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Propylene Complexes of Cu, Ag, and Au Atoms: Matrix Isolation ESR Study

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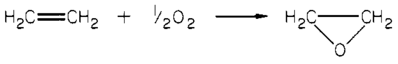
Abstract: Cu, Ag, and Au atoms were trapped in argon matrices containing propylene and were examined by electron spin resonance spectroscopy. Spectral analyses revealed the formation of mono- and diligand complexes in the cases of Cu and Au atoms. The Ag atoms failed to form any bona fide complex. The g tensors and the hyperfine coupling tensors of the complexes were determined and analyzed. The monopropylene complexes are held by the dative interaction between the filled d_{xy} orbital of the metal and the antibonding π_y^* orbital of the ligand. The semifilled orbital is an sp-hybridized orbital of the metal pointing away from the ligand. In the dipropylene complexes the metal atom is flanked by two ligand molecules oriented parallel to each other. They are held by the dative interaction between the antibonding π_y^* orbitals of the ligands and the filled d_{xy} orbital and/or the semifilled p_x orbital of the metal atom parallel to the ligands.

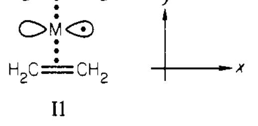
Partial oxidation of ethylene to ethylene oxide using Ag metal as a catalyst is an important industrial process. Other group 1B metals (Cu and Au) do not catalyze this reaction. Partial oxidation of propylene to propylene oxide, however, cannot be carried out by this route. The difficulty with propylene has been attributed to facile formation of allylic species through intramolecular hydrogen transfer from the methyl group.[1]



Recently we reported on our matrix isolation ESR (electron spin resonance) studies of interactions between the group 1B metal atoms and ethylene or acetylene molecules cocondensed in rare gas matrices.[2,3] In the case of ethylene it was shown that, while the Cu and Au atoms formed both mono- and bisligand complexes, the Ag atoms complexed only with the bis(ethylene) system. In the case of acetylene, while the Cu atoms formed the mono- and bisligand complexes, the Au atoms formed only the monoligand species, and the Ag atoms failed to form any bona fide complex.

Structural features of these complexes were elucidated as exemplified in I and II. In the monoligand structure I the unpaired electron is localized in an sp_y orbital of the metal atom pointing away from the ligand, and in the bisligand structure II it is located in the p_x orbital of the metal parallel to the ligands. Formally both structures can be stabilized by the dative interaction of the Dewar–Chatt–Duncanson scheme,[4,5] donation from the filled π_y orbital(s) of the ligand(s) into the vacant s and p_y orbitals of the metal atom, and back-donation from the filled d_{xy} orbital of the metal into the vacant π_y^* orbital(s). In structure II additionl dative interaction is possible between the semifilled p_x orbital and the vacant π_y^* orbitals.

I



II

The energy levels of the valence d orbitals determined from the optical data are −9.11, −11.32, and −10.36 eV for the Cu, Ag, and Au atoms, respectively.[6] The singularly weak complexing ability of Ag(0) has been attributed to the exceptional stability of its d orbital.[2] Bis(ethylene)silver(0), the only bona fide complex of Ag(0) thus far detected, is believed to be held essentially by the one electron dative interaction between the semifilled p_x orbital of the metal and the vacant π_y^* orbitals of the ligands. Obviously one should be cautious in relating reactions catalyzed by a condensed metal phase to reactions observed on metal atoms. It is nonetheless extremely enticing to predicate the unique catalytic capability of Ag metal in ethylene epoxidation on the unique complexing behavior of Ag atom with ethylene.

The present study was undertaken to examine the complexing ability of the Cu, Ag, and Au atoms with propylene. The study revealed that, while Cu and Au atoms interact with propylene exactly as they do with ethylene forming the mono- and bisligand complexes of structures I and II, the Ag atoms do not form any bona fide complex with propylene.

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[1] Cant, N. W.; Hall, W. K. *J. Catal.*, **1978**, *52*, 81.

[2] Kasai, P. H.; McLeod, D., Jr.; Watanabe, T. *J. Am. Chem. Soc.* **1980**, *102*, 179.

[3] Kasai, P. H. *J. Am. Chem. Soc.* **1983**, *105*, 6704.

[4] Dewar, M. J. S. *Bull. Soc. Chim. Fr.* **1951**, *18*, C79.

[5] Chatt, J.; Duncanson, L. A. *J. Chem. Soc.* **1953**, 2939.

[6] Moore, C. E. *Nat. Bur. Stand.* (*U.S.*) *Circ.* **1949**, *No. 467*, 1; **1952**, 2; **1958**, 3.

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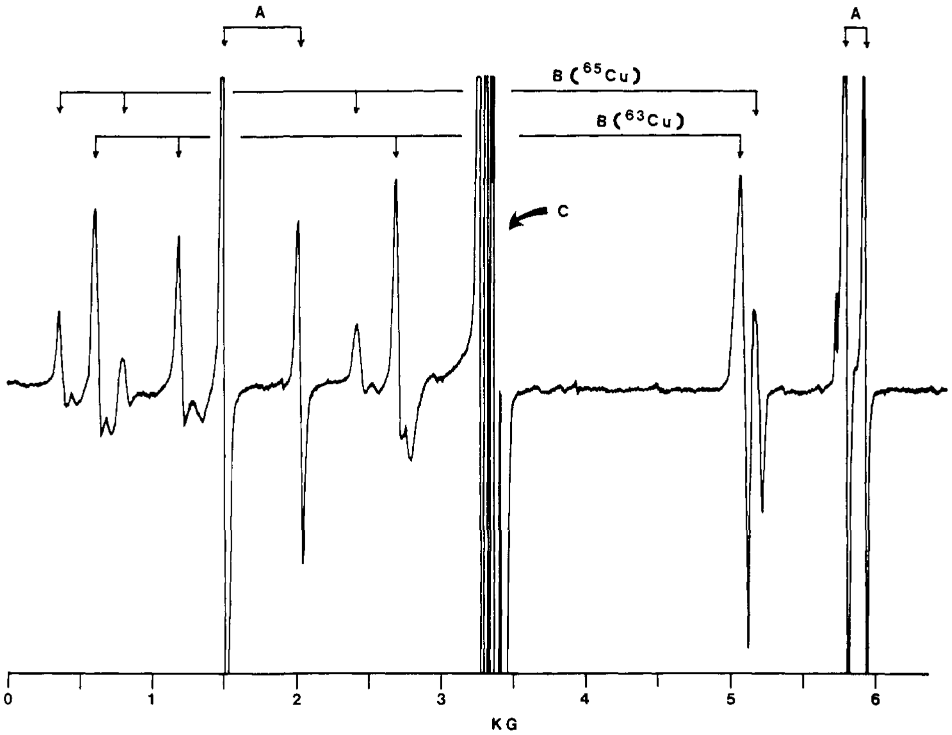

Figure 1. ESR spectrum observed from an argon matrix containing Cu atoms and propylene-d_6 (3%).

Experimenal Section

A liquid helium cryostat and an X-band ESR spectrometer system that would allow trapping of high temperature vapor-phase species in an inert gas matrix, and observation of the resulting matrix by ESR has already been described.[7] In the present series of experiments, the Cu, Ag, and Au atoms were generated from resistively heated tantalum cells and were trapped in argon or neon matrices containing propylene (0.1 ~ 10 mol %). The cells were heated to 1350, 1450, and 1500 °C for the Cu, Ag, and Au cases, respectively. In the case of Au, in order to mitigate the problem caused by the wetting and alloying property of molten gold, gold pellets were first placed in an alumina tube, capped with a molybdenum plug, and then placed in the tantalum cell.

Normal propylene (C_3H_6) obtained from Matheson, and deuterated propylene (C_3D_6) obtained from Merck Chemical Division were used as received. All the ESR spectra reported here were recorded while the matrices were maintained at ~4 K. The spectrometer frequency locked to the sample cavity was 9.4245 GHz.

Spectra and Assignments

Cu Atom–Propylene Complexes. The ESR spectrum of Cu atoms ($3d^{10}4s^1$) isolated in rare gas matrices has already been reported.[8] There are two naturally abundant Cu isotopes, ^{63}Cu (natural abundance = 69%, $I = {}^3/_2$, $\mu = 2.2206\beta_n$) and ^{65}Cu (natural abundance = 31%, $I = {}^3/_2$, $\mu = 2.3790\beta_n$). Owing to the large hf (hyperfine) interactions with those nuclei, the ESR spectrum of Cu atoms observed with an X-band spectrometer shows only two resonance transitions; one corresponding to the "NMR" transition ($M_s = -{}^1/_2$, $m_I = -{}^1/_2 \leftrightarrow -{}^3/_2$) occurs at 1.5 and 2.0 KG for ^{63}Cu and ^{65}C, respectively, and the other corresponding to the ESR transition ($M_s = -{}^1/_2 \leftrightarrow +{}^1/_2$, $m_I = -{}^3/_2$) occurs at 5.8 and 6.0 KG.

Figure 1 shows the ESR spectrum observed from an argon matrix containing Cu atoms and perdeuteriopropylene, C_3D_6 (3%). It is very similar to the spectrum of the Cu/ethylene/Ar system reported earlier.[2] Three types of signals, A, B, and C, are indicated. The signals A are due to isolated Cu atoms. The signals B and C were assigned to the Cu(O)-monopropylene and Cu(O)–dipropylene complexes, respectively, following the assignments made in the Cu/ethylene/Ar situation.

Table I. Observed Resonance Positions of ^{63}Cu(O)-Monopropylene and ^{197}Au(O)-Monopropylene Generated in Argon Matrices[a]

		H(m)[b]			
complex	axis	$+{}^3/_2$	$+{}^1/_2$	$-{}^1/_2$	$-{}^3/_2$
Cu-propylene	1	629	1364	2812	5162
	2	655	1203	2714	5075
	3	749	1223	2704	5126
Au-propylene	1	2348	2871	3505	4263
	2	2385	2896	3525	4283
	3	2560	(3101)	3779	4583

[a] Given in G; microwave frequency 9.425 GHz. [b] Accuracy: ±5 G for Cu-propylene and ±3 G for Au-propylene. When the signal is masked by others, the computed value is given in parentheses.

The quartet patterns of the B signals are the hf structures due to the ^{63}Cu and ^{65}Cu nuclei. Their spacings, however, are too large to be analyzed by the usual second-order solution of a spin Hamiltonian. For a radical ($S = {}^1/_2$) with one magnetic nucleus, if the principal axes of the g tensor and the hf coupling tensor coincide, and the magnetic field is parallel to the z axis, the spin Hamiltonian can be written as follows:

$$\mathcal{H}_{\text{spin}} = g_z\beta HS_z + A_zS_zI_z + A_xS_xI_x + A_yS_yI_y \tag{1}$$

where A_x, A_y, and A_z are the elements of the principal hf coupling tensor. It has been shown that the resonance field $H_z(m)$ of a hf component ($m_I = m$) is then given accurately by the following "continued fraction" expression[2]

$$H_z(m) = H_z{}^0 - mA'_z - F - G \tag{2}$$

where

$$F = \frac{Q^2[I(I+1) - m(m+1)]}{H_z(m) + (m + {}^1\!/_2)A'_z + F}$$

$$G = \frac{Q^2[I(I+1) - m(m-1)]}{H_z(m) + (m - {}^1\!/_2)A'_z + G}$$

and $H_z{}^0 = h\nu/g_z\beta$, $A'_x = A_x/g_x\beta$, $A'_y = A_y/g_y\beta$, $A'_z = A_z/g_z\beta$,

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[7] Kasai, P. H. *Acc. Chem. Res.* **1971**, *4*, 329.

[8] Kasai, P. H.; McLeod, D., Jr. *J. Chem. Phys.* **1971**, *55*, 1566.

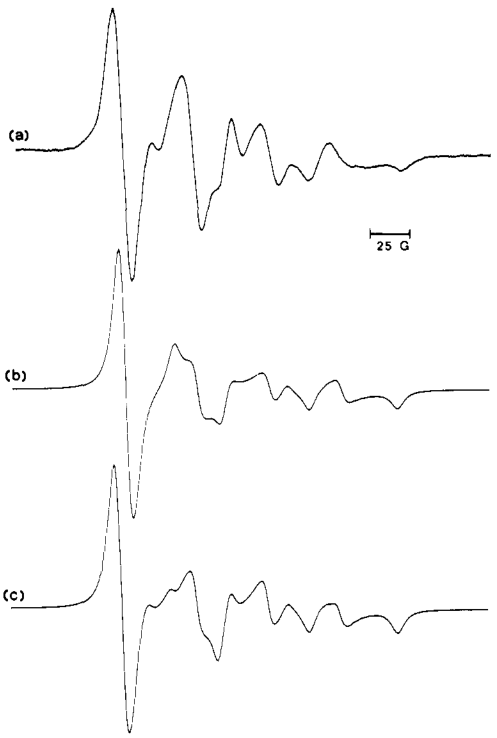

Figure 2. (a) C signal (of Figure 1) shown in an expanded scale. (b) Simulated spectrum based upon the parameters given in the text, allowing only the normal transitions. (c) Simulated spectrum based upon the same parameters but allowing both the normal and forbidden transactions.

and $Q = (1/4g_z)(A'_x g_x + A'_y g_y)$. The expressions for resonance positions $H_x(m)$ and $H_y(m)$ can be generated by appropriate permutations of (g_x, g_y, g_z) and (A'_x, A'_y, A'_z) in eq 2.

The B signals, when examined in an expanded scale, revealed characteristic powder patterns of an orthorhombic system ($g_x \neq g_y \neq g_z$, and/or $A_x \neq A_y \neq A_z$).[9] The resonance positions $H_i(m)$ ($i = x, y, z$) determined from the B signals due to $^{63}Cu(C_3D_6)$ are given in Table I. From the resonance positions of the $m_1 = \pm^3/_2$ components and the set of eq 2 developed above for $H_x(m)$, $H_y(m)$, and $H_z(m)$, the consistent set of g values and hf coupling constants can be determined through a computer-assisted iteration process. The g tensor and the ^{63}Cu hf coupling tensor of the Cu(O)–monopropylene complex were thus determined as follows: follows:

$$g_1 = 2.025\ (4) \qquad g_2 = 2.010\ (4) \qquad g_3 = 1.964\ (4)$$
$$A_1 = 3.991\ (8) \qquad A_2 = 4.067\ (8) \qquad A_3 = 3.829\ (8)\ \text{GHz}$$

The resonance positions of $^{63}Cu(C_3D_6)$ and $^{65}Cu(C_3D_6)$ computed from eq 2 based upon these parameters and the known ratio of the nuclear magnetic moments of ^{63}Cu and ^{65}Cu are all within the experimental uncertainty (±5 G) of the observed values.

When the experiment was repeated with normal propylene (C_3H_6), no discernible change was noted in the B signals. The large, essentially isotropic, hf interaction with the Cu nucleus and the absence of hf structure due to protons are consistent with the monoligand structure I discussed earlier.

Figure 2a shows the C signals (of Figure 1) in an expanded scale. Other than the slightly increased line width and several minor features the overall pattern seen here is essentially identical with that observed from bis(ethylene)copper(0). The spectrum is hence assigned to Cu(0)–dipropylene having the diligand structure II discussed earlier. As shown for the spectrum of bis(ethylene)copper(0), the complex, irregular pattern seen here is the composite result of an anisotropic g tensor, a small but highly anisotropic hf coupling tensor of the Cu nucleus, and a nuclear quadrupole interaction of the Cu nucleus.

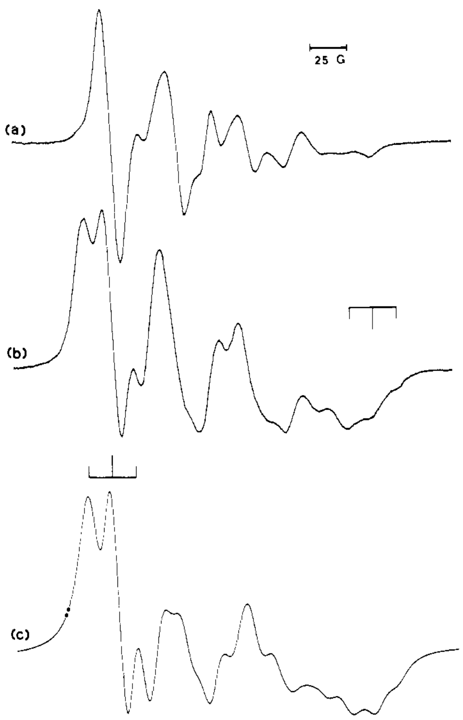

Figure 3. ESR spectra observed from (a) Cu/propylene(C_3D_6, 3%)/Ar and (b) Cu/propylene(C_3H_6, 3%)/Ar. (c) Simulated spectrum based upon the parameters used in Figure 2c and an additional isotropic hf interaction of 15 G with two protons.

For a radical ($S = {}^1/_2$) with one magnetic nucleus ($I > {}^1/_2$) a spin Hamiltonian including the nuclear quadrupole interaction may be written as follows:

$$\mathcal{H}_{\text{spin}} = g_x\beta H_x S_x + g_y\beta H_y S_y + g_z\beta H_z S_z + A_x S_x I_x + A_y S_y I_y + A_z S_z I_z + P_x I_x^2 + P_y I_y^2 + P_z I_z^2 \quad (3)$$

Here (g_x, g_y, g_z), (A_x, A_y, A_z), and (P_x, P_y, P_z) are the diagonal elements of the principal g tensor, the hf coupling tensor, and the quadrupole interaction tensor. A treatment of this Hamiltonian by the second-order perturbation theory ($g\beta H >> A >> P$) for an axially symmetric case has been shown by Bleaney.[10] A similar treatment for an orthorhombic case has also been performed; the equations relating to the resonance fields and the transition probabilities of the normal transitions ($\Delta M_s = \pm 1$, $\Delta m_I = 0$) and those of the forbidden transitions ($\Delta M_s = \pm 1$, $\Delta m_I = \pm 1$ or ± 2) have been reported.[2] The parametric assignment of the spin Hamiltonian (3) from a powder pattern is then possible through a trial-and-error simulation of the spectrum based on these equations.[11] The g tensor, the hf coupling tensor, and the quadrupole interaction tensor of the Cu(0)–dipropylene comlex were thus determined as follows:

	1	**2**	**3**
g	2.013 (2)	2.001 (2)	1.989 (2)
A (in G)	35.0 (5)	45.0 (5)	55.0 (5)
P (in G)	−2.0 (2)	4.0 (2)	−2.0 (2)

Figure 2b is the computer-simulated spectrum based upon these parameters allowing only the normal transitions. A Lorentzian line shape with a line width of 10 G was assumed for the simulation. Figure 2c shows the computer-simulated spectrum based upon the same parameters but allowing both the normal and the forbidden transitions caused by the nuclear quadrupole effect.

ESR spectra of Cu(0)–dipropylene observed from the Cu/C_3D_6 (3%)/Ar and Cu/C_3H_6 (3%)/Ar systems are compared in Figure

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[9] For discussion of ESR powder patterns, see, for example: Ayscough, P. B. "Electron Spin Resonance in Chemistry"; Methuen: London, 1967; Chapter 9.

[10] Bleaney, B. *Philos. Mag.* **1951**, *42*, 441.

[11] The powder pattern simulation program used is described in [Kasai, P. H. *J. Am. Chem. Soc.* **1972**, *94*, 5950] and also in ref 2.

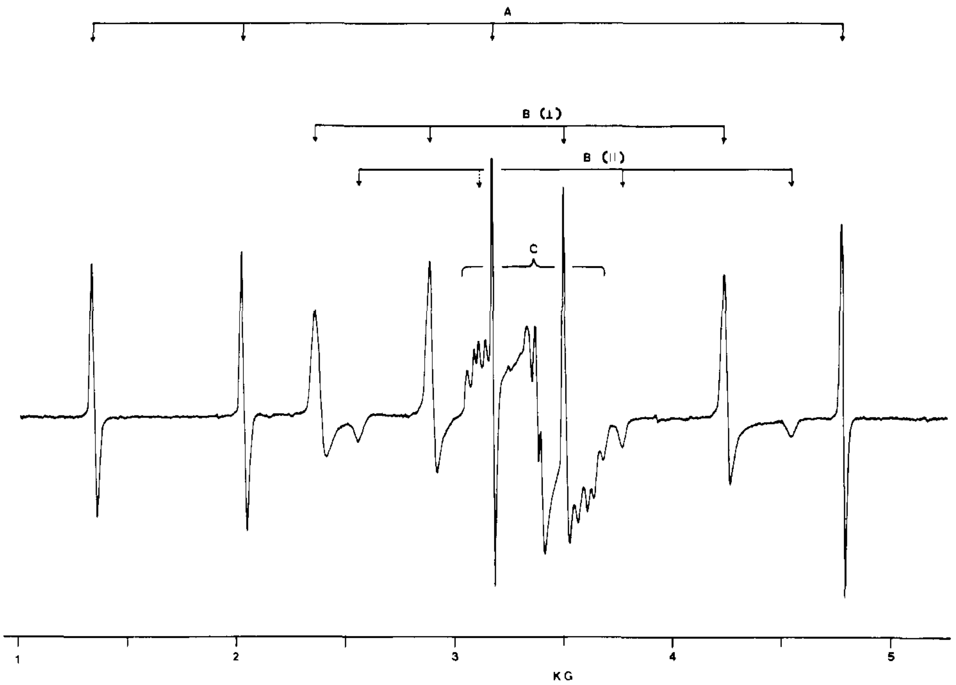

Figure 4. ESR spectrum observed from an argon matrix containing Au atoms and propylene-d_6 (10%).

3. The proton substitution clearly leads to additional splitting of the signals. In particular it appears to render a "1:2:1" triplet pattern to the outer components of the main quartet as indicated. Figure 3c shows the computer-simulated spectrum based upon the parameters given above and additional isotropic hf interactions of 15 G with two protons. The agreement between the observed and simulated spectra is considered reasonable. In the case of bis(ethylene)copper(0) no discernible difference was noted between the ESR spectra of deuterated and nondeuterated complexes. Thus, it is strongly suggested that the proton hf structures observed with Cu(0)–dipropylene are due to protons in the methyl groups, most probably one proton participtating from each methyl group.

Au Atom–Propylene Complexes. The ESR spectrum of Au atoms ($5d^{10}6s^1$) isolated in rare gas matrices has already been reported.[8] It is characterized by a large, isotropic hf interaction with the ^{197}Au nucleus (natural abundance = 100%, $I = {}^3/_2$, $\mu = 0.1439\beta_n$). Figure 4 shows the ESR spectrum observed from the Au/C_3D_6 (10%)/Ar system. It is quite similar to the spectrum observed from the Au/ethylene/Ar system. Three types of signals, A, B, and C, are again recognized, as indicated. The signals A are due to isolated Au atoms. When the propylene concentration was lowered to 3.3%, the intensities of signals B and C decreased, respectively, by factors of ~3 and ~9. The B and C signals were hence assigned to Au(0)–monopropylene and Au(0)–dipropylene, respectively.

When examined in an expanded scale, the B signals of Au(0)–monopropylene also revealed characteristic powder patterns of an orthorhombic system. The observed resonance positions $H_i(m)$ ($i = x, y, x$) of the four hf components are shown in Table I. From the resonance positions of the $m_I = \pm{}^3/_2$ components and the set of eq 2 discussed earlier, the g tensor and the ^{197}Au hf coupling tensor of the Au(0)–monopropylene complex were determined as follows:

$$g_1 = 1.986\ (2) \qquad g_2 = 1.968\ (2) \qquad g_3 = 1.837\ (2)$$

$$A_1 = 1.759\ (2) \qquad A_2 = 1.728\ (2) \qquad A_3 = 1.719\ (2)\ \text{GHz}$$

The resonance positions $H_i(m)$ ($i = x, y, x$) of Au(C_3D_6) computed from eq 2 based on these parameters were all within the experimental uncertainty (±3 G) of the observed values. Again no discernible difference was noted betweenthe ESR spectra of deuterated and nondeuterated Au(0)–monopropylene. The large, essentially isotropic hf interaction with the Au nucleus and the absence of hf interaction with protons are consistent with the monoligand structure I.

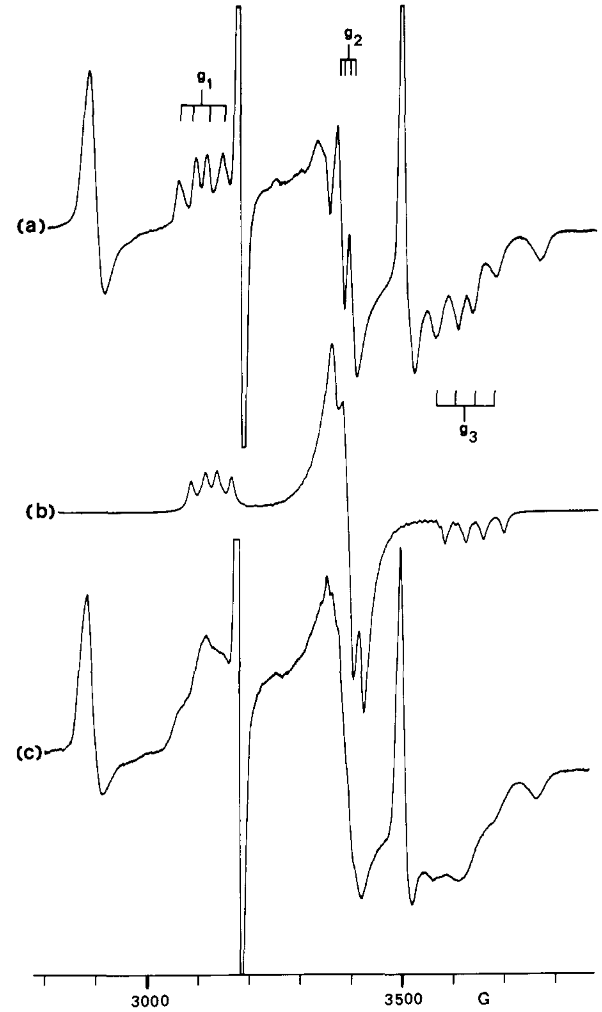

Figure 5. (a) C signal region (of Figure 4) shown in an expanded scale. (b) Simulated spectrum based upon the parameters given in the text. (c) C signal region observed from the Au/propylene(C_6H_6, 10%)/Ar system.

Figure 5a shows the C signals (of Figure 4) in an expanded scale. They overlap with the $m_I = -{}^1/_2$ component of the Au atom

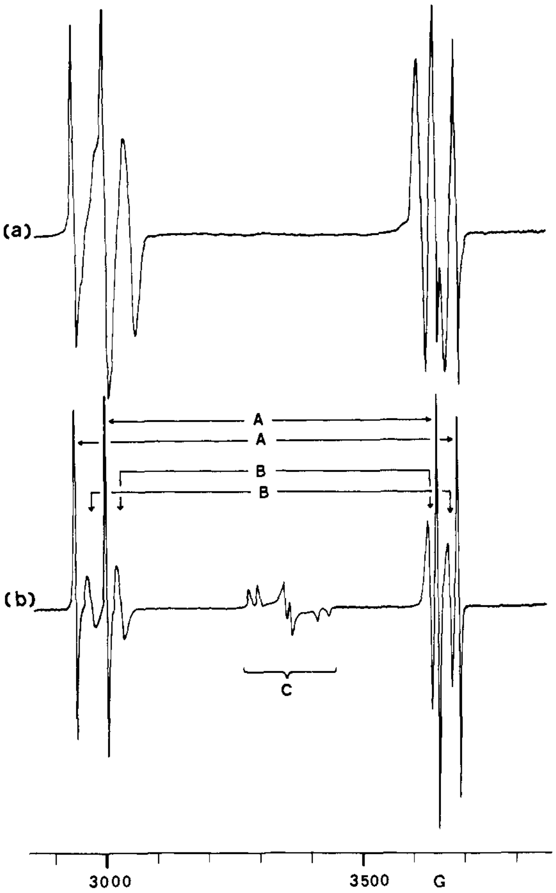

Figure 6. ESR spectra observed from (a) the Ag/propylene(C_3D_6, 3%)/Ar system and (b) the Ag/ethylene(C_2D_4, 3%)/Ar system.

spectrum and the $m_I = \pm^1/_2$ components of the Au(0)-monopropylene spectrum. The C signals themselves can be recognized as the powder pattern of a system having a highly anisotropic g tensor and small hf structures (a quartet due to ^{197}Au) resolved along two principal axes of the g tensor. The recognized pattern is essentially identical with that of bis(ethylene)gold(0). The spectrum was hence assigned to Au(0)-dipropylene having the diligand structure II. The g tensor and the ^{197}Au hf coupling tensor of the complex were determined as follows:

$$g_1 = 2.159\ (2) \quad g_2 = 1.988\ (2) \quad g_3 = 1.853\ (2)$$
$$A_1 = 28.1 \pm 0.5 \quad A_2 = 10.0 \pm 2.0 \quad A_3 = 40.0 \pm 0.5\ \mathrm{G}$$

The computer-simulated spectrum based on these parameters and a Lorentzian line shape with the line width of 14 G is shown in Figure 5b.

Figure 5c shows the C signal region of the spectrum observed from the Au/C_3H_6/Ar system. The spectrum of Au(0)-monopropylene is clearly not affected by the proton substitution. In contrast the spectrum of Au(0)-dipropylene is severely broadened by the hf interaction with protons. In the case of bis(ethylene)gold(0) no difference was noted between the ESR spectra of deuterated and nondeuterated complexes. It is therefore concluded that the proton hf interactions noted for Au(0)-dipropylene are due to protons in the methyl groups.

Ag Atom-Propylene Complexes. The ESR spectrum of Ag atoms ($4d^{10}5s^1$) isolated in rare gas matrices has also been reported.[8] The spectrum consists of two sets of sharp doublets with the respective spacings of 650 and 750 G. The doublets are due to ^{107}Ag (natural abundance = 51%, $I = ^1/_2$, $\mu = -0.1130\beta_n$), and ^{109}Ag (natural abundance = 49%, $I = ^1/_2$, $\mu = -0.1299\beta_n$).

Figure 6a shows the ESR spectrum observed from the Ag/C_3D_6 (3%)/Ar system. It is compared with the spectrum of the Ag/C_2D_4 (3%)/Ar system reported earlier (Figure 6b).[2] Three signals, A, B, and C, are indicated in the latter. The signals A are due to isolated Ag atoms. The signals B have been attributed to the Ag(0)-ethylene pseudocomplex, Ag atoms interacting weakly with ethylene monomers; the Ag hf coupling constants of the B signals are only 6% less than those of isolated Ag atoms. The signals C are due to bis(ethylene)silver(0); the presence of two ethylene molecules in the complex and its bisligand structure II have been substantiated by the ESR spectrum of ^{13}C enriched species.[12] It is thus extremely intriguing that, in Figure 6a, signals due to pseudocomplexes are strong, but signals attributable to a bona fide diligand complex are totally absent. Increasing the propylene concentration to 10% did not alter the conclusion.

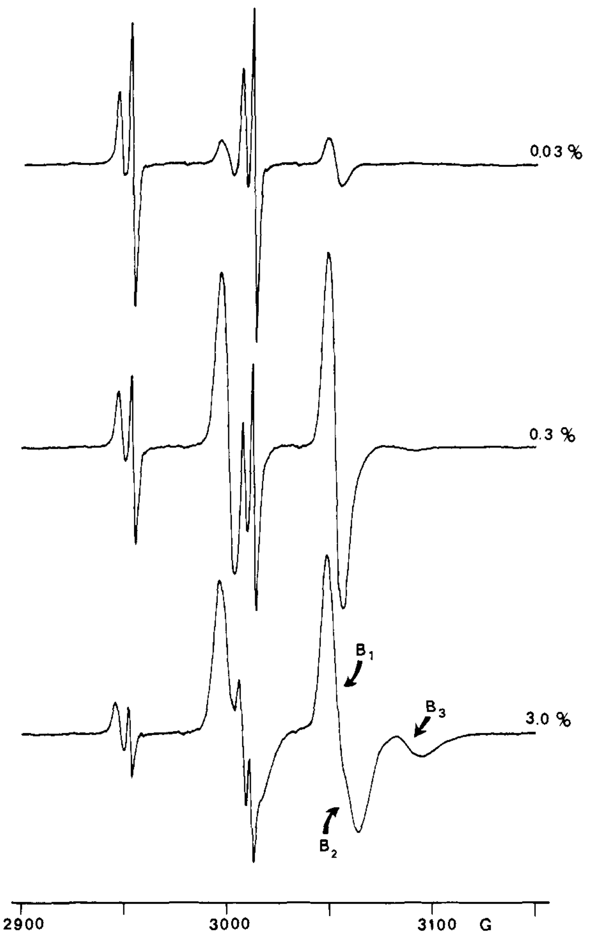

Figure 7. ESR spectra (the lower field section of the Ag atom doublet) observed from neon matrices containing Ag atoms and propylene (C_3D_6) of indicated concentration.

Generally neon matrices afford ESR signals with the narrowest matrix line broadening due presumably to more complete annealing of the matrix. Figure 7 shows the lower field section of the ESR spectra observed from a series of matrices, Ag/C_3D_6 (0.03, 0.3, 3.0%)/Ne. In neon matrices signals A due to isolated Ag atoms are split by a site effect. The figure clearly reveals that the B signals grow with increasing propylene concentration and that there are several different types of B signals. Three types of B signals, B_1, B_2, and B_3, can be recognized. It is suggested that they belong to Ag atoms weakly interacting with propylene monomers, dimers, and oligomers ($n \geq 3$), respectively. The g values and the hf coupling constants of these species were assessed as follows:

	g	A(^{107}Ag), GHz
B_1	1.999 (1)	1.573 (3)
B_2	1.998 (1)	1.531 (3)
B_3	1.999 (1)	1.391 (3)

These Ag coupling constants are 9%, 12%, and 20%, respectively, less than those of the A signels (1.735 GHz) in the same neon matrices.

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(12) Kasai, P. H. *J. Phys. Chem.* **1982**, *86*, 3684.

Table II. g Tensors and ^{63}Cu or ^{197}Au hf Coupling Tensors of Mono- and Bis(propylene) Complexes of Cu and Au Atoms

complex	g tensor	hf tensor, MHz	other parameters
$H_2C{=}CHMe$ ⋮ Cu	$g_x = 2.025\ (4)$ $g_y = 2.010\ (4)$ $g_z = 1.964\ (4)$	$A_x = 3991\ (8)$ $A_y = 4067\ (8)$ $A_z = 3829\ (8)$	
$H_2C{=}CHMe$ ⋮ Au	$g_x = 1.968\ (2)$ $g_y = 1.986\ (2)$ $g_z = 1.837\ (2)$	$A_x = 1728\ (2)$ $A_y = 1759\ (2)$ $A_z = 1719\ (2)$	
$H_2C{=}CHMe$ ⋮ Cu ⋮ $H_2C{=}CHMe$	$g_x = 2.001\ (2)$ $g_y = 1.989\ (2)$ $g_z = 2.013\ (2)$	$\lvert A_x\rvert = 126\ (2)$ $\lvert A_y\rvert = 153\ (2)$ $\lvert A_z\rvert = 99\ (2)$	quad. coupl (G) $P_x = 4, P_y = -2, P_z = -2$ coupl. to two H's in methyls = 15 G
$H_2C{=}CHMe$ ⋮ Au ⋮ $H_2C{=}CHMe$	$g_x = 1.988\ (2)$ $g_y = 1.853\ (2)$ $g_z = 2.159\ (2)$	$\lvert A_x\rvert = 28\ (6)$ $\lvert A_y\rvert = 104\ (2)$ $\lvert A_z\rvert = 85\ (2)$	

Discussion

The g tensors and the hf tensors of the bona fide Cu(0)– and Au(0)–propylene complexes detected in the present study are compiled in Table II. The table incorporates the results of g tensor analysis (presented below) which allowed determination of the orientation of the tensors relative to the respective molecular axes. As adopted in the mono- and bisligand structures I and II, the z axis is perpendicular to the molecular plane, while the x axis is parallel to the C=C bond(s). The coupling constants determined in G were converted to those in MHz through multiplication by $g_i\beta$. For the dipropylene complexes four structural isomers are possible depending upon the relative positions of the two methyl groups. Though the structure with the trans arrangement of the methyl groups is the most likely one, the exact structure cannot be determined presently.

As inferred earlier in describing structures I and II and as discussed in detail in the previous reports,[2,3] the semifilled orbitals of the mono- and bis(ethylene) complexes of the group 1B metal atoms are given by the following LCAO molecular orbitals, respectively.

$$\phi_1 = a_1\phi_M(s) - b_1\phi_M(p_y) + C_1\pi_y \tag{4}$$

$$\phi_2 = a_2\phi_M(p_x) + (b_2/2^{1/2})(\pi_y{}^* - \pi_y{}^{*\prime}) \tag{5}$$

Here $\phi_M(s)$ and $\phi_M(p_y)$, etc. represent the indicated valence orbitals of the metal atom, and π_y and $\pi_y{}^*$ the indicated bonding and antibonding π orbitals of the ligand(s). The π_y orbital in eq 4 is due to the orthogonality requirement. These equations should then also describe the semifilled orbitals of the mono- and dipropylene complexes of Cu and Au atoms observed here.

It has been shown that, for a radical with a nondegenerate ground state $|0\rangle$, deviation of the g tensor from the spin only value (g_e = 2.0023) is given by eq 6.[13] Here i (x, y, z) represents an

$$g_i - g_e = -2\lambda\sum_n \frac{\langle 0|L_i|n\rangle\langle n|L_i|0\rangle}{E_n - E_o} \tag{6}$$

axis of the principal g tensor, L_i the orbital angular momentum operator, and λ the one-electron spin–orbit coupling constant. The summation is performed over all the excited states. In evaluating eq 6 in terms of LCAO–MO's, only one-centered integrals need to be retained, and for each atomic integral the spin–orbit coupling constant of the particular atom is chosen. The spin–orbit coupling constants of Cu (evaluated from its $3d^{10}4p^1$ state) and Au (evaluated from its $5d^{10}6p^1$ state) are 165 and 2544 cm^{-1}, respectively.[6] The spin–orbit coupling constant of carbon is only 15 cm^{-1}. It follows that the g tensors of the Cu(0) and Au(0) complexes examined here should be determined essentially by the $\phi_M(p)$ parts of eq 4 and eq 5.

Recalling that the matrix element $\langle p_i|L_j|p_k\rangle$ would have nonvanishing value only when the indices i, j, and k are all different from each other, it is asserted that g_y should show the smallest deviation from g_e in the case of the monopropylene complexes and g_x in the case of the dipropylene complexes. In the monopropylene complexes the lowest unoccupied orbital ($E_n - E_o > 0$) would be the antibonding $\pi_y{}^*$ orbital of the ligand mixed with the metal p_x orbital. The g value showing the largest negative shift was hence assigned as g_z. In the dipropylene complexes the highest occupied orbital ($E_n - E_o < 0$) would be the bonding π_y orbitals of the ligands mixed with the metal p_y orbital, and the lowest unoccupied orbital ($E_n - E_o > 0$) would be the metal p_z orbital. The g value with a large positive shift was hence identified as g_z, and the g value with a large negative shift was assigned as g_y.

The essential feature of the hf coupling tensor to a magnetic nucleus is determined by the distribution of the unpaired electron in the vicinity of the nucleus. The hf coupling tensors to the metal nuclei of the monopropylene complexes should hence be axially symmetric about the y axis, and those of the diproyplene complexes about the x axis. It has been shown that the principal elements, $A_\parallel$ and $A_\perp$, of an axially symmetric hf coupling tensor can be related to the isotropic term $A_{\rm iso}$ and the anisotropic term $A_{\rm dip}$ as follows:[14]

$$\begin{aligned} A_\parallel &= A_{\rm iso} + 2A_{\rm dip} \\ A_\perp &= A_{\rm iso} - A_{\rm dip} \end{aligned} \tag{7}$$

where

$$A_{\rm iso} = g_e\beta_e g_n\beta_n \frac{8\pi}{3}|\phi(o)|^2$$

$$A_{\rm dip} = g_e\beta_e g_n\beta_n\left\langle \frac{3\cos^2\theta - 1}{2r^3}\right\rangle = g_e\beta_e g_n\beta_n \frac{2}{5}\left\langle\frac{1}{r^3}\right\rangle_p \text{ or } -g_e\beta_e g_n\beta_n \frac{2}{7}\left\langle\frac{1}{r^3}\right\rangle_d$$

Here $|\phi(o)|^2$ respresents the spin density at the nucleus, r the separation between the unpaired electron and the nucleus, and θ the angle between r and the symmetry axis. In an LCAO approximation of the semifilled orbital only the spin density in an s orbital contributes to $A_{\rm iso}$, and that in a non-s orbital contributes to $A_{\rm dip}$. The last two expressions for $A_{\rm dip}$ are for a unit spin density in a p orbital and for a unit spin density in the $d_{x^2-y^2}$ orbital, respectively.

Contrary to the discussion presented above the observed Cu hf coupling tensor of Cu(0)–monopropylene is not axially symmetric. The variance is ascribed to admixture of the Cu $3d_{x^2-y^2}$ orbital in the semifilled orbital. Admixture of a 3d orbital would also account for the unusually large positive g shifts observed along the x and y directions. For the semifilled orbital of Cu(0)–monopropylene containing both the Cu $4p_y$ and $3d_{x^2-y^2}$ orbitals, eq 7 predicates the following orthorhomic expressions for the Cu hf coupling tensor:

$$\begin{aligned} A_x &= A_{\rm iso} - A_{\rm dip} - B_{\rm dip} \\ A_y &= A_{\rm iso} + 2A_{\rm dip} - B_{\rm dip} \\ A_z &= A_{\rm iso} - A_{\rm dip} + 2B_{\rm dip} \end{aligned} \tag{8}$$

where $A_{\rm dip}$ and $B_{\rm dip}$ represent the anisotropic terms due to the p_y and $d_{x^2-y^2}$ orbitals, respectively. Analysis of the observed coupling constants in terms of eq 8 yields $A_{\rm iso}$ = 3962 MHz, $A_{\rm dip}$ = 25 MHz, and $B_{\rm dip}$ = −54 MHz. These values may be compared with $A^0_{\rm iso}$ = 6151 MHz, the hf coupling constant of ^{63}Cu atoms ($4s^1$) isolated in an argon matrix,[2] $A^0_{\rm dip}$ = 206 MHz, a value estimated for a unit spin density in the Cu 4p orbital from the known hf splitting term $a_{(J=1/2)}$ of the ^{69}Ga atoms ($4s^24p^1$),[15] and $B_{\rm dip}$ = −342 MHz,

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(13) Pryce, M. H. L. *Proc. Phys. Soc. London, Sect. A* **1950**, *63*, 25.

(14) See, for example: Atkins, P. W.; Symons, M. C. R. "The Structure of Inorganic Radicals"; Elsevier: Amsterdam, 1967; Chapter 2.

a value computed by Morton and Preston for a unit spin density in the Cu 3d orbital from the Hartree–Fock–Slater atomic orbital.[16] We may thus conclude that the unpaired electron distribution among the Cu valence orbitals in Cu(0)–monopropylene is 0.64 in 4s, 0.13 in $4p_y$, and 0.16 in $3d_{x^2-y^2}$. These values should be regarded with due reservation since many approximations were made in the computation.

A similar analysis of the ^{197}Au hf coupling tensor observed on Au(0)–monopropylene yields $A_{iso} = 1735$ MHz, $A_{dip} = 11$ MHz, and $B_{dip} = -3$ MHz. They may be compared with $A^0_{iso} = 3138$ MHz, the hf coupling constant of Au atoms ($6s^1$) isolated in an argon matrix,[8] $A^0_{dip} = 48$ MHz, a value estimated for a unit spin density in the Au 6p orbital from the known hf splitting term $a_{(j={}^1/_2)}$ of the ^{205}Tl atoms ($6s^26p^1$),[15] and $B^0_{dip} = -38$ MHz, a value computed for a unit spin density in the Au $5d_{x^2-y^2}$ orbital by Morton and Preston.[16] The unpaired electron distribution among the Au valence orbitals in Au(0)–monopropylene is hence concluded to be 0.55 in 6s, 0.23 in $6p_y$, and 0.08 in $5d_{x^2-y^2}$.

As for the hf coupling tensors to the metal nuclei of the dipropylene complexes, owing to the dominance of the dipolar term, the signs of the coupling constants cannot be determined a priori. However, the axial symmetry of the coupling tensor about the x axis consistent with the semifilled orbital of eq 5 can be approximately realized if we assume as follows. For Cu(0)–dipropylene $A_x = +126$, $A_y = -153$, and $A_z = -99$ MHz, and for Au(0)–dipropylene $A_x = \pm 28$, $A_y = -104$, and $A_z = -85$ MHz. We should note that the proposed structure of the dipropylene complexes does not permit mixing of a d orbital into the semifilled orbital of eq 5. The departure of the coupling tensor from the axial symmetry must hence be ascribed to a spin density in the ligands and more likely to a negative spin density induced in the filled d orbitals. Since the contribution of these terms is difficult to assess, and it is relatively small, we shall assume $A_\parallel = A_x$ and $A_\perp = (A_y + A_z)/2$ and proceed to analyze the tensors based on eq 7. We then obtain for Cu(0)–dipropylene $A_{iso} = -42$ and $A_{dip} = +84$ MHz and for Au(0)–dipropylene $A_{iso} = -73$ and $A_{dip} = +22$ MHz. For the Au complex A_x was chosen to be -28 MHz since it yielded a much more reasonable distribution of the unpaired electron. The small, negative A_{iso}'s deduced here are attributed to polarization of filled s orbitals. The A_{dip}'s determined here, when compared with the A^0_{dip}'s cited earlier for the Cu 4p and Au 6p orbitals, show that the unpaired electron density in the metal p_x orbital is ~0.4 for both Cu(0)– and Au(0)–dipropylene. As reported earlier the spin density in the ligand section of Ag(0)–diethylene has been determined explicitly from the ^{13}C hf structure, the result being ~0.6.[12] The semifilled orbitals of these complexes are apparently similar.

As stated earlier, the proton hf interaction of 15 G observed with Cu(0)–dipropylene must be ascribed to two protons in the methyl groups. It strongly suggests a conformation in which each methyl group is locked in a position whereby one of its C–H bonds projects toward the Cu p_x orbital. In Cu(0)–diacetylene, where all the protons lie in the x–y molecular plane, a hf interaction of 28 G with the four equivalent protons has been observed.[2]

The most intriguing revelation of the present study is that, in sharp contrast to the Cu and Au atoms, the Ag atoms do not form any bona fide complex with propylene. As expected, the ESR spectra, hence the bonding characteristics of the mono- and dipropylene complexes of Cu and Au atoms revealed here, are essentially identical with those of the corresponding mono- and bis(ethylene) complexes reported earlier.[2] The mono- and bis(acetylene) complexes of Cu(0)[2] and monoacetylene complex of Au(0)[3] are also known; their ESR spectra and the indicated complexing schemes are also quite similar to those of the mono- and bis(ethylene) complexes of the respective atoms. The only bona fide complex thus far found between Ag atoms and ethylene or acetylene is bis(ethylene)silver(0). As stated earlier the energy levels of the valence d orbitals of the Cu, Au, and Ag atoms are -9.11, -10.36, and -11.32 eV, respectively.[6] Thus, the singularly weak complexing abilty of Ag(0) is attribued to the exceptional stability of its d orbitals, hence a decreased interaction between the filled d_{xy} orbital and the vacant, antibonding $\pi_y{}^*$ orbital of the ligand(s). The EHT (extended Hückel theory) molecular orbital calculation places the bonding and antibonding π orbitals of ethylene at -13.22 and -8.24 eV, respectively.[17] The same theory places the corresponding orbitals of propylene at -12.95 and -8.06 eV. The slightly higher level of the antibonding π^* orbital of the latter may account for nonexistence of Ag(0)–dipropylene. It is apparent that the formation of complexes between neutral atoms of group 1B and olefinic molecules through dative interaction is dependent with extreme delicacy upon the relative energy levels of interacting orbitals.

Registry No. $Cu(H_2C{=}CHMe)$, 89638-10-8; $Au(H_2C{=}CHMe)$, 89638-11-9; $Cu(H_2C{=}CHMe)_2$, 89638-12-0; $Au(H_2C{=}CHMe)_2$, 89638-13-1; Cu, 7440-50-8; Au, 7440-57-5; Ag, 7440-22-4; C_3D_6, 1517-52-8; C_3H_6, 115-07-1; C_2D_4, 683-73-8; $Au(C_3D_6)$, 89638-14-2; $Ag(C_2D_4)_2$, 82807-01-0.

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(15) See, for example: Kopfermann, H., "Nuclear Moments"; Academic Press: New York, 1958; pp 123–138. The A^0_{dip} obtained here is considerably larger than that estimated from the fine structure spacings of Cu atoms at the $3d^{10}4p^1$ state (ref 2). Available data show that A^0_{dip} values determined from the hf splitting terms are larger than those estimated from the fine structure spacing, and are in better agreement with theoretical values (ref 16).

(16) Morton, J. R.; Preston, K. F. *J. Magn. Reson.* **1978**, *30*, 577.

(17) Hoffman, R. *J. Chem. Phys.* **1963**, *39*, 1397.