mole of **4** decomposed. This reaction was not studied further.

Other examples of reduced quantum yields for photoreduction of Co^{III} in systems where ammonia has been replaced by chelating organic amines have been reported,[10] but the present example is the only one of which we are aware in which the ligands being substituted are not chemically changed (except for being released from the cobalt coordination sphere and subsequently protonated) during the reaction. It is conceivable that the chelated organic amine offers mechanical hindrance to reorganization of the cobalt coordination sphere necessary to proceed from photoexcited complex to products. On the other hand, organic amines are somewhat better donors than ammonia. This is reflected in the ground state of **3**, in which the O–O bond distance is 1.36 Å,[11] compared to 1.32 Å in **2**, and might result in the excited states of **3** having more electron density on the bridging superoxide than the corresponding excited state of **2** and a consequently lower tendency to complete electron transfer from O_2^- to Co^{III}.

Experimental Section

Sodium perchlorate was prepared following Olin.[12] Mononuclear cobalt(III) ammines were prepared by standard methods. A sample of the perchlorate of **4** was kindly supplied by Professor W. K. Wilmarth. Analyses for Co^{2+} were made by the method of Gould and Taube.[13] Ion-exchange chromatography was done with a Dowex 50W-X8 resin. Divalent fractions were eluted with 1.00 *M* $NaClO_4$ containing 10^{-3} *M* $HClO_4$ and trivalent fractions were eluted with 3 *M* HCl.

Stoichiometric determinations were made using as light source a 450-W Hanovia medium-pressure mercury arc whose output was filtered through a 2-mm thickness of Pyrex to remove light of wavelengths shorter than 300 nm. Solutions were not deaerated before or during photolyses because preliminary comparison experiments showed that this made no difference in the observed results. All irradiations were terminated when the 700-nm absorbance had been reduced to zero.

Quantum yield measurements were made using the same monochromator and approximate light intensities employed in our previous work.[1] All solutions for kinetic experiments were optically dense at the irradiating wavelength. Because of the geometry of our apparatus it was not possible to stir solutions during photolyses for kinetic measurements. All quantum yields were determined using less than 10% conversion to products so as to minimize local bleaching and for these low conversions the observed quantum yields did not depend on the amount of conversion to products. Reaction 2 was used as the actinometric system.[1] Spectrophotometric analyses were made with a Cary 14 spectrometer.

μ-Amido-μ-superoxo-bis[bis(ethylenediamine)cobalt](4+), 3.—A concentrated solution of the nitrate of **6**, prepared following Werner,[2] in 0.1 *M* $HClO_4$ was treated with 100-mg portions of ceric ammonium nitrate until the solution color was deep green. Excess ammonium nitrate was added and the solution was refrigerated for several hours. The green precipitate of the nitrate of **3** was recovered by filtration, washed with ethanol and ether, and air dried. *Anal.* Calcd for $C_8H_{34}N_{13}O_{14}Co_2$: Co, 18.1. Found: Co, 18.1.

Acknowledgment.—We are grateful to Professor Henry Taube for his interest in this work and for helpful discussions. We also acknowledge support of this work by the Petroleum Research Fund administered by the American Chemical Society.

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[10] J. F. Endicott and M. Z. Hoffman, *J. Amer. Chem. Soc.*, **87**, 3348 (1965).

[11] U. Thewalt and R. E. Marsh, *ibid.*, **89**, 6364 (1967); R. E. Marsh private communication.

[12] A. Olin, *Acta Chem. Scand.*, **11**, 1445 (1957).

[13] E. S. Gould and H. Taube, *J. Amer. Chem. Soc.*, **86**, 1318 (1964).

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Behavior of Silver(I)–Olefin Complexes in Organic Media[1]

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A series of papers[2] has recently appeared in which the nature of the bonding in silver(I)–olefin complexes is examined by nmr techniques; *i.e.*, conclusions have been drawn concerning the structure of the silver–olefin bond from differences in chemical shifts and coupling constants between free and complexed olefins.

The most severe restriction to the use of this technique is that the ligands may be so labile that one records time-averaged spectra of rapidly equilibrating free and complexed ligands which renders the intended conclusions useless. Nmr detection of ligand lability is well established for many transition metal complexes[3] but is virtually unreported for silver(I)–olefin compounds.[4]

Our nmr investigation of solutions of silver(I)–olefin complexes in organic solvents shows that these systems do involve time-averaged equilibria and suggests that the work in the papers cited above be reconsidered in the light of our results. Especially interesting is the fact that the equilibrium constants are very much solvent dependent and may vary over a wide range.

Experimental Section

Nmr Studies.—All nmr spectra were recorded on a Varian A-60 proton resonance spectrometer at a probe temperature of 33° and at a sweep width of 500 Hz. Cyclohexane[5] (1% by volume) was used as an internal standard except in those cases in which cyclohexane could not be seen under a solvent peak. In these cases, a solvent peak was used as the standard. All chemical shifts were tabulated in hertz relative to the standard.

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[1] Presented in part at the 25th Southwest Regional Meeting of the American Chemical Society, Tulsa, Okla., Dec. 5, 1969.

[2] (a) G. Bressan, R. Broggi, M. P. Lachi, and A. L. Segre, *J. Organometal. Chem.*, **9**, 355 (1967); (b) H. W. Quinn, J. S. McIntyre, and D. J. Peterson, *Can. J. Chem.*, **43**, 2896 (1965); (c) J. C. Schug and R. J. Martin, *J. Phys. Chem.*, **66**, 1554 (1962); (d) D. B. Powell and N. Sheppard, *J. Chem. Soc.*, 2519 (1960); (e) H. W. Quinn and R. L. Van Gilder, *Can. J. Chem.*, **47**, 4691 (1969).

[3] For example, M. Orchin and P. J. Schmidt, *Inorg. Chim. Acta*, **2**, 123 (1968); R. Cramer, *J. Amer. Chem. Soc.*, **86**, 217 (1964).

[4] In ref 2b Quinn noted a change of $\Delta\delta$ with temperature for the *trans*-2-butene–$AgBF_4$ system only and correctly concluded that a rapid equilibrium is involved in this particular case. This is the only mention we could find of any prior hint of the extent of the equilibria involved.

[5] We have found that an external standard is unsatisfactory due to the fact that the changes in bulk magnetic susceptibility which occur with silver salt addition are normally quite significant with respect to the size of $\Delta\delta$. Internal TMS was also unsatisfactory as it was attacked by silver ion in some solvents.

Solutions.—All solutions were made up in 1.0-ml volumetric tubes. Weighed amounts of $AgBF_4 \cdot C_6H_{10}$ and $AgClO_4 \cdot 2C_6H_{10}$[6] were dissolved in the desired solvents to make up solutions containing those components. For the other olefins and for cases in which the charged silver:olefin ratio was not the same as in the solid complexes, weighed amounts of silver salt and olefin were used.

$AgBF_4 \cdot C_6H_{10}$.—Cyclohexene (2.2 g, 0.027 mol) in 75 ml of cyclohexane was added to anhydrous $AgBF_4$ (2.2 g, 0.011 mol, Alfa Inorganics). After being stirred vigorously for 90 min, the mixture was filtered under nitrogen, washed quickly with cyclohexane, and sucked dry for 60 sec. The product is hygroscopic and efflorescent. *Anal.* Calcd for $AgBF_4 \cdot C_6H_{10}$: Ag, 38.97; weight loss under vacuum, 29.6. Found: Ag, 39.02, 39.11; weight loss under vacuum, 29.[7]

Calculation of Equilibrium Constants

The equilibrium constants were calculated using eq 3 or 4[8,9] assuming eq 1 and assuming that eq 2 is not

$$Ag^+ + \text{olefin} \underset{}{\overset{K_1}{\rightleftarrows}} [Ag \cdot \text{olefin}]^+ \qquad (1)$$

$$[Ag \cdot \text{olefin}]^+ + \text{olefin} \underset{}{\overset{K_2}{\rightleftarrows}} [Ag \cdot 2(\text{olefin})]^+ \qquad (2)$$

significant. For equal total molar content of Ag^+ and olefin

$$K = \frac{\dfrac{\Delta\delta_{obsd}}{\Delta\delta_{max}}[\text{complex}]}{\left(\dfrac{\Delta\delta_{max} - \Delta\delta_{obsd}}{\Delta\delta_{max}}[\text{complex}]\right)^2} \qquad (3)$$

and for unequal total molar content of Ag^+ and olefin

$$K = \frac{\dfrac{\Delta\delta_{obsd}}{\Delta\delta_{max}}[\text{olefin}]}{\left([Ag^+] - \dfrac{\Delta\delta_{obsd}}{\Delta\delta_{max}}[\text{olefin}]\right)\left([\text{olefin}] - \dfrac{\Delta\delta_{obsd}}{\Delta\delta_{max}}[\text{olefin}]\right)} \qquad (4)$$

where [complex] is the total molarity of the originally charged complex, $[Ag^+]$ is the total molarity of the originally charged silver salt, and [olefin] is the total molarity of the originally charged olefin.

Results

Our detection of equilibria in these systems resulted from noting the concentration dependence of the downfield shift of the olefinic protons in silver tetrafluoroborate–cyclohexene. By adding increasingly larger excesses of $AgBF_4$ to dilute solutions of cyclohexene we have found that a point is reached at which the downfield shift ($\Delta\delta$) increases no further. We have called this the maximum downfield shift ($\Delta\delta_{max}$) and assumed that at this point essentially all of the cyclohexene is complexed. By relating $\Delta\delta_{obsd}$ at any concentration of charged complex to $\Delta\delta_{max}$ by eq 3 we have been able to calculate the corresponding association constants in a varity of solvents.[9] These are listed in Table I and range over a factor of 420.[10] A large variation can also be seen in $\Delta\delta_{max}$ but no correlation with K appears to exist.

TABLE I

NMR SPECTRA OF $AgBF_4 \cdot c\text{-}C_6H_{10}$

Solvent	Concn × 10, M	$\Delta\delta_{obsd}$, Hz	$\Delta\delta_{max}$, Hz	K	Av K
CH_2Cl_2	0.31	40	56	280	230
	2.0	48		210	
	3.9	50		200	
$C_6H_5NO_2$	0.58	40	65	72	76
	2.3	51		74	
	4.3	55		83	
C_6H_5Cl	0.32	15	38	34	32
	2.0	25		28	
	4.05	37		35	
CH_3NO_2	0.44	10	54.5	6.2	15
	1.4	28		16	
	3.4	38		22	
C_2H_5OAc	0.58	15	44	14	14
	0.83	18.5		15	
	2.1	23		11	
	5.1	31		16	
CD_3COCD_3	0.7	7	56	2.3	2.6
	2.0	17		3.1	
	4.9	23		2.4	
Dimethoxyethane	0.44	2	53	0.93	0.98
	2.5	9		0.98	
	4.7	14		1.04	
DMF	0.60	1.5	51	0.52	0.55
	1.6	4		0.58	
	3.8	8		0.58	
	6.4	10.5		0.51	

Table II shows the equilibrium constants for the $AgBF_4$ complexes of norbornene, cyclohexene, and 1-methylcyclohexene in deuterioacetone. This series (K = 420, 2.6, 0.52) compares favorably with the values reported by Muhs and Weiss[11] for the association constants of $[AgNO_3 \cdot \text{olefin}]$ in ethylene glycol (K = 62, 3.6, 0.5, respectively).

TABLE II

$AgBF_4$ COMPLEXES IN CD_3COCD_3

Olefin	Concn × 10, M	$\Delta\delta_{obsd}$, Hz	$\Delta\delta_{max}$, Hz	K	Av K
Norbornene	1.6	31	35	420	
	3.8	33		>350[a]	
Cyclohexene	0.7	7	56	2.3	2.6
	2.0	17		3.1	
	4.9	23		2.4	
1-Methylcyclohexene	1.6	4	52.5	0.56	0.52
	3.1	6		0.47	

[a] Too close to $\Delta\delta_{max}$ to determine accurately.

The association constants for cyclohexene and 1-methylcyclohexene with silver perchlorate in CD_3COCD_3 in the presence of up to 2 mol of olefin/mol of Ag(I) are listed in Table III. It is interesting to note that $\Delta\delta_{max}$ for both olefins is smaller with $AgClO_4$ than with $AgBF_4$ but that K is larger.

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(6) A. E. Comyns and H. J. Lucas, *J. Amer. Chem. Soc.*, **79**, 4339 (1957).

(7) (a) Multiple attempts to obtain good C and H analyses were hindered by the fact that our microanalytical laboratory is maintained at 50% relative humidity. At these levels, with a 3-mg sample, the effects of hygroscopicity and olefin efflorescence become intolerable and the actual analysis obtained depends on the length of time it takes to weigh the sample. *Anal.* Calcd: C, 26.03. Found: C, 18.7–23.1. The silver content and weight loss analyses were conducted on 1-g samples under dry conditions and were not susceptible to the above problem. (b) The synthesis of the 1:1 complex is admittedly more fortuitous than planned. The 90-min reaction time is important since one reaction which was allowed to run 19–20 hr gave a product which came close to a 1:2 complex. *Anal.* Calcd for $AgBF_4 \cdot 2C_6H_{10}$: Ag, 30.05. Found: 28.75, 29.21. It should be pointed out that the 1:1 complex is very uniform in texture and appears not to be a mixture of $AgBF_4$ and $AgBF_4 \cdot 2C_6H_{10}$.

(8) *Cf.* the Discussion concerning the validity of the assumptions herein.

(9) Implicit in the use of eq 3 and 4 is the assumption of a linear relationship between $\Delta\delta_{obsd}/\Delta\delta_{max}$ and changes in concentration.

(10) Solutions of $2AgClO_4 \cdot 3(1,5\text{-hexadiene})$ in pyridine and in acetonitrile exhibited no $\Delta\delta$. These solvents evidently tie up the silver ion so completely that no silver(I)–olefin complex survives.

(11) M. A. Muhs and F. T. Weiss, *J. Amer. Chem. Soc.*, **84**, 4697 (1962).

Table III

$AgClO_4$ Complexes in CD_3COCD_3

Concn × 10, *M*		$\Delta\delta_{obsd}$, Hz	$\Delta\delta_{max}$, Hz	*K*	Av *K*
Ag^+	Olefin				
		Cyclohexene			
1.9	3.8	18	51	8.7	8.1
3.7	3.7	29		8.2	
3.7	1.5	34		7.4	
4.9	3.9	33		7.4	
7.6	3.6	41		8.8	
		1-Methylcyclohexene			
1.6	3.2	4	49	0.80	0.72
3.1	6.2	6		0.64	

Discussion

The results which we have obtained clearly show that a variety of silver(I)–olefin complexes do dissociate in organic solvents to give a mixture of free and complexed olefin and free Ag(I)+. Within the limits of experimental technique and some assumptions in the calculations, nmr appears to be the most efficient tool available for determining the equilibrium constants in a wide variety of organic media.

The accuracy of the determination of the equilibrium constants is greatly dependent on the accuracy of the measurement of $\Delta\delta_{max}$ and on the correctness of the assumption that equilibrium 2 can be ignored.[12] The ideal situation for the determination of $\Delta\delta_{max}$ would be one involving a slow enough equilibrium so that separate resonances for the free and for the complexed olefin could be seen. This is not the case for any of the systems which we have studied and an attempt at resolving this question with cooling methods offered no hope of success down to −55° with $AgBF_4 \cdot C_6H_{10}$ in CD_3COCD_3 although a slight increase in $\Delta\delta_{obsd}$ was noted.

Although the method which we were forced to use to determine $\Delta\delta_{max}$ is not ideal, we feel that it is sound nonetheless. In all cases we added sufficient excess silver salt so that some solid remained undissolved in the bottom of the nmr tube. This allowed for the removal of free olefin from solution as the solid complex. While we must admit to having no exact knowledge of the position of the equilibrium for this latter process, we must assume that it is far enough to the side of removal of olefin from solution so that nmr measurements on the saturated solutions recorded spectra of complexed olefin only. To the extent that this latter assumption is incorrect, $\Delta\delta_{max}$ as recorded is too small and *K*, as presently calculated, is too large. This possibility, which is greatest when *K* is smallest, does define an area of uncertainty and indicates that the range of *K* in this series of solvents may be greater than we have calculated.[13]

We have ignored the possibility of the participation of equilibrium 2 and assumed that it is not significant. The validity of this assumption is shown by the fact that, in most cases, *K* does not vary considerably with concentration. Deviations at higher concentrations and large *K* values indicate that some $[Ag \cdot 2(olefin)]^+$ formation may be occurring.

One important question raised by the current work is why earlier workers in this field did not detect the equilibria which we have found. We believe that the answer lies in the methods of detection employed. Quinn's group searched for equilibria by the conventional technique of lowering the probe temperature while keeping the species concentration constant.[2b] This technique has been applied with great success in the past, but it is limited, perforce, to those situations in which the equilibria are temperature dependent. Clearly, the Ag(I)–olefin equilibria are only very slightly temperature dependent and their detection is possible only by use of the more time-consuming method of making measurements at different concentrations.

If the original intention of using nmr in these studies (to obtain information concerning the nature of the silver–olefin bond) is to be fulfilled, then perhaps the really significant relationship which should be considered is that between the equilibrium constants of a series of complexes in one solvent and the strength of the coordinate bond.

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d-Orbital Orderings of Tetragonal Chromium(III) Complexes

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The considerable interest in low-symmetry complexes of the first transition series has generated a large number of publications, both experimental and theoretical.[1–5] Since the work of Wentworth and Piper on Co(III) complexes,[2] the analysis of low-symmetry complexes has been extended to Ni(II),[1] Fe(II),[3] and Cr(III).[4] The analysis of Ni(II)[1] and Fe(II)[3] complexes has been adequately stated elsewhere and valuable insights into the electronic structure of the complexes were obtained. The case of Cr(III) has presented a variety of problems resulting from qualitative interpretation of the experimental data. These problems are differing

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[12] If the energy level of $[Ag \cdot 2(olefin)]^+$ is less than that of $[Ag \cdot olefin]^+$, then K_2 can become an important factor, especially for large K_1. The necessity for ignoring equilibrium 2 is dictated by the fact there is no way of measuring $\Delta\delta_{max}$ for $[Ag \cdot 2(olefin)]^+$, and any attempt to include a term for K_2 thus renders the algebraic equations insoluble.

[13] The *K* values (Table I) for CH_3NO_2 do vary considerably with concentration and may indicate participation of equilibrium 2. In this case we would suspect that K_1 as measured is much smaller than the real K_1 and that the energy level of $[Ag \cdot 2(olefin)]^+$ is much less than that of $[Ag \cdot olefin]^+$ in this solvent.

(1) (a) D. A. Rowley and R. S. Drago, *Inorg. Chem.*, **7**, 795 (1968); (b) D. A. Rowley and R. S. Drago, *ibid.*, **6**, 1092 (1967).

(2) (a) R. A. D. Wentworth and T. S. Piper, *ibid.*, **4**, 709 (1965); (b) R. A. D. Wentworth and T. S. Piper, *ibid.*, **4**, 1524 (1965).

(3) D. M. L. Goodgame, M. Goodgame, M. A. Hitchman, and M. J. Waks, *ibid.*, **5**, 635 (1966).

(4) W. A. Baker and M. S. Philips, *ibid.*, **5**, 1042 (1966).

(5) L. Dubicki, M. A. Hitchman, and P. Day, *ibid.*, **9**, 188 (1970).