

metal center on the development of stereochemistry at an adjacent carbon. Since other nucleophiles can be expected to react similarly to $\text{Li}(\text{C}_2\text{H}_5)_3\text{BH}$, and stereospecific methods for metal-alkyl bond cleavages have been developed for related systems,¹⁷ important extensions of these reactions in asymmetric organic synthesis can be anticipated.

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- Alkyl **1** has been reported previously.³ Data for **2**: ¹H NMR (CDCl_3) δ 7.54–7.22 (m, 15 H), 4.92 (s, 5 H), 2.10 (m, 1 H); 1.68 (m, 1 H), 1.58 (distorted t, 3 H); ¹³C NMR (CDCl_3) 89.5, 26.0, –17.4 ppm, and phenyl carbons; IR (CH_2Cl_2) ν_{NO} 1614 cm^{-1} ; mp 220 °C dec. Anal. Calcd for $\text{C}_{25}\text{H}_{25}\text{NOPr}$: C, 52.44; H, 4.40; N, 2.44; P, 5.41. Found: C, 52.19; H, 4.41; N, 2.30; P, 5.19. Data for **3**: ¹H NMR (CD_2Cl_2) δ 7.57–7.38 (m, 15 H), 4.92 (s, 5 H), 2.03–1.64 (m, 4 H), 0.83 (t, $J = 7$ Hz, 3 H); ¹³C NMR (acetone- d_6) 90.3, 35.3, 20.5, –5.9 ppm, and phenyl carbons; IR (CH_2Cl_2) ν_{NO} 1618 cm^{-1} ; mp 184–185 °C; mass spectrum (16 eV) m/e 587 (M^+ , ¹⁸⁷Re, 100%).
- ¹H NMR spectra were recorded at 200 MHz and ¹³C NMR spectra were recorded at 50.32 MHz on a spectrometer provided by a NSF departmental instrument grant (CHE76-05926). Probe temperatures were ambient unless noted and chemical shifts were measured relative to $(\text{CH}_3)_4\text{Si}$.
- (a) Data for **5t**: ¹H NMR (CDCl_3) δ 15.30 (s, 1 H), 7.52–7.18 (m, 20 H), 6.06 (s, 5 H); ¹³C NMR (acetone- d_6) 289.0, 101.2 ppm, and phenyl carbons; IR (CH_2Cl_2) ν_{NO} 1708 cm^{-1} ; mp 215 °C dec. (b) We have not been able to obtain solvent-free analytically pure crystals of the alkylidene complexes reported herein. However, **5t** and **6t** react with $\text{Li}(\text{C}_2\text{H}_5)_3\text{BH}$ to afford high yields of **1** and **2**, respectively, which have been microanalyzed.
- Restricted rotation about the rhenium–methylidene bond of **4** is evident from its ¹H NMR spectrum.³ For the isolation of an isoelectronic and isostructural benzylidene complex without the observation of geometric isomers, see Brookhart, M.; Nelson, G. O. *J. Am. Chem. Soc.* **1977**, *99*, 6099.
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- Wong, W.-K.; Tam, W.; Strouse, C. E.; Gladysz, J. A. *J. Chem. Soc., Chem. Commun.* **1979**, 530. The dihedral angle is $\sim 4.4^\circ$.
- ¹H NMR of **6k** (CD_2Cl_2 , –70 °C)⁵ δ 16.27 (q, $J = 8$ Hz, 1 H), 5.92 (s, 5 H), 2.68 (d, $J = 8$ Hz, 3 H); phenyl protons overlap with Ph_3CH in the reaction mixture. Data for **6t**: ¹H NMR (CD_2Cl_2) δ 15.82 (q, $J = 8$ Hz, 1 H), 7.62–7.28 (m, 15 H), 5.94 (s, 5 H), 2.53 (d, $J = 8$ Hz, 3 H); ¹³C NMR (acetone- d_6) 310.7, 100.7, 44.0 ppm, and phenyl carbons; IR (CH_2Cl_2) ν_{NO} 1720 cm^{-1} ; mp 165 °C dec.
- (a) The reaction of $[\eta\text{-C}_5\text{H}_5]\text{Re}(\text{NO})(\text{PPh}_3)(\text{CO})^+[\text{PF}_6]^-$ with LiAlD_4 or NaBD_4 afforded $(\eta\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{CD}_3)$, which was reacted with $\text{Ph}_3\text{C}^+\text{PF}_6^-$ at –70 °C to yield **4- α -d₂**. Subsequent addition of CH_3Li gave **2- α -d₂**. (b) It is significant that the triphenylmethane accompanying the preparation of **4- α -d₂**^{1a} was found to be an $\sim 96:4$ mixture of Ph_3CD and Ph_3CH by mass spectrometry. Hence $\text{Ph}_3\text{C}^+\text{PF}_6^-$ may competitively abstract H^- from nondeuterated ligands or other sources. Therefore the presence of small amounts of Ph_3CH when only Ph_3CD is expected cannot be taken as evidence against specificity.
- (a) Data for **6t- α -d₁**: ¹H NMR (CD_2Cl_2): δ 7.62–7.30 (m, 15 H), 5.94 (s, 5 H), 2.52 (s, 3 H); ¹³C NMR identical with that of **6t- α -d₁₀** except deuterated carbon was absent owing to increased relaxation time. (b) A 79% yield of an $\sim 96:4$ $\text{Ph}_3\text{CD-Ph}_3\text{CH}$ mixture (mass spectrometric determination) was also isolated from this reaction.^{1b}
- Data for **7k**: ¹H NMR (CD_2Cl_2 , –70 °C) δ 15.98 (t, $J = 8$ Hz, 1 H), 5.94 (s, 5 H), 3.22–3.18 (m, 1 H), 2.63–2.55 (m, 1 H), 0.87 (t, $J = 7$ Hz, 1 H); phenyl protons overlap with Ph_3CH in the reaction mixture. Data for **7t**: ¹H NMR (CD_2Cl_2) δ 15.55 (t, $J = 8$ Hz, 1 H), 7.62–7.30 (m, 15 H), 5.93 (s, 5 H), 3.29–3.06 (m, 1 H), 2.74–2.52 (m, 1 H), 0.79 (t, $J = 7$ Hz, 3 H); ¹³C NMR (acetone- d_6) 315.5, 100.7, 51.5, 12.6 ppm, and phenyl carbons; IR (CH_2Cl_2) ν_{NO} 1718 cm^{-1} ; mp 120 °C dec.
- ¹H NMR (CD_2Cl_2): **5k- α -d₁**, δ 5.89 (s), no benzylidene proton; **5t- α -d₁**, δ 6.08 (s), no benzylidene proton.
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Metal Atom to Cluster to Bulk Transformations. Electron Spin Resonance Studies of Silver Atoms in Rare Gas Matrices at 12 K. Quantum Size Effect

Sir:

The controlled clustering of silver atoms in a wide variety of matrices has directed attention to the general question of the fundamental interrelationship between metal cluster nuclearity and molecular and bulk properties, as seen through the eye of various spectroscopies. A number of groups have recently examined the optical absorption spectra of very small silver clusters generated by matrix cryochemical methods and have used the appearance of a surface plasma absorption as one criterion for establishing the onset of bulk silver microcrystalline properties, from that of molecular silver cluster behavior.^{1–3} Although the nuclearity determination above six silver atoms is not yet firmly established, a relatively smooth conversion from a one-electron molecular eigenstate cluster picture into that of conduction band bulk-like character is emerging from this "optical-electronic" image of the very early stages of silver nucleation.^{1–3}

Along with the optical absorption measurements of the embryonic stages of silver cluster growth, we have also recently conducted a series of ESR measurements, in a designed attempt to collect complementary structural and electronic information for the paramagnetic species present in the silver cluster system. It is the purpose of this communication to report that, by simultaneously monitoring the optical and ESR spectra for Ag/inert gas samples deposited onto a sapphire rod,¹² it is possible to establish that the onset of collective electronic excitations in silver clusters around a nuclearity of ~ 6 –13 atoms^{1,2,3} is accompanied in the ESR spectrum by the appearance of a conduction electron spin resonance (CESR) whose band width and g -shift behavior provides one of the few, direct experimental verifications of "quantum size effects" in very small metal particles.⁴

At high silver concentrations in Ar or Kr matrices ($1:10^{2-3}$), or after extensive matrix annealing or photoaggregation¹ of matrices dilute in silver ($1:10^{3-4}$), the samples showed only weak ESR lines corresponding to the hyperfine components of isolated ¹⁰⁷Ag/¹⁰⁹Ag atoms⁵ (nuclear spin $I = 1/2$ in both cases, with roughly equal natural isotopic abundances), as well as a resonance around the free electron value of $g = 2$, whose intensity, band width, and associated fine structure depended on the matrix preparation and pretreatment mentioned above (Figure 1). According to earlier ESR studies of small metal particles,⁶ it would appear that this latter resonance is a composite of two contributions: (i) sharp lines associated with a range of silver aggregates with molecular cluster properties (four to six atoms suggested optically),^{1,2,3} rather than metal microcrystallite properties, and (ii) a broader CESR line ascribable to small silver microcrystallites on which the sharp lines (i) are superimposed. The temperature dependence of these ESR spectra indicate that silver atomic features decay to 0 in Ar at ~ 30 –35 K, while the resonances associated with molecular silver clusters disappear at ~ 40 –45 K, leaving behind the broader, small-particle CESR. This type of behavior seems to be mirroring the metal atom to cluster to bulk transformations observed in the corresponding optical spectra.^{1–3}

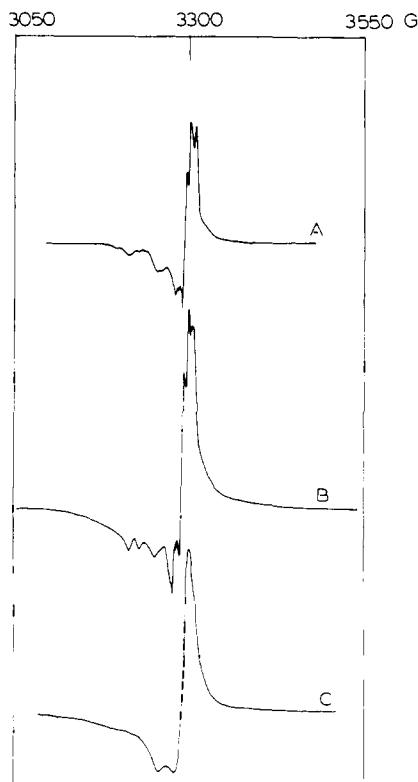


Figure 1. Representative matrix ESR spectra of Ag/inert gas samples deposited at 10–12 K after various photoaggregation¹ and annealing pretreatments (A) Ag/Ar $\approx 6 \times 10^{-4}$, after a 60-min irradiation at 315 nm (Oriel 600-W xenon lamp, Schoeffel monochromator assembly, band pass 8 nm) followed by 40-min annealing in the range of 10–40 K ($\nu = 9.330$ GHz), (B) Ag/Ar $\approx 3 \times 10^{-4}$, after 60-min annealing in the range of 10–43 K ($\nu = 9.330$ GHz), (C) Ag/Kr $\approx 4.5 \times 10^{-3}$, after a 15-min irradiation at 322 nm followed by 20-min annealing in the range of 10–50 K ($\nu = 9.270$ GHz), showing a composite picture of sharp lines associated with a range of silver aggregates with molecular properties, superimposed on a broader conduction electron spin resonance line (C ESR) ascribed to silver microcrystals; see text. (Note that the data displayed in Figure 2 refers to the C ESR band widths and g shifts measured under conditions such that the narrower lines associated with molecular silver aggregates were sufficiently small, not to adversely affect the accuracy of the experimental analysis of the C ESR spectra.)

For very small metal crystals, the boundary conditions imposed on the conduction electrons cause the conduction energy levels to become discrete and separated by energies which are large compared with thermal or other important energies. Properties which arise from the energy gap δ near the Fermi level are known as quantum size effects.⁴ Kubo,⁷ Gor'kov,⁸ and Kawabata⁹ have principally developed the electronic theory for such fine metal particles. In particular, Kawabata⁹ predicted that the quantum size effect associated with these small aggregates could, under certain conditions, be observed in the conduction electron spin resonance spectra, which should differ markedly from that of the bulk. Particle size dependencies of the C ESR line widths and g shifts have been proposed and should be observable in microcrystals smaller than roughly 100 Å.^{6–10} With this in mind, the experimental results of the present study for Ag/Ar and Ag/Kr deposits are collected together in Figure 2, for both the line width and g shift of the C ESR as a function of silver atom density (related to particle size). To appreciate the significance of these data, a brief look at the related background theory is in order.^{6–10}

As the silver particle size decreases, the electron levels of the conduction band become discrete rather than quasicontinuous, and the average spacing δ between adjacent levels near the Fermi level eventually dominates the Zeeman energy, $\hbar\omega_z$. To understand the accompanying changes in the C ESR line width and g shift, one must enquire into the mechanism of the re-

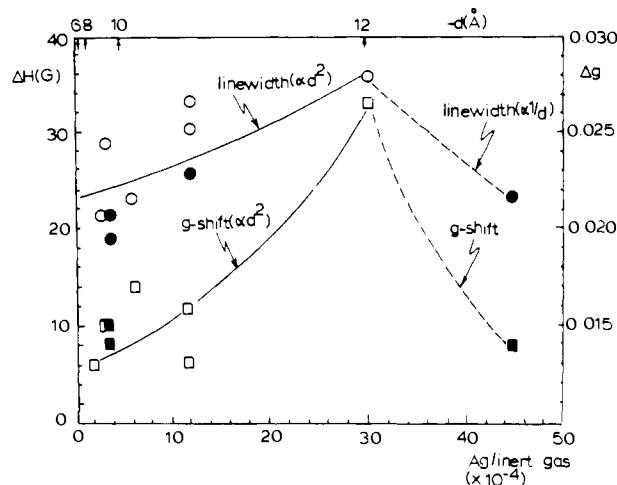


Figure 2. Collected data for the C ESR line widths and g shifts for Ag/inert gas $\approx 1/5 \times 10^3$ to $1/2 \times 10^2$ mixtures deposited at 10–12 K, annealed to 40–60 K, and recooled to 10–12 K for spectral recording purposes: argon results, open squares and circles; krypton results, solid squares and circles.

laxation of conduction electron spins. Following Smithard,^{6a} the spin-relaxation time, τ_2 , of the bulk metal, originally discussed by Elliot,¹¹ can be related approximately to the resistivity scattering τ_R by

$$1/\tau_2 = C/\tau_R \quad (1)$$

where C depends on the square of the spin-orbit coupling contribution, Δg_{SO}^2 , to the g shift of the bulk metal (where $\Delta g_{SO} \approx \Delta g_{bulk} \approx \lambda/\Delta E$, where λ is the spin-orbit coupling constant and ΔE the band-gap energy). However, surface scattering effects, as well as resistivity collisions, must be considered for the total electron scattering time in small metal particles, and, following Kawabata,⁹ the spin-relaxation time becomes

$$1/\tau_2 = C(1/\tau_R + 2V_F/d) \quad (2)$$

where V_F is the Fermi velocity and d the particle diameter, replacing the electron mean free path. It is assumed that C , the spin relaxation probability per scattering collision, is the same for both processes. (Classically speaking, when an electron is scattered at the surface of a small particle, translational invariance is broken and a spin flip occurs, the probability of the latter depending on the spin-orbit coupling strength.) For particles sufficiently small to satisfy both conditions, $\delta \gg \hbar\omega_z$ and $\tau\delta \gg \hbar$, Kawabata⁹ showed that the normal relaxation effect expressed in eq 2 would be quenched by a factor $\hbar\omega_z/\delta$ (because electron movement between the discrete levels will be blocked), and quantum size effects would be manifested in the form of a modified relaxation time given by

$$1/\tau_2 = C(1/\tau_R + 2V_F/d)\hbar\omega_z/\delta \quad (3)$$

Remembering that, for particles of arbitrary shape, δ near the Fermi level is given approximately by E_F/N (the Fermi energy divided by the total number of conduction electrons in the particle) and therefore δ varies as d^{-3} , one can easily see that the C ESR line width will *increase* at first from the bulk value as the particle size decreases because of the d^{-1} surface effect (eq 2) and will then continue to *decrease* sharply (with the g shift⁹), owing to the d^2 quantum size effect (eq 3). With this basic information at hand, the C ESR line widths (and g shifts) for Ag/Ar and Ag/Kr deposits in the range of $1/5 \times 10^3$ to $1/2 \times 10^2$ displayed in graphical form in Figure 2, can be understood. The observed changes in C ESR band widths (15–35 G) and g shifts (2.013–2.028) shown in Figure 2, together with the accompanying growth in amplitude with silver concentration, matrix annealing, and silver atom photoaggregation,¹

can be considered to verify the predictions of the theory of Kawabata,⁹ and represents one of the few, direct experimental observations of quantum size effects (see ref 4 for an excellent up to date account of the field) in fine metallic particles, as first discussed some 43 years ago by Fröhlich.¹⁰

It is also worth noting that a plot of the measured g shift vs. line width yields a reasonably linear correlation (in agreement with the prediction of the theory⁹) which gives an extrapolated $\Delta g_{SO} = 0.026 \pm 0.006$. This corresponds to the experimental value of the contribution of the spin-orbit coupling to the g shift of the bulk, which is reasonably close to the value $\Delta g_{SO} = 0.03$ calculated for bulk silver⁶ by Elliot's theory¹¹ (using $\Delta g_{bulk} \approx \Delta g_{SO} \approx \lambda/\Delta E$, with $\lambda = 0.115$ and $\Delta E = 3.87$ eV).

According to the theory of Kawabata,⁹ a C ESR line width of ~ 25 G corresponds to a silver particle diameter of roughly 10 \AA (see Figure 2), a dimension close to that expected for a close-packed, 13-atom silver cluster. This estimate places the ESR data in line with the conclusions drawn from the corresponding optical experiments,¹⁻³ which used the appearance of the surface plasma absorption as a criterion for establishing the onset of the molecular silver cluster to bulk silver particle transformation. Although the details of these spectra have yet to be deciphered, it would appear that the quantum size effect is being detected in these ESR-optical matrix experiments, and can therefore provide crucial information on the transition metal cluster to bulk metal.

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- In the ESR experiments, the sample was deposited onto an optically polished sapphire rod (dimensions $1.75 \times 0.12 \times 0.14$ in.) cooled to 10–12 K by means of an Air Products Displex closed cycle helium refrigerator using techniques similar to those described previously.¹ By employing a specially designed telescopic vacuum shroud-furnace assembly, the sample could be lowered into an extension quartz tailpiece, held in the microwave cavity of a standard Varian E4 spectrometer. ESR spectra were recorded in the range of 0–6000 G with microwave powers varied between 0.1 and 10 mW for optimum resolution conditions. UV-visible spectra were recorded on the same sample using a standard Varian Techtron instrument in the range of 190–900 nm.

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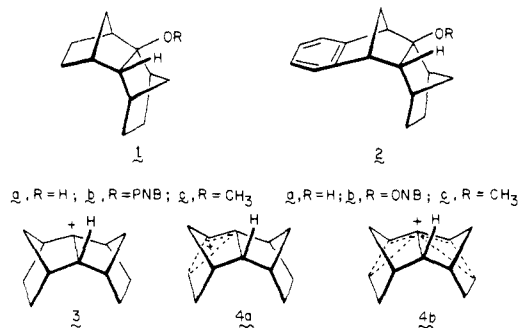
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syn,endo-Tetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodec-2-ylum Cations. Kinetic and Chemical Consequences of Fusing Norbornyl Systems across Common C₂,C₃ Segments

Sir:

We wish to draw attention to some of the novel structural features of compound **1**, a molecule constructed of two amalgamated norbornyl frameworks having the tertiary substituent simultaneously oriented exo to both bicyclic units. The solvolysis of **1b** proceeds at a rate in excess of that of 2-*tert*-butyl-2-*exo*-norbornyl *p*-nitrobenzoate,¹ qualifying this substance as the most highly reactive saturated tertiary derivative presently known. Further, **1** is seen to ionize 1.25×10^3 times faster than its benzologue **2** in 80% dioxane, this margin being substantially larger than any heretofore uncovered in norbornyl-benzonorbornenyl structural pairs. The studies involving **1** and **2** supplement extensive previous work on norbornyl cations² and, in particular, permit assessment of several aspects of the chemistry of these species not possible before. For example, it is our belief that σ participation in **1** to form either or both of the nonclassical intermediates **4a** and **4b** cannot be important in this system. These canonical structures differ so greatly in energy from their classical counterpart **3** that resonance between them is not considered significant.



Alcohols **1a** and **2a** were prepared from the corresponding olefins³ by sequential epoxidation and reduction. The action of lithium in anhydrous ethylenediamine gave **1a**, mp 100–101 °C, in 94% yield, whereas lithium in liquid ammonia-tetrahydrofuran at -40 °C provided **2a**, mp 95–96 °C.^{4,5} The esters were obtained by conventional reaction with the appropriate acid chloride in pyridine solution. *p*-Nitrobenzoate **1b** was solvolyzed in 80% acetone and 80% dioxane. The analogous derivative of **2** proved too unreactive under the same conditions. Consequently, recourse was made to the 3,5-dinitrobenzoate (**2b**), where solubility considerations dictated the use of 80% dioxane as solvent. The kinetic determinations and thermodynamic parameters are summarized in Table I.⁶ Product distribution and yield data for both solvolysis and methanolysis are collected in Table II.

Theory and previous experience with solvent polarity effects lead one to expect a slight rate enhancement for **1b** in 80% acetone ($Y = -0.673$) relative to 80% dioxane ($Y = -0.833$).⁷ As is clear from Table II, both **1b** and **2b** ionize without skeletal isomerization to return unrearranged alcohol or methyl ether, as well as substantial levels of the internal olefins from which they were originally derived. The factor of 1250 by which the fused benzene ring in **2b** decelerates ionization of the tertiary exo leaving group (at 25 °C) is much larger in magnitude than values obtained for either the secondary pair **5/6**⁸ or the series of tertiary *p*-nitrobenzoates **7/8**.⁹ This phenomenon should not be viewed as the result of decreased levels of anchimeric assistance in **2** relative to the model systems, where it is already recognized to be at a low level or nonexistent.⁹⁻¹¹ Rather, molecular models of **1** dramatically reflect the fact that ground states of *syn,endo*-tetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodecanes (e.g.,