

ordinating ability of dipeptide esters as compared to the dipeptides themselves.

The higher K_1 value for coordination of GGOMe by $\text{Cu}(\text{H}_{-1}\text{GGOMe})^+$ ($\log K_2^1 = 3.30$) as compared to $\text{Cu}(\text{H}_{-1}\text{GG})$ reflects the availability of more coordination sites and a higher positive charge on the $\text{Cu}(\text{H}_{-1}\text{GGOMe})^+$ complex.

Unlike the complexes of GS and GSOMe, the Cu(II) complexes of GG and GGOMe undergo amide proton ionization. Dissociation constants for this ionization in $\text{Cu}(\text{GG})^+$ and $\text{Cu}(\text{GGOMe})^{2+}$ are given in Table III as K_{1a} . As has been suggested by Kaden and Zuberbuhler¹⁵ and by Nakon and Martell,¹⁶ part of the driving force for this ionization is the formation of a second stable chelate ring as occurs when $\text{Cu}(\text{GG})^+$ loses a proton to give $\text{Cu}(\text{H}_{-1}\text{GG})$, as in eq 1. Thus, as compared to $\text{Cu}(\text{GG})^+$ ($\log K_{1a} = -4.38$),⁵ amide

(15) Th. Kaden and A. Zuberbuhler, *Helv. Chim. Acta*, **54**, 1361 (1971).

(16) R. Nakon and A. E. Martell, *Bioinorg. Chem.*, submitted for publication.

proton ionization occurs significantly less readily ($\log K_{1a} = -7.01$)¹⁷ in $\text{Cu}(\text{glycinamide})^{2+}$ in which no additional chelate ring is formed. The value of $\log K_{1a}$ (-5.23) for $\text{Cu}(\text{GGOMe})^{2+}$ is intermediate between the above extremes, suggesting that the ester group is perhaps weakly coordinated to the Cu^{2+} , as in structure III. Whether the ester actually binds to the metal is not clear, but amide ionization and nitrogen coordination definitely place the ester group in a position near the metal ion where the metal ion may promote the hydrolysis of the ester, as will be discussed in a following paper.³

Registry No. 2:1 GGOMe-Cu(II), 38671-67-9; 1:1 GGO-Me-Cu(II), 38671-68-0; 2:1 GSOMe-Cu(II), 38671-69-1; 2:1 GS-Cu(II), 38671-70-4.

Acknowledgment. This research was supported by the U. S. Public Health Service through Grant No. GM-12626 of the National Institute of General Medical Sciences.

(17) H. Sigel, *Angew. Chem., Int. Ed. Engl.*, **7**, 137 (1968).

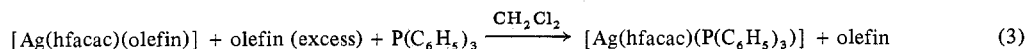
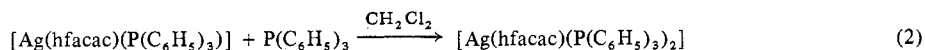
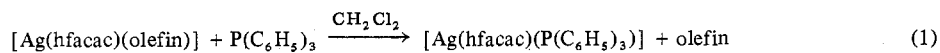
Contribution from the Department of Chemistry,
Clarkson College of Technology, Potsdam, New York 13676

Heats of Reaction of Triphenylphosphine with Compounds of the Type Hexafluoroacetylacetonato(olefin)silver(I)

WALTER PARTENHEIMER* and EARL H. JOHNSON

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Characterization of and heats of the following reactions are reported where hfacac is the conjugate base of hexafluoroacetylacetonate, and the olefins are cyclopentene, cyclohexene, cycloheptene, *cis*-cyclooctene, 1,5-cyclooctadiene, and 1,3,5,7-cyclooctatetraene. Relative base-silver dissociation energies are found to be 18.4 ($\text{P}(\text{C}_6\text{H}_5)_3$), 8.6 (C_8H_{14}), 6.7 (C_8H_{12}), 5.1 (C_6H_{10}), 4.1 (C_7H_{12}), and 0.0 kcal/mol (C_5H_8) (ignoring solvation contributions). This ordering is in disagreement with all other available thermodynamic silver olefin data indicative of substantial solvation and entropic contributions in the previously reported data. Evidence is given for the formation of species of the type $[\text{Ag}(\text{hfacac})(\text{olefin})_2]$. The proton nmr spectra for these compounds are briefly discussed.



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Introduction

We have been interested in preparing suitable metal-olefin compounds and obtaining relative metal-olefin dissociation energies by calorimetric studies on these compounds.¹ We previously have calorimetrically studied the interaction of dichlorobis(benzonitrile)palladium(II) with various chelating bases² and prepared a series of nonionic compounds of the type $[\text{Ag}(\text{hfacac})(\text{olefin})]$ (hfacac is the anion of hexafluoroacetylacetonate) which are soluble in relatively nonpolar solvents.¹ We now wish to report the interaction of triphenylphosphine with the latter compounds and the enthalpic changes associated with these reactions.

Thermodynamic information regarding the metal-olefin

interaction is significant for at least three reasons. Information regarding the metal-olefin bond can be gained by varying the electronic, steric, and strain characteristics of the olefin and observing the changes in the metal-olefin interaction. It can be used to test the various spectroscopic parameters that have been thought to reflect metal-olefin "bond strength," such as the decrease in the double-bond stretching frequency upon coordination of an olefin to a metal. Since heats of formation of compounds in the gas phase have been found to parallel closely heats of chemisorption on solids,³ valuable information relating to the catalytic activity of surfaces can be obtained.

Extensive thermodynamic information on silver-olefin compounds is available and has been reviewed.⁴ Since that

(1) W. Partenheimer and E. H. Johnson, *Inorg. Chem.*, **11**, 2840 (1972).

(2) W. Partenheimer, *Inorg. Chem.*, **11**, 743 (1972).

(3) D. O. Hayward and B. M. W. Trapnell, "Chemisorption," 2nd ed, Butterworths, London, 1964, p 208.

Table I. Molecular Weights of Compounds of the Type [Ag(hfacac)(olefin)]

Olefin	Calcd	Found	Solvent
Cyclooctadiene	423	435	CHBr ₃
Cyclooctatetraene	419	513	HCCl ₃ ^a
Cyclooctene	425	425	CHBr ₃
		430	CH ₂ Cl ₂
Cyclopentene	383	374, 376	CH ₂ Cl ₂

^a Determined osmotically by Schwarzkopf Microanalytical Laboratories.

Table II. Proton Nmr Data^a for Some Olefins and Compounds of the Type [Ag(hfacac)(olefin)]

Compd	$\delta(-CH)^b$	$\delta(=CH)$	$\delta(>CH_2)$
Cyclopentene		4.19 (2.1) ^c	7.65 (4.0) 8.14 (1.9)
[Ag(hfacac)(C ₅ H ₈)]	3.95 (1.0)	3.48 (2.1)	7.40 (4.1) 7.95 (2.0)
Cyclohexene		4.31 (1.9)	8.02 (4.2) 8.37 (3.9)
[Ag(hfacac)(C ₆ H ₁₀)]	4.02 (0.9)	3.64 (1.8)	7.71 (4.3) 8.27 (4.0)
Cycloheptene		4.15 (1.8)	7.81 (4.1) 8.36 (6.2)
[Ag(hfacac)(C ₇ H ₁₂)]	4.00 (1.9)	3.55 (2.0)	7.65 (3.8) 8.30 (5.9)
Cyclooctene		4.35 (1.9)	7.86 (3.9) 8.49 (8.2)
[Ag(hfacac)(C ₈ H ₁₄)]	4.09 (1.0)	3.98 (1.9)	7.58 (3.9) 8.45 (8.3)

^a Chemical shifts reported using the τ scale with TMS as the standard. ^b Methine proton on the hexafluoroacetylacetonate anion.

^c Integrated intensities given in parentheses.

time more work has appeared.^{5,6} All of the available data have been obtained either in polar solvent systems such as water or alcohols or on systems where the reactants and products are in different phases. The ordering of equilibrium constants involving the interaction of the argentous ion with olefins are different in water and ethylene glycol⁷ clearly illustrating that solvation effects in these systems are significant. As a further check on the reliability of previously reported silver-olefin thermodynamic data we have undertaken this study which reports accurate enthalpic changes in a relatively nonpolar solvent using olefins for which extensive pertinent information is already available.

Experimental Section

Materials. J. T. Baker 1,5-cyclooctadiene (C₈H₁₂), Columbia organic 1,3,5,7-cyclooctatetraene (C₈H₈), and Aldrich *cis*-cyclooctene (C₈H₁₄), cycloheptene (C₇H₁₂), cyclohexene (C₆H₁₀), and cyclopentene (C₅H₈) were used as received. Aldrich triphenylphosphine was recrystallized from benzene-cyclohexane. Baker AR grade dichloromethane, used in the calorimetric studies, was dried with Linde 4A molecular sieves at least 24 hr before use. The compounds [Ag(hfacac)(olefin)] (olefin = C₅H₈, C₆H₁₀, C₇H₁₂, C₈H₁₄) were prepared as previously described.¹ [Ag(hfacac)(C₅H₈)] was prepared in a similar manner in a 50% yield. Nmr spectra were recorded on a Varian A-60 spectrometer, ir spectra with a Beckman IR-12, molecular weights in dichloromethane with a Coleman Model 155, and calorimetric measurements with a Guild solution microcalorimeter⁸ using a base line compensator. Molecular weights in bromoform were determined cryoscopically.

(4) C. D. M. Beverwijk, G. J. M. Van der Kerk, A. J. Leusink, and J. G. Noltes, *Organometal. Chem. Rev.*, 5, 215 (1970).

(5) H. W. Quinn and R. L. Van Gilder, *Can. J. Chem.*, 49, 1323 (1971).

(6) Y. Inaki, S. Nozakura, and S. Murahashi, *Bull. Chem. Soc. Jap.*, 42, 2605 (1969).

(7) S. P. Wasik and W. Tsang, *J. Phys. Chem.*, 74, 2970 (1970).

(8) Design of instrument is essentially the same as that described by E. M. Arnett, W. G. Bentrude, J. J. Burke, and P. Duggleby, *J. Amer. Chem. Soc.*, 87, 1541 (1965).

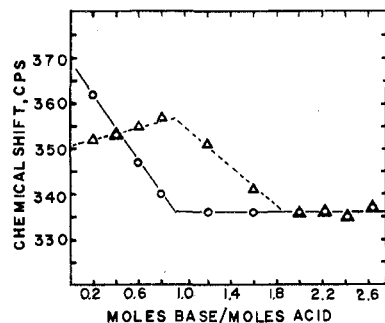


Figure 1. Partial proton nmr spectrum resulting from the incremental addition of triphenylphosphine to [Ag(hfacac)(1,5-cyclooctadiene)]: \circ , olefinic protons; Δ , methine proton on β -diketonate.

Calorimetric Experiments. The silver compound, 2.2–3.9 mmol, was dissolved in 200 ml of dichloromethane and titrated incrementally with a concentrated triphenylphosphine-dichloromethane solution *via* a 2-ml Gilmont micrometer buret. All heats were corrected for the heat of solution of the added triphenylphosphine. The compounds [Ag(hfacac)(olefin)] (olefin = C₇H₁₂, C₆H₁₀, C₅H₈) lose olefin readily. The calorimetric experiments were therefore performed immediately after the preparation of the compounds. Nmr spectra were also obtained on most of the samples before the calorimetric experiments as a check on the purity of the samples. The white solid, obtained by evaporation of the solutions obtained after the calorimetry experiments, had an ir spectrum similar to that reported for [Ag(hfacac)(P(C₆H₅)₃)₂]⁹ and gave a satisfactory analysis. *Anal.* Calcd for AgP₂F₆O₂C₄₁H₃₁: C, 58.65; H, 3.73. Found: C, 59.69; H, 3.92.

Results

Molecular weights of the silver-olefin compounds are given on Table I. The cyclooctadiene, cyclooctene, and cyclopentene derivatives are monomers in the halogenated hydrocarbon solvents, while the cyclooctatetraene derivative is partially polymeric in chloroform. The nmr data for the monoolefins and their silver compounds is given on Table II. The integrated intensities are consistent with the formulation [Ag(hfacac)(olefin)].

Figure 1 illustrates the changes that occur in the proton nmr spectrum when triphenylphosphine is incrementally added to a deuteriochloroform solution of [Ag(hfacac)(1,5-cyclooctadiene)]. In the 0–1 mole ratio region, the olefinic protons shift upfield. At approximately a 1:1 mole ratio of added triphenylphosphine to silver complex the chemical shift is identical with that of uncoordinated 1,5-cyclooctadiene.¹⁰ The chemical shift of the methine proton on the β -diketonate shifts downfield until a 1:1 mole ratio and then upfield until a 2:1 mole ratio is obtained. The chemical shift of the methine proton and the uncoordinated olefinic protons are the same after the 2:1 mole ratio. This experiment was repeated with [Ag(hfacac)(cyclooctene)] with the same qualitative results, except that the chemical shifts of the methine protons and olefinic protons are not identical in the final products.

The calorimetric data are summarized in Table III and illustrated *via* calorimetric titration curves on Figure 2. Addition of triphenylphosphine to [Ag(hfacac)(olefin)] results in a linear plot from 0 to 1 mole ratio, a break occurs, and another line is observed in the 1–2 mole ratio region (see Figure 2). Exceptions to the previous statement occur for the cyclohexene- and cycloheptenesilver compounds where a slight curva-

(9) D. Gibson, B. F. G. Johnson, and J. Lewis, *J. Chem. Soc. A*, 367 (1970).

(10) The error in the given mole ratios is high since the weights of the acid and base were in the milligram range. Linearity of lines is assumed.

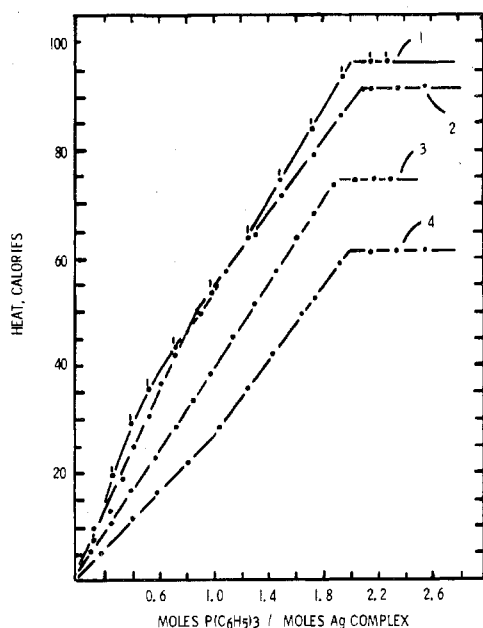


Figure 2. Calorimetric titration curves for the reaction of triphenylphosphine with $[\text{Ag}(\text{olefin})(\text{hfacac})]$: curve 1, cycloheptene (3.791 mg-atoms of Ag); curve 2, cyclopentene (2.154 mg-atoms of Ag); curve 3, 1,3,5,7-cyclooctatetraene (3.567 mg-atoms of Ag); curve 4, cyclohexene with excess cyclohexene added (3.934 mg-atoms of Ag).

Table III. Calorimetric Data for the Silver Olefin Compounds

Olefin	ΔH , kcal/mol	SD in slope ^a	No. of data points
$[\text{Ag}(\text{hfacac})(\text{olefin})] + \text{P}(\text{C}_6\text{H}_5)_3 \xrightarrow{\text{CH}_2\text{Cl}_2} [\text{Ag}(\text{hfacac})(\text{P}(\text{C}_6\text{H}_5)_3)] + \text{olefin} \quad (1)$			
Cyclopentene	18.0 ± 0.5	0.39	5
	18.8 ± 0.4	0.26	7
Cyclohexene	13.3 ± 0.3	0.34^b	9
Cycloheptene	14.3 ± 0.3	1.14^b	5
Cyclooctene	9.88 ± 0.20	0.05	4
	9.76 ± 0.5	0.29	6
1,5-Cyclooctadiene	11.7 ± 0.2	0.08	11
1,3,5,7-Cyclooctatetraene	10.7 ± 0.2	0.03	7
$[\text{Ag}(\text{hfacac})(\text{P}(\text{C}_6\text{H}_5)_3)] + \text{P}(\text{C}_6\text{H}_5)_3 \xrightarrow{\text{CH}_2\text{Cl}_2} [\text{Ag}(\text{hfacac})(\text{P}(\text{C}_6\text{H}_5)_3)_2] \quad (2)$			
Cyclopentene ^c	11.5 ± 0.3	0.06	5
	11.2 ± 0.2	0.10	6
Cyclohexene	11.1 ± 0.4	0.06	7
Cycloheptene	11.3 ± 0.3	0.12	5
Cyclooctene	11.1 ± 0.5	0.28	5
	11.3 ± 0.6	0.33	5
1,5-Cyclooctadiene	11.6 ± 0.6	0.09	7
1,3,5,7-Cyclooctatetraene	10.9 ± 0.5	0.12	6
Cyclohexene + excess olefin	11.1 ± 0.4	0.06	7
Cycloheptene + excess olefin	11.5 ± 0.4	0.09	5
Cyclooctene + excess olefin	11.4 ± 0.4	0.07	6
$[\text{Ag}(\text{hfacac})(\text{olefin})] + \text{P}(\text{C}_6\text{H}_5)_3 + \text{olefin} \xrightarrow{\text{CH}_2\text{Cl}_2} [\text{Ag}(\text{hfacac})(\text{P}(\text{C}_6\text{H}_5)_3)] + \text{olefin} \quad (3)$			
Cyclohexene	11.0 ± 0.2	0.11	6
Cycloheptene ^d	10.3 ± 0.2	0.03	4
Cyclooctene ^e	9.22 ± 0.18	0.06	3
	8.75 ± 0.18	0.07	4

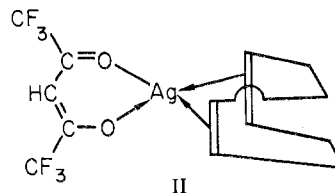
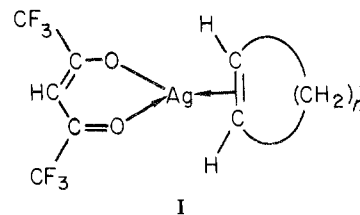
^a Standard deviation from least-squares calculation. ^b Data points from a curve. See text for further discussion. ^c Olefin indicates starting material, $[\text{Ag}(\text{hfacac})(\text{olefin})]$, from which enthalpies are derived. ^d 1.46 mmol of C_7H_{12} added. ^e 1.56 and 1.945 mmol of C_8H_{14} added, respectively.

ture can be detected in the 0-1 mole ratio region. For the cyclooctatetraene derivative, no break is observed indicating that the enthalpies for reactions 1 and 2 are the same. All of the enthalpies reported on Table III were evaluated by determining the slopes of the calorimetric titration curves using the least-squares method. The precision for the individual determinations was excellent as evidenced by the standard deviations of the slope given in Table III (except for the cyclohexene and cycloheptene derivatives where curvature is observed). The enthalpies of the cyclohexene- and cycloheptenesilver compounds can be evaluated by an alternative method. Knowing the value of the enthalpy of the second concomitant reaction, 11.3 kcal/mol (see below), and the gram-atoms of silver present, the heat contribution to the second reaction can be calculated. This latter quantity can be subtracted from the total heat evolved in the calorimetric titration, giving the amount of heat evolved in the first reaction. The heat evolved in the first reaction can then be divided by the moles of silver present to obtain the enthalpy. The enthalpies calculated by this method are 13.2 and 14.2 kcal/mol for cyclohexene and cycloheptene, respectively, compared to the values 13.3 and 14.3 kcal/mol in Table III.

The reaction given by eq 2 has been measured 11 times. The weighted mean of these enthalpies is 11.3 ± 0.1 , the error being the precision of the mean at the 70% confidence level.

Discussion

The molecular weight data (Table I) indicate that the silver-olefin compounds, except for the cyclooctatetraene complex, are monomeric in halogenated hydrocarbon solvents. We have previously established that the β -diketonate moiety is attached *via* the oxygens to the silver atom.¹ The probable

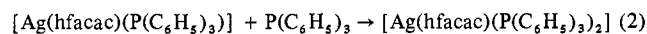
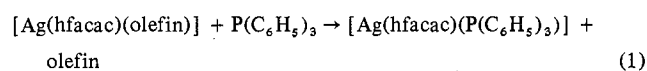


structure of these compounds is given by I. The silver atom has a trigonal-planar geometry. This is consistent with a number of X-ray crystal structures of silver-olefin compounds where the metal has an approximate trigonal-planar array of ligands around it.¹¹⁻¹⁵ The cyclooctadiene derivative may be bonded *via* double bonds as in II; however, the calorimetric data, to be discussed, indicate that the interaction of a second double bond is either weak or nonexistent. A large number of structures is possible for the cyclooctatetraene

- (11) J. S. McKechnie, M. G. Newton, and I. C. Paul, *J. Amer. Chem. Soc.*, **89**, 4819 (1967).
 (12) A. T. McPhail and G. A. Sim, *J. Chem. Soc. B*, 112 (1966).
 (13) J. S. McKechnie and I. C. Paul, *J. Chem. Soc. B*, 1445 (1968).
 (14) F. S. Matthews and W. N. Lipscomb, *J. Phys. Chem.*, **63**, 845 (1959).
 (15) N. C. Baenziger, H. L. Haight, R. Alexander, and J. R. Doyle, *Inorg. Chem.*, **5**, 1399 (1966).

derivative because it is partially polymeric in chloroform but will not be discussed here.

The proton nmr studies (Figure 1) and the calorimetric titration curves (Figure 2) strongly suggest that two concomitant reactions are occurring. In the first reaction olefin is being liberated (nmr data). The product for the second reaction is $[\text{Ag}(\text{hfacac})(\text{P}(\text{C}_6\text{H}_5)_3)_2]$ which has previously been characterized.⁹ The two concomitant reactions consistent with these observations are

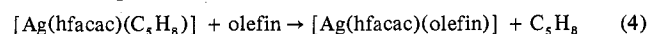


The reaction given in eq 2 has been shown to occur for $[\text{Cu}(\text{hfacac})(\text{P}(\text{C}_6\text{H}_5)_3)_2]$.⁹

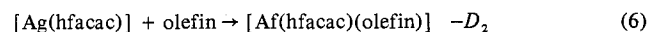
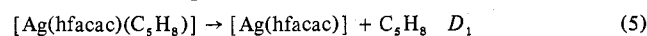
As reaction 1 occurs, there is only one nmr signal due to the olefinic protons indicative that fast exchange between the coordinated and free olefin is occurring. This is normally observed for silver-olefin compounds.¹⁶

Calculation of Relative Silver-Base Dissociation Energies.

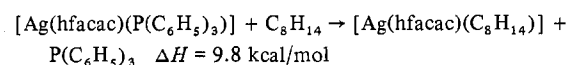
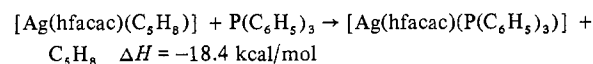
An enthalpic change in a reaction of the type



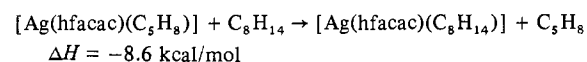
where C_5H_8 is cyclopentene, can be written as a sum of two dissociation energies, D



If we choose the dissociation energy of cyclopentene as our standard (eq 5) and allow it to have a value of zero, we can then obtain a series of *relative* dissociation energies. The enthalpic change in eq 5 is defined as zero; hence the enthalpic change in eq 6 is identical with that in eq 4. The enthalpic change in eq 4 can be calculated from the calorimetric data in Table II as follows, using cyclooctene as an example

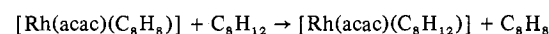


Adding the last two equations gives



Hence the dissociation energy of cyclooctene is 8.6 kcal/mol higher than that of cyclopentene. The relative dissociation energies are summarized in Table IV.

Dissociation energies are properly defined as enthalpic changes occurring in the gas phase. We believe that the relative dissociation energies have negligible solvent effects for the following reasons. We will report in detail elsewhere the data for the reaction



where acac is the anion of acetylacetonate, C_8H_8 is 1,3,5,7-cyclooctatetraene, and C_8H_{12} is 1,5-cyclooctadiene.

The enthalpic change for this reaction, -4.4 kcal/mol, is exactly the same in dichloromethane and carbon tetrachloride. This most probably means that the olefins are not interacting specifically with the solvent; *i.e.*, only van der Waals interactions are present. It has been shown that the enthalpic changes occurring in reactions of the type given in eq 4 and 5 are free from significant solvation effects when only

(16) J. Solodar and J. P. Petrovich, *Inorg. Chem.*, **10**, 395 (1971), and references cited therein.

Table IV. Relative Silver-Base Dissociation Energies^a (kcal/mol)

Base	D	Base	D
Triphenylphosphine	18.4 ± 0.5	Cyclohexene	5.1 ± 0.3
<i>cis</i> -Cyclooctene	8.6 ± 0.4	Cycloheptene	4.1 ± 0.3
1,5-Cyclooctadiene	6.7 ± 0.2	Cyclopentene	0.0

^a Relative to silver-cyclopentene. All dissociation energies given are higher than that of silver-cyclopentene.

van der Waals interactions occur at the site on each molecule where the exchange occurs.^{17,18} Thus specific interactions may occur on the oxygens of the acetylacetonate in the silver compounds but these would be present in both the reactants and the products. In exchange reactions, as given in eq 4, the acid site on the silver is always protected by the coordinated olefin. The only exposed acid-base sites in the molecules given in eq 4 are those basic ones on the olefins which, as shown above, probably interact nonspecifically with the solvent.

We have chosen the monoolefins reported in Table IV because there already exists a considerable amount of information on these olefins. In the following discussion the values will always be given in the same order as the dissociation energies reported in Table IV, namely, cyclopentene, cycloheptene, cyclohexene, and *cis*-cyclooctene (increasing dissociation energies). Muhs and Weiss reported equilibrium constants determined in ethylene glycol using a gas chromatographic technique for the interaction of silver nitrate and olefins. Their values are 7.3 (C_5H_8), 12.8 (C_7H_{12}), 3.6 (C_6H_{10}), and $14.4 M^{-1}$ (C_8H_{14}).¹⁹ Traynham and Olechowski, using the distribution method between water and carbon tetrachloride, reported equilibrium constants of 0.119, 0.0212, 0.0184, and $0.00504 M^{-1}$ and enthalpies of -6.63 , -6.49 , -5.74 , and -4.11 kcal/mol²⁰ for the interaction of the argentous ion and these olefins. These comparisons point out that the ordering in equilibrium constants for a series of olefins is not determined by the enthalpic contribution to the free energy and/or that solvation energies are a significant factor responsible for the orderings in all of the previously reported silver-olefin data.^{19,20} These results cast doubt on the validity of the conclusions derived from previous silver-olefin thermodynamic data. The differences between our work and others may also be due to significant structural differences in the compounds being prepared, $[\text{Ag}(\text{hfacac})(\text{olefin})]$ and $[\text{Ag}(\text{olefin})(\text{solvent})_x]^+$. The unknown structure of the latter compound certainly makes it a rather poor model compound. For example, the number of solvent molecules present in $[\text{Ag}(\text{olefin})(\text{solvent})_x]^+$ may not remain the same as different olefins are being compared.

The correspondence between the equilibrium constants and enthalpies with the amount of strain energy present in the olefin has been discussed.^{19,20} Conventional ring strain energies are 5.7 (C_5H_8), 1.3 (C_7H_{12}), 5.1 (C_6H_{10}), and 5.8 kcal/mol (C_8H_{14}).²¹ These values do not correlate to any of the reported orderings^{19,20} and that reported here.²² Van Gilder and Quinn²³ have reported the shift in the carbon

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double-bond stretching frequency upon coordination for compounds of the type $\text{Ag}(\text{olefin})_2\text{BF}_4$. The reported values in cm^{-1} are 75, 62, 68, and 64. Failure to observe a correspondence between these shifts and the silver-olefin dissociation energies may be due to the different types of compounds being compared and/or to a number of theoretical reasons previously discussed.²⁴

All of the chemical shifts of the protons in an olefin experience a paramagnetic shift upon coordination to the silver ion. The shift becomes less as the carbon atoms become farther away from the metal. Thus the olefinic protons in the monoolefins are shifted downfield 0.59 ± 0.15 ppm when coordinated to the metal. The protons on the methylenic carbons next to the olefinic bond are shifted 0.25 ± 0.06 ppm, and those one carbon removed are shifted 0.10 ± 0.07 ppm. All of the protons in compounds of the type $\text{Ag}(\text{olefin})_2\text{BF}_4$ are similarly shifted relative to the uncoordinated olefin, 0.79 ± 0.10 ppm.²³ There is a correspondence between the chemical shifts of the coordinated olefinic protons and the relative dissociation energies (see Tables II and IV) but there is not between the shift of the chemical shift of the olefinic protons upon coordination and the relative dissociation energies. We have also found such a correspondence in the chelating olefinic compounds of the type $[\text{PdCl}_2(\text{olefin})]$ and $[\text{RhCl}(\text{olefin})_2]$ which will be reported elsewhere. Since theoretic

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cal calculations of chemical shifts in molecules are at a primitive stage of development, discussion on the reasons for the above correspondence is premature.

We observe that in all cases addition of excess olefin results in a lower enthalpic change when $[\text{Ag}(\text{hfacac})(\text{olefin})]$ is treated with triphenylphosphine (Table III, eq 3). We also observe a lower enthalpic change when increasing amounts of olefin are present. This is probably due to the formation of species of the type $[\text{Ag}(\text{hfacac})(\text{olefin})_2]$, which is not unexpected since similar silver olefin compounds exist.^{3,23} The dissociation energy of 1,5-cyclooctadiene is intermediate between cyclooctene and cyclohexene which suggests that only one double bond is coordinated or that on the average both double bonds coordinate more weakly than the monoolefins. The significance of the cyclooctatetraene enthalpic data cannot be discussed at this time due to its partially polymeric state in solution.

Registry No. $\text{P}(\text{C}_6\text{H}_5)_3$, 603-35-0; $[\text{Ag}(\text{hfacac})(\text{cyclopentene})]$, 38882-87-0; $[\text{Ag}(\text{hfacac})(\text{cyclohexene})]$, 38892-26-1; $[\text{Ag}(\text{hfacac})(\text{cycloheptene})]$, 38882-89-2; $[\text{Ag}(\text{hfacac})(\text{cis-cyclooctene})]$, 38882-85-8; $[\text{Ag}(\text{hfacac})(1,5\text{-cyclooctadiene})]$, 38892-25-0; $[\text{Ag}(\text{hfacac})(1,3,5,7\text{-cyclooctatetraene})]$, 37333-35-0; $[\text{Ag}(\text{hfacac})(\text{PPh}_3)]$, 38960-88-2; $[\text{Ag}(\text{hfacac})(\text{PPh}_3)_2]$, 26582-28-5.

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Studies on Coordination Complexes of Silver(II). VIII.¹ Synthesis and Characterization of Mixed-Ligand Complexes of the Pyridinecarboxylic Acids and Other Nitrogen Heterocyclic Donor Molecules

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When the silver(II) complex $\text{Ag}(\text{dipic})(\text{dipicH}_2) \cdot 4\text{H}_2\text{O}$ ($\text{dipicH}_2 = \text{pyridine-2,6-dicarboxylic acid}$) is allowed to react with 2,2',2''-terpyridyl, 2,2'-bipyridyl, or 1,10-phenanthroline in aqueous solution, the neutral terdentate ligand molecule dipicH_2 is readily replaced to yield mixed-ligand complexes of the general formula $\text{Ag}(\text{dipic})(\text{L}) \cdot x\text{H}_2\text{O}$. From the related reactions of other bis(pyridinecarboxylate) complexes of silver(II) with 1 mol of 2,2',2''-terpyridyl in the presence of diammonium peroxydisulfate, ionic derivatives of the general formula $\text{Ag}(\text{pyridinecarboxylate})(\text{terpy})(\text{S}_2\text{O}_8)_{1/2} \cdot x\text{H}_2\text{O}$ are formed. Infrared spectral studies and X-ray powder data provide good evidence for the formulation of these compounds as authentic mixed-ligand complexes. The physical properties and spectra of these compounds are discussed.

Introduction

The majority of silver(II) complexes which have been reported in the literature are four-coordinate species whose stereochemistry most probably approximates to square planar.³⁻¹¹ The very limited amount of unambiguous structural

information available for these complexes¹²⁻¹⁵ confirms an essentially square-planar structure. Morgan and Burstall previously reported the synthesis of several tris(2,2'-bipyridyl) complexes of silver(II)⁴ which were believed to be six-coor-

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