH_3)_2$, $OS(CH_3)_2$, $OC(NH_2)_2$, $NCNH_2$, $^-OOCCH_3$, $^-OOCCHCl_2$) in high yield are reported. The kinetics and the stereochemical course of aquation of the labile trifluoromethanesulfonato complexes and derivatives are reported.

Introduction

The trifluoromethanesulfonyl group (CF_3SO_2), by virtue of the large inductive effect of the trifluoromethyl group, is one of the strongest electron-withdrawing groups known.[2–4] Consequently, the trifluoromethanesulfonate anion ($CF_3SO_3^-$, triflate) has found use as an excellent leaving group in nucleophilic substitution reactions in organic chemistry.[4,5] The triflate anion may act as a unidentate ligand in inorganic coordination chemistry. Recently, characterizations of the labile pentaamminecobalt(III) complexes of both trifluoromethanesulfonate ($OSO_2CF_3^-$) and perchlorate ($OClO_3^-$) have been reported.[6,7] The perchlorato and triflato ligands aquate with rate constants of 0.1 and 0.027 s^{-1}, respectively (25 °C, $\mu = 1.0$ M). The lability of these coordinated anions raises the prospect of their complexes providing facile routes to a range of cobalt(III) complexes via substitution reactions. However, since complexes containing the more labile perchlorate ligand are potentially explosive, we have chosen to concentrate attention on the triflato complexes.

Prior to this study, synthesis of $Co(NH_3)_5OSO_2CF_3^{2+}$ has involved nitrosation of azidopentaamminecobalt(III) in triflate medium and rapid isolation of the product.[7,8] We have now developed a simple procedure which yields the triflate complex quantitatively from chloropentaamminecobalt(III) and have extended this preparative concept to other cobalt(III) amine systems.

Dissolution of the triflato complexes in a range of solvents provides facile routes to complexes containing the coordinated solvents, while reaction with ligands in poorly coordinating solvents such as sulfolane (1,1-dioxothiolane) or acetone proceeds smoothly with substitution of the coordinated triflate by the ligand. Examples of the use of these procedures in some otherwise difficult syntheses are presented.

Experimental Section

Visible absorption spectra were recorded in duplicate by using Cary 14 or Cary 118 recording spectrophotometers. ^1H NMR spectra were measured with JEOL Minimar (100 MHz) or JEOL AMX60 spectrometers at ~30 °C, with use of sodium trimethylsilylpropionate as internal reference. Infrared spectra (KBr disk) were recorded with a Perkin-Elmer Model 457 instrument.

Anhydrous trifluoromethanesulfonic acid (CF_3SO_3H, 3M Company) was vacuum distilled (bp 52 °C at 10 mmHg). The precursor complexes $[Co(NH_3)_5Cl]Cl_2$,[9] *cis*-$[Co(en)_2Cl_2]Cl$,[10] *trans*-$[Co(en)_2Cl_2]Cl$,[10] *cis*-$[Co(en)_2CO_3]Cl$,[11] and $Co(dien)Cl_3$[12] were synthesized by reported methods.[13] Analytical reagent grade or redistilled

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