The isomeric nature of the present complexes, [Ru(OH)$_2$(py)$_2$bipy] and [Ru(OH)$_2$(py)$_2$phen], will be discussed in the following paper by the comparison of the results of the cis–trans isomeric pair.

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# The Syntheses of Some New Silver Olefin Compounds of the Type (Olefin)($\beta$-diketonato)silver(I)

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It has been well established that the silver(I) cation has a strong propensity to react with olefins to form labile, relatively weakly bonded olefin complexes.[1] Most of the available isolable Ag(I) olefin compounds are salts in which the anion is perchlorate, nitrate, or tetrafluoroborate. We were interested in obtaining some nonionic silver(I) olefin compounds that would be isolable and soluble in relatively nonpolar solvents such as dichloromethane or cyclohexane. This paper reports a series of compounds with such characteristics.

The compounds which have been characterized are of the type [Ag(hfacac)(olefin)] (hfacac is the conjugate base of hexafluoroacetylacetone; olefins are 1,5-cyclooctadiene ($C_8H_{12}$), 1,3,5,7-cyclooctatetraene ($C_8H_8$), cyclohexene ($C_6H_{10}$), cycloheptene ($C_7H_{12}$), and cyclooctene ($C_8H_{14}$)) and [Ag(tfacac)(olefin)] (tfacac is the conjugate base of trifluoroacetylacetone; olefins are 1,5-cyclooctadiene and 1,3,5,7-cyclooctatetraene).

## Experimental Section

J. T. Baker 1,5-cyclooctadiene, Columbia Organic 1,3,5,7-cyclooctatetraene, and Aldrich cyclooctene, cycloheptene, and cyclohexene were used in the preparation of the olefin compounds. Nmr spectra were recorded on a Varian A-60 spectrometer and are reported in Table I. Molecular weights were determined cryoscopically. Elemental analyses were performed by Instranal Labs. Silver analyses were performed gravimetrically by precipitation of the bromide salt. Conductance measurements were performed with an Industrial Instruments Model 16B2.

**Preparation of Ag(hfacac)($C_8H_8$).**—A 5.92-g (34.9-mmole) amount of silver nitrate was dissolved in 30 ml of water and 4 ml of 1,3,5,7-cyclooctatetraene was added. To this solution was added a solution of Na$^+$ hfacac$^-$, prepared by addition of 1.125 g (28.14 mmol) of sodium hydroxide to 5.876 g (28.14 mmol) of Hfacac in water, yielding a flocculent white precipitate. (Occasionally a dark oil forms which may be due to a slight excess of sodium hydroxide. This oil can be extracted from the aqueous solution with benzene and recrystallized yielding the desired product.) Filtration and subsequent recrystallization from benzene–cyclohexane yielded 5.029 g (12.0 mmol) of the desired product. *Anal.* Calcd for $AgC_{13}H_9O_2F_6$: C, 37.25; H, 2.17; Ag, 25.75; mol wt 419. Found: C, 37.22; H, 2.26; Ag, 25.71; mol wt 354 (benzene).

**Preparation of Ag(hfacac)($C_8H_{12}$).**—Procedure identical with that of [Ag(hfacac)($C_8H_8$)] except that recrystallization was from chloroform. *Anal.* Calcd for $AgC_{13}H_{13}O_2F_6$: C, 36.90; H, 3.10; Ag, 25.50; mol wt 423. Found: C, 36.78; H, 3.22; Ag, 25.51; mol wt 391 (benzene), 734 (cyclohexane), 435 (bromoform). Conductivity data: Ag(hfacac)($C_8H_{12}$), 84 mhos; NaI, 1125 mhos ($10^{-3}$ *M* nitromethane solutions).

**Preparation of Ag(hfacac)($C_8H_{14}$).**—The procedure was identical with that of Ag(hfacac)($C_8H_8$) except that addition of Na$^+$-hfacac$^-$ to the aqueous solution containing Ag$^+$ and cyclooctene yielded an oil. This oil was extracted with benzene–cyclohexane and filtered, and the solution was allowed to evaporate yielding the desired product in 59% yield. *Anal.* Calcd for $AgC_{13}H_{15}O_2F_6$: C, 36.72; H, 3.56; mol wt 425. Found: C, 36.15; H, 3.47; mol wt 425 (bromoform).

**Preparation of Ag(hfacac)($C_6H_{10}$), Ag(hfacac)($C_7H_{12}$), Ag(tfacac)($C_8H_{12}$), and Ag(tfacac)($C_8H_8$).**—The procedure was identical with the preparation of Ag(hfacac)($C_8H_8$). The compounds were recrystallized from chloroform, dichloromethane, dichloromethane, and benzene and the yields were 45, 31, 29, and 52%, respectively. Satisfactory carbon and hydrogen analyses were not obtainable since these compounds lose olefin readily. The integrated nmr signals of freshly prepared samples were consistent with the given stoichiometries.

## Discussion

The preparation of the compounds reported in this work can be summarized by the equations

$$Ag^+NO_3^- + \text{olefin} \xrightarrow{H_2O} [Ag(\text{olefin})]^+NO_3^-$$

$$[Ag(\text{olefin})]^+NO_3^- + Na^+Xacac^- \xrightarrow{H_2O} [Ag(\text{olefin})(Xacac)] \downarrow + Na^+NO_3^-$$

where X = hf or tf.

The qualitative stability of these compounds is dependent upon the type of $\beta$-diketonate anion present in the compound. For example, Ag(hfacac)(cyclooctadiene) can be stored for weeks at 0° without any appreciable change, while Ag(tfacac)(cyclooctadiene) loses olefin fairly rapidly and decomposes in a few days. We have attempted to prepare analogous compounds using the conjugate base of acetylacetone, but these failed. It may be that the qualitative stability of these compounds are inversely proportional to the basicity of the acetylacetonate derivative used.[2]

The vibrational spectra of the silver olefin compounds have been compared to those of the known compounds Cu(hfacac)$_2$ and Cu(tfacac)$_2$. All of the major bands associated with the hfacac and tfacac anion appear in the spectra of the silver compounds. The purpose of Table II is to provide evidence that the hfacac is bonded to silver *via* the oxygen atoms, rather than the $\gamma$-carbon atom. The first three compounds in Table II are thought to be bonded to the metal *via* the oxygens. The absorptions in the 1500–1700-cm$^{-1}$ region are thought to be due to the $\nu$(C$\overset{\dots}{-}$O) and $\nu$(C$\overset{\dots}{-}$C) modes.[3] Pd(acac)$_2$(P(C$_6$H$_5$)$_3$) has been shown to have one acac group attached to the metal *via* the oxygen atoms and the other *via* the $\gamma$-carbon atom.[4] The ir spectrum of

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[1] D. C. M. Beverwijk, G. J. M. van der Kerk, A. J. Leusink, and J. G. Noltes, *Organometal. Chem. Rev.*, **6**, 215 (1970), and references quoted therein.

[2] The variation of substituents on the acetylacetonate ligand and its effects upon stability constants, force constants, and adduct formation in copper(II) acetylacetonates are discussed in the following two references: (a) K. Nakamoto, Y. Morimoto, and A. E. Martell, *J. Phys. Chem.*, **66**, 346 (1962); (b) W. Partenheimer and R. S. Drago, *Inorg. Chem.*, **9**, 47 (1970).

[3] These frequencies are thought to be coupled. See K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," Wiley-Interscience, New York, N. Y., 1970, pp 247–256.

[4] See Table II, ref *d*.

TABLE I
$^1$H NMR DATA OF COMPOUNDS OF THE TYPE [Ag(Xacac)(olefin)][d]

| Compound | $\delta^c$(–CH) | $\delta$(>$CH_2$) | $\delta$(>CH)[a] | $\delta$($CH_3$) |
|---|---|---|---|---|
| [Ag(hfacac)(cyclooctadiene)] | 3.70 (3.6)[b] | 7.38 (8.3) | 3.93 (1.1) | |
| [Ag(hfacac)(cyclooctatetraene)] | 3.58 (8.0) | | 3.90 (1.0) | |
| [Ag(hfacac)(cyclooctene)] | 3.90 (1.9) | 7.55 (3.9)<br>8.41 (8.3) | 4.09 (1.0) | |
| [Ag(hfacac)(cycloheptene)] | 3.55 (2.0) | 7.65 (3.8)<br>8.30 (5.9) | 4.00 (1.3) | |
| [Ag(hfacac)(cyclohexene)] | 3.64 (1.8) | 7.71 (4.3)<br>8.27 (4.0) | 4.02 (0.9) | |
| [Ag(tfacac)(cyclooctadiene)] | 3.93 (3.8) | 7.48 (7.9) | 4.46 (1.2) | 7.92 (3.1) |
| [Ag(tfacac)(cyclooctatetraene)] | 3.83 (8.5) | | 4.43 (0.8) | 7.91 (2.7) |

[a] Methine proton on $\beta$-diketonate. [b] Integrated intensities in parentheses. [c] Chemical shifts reported using the $\tau$ scale with TMS as a standard. [d] X is hf or tf.

TABLE II
VIBRATIONAL FREQUENCIES OF SOME METAL $\beta$-DIKETONATES IN THE REGION 1600–1800 CM$^{-1}$

| Compound | Frequencies |
|---|---|
| Pd(hfacac)$_2$[a] | 1603 |
| Rh(hfacac)($C_8H_{14}$)$_2$[b] | 1621, 1602 |
| Cu(hfacac)$_2$[c] | 1646, 1617 |
| Pd(hfacac)$_2$(P($C_6H_5$)$_3$)[d] | 1768, 1723, 1656, 1629 |
| Ag(hfacac)(P($C_6H_5$)$_3$)$_2$[e] | 1663, 1640 sh |
| Ag(hfacac)($C_8H_{12}$) | 1667, 1634 |
| Ag(hfacac)($C_8H_8$) | 1660, 1636 |
| Ag(hfacac)($C_8H_{14}$) | 1667, 1640 sh |
| Ag(hfacac)($C_7H_{12}$) | 1663, 1644 sh |
| Ag(hfacac)($C_6H_{10}$) | 1678, 1644, 1615 |
| Ag(tfacac)($C_8H_{12}$) | 1635, 1620 sh |
| Ag(tfacac)($C_8H_8$) | 1645, 1625 sh |

[a] Prepared by addition of sodium hexafluoroacetylacetonate to a palladium chloride suspension in hot water. Product sublimed at 90° (1 Torr). [b] Prepared by addition of potassium carbonate and hexafluoroacetylacetone to [RhCl($C_8H_{14}$)$_2$]$_2$ in dichloromethane. Recrystallized from dichloromethane–petroleum ether. [c] Prepared by method given by C. H. Ke and N. C. Li, *J. Inorg. Nucl. Chem.*, **28**, 2255 (1966). [d] Prepared in a manner identical with that for Pd(acac)$_2$(P($C_6H_5$)$_3$) given by S. Baba, T. Ogura, and S. Kawaguchi, *Inorg. Nucl. Chem. Lett.*, **7**, 1195 (1971). [e] D. Gibson, B. F. G. Johnson, and J. Lewis, *J. Chem. Soc. A*, 367 (1970).

Pd(hfacac)$_2$(P($C_6H_5$)$_3$) is also consistent with this formulation. One observes the $\nu$(C=O) modes in the carbon-bonded hfacac at 1768 and 1723 cm$^{-1}$. These absorptions are absent in the silver compounds indicative that the bonding of the hfacac to the silver is *via* the oxygen atoms.

The nmr spectra in chloroform-*d* are consistent with the formulation Ag(Xacac)(olefin). The chemical shifts of the coordinated olefinic protons are all approximately 0.6 ppm downfield (to a lower $\tau$ value) from the uncoordinated "free" olefin. Addition of free olefin to a solution of the silver olefin compounds results in an upfield shift of the olefinic peak indicative that a rapid dissociation of the olefin from the Ag(Xacac) moiety occurs in solution. This is commonly observed with silver olefin compounds.[5] This labile dissociation of the olefin moiety would explain why the chemical shift of all the olefinic protons in cyclooctatetraene are the same. The lability of the olefin–metal bond prevents definitive structural assignments *via* nmr from being made, such as the differentiation of oxygen and carbon bonding of the $\beta$-diketonate group. The nmr spectrum of Ag($C_8H_8$)(hfacac) does not change significantly when cooled to −30°.

Molecular weight measurements indicate that Ag(hfacac)(cyclooctadiene) and Ag(hfacac)(cyclooctene) are monomers in bromoform and Ag(hfacac)(cyclooctadiene) is partially polymeric in cyclohexane. The molecular weights of Ag(hfacac)(cyclooctadiene) and Ag(hfacac)(cyclooctatetraene) in benzene are lower than theoretically calculated for these compounds and correspond closely to the compound [Ag(hfacac)(benzene)] (mol wt 393). The conductance data suggest that [Ag(hfacac)($C_8H_{12}$)] is nonionic in nitromethane.

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

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## Titanium(III) Chloride–Bis(alkylphosphine) Complexes

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Titanium(III) chloride–bis(alkylphosphine) complexes have been prepared by direct combination of the components in toluene at elevated temperature. The alkylphosphines include methylphosphine, dimethylphosphine, trimethylphosphine, and triethylphosphine. Attempts to prepare titanium trichloride complexes of the more weakly basic phosphorus trifluoride, phosphorus trichloride, and triphenylphosphine under a variety of experimental conditions were unsuccessful. The only other reported titanium(III) phosphine complex is $TiCl_3 \cdot [(C_2H_5)_2P]_2C_2H_4$.[1]

These complexes are soluble in benzene and the molecular weight of the triethylphosphine adduct in benzene was shown by freezing point depression to be equal to that of the titanium(III) chloride–bis(triethylphosphine) monomer. The remaining compounds of the series are by analogy regarded as monomers. Our interest in these complexes centered around their use as homogeneous hydrogenation and polymerization catalysts.

The complexes possess two properties which make their consideration as homogeneous catalysts attractive. (1) They are soluble in nonpolar or slightly polar,

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(1) J. Chatt and R. G. Hayter, *J. Chem. Soc.*, 1343 (1963).