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Synthesis and characterization of (β-diketonato)silver complexes of 7-*tert*-butoxynorbornadiene. Single-crystal structures of (hfac)(7-Bu^t-O-NBD)Ag and [(hfac)$_2$(7-Bu^t-O-NBD)Ag$_2$]$_n$

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Abstract—Silver complexes of the empirical formula [(β-diketonato)Ag]$_n$(7-Bu^{t}O-NBD), where β-diketonato = 1,1,1,5,5,5-hexafluoro-2,4-pentanedionato (hfac), 1,1,1-trifluoro-2,4-pentanedionato (tfac), 4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedionato (Ttfac), 4,4,4-trifluoro-1-phenyl-1,3-butanedionato (Btfac), 2,2-dimethyl-6,6,7,7,8,8,8-heptafluoro-3,5-octanedionato (fod), 7-Bu^{t}O-NBD = 7-*tert*-butoxynorbornadiene and $n = 1$ or 2, have been prepared from reaction of Ag$_2$O with the corresponding β-diketone in the presence of 7-Bu^{t}O-NBD. These compounds were characterized by elemental analyses, ^{1}H, ^{13}C and ^{19}F NMR and IR spectroscopic methods. Single-crystal structures of two compounds (hfac) (7-Bu^{t}O-NBD)Ag and [(hfac)$_2$(7-Bu^{t}O-NBD)Ag$_2$]$_n$ were determined by X-ray diffraction analyses. © 1997 Elsevier Science Ltd

Keywords: β-diketonate, silver complex, 7-*tert*-butoxynorbornadiene, crystal structure.

Chemical vapor deposition of silver thin films has recently attracted much research interest as the result of potential applications in the microelectronics industry [1]. Unlike (β-diketonato)copper complexes of alkenes which are widely used for CVD processes [2], very few analogous silver compounds have been reported to be suitable for CVD, although such complexes have been known for years [3]. It is probably due to weak bonding between the alkene and silver center that causes the loss of the alkene during or before these complexes are vaporized. In our previous studies of (β-diketonato)copper complexes of alkenes [4], we found 7-substituted norbornadienes, namely 7-*tert*-butoxynorbornadiene (7-Bu^{t}O-NBD) and 7-acetoxynorbornadiene (7-AcO-NBD) provide additional coordination from the oxygen atom to the metal center and stabilized the copper complexes. We have continued this synthetic strategy and successfully used this type of alkene ligand to make stable silver-alkene complexes. Here, we report the synthesis and characterization of a series of silver complexes of the empirical formula [(β-diketonato)Ag]$_n$(7-Bu^{t}O-NBD), where $n = 1$, β-diketonato = 1,1,1,5,5,5-hexafluoro-2,4-pentanedionato (hfac, **1**), 4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedionato (Ttfac, **4**), 4,4,4-trifluoro-1-phenyl-1,3-butanedionato (Btfac, **5**), 2,2-dimethyl-6,6,7,7,8,8,8-heptafluoro-3,5-octanedionato (fod, **6**); $n = 2$, β-diketonato = 1,1,1,5,5,5-hexafluoro-2,4-pentanedionato (hfac, **2**), 1,1,1-trifluoro-2,4-pentane-dionato (tfac, **3**), and single-crystal structures of compounds **1** and **2**.

EXPERIMENTAL

Synthesis and characterization of (β-diketonato)silver complexes of 7-tert-*butoxynorbornadiene*

All operations were performed under nitrogen purified by passage through columns of activated BASF

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catalyst and molecular sieves and using standard Schlenk techniques [5] in conjunction with a double manifold vacuum line. Tetrahydrofuran and *n*-hexane were dried and distilled from sodium benzophenone ketyl at atmospheric pressure before use. Silver(I) oxide, 1,1,1,5,5,5-hexafluoro-2,4-pentanedione, 1,1,1-trifluoro-2,4-pentanedione, 4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione, 4,4,4-trifluoro-1-phenyl-1,3-butanedione and 2,2-dimethyl-6,6,7,7,8,8,8-heptafluoro-3,5-octanedione (Aldrich Chemical Co.) were used without further purification. The diene 7-*tert*-butoxynorbornadiene was prepared by the method previously described in the literature [6]. Elemental analyses were made at the National Science Council Southern Instrument Center (Department of Chemistry, National Cheng Kung University). NMR data were recorded on a Varian Gemini-200 NMR spectrometer by using the protio impurities of deuterated solvents as references for the ^{1}H NMR and the ^{13}C signals of the solvents as references for ^{13}C NMR spectroscopies. ^{19}F NMR spectra were externally referred to $CFCl_3$. IR data were recorded on a Perkin–Elmer Model 16 PC FTIR spectrophotometer. Melting points were measured in sealed capillaries on a Thomas–Hoover Unimelt instrument without calibration.

(a) (hfac)(7-BuO^t-NBD)Ag (**1**) *and* $(hfac)_2$(7-BuO^t-NBD)Ag_2 (**2**). Addition of 7-Bu^{t}O-NBD (1.42 g, 8.66 mmol) to a 250 cm^3 Schlenk flask containing Ag_2O (1.07 g, 4.32 mmol) and *n*-hexane (50 cm^3) gave a slurry solution. A solution of Hhfac (1.3 cm^3, 8.64 mmol) in *n*-hexane (50 cm^3) was transferred dropwise into the reaction flask with stirring. A white powder precipitated after the solution mixture was stirred for 4 h at room temperature. After filtration and removal of the volatile components from the filtrate, a white crystalline product **1** was obtained (2.27 g, 55% yield). Dissolution of the precipitate in THF (20 mL), followed by filtration and removal of THF afforded a white solid product **2** (1.37 g, 46% yield).

Characterization of compound **1**. Found: C, 40.0; H, 3.6. Calc. for $C_{16}H_{17}O_3F_6Ag$: C, 40.1; H, 3.6%.

NMR data (C_6D_6, 18°C): ^{1}H: δ 6.30 (s, 1H, C*H* on hfac), 6.08 (m, 2H, noncoordinated C*H*=C*H* on 7-Bu^{t}O-NBD), 5.95 (br, s, 2H, coordinated C*H*=C*H* on 7-Bu^{t}O-NBD), 3.35 (br, s, 1H, bridge *H* on 7-Bu^{t}O-NBD), 2.84 (br, s, 2H, bridgehead *H* on 7-Bu^{t}O-NBD), 0.83 [s, 9H, C(C*H*$_3$)$_3$ on 7-Bu^{t}O-NBD] ppm. ^{13}C ^{1}H: δ 177.6 (q, J_{F-C} = 31.8 Hz, CF_3*C*O on hfac), 139.8 (s, noncoordinated *C*H=*C*H on 7-Bu^{t}O-NBD), 126.4 (s, coordinated *C*H=*C*H on 7-Bu^{t}O-NBD), 118.6 (q, J_{F-C} = 289.4 Hz, *C*F$_3$ on hfac), 97.1 (s, bridge *C* on 7-Bu^{t}O-NBD), 87.3 (s, *C*H on hfac), 75.8 [s, $(CH_3)_3$*C* on 7-Bu^{t}O-NBD], 55.9 (s, bridgehead *C* on 7-Bu^{t}O-NBD), 27.6 [s, (*C*H$_3$)$_3$C on 7-Bu^{t}O-NBD] ppm. ^{19}F ^{1}H: δ −76.4 (s) ppm.

IR data (KBr disc, ν_{CO}): 1678 (s), 1541 (s), 1510 (s) cm^{-1}.

Characterization of compound **2**. Found: C, 31.4; H, 2.3%. Calc. for $C_{21}H_{18}O_5F_{12}Ag_4$: C, 31.8; H, 2.3%.

NMR data (C_6D_6, 18°C): ^{1}H: δ 6.21 (s, 2H, C*H* on hfac), 6.04 (m, 2H, noncoordinated C*H*=C*H* on 7-Bu^{t}O-NBD), 5.89 (br, s, 2H, coordinated C*H*=C*H* on 7-Bu^{t}O-NBD), 3.31 (br, s, 1H, bridge *H* on 7-Bu^{t}O-NBD), 2.79 (br, s, 2H, bridgehead *H* on 7-Bu^{t}O-NBD), 0.81 [s, 9H, C(C*H*$_3$)$_3$ on 7-Bu^{t}O-NBD] ppm. ^{13}C ^{1}H: δ 177.4 (q, J_{F-C} = 32.2 Hz, CF_3*C*O on hfac), 139.7 (s, noncoordinated *C*H=*C*H on 7-Bu^{t}O-NBD), 125.7 (s, coordinated *C*H=*C*H on 7-Bu^{t}O-NBD), 118.6 (q, J_{F-C} = 289.4 Hz, *C*F$_3$ on hfac), 96.7 (s, bridge *C* on 7-Bu^{t}O-NBD), 86.9 (s, *C*H on hfac), 75.9 [s, $(CH_3)_3$*C* on 7-Bu^{t}O-NBD), 55.9 (s, bridgehead *C* on 7-Bu^{t}O-NBD), 27.5 [s, (*C*H$_3$)$_3$C on 7-Bu^{t}O-NBD] ppm. ^{19}F ^{1}H: δ −76.3 (s) ppm.

IR data (KBr disc, ν_{CO}): 1678 (s), 1547 (s), 1515 (s) cm^{-1}. M.p.: compound **1**, 73°C (dec.); compound **2**, 85°C (dec.).

(b) $(tfac)_2$(7-Bu^{t}O-NBD)Ag_2 (**3**). Addition of 7-Bu^{t}O-NBD (0.71 g, 4.32 mmol) to a 250 cm^3 Schlenk flask containing Ag_2O (1.05 g, 4.32 mmol) and THF (50 cm^3) gave a slurry. A solution of Htfac (1.1 cm^3, 8.64 mmol) in THF (20 cm^3) was transferred dropwise into the reaction flask with stirring. The solution mixture was continuously stirred for 4 h at room temperature. After filtration and removal of the volatile components from the filtrate, a white crystalline product **3** was obtained (2.41 g, 81% yield).

Found: C, 36.9; H, 3.5. Calc. for $C_{21}H_{24}O_5F_6Ag_2$: C, 36.8; H, 3.5%.

NMR data (C_6D_6, 18°C): ^{1}H: δ 6.05 (m, 2H, noncoordinated C*H*=C*H* on 7-Bu^{t}O-NBD), 5.95 (br, s, 2H, coordinated C*H*=C*H* on 7-Bu^{t}O-NBD), 5.70 (s, 2H, C*H* on tfac), 3.36 (br, s, 1H, bridge *H* on 7-Bu^{t}O-NBD), 2.90 (br, s, 2H, bridgehead *H* on 7-Bu^{t}O-NBD), 1.86 (s, 6H, C*H*$_3$ on tfac), 0.91 [s, 9H, C(C*H*$_3$)$_3$ on 7-Bu^{t}O-NBD] ppm. ^{13}C ^{1}H: δ 197.9 (s, CH_3*C*O on tfac), 171.8 (q, J_{F-C} = 30.5 Hz, CF_3*C*O on tfac), 139.8 (s, noncoordinated *C*H=*C*H on 7-Bu^{t}O-NBD), 122.7 (s, coordinated *C*H=*C*H on 7-Bu^{t}O-NBD), 120.8 (q, J_{F-C} = 284.1 Hz, *C*F$_3$ on tfac), 96.3 (s, bridge *C* on 7-Bu^{t}O-NBD), 91.0 (s, *C*H on tfac), 75.7 [s, $(CH_3)_3$*C* on 7-Bu^{t}O-NBD], 55.8 (s, bridgehead *C* on 7-Bu^{t}O-NBD), 30.2 (s, *C*H$_3$ on tfac), 27.7 [s, (*C*H$_3$)$_3$C on 7-Bu^{t}O-NBD] ppm. ^{19}F ^{1}H: δ −75.1 (s) ppm.

IR data (KBr disc, ν_{CO}): 1668 (s), 1568 (s) cm^{-1}. M.p.: 95°C (dec.).

(c) (Ttfac)(7-Bu^{t}O-NBD)Ag (**4**). Addition of 7-Bu^{t}O-NBD (1.42 g, 8.66 mmol) to a 250 cm^3 Schlenk flask containing Ag_2O (1.01 g, 4.32 mmol) and THF (50 cm^3) gave a slurry. A solution of HTtfac (1.92 g, 8.64 mmol) in THF (20 cm^3) was transferred dropwise into the reaction flask with stirring. The solution mixture was continuously stirred for 4 h at room temperature. After filtration and removal of the volatile components from the filtrate, a pale yellow solid product **4** was obtained (3.31 g, 78% yield).

Found: C, 46.2; H 4.1. Calc. for $C_{19}H_{20}O_3F_3AgS$: C, 46.3; H, 4.1%.

NMR data (C_6D_6, 18°C): ^{1}H: δ 7.37 (d, 1H, J = 2.9 Hz, thienyl *H* on Ttfac), 6.91 (d, 1H, J = 4.1 Hz, thienyl *H* on Ttfac), 6.62 (m, 1H, thienyl *H* on Ttfac), 6.53 (s, 1H, methine C*H* on Ttfac), 6.09 (br, s, 2H, noncoordinated C*H*=C*H* on 7-Bu^{t}O-NBD), 6.00 (br, s, 2H, coordinated C*H*=C*H* on 7-Bu^{t}O-NBD), 3.39 (br, s, 1H, bridge *H* on 7-Bu^{t}O-NBD), 2.90 (br, s, 2H, bridgehead *H* on 7-Bu^{t}O-NBD), 0.91 [s, 9H, C(CH_3)$_3$ on 7-Bu^{t}O-NBD] ppm. ^{13}C ^{1}H: δ 183.1 (s, *C*O on Ttfac), 172.6 (q, J_{F-C} = 30 Hz, CF$_3$*C*O on Ttfac), 148.5 (s, thienyl *C* on Ttfac), 139.9 (s, noncoordinated *C*H=*C*H on 7-Bu^{t}O-NBD), 130.7 (s, thienyl *C* on Ttfac), 122.9 (s, coordinated *C*H=*C*H on 7-Bu^{t}O-NBD), 120.1 (q, J_{F-C} = 287 Hz, *C*F$_3$ on Ttfac), 96.7 (s, bridge *C* on 7-Bu^{t}O-NBD), 89.3 (s, methine *C*H on Ttfac), 75.7 [s, (CH$_3$)$_3$*C* on 7-Bu^{t}O-NBD), 55.9 (s, bridgehead *C* on 7-Bu^{t}O-NBD), 27.8 [s, (*C*H$_3$)$_3$C on 7-Bu^{t}O-NBD] ppm. ^{19}F ^{1}H: δ −75.1 (s) ppm.

IR data (KBr disc, ν_{CO}): 1626 (s), 1552 (s), 1515 (s) cm^{-1}. M.p.: 95°C (dec.).

(d) (Btfac)(7-Bu^{t}O-NBD)Ag (**5**). Pale yellow, crystalline (Btfac)Ag(7-Bu^{t}O-NBD) was prepared in 74% yield by using a procedure analogous to that of the synthesis of compound **4**. Found: C, 51.8; H, 4.6. Calc. for $C_{21}H_{22}O_3F_3Ag$: C, 51.8; H, 4.5%.

NMR data (C_6D_6, 18°C): ^{1}H: δ 8.04 (m, 2H, phenyl *H* on Btfac), 7.13 (m, 3H, phenyl *H* on Btfac), 6.66 (s, 1H, methine C*H* on Btfac), 6.07 (br, s, 2H, noncoordinated C*H*=C*H* on 7-Bu^{t}O-NBD), 6.00 (br, s, 2H, coordinated C*H*=C*H* on 7-Bu^{t}O-NBD), 3.39 (br, s, 1H, bridge *H* on 7-Bu^{t}O-NBD), 2.93 (br, s, 2H, bridgehead *H* on 7-Bu^{t}O-NBD), 0.91 [s, 9H, C(CH_3)$_3$ on 7-Bu^{t}O-NBD] ppm. ^{13}C ^{1}H: δ 190.2 (s, C$_6$H$_5$*C*O on Btfac), 172.9 (q, J_{F-C} = 30 Hz, CF$_3$*C*O on Btfac), 141.8 (s, phenyl *C* on Btfac), 139.9 (s, noncoordinated *C*H=*C*H on 7-Bu^{t}O-NBD), 131.0 (s, phenyl *C* on Btfac), 123.5 (s, coordinated *C*H=*C*H on 7-Bu^{t}O-NBD), 120.1 (q, J_{F-C} = 287 Hz, *C*F$_3$ on Btfac), 96.5 (s, bridge *C* on 7-Bu^{t}O-NBD), 89.8 (s, methine *C*H on Btfac), 75.7 [s, (CH$_3$)$_3$*C* on 7-Bu^{t}O-NBD), 55.9 (s, bridgehead *C* on 7-Bu^{t}O-NBD), 27.7 [s, (*C*H$_3$)$_3$C on 7-Bu^{t}O-NBD] ppm. ^{19}F ^{1}H: δ −75.1 (s) ppm.

IR data (KBr disc, ν_{CO}): 1647 (s), 1589 (m), 1546 (s), 1504 (s) cm^{-1}. M.pt: 85°C (dec.).

(e) (fod)(7-Bu^{t}O-NBD)Ag (**6**). White, crystalline (fod)Ag(7-Bu^{t}O-NBD) was prepared in 71% yield by using a procedure analogous to that of the synthesis of compound **4**. Found: C, 44.2; H, 4.5. Calc. for $C_{21}H_{26}O_3F_7Ag$: C, 44.5; H, 4.6%.

NMR data (C_6D_6, 18°C): ^{1}H: δ 6.15 (s, 1H, methine C*H* on fod), 6.04 (br, s, 2H, noncoordinated C*H*=C*H* on 7-Bu^{t}O-NBD), 5.91 (br, s, 2H, coordinated C*H*=C*H* on 7-Bu^{t}O-NBD), 3.37 (br, s, 1H, bridge *H* on 7-Bu^{t}O-NBD), 2.86 (br, s, 2H, bridgehead *H* on 7-Bu^{t}O-NBD), 1.24 [s, 9H, C(CH_3)$_3$ on fod], 0.92 [s, 9H, C(CH_3)$_3$ on 7-Bu^{t}O-NBD] ppm. ^{13}C ^{1}H δ 205.7 [s, (CH$_3$)$_3$C *C*O on fod], 172.3 (t, J_{F-C} = 21 Hz, CF$_2$*C*O on fod), 139.9 (s, noncoordinated *C*H=*C*H on 7-Bu^{t}O-NBD), 122.8 (s, coordinated *C*H=*C*H on 7-Bu^{t}O-NBD), 122.5–103.7 (m, *C*F$_3$*C*F$_2$*C*F$_2$ on fod), 96.3 (s, bridge *C* on 7-Bu^{t}O-NBD), 89.6 (s, methine *C*H on fod), 75.6 [s, (CH$_3$)$_3$ *C* on 7-Bu^{t}O-NBD], 55.8 (s, bridgehead *C* on 7-Bu^{t}O-NBD), 42.8 [s, (CH$_3$)$_3$*C* on fod], 28.3 [s, (*C*H$_3$)$_3$C on fod], 27.7 [s, (*C*H$_3$)$_3$C on 7-Bu^{t}O-NBD] ppm. ^{19}F ^{1}H: δ −80.5 (br, s), −118.5 (br, s), −126.2 (br, s) ppm.

IR data (KBr disc, ν_{CO}): 1652 (s), 1510 (s) cm^{-1}. M.p.: 73°C (dec.).

X-ray single-crystal structural determination

Two examples of the title compounds were characterized structurally in the solid state by single-crystal X-ray diffraction. All diffraction data were collected at 293 K on an Enraf–Nonius CAD-4 diffractometer with graphite-monochromated Mo-K_α radiation (λ = 0.71069 Å) by using an ω–2θ scan mode. The structures were solved by direct methods using NRCVAX [7] and refined by full-matrix least squares (based on F^2) using SHELXL-93 [8]. All non-hydrogen atoms were refined with anisotropic displacement parameters and all hydrogen atoms were constrained to geometrically calculated positions.

(a) *Compound* **1**. Colorless crystals of (hfac)Ag(7-Bu^{t}O-NBD) were grown by crystallization from hexane solution at −20°C and a single crystal of dimensions 0.34 × 0.30 × 0.24 mm^3 was selected for X-ray analysis. Cell parameters and orientation matrix were established from a least-squares fit of 25 reflections ($22 < 2\theta < 25°$). A total of 2776 reflections was collected, but only 2276 unique reflections with $I > 2.0\sigma(I)$ were used for structure solution and refinement after Lorentz–polarization and empirical absorption corrections. On the basis of systematic absences and successful solution and refinement of the structure, the space group was determined to be $P2_12_12_1$ (no. 19).

(b) *Compound* **2**. Hexane was layered on and allowed to slowly diffuse through a colorless solution of [(hfac)$_2$Ag$_2$(7-Bu^{t}O-NBD)]$_n$ in diethyl ether at −20°C. After 3 days, colorless crystals of the compound formed. A single crystal of dimension 0.22 × 0.20 × 0.16 mm^3 was selected for X-ray analysis. Cell parameters and orientation matrix were established from a least-square fit of 25 reflections ($2.1 < 2\theta < 24.9°$). A total of 2578 reflections was collected, but only 1289 unique reflections with $I < 2.0\sigma(I)$ were used for structure solution and refinement after Lorentz–polarization and empirical absorption corrections. On the basis of systematic absences and successful solution and refinement of the structure, the space group was determined to be $P2_1nm$ (alt. no. 31).

RESULTS AND DISCUSSION

Synthesis of (β-diketonato)silver complexes of 7-Bu^{t}O-NBD

The title compounds were prepared from reactions of Ag$_2$O with the corresponding β-diketone in the presence of 7-Bu^{t}O-NBD according to eq. (1). A similar method was used to prepare analogous complexes of other alkenes [1i,3c,9].

$$Ag_2O + 2\,\beta\text{-diketone} + 2\ 7\text{-Bu}^t\text{-O-NBD} \longrightarrow$$

$$[(\beta\text{-diketonato})Ag]_n(7\text{-Bu}^t\text{-O-NBD}) + H_2O \qquad (1)$$

$$n = 1 : \beta\text{-diketonato} = \text{hfac}\ (\mathbf{1}), \text{Ttfac}\ (\mathbf{4}),$$

$$\text{Btfac}\ (\mathbf{5}), \text{fod}\ (\mathbf{6})$$

$$n = 2 : \beta\text{-diketonato} = \text{hfac}\ (\mathbf{2}), \text{tfac}\ (\mathbf{3})$$

The reactions were carried out in THF solutions at room temperature and products were isolated after removal of volatile species *in vacuo*. Among these reactions, the reaction using hfacH as a starting material provided two products with different Ag/7-Bu^{t}O-NBD ratios. They can be separated by means of the solubility difference in *n*-hexane. Only one thermodynamically stable product was obtained from each of the other reactions [see eq. (1)]. These white to pale yellow silver complexes are moderately sensitive to air and moisture and decompose before sublimation, thus they are not suitable for CVD. All compounds gave satisfactory elemental analyses and were characterized by solution ^{1}H, ^{13}C and ^{19}F NMR and IR spectroscopic methods.

The integrated ^{1}H and ^{13}C NMR spectra of the title compounds are consistent with the empirical formula $[(\beta\text{-diketonato})Ag]_n(7\text{-Bu}^t\text{O-NBD})$ and exhibit olefinic resonances of two types presented in Table 1. Both resonances have smaller chemical shifts than those of free 7-Bu^{t}O-NBD. The signal at higher field belongs to proton or carbon of the coordinated olefin and the other is attributed to that of the non-coordinated olefin. Chemical shift variations ($\Delta\delta$) of olefinic protons and carbons, that have been used to evaluate the bonding feature in the silver complexes of alkenes [10], for compounds **1–6** are slightly larger than those for the analogous complexes of norbornadiene that were found to be between -0.35 and -0.58 ppm and between -0.6 and -5.6 ppm for ^{1}H and ^{13}C resonances, respectively. This feature implies the existence of relatively stronger π-complexation between alkene and silver center in the title compounds, which is probably resulted from extra coordination of oxygen atom of *tert*-butoxy substituent.

Single-crystal structural determination of compounds **1** *and* **2**

The molecular structures of (hfac)(7-Bu^{t}O-NBD)Ag (**1**) and (hfac)$_2$(7-Bu^{t}O-NBD)Ag$_2$ (**2**) were determined in the solid state by single-crystal X-ray diffraction analyses. The crystal, collection and refinement data are summarized in Table 2; selected bond lengths and bond angles are given in Tables 3 and 4 for compounds **1** and **2**, respectively.

There are two independent molecules of compound **1** in the unit cell. An ORTEP diagram of one molecule is presented in Fig. 1. This compound is mononuclear in the solid state and the coordination geometry about silver is best described as a highly distorted tetrahedron. The central silver atom is coordinated by the chelating hfac ligand through two oxygen atoms and the 7-Bu^{t}O-NBD through one C═C double bond and an oxygen atom. The bond distances and angles within the β-diketonato ligand are similar to those of other previously reported mononuclear (β-diketonato)Ag complexes [1f,h,i,9d]. The atoms O(1), O(2), C(6) and C(7) are mutually coplanar and silver atom lies slightly (for example, 0.078 Å) apart from the plane. The O(3) atom occupies the fourth coordination site with a relatively weak interaction to the silver atom [Ag—O(3) distance is *ca* 2.48 Å] compared with bonding between silver and oxygens of β-diketonato ligand in the same molecule [Ag—O(1), Ag—O(2) bond distances are 2.26–2.30 Å]. Thus, the structure is best described as "3 + 1" coordination of the silver center, which is also observed in that of the copper analogue (hfac)(7-Bu^{t}O-NBD)Cu [4b]. Slightly longer distance of the coordinated C(6)═C(7) than that of the non-coordinated C(9)═C(10) indicates the existence of weak π-bonding between alkene and silver center in this compound. No other distances and angles within the 7-Bu^{t}O-NBD are exceptional.

Table 1. Chemical shifts^a of olefinic ^{1}H and ^{13}C NMR resonances for 7-Bu^t-O-NBD and compounds **1–6**

Compound	$\delta(\Delta\delta^b)$ (ppm)			
	^{1}H		^{13}C	
7-Bu^t-O-NBD	6.56	6.54	140.6	137.9
1	6.08 (−0.48)	5.95 (−0.59)	139.8 (−0.8)	126.4 (−11.5)
2	6.04 (−0.52)	5.89 (−0.65)	139.7 (−0.9)	125.7 (−12.2)
3	6.05 (−0.51)	5.95 (−0.59)	139.8 (−0.8)	122.7 (−15.2)
4	6.09 (−0.47)	6.00 (−0.54)	139.9 (−0.7)	122.9 (−15.0)
5	6.07 (−0.49)	6.00 (−0.54)	139.8 (−0.8)	123.5 (−14.4)
6	6.04 (−0.48)	5.91 (−0.63)	139.9 (−0.7)	122.8 (−15.1)

^{a}In C_6D_6.

^{b}$\Delta\delta = \delta_{\text{silver compound}} - \delta_{7\text{-Bu}^t\text{-O-NBD}}$.

Table 2. Summary of crystallographic data for compounds **1** and **2**.

	Compound **1**	Compound **2**
Empirical formula	$C_{16}H_{17}O_3AgF_6$	$C_{21}H_{16}O_5Ag_2F_{12}$
Formula weight	479.16	792.08
Space group	Orthorhombic; $P2_12_12_1$	Orthorhombic; $P2_1nm$
a (Å)	10.245(2)	7.939(2)
b (Å)	15.192(3)	8.710(2)
c (Å)	24.079(3)	19.010(2)
V (Å^3)	3747(1)	1314.5(5)
Z	8	2
d (calcd) (g cm^{-3})	1.699	2.001
F(000)	1904	768
Scan speed (° min^{-1})	2.06–8.24	0.82–2.75
$\theta/2\theta$ scan width (°)	$0.70+0.35\tan\theta$	$0.75+0.35\tan\theta$
$2\theta_{max}$	45	50
μ (mm^{-1})	1.144	1.605
Transmission	0.716; 0.880	0.709; 0.780
Index ranges	$0<h<11$ $-16<k<0$ $0<l<25$	$0<h<9$ $-10<k<10$ $-25<l<25$
Unique reflections	2776	2578
Observed reflections [$I>2\sigma(I)$]	2276	1289
R;[a] wR[b]	0.0353; 0.0996	0.0642; 0.1793
Goodness-of-fit[c]	1.029	1.086
No. of atoms	86	56
No. of parameters refined	479	159
Chirality parameter	0.57(7)	0.08(14)
Extinction coefficient	0.0014(3)	0.002(2)
$(\Delta\rho)_{max., min}$ (e Å^{-3})	0.427; −0.320	1.692; −0.837

[a] $R=\Sigma(||F_O|-|F_C||)/\Sigma|F_O|$.

[b] $wR=[(\Sigma w(F_O^2-F_C^2)^2)/\Sigma(wF_O^2)^2]^{1/2}$; $w=1/[\sigma^2(F_O^2)+(0.0722p)^2+0.15p]$;
$p=(\max(F_O^2+2F_C^2)^{1/3}$.

[c] Goodness-to-fit $=[(\Sigma w(F_O^2-F_C^2)^2]/(\text{no. of reflections}-\text{no. of parameters})]^{1/2}$.

Table 3. Selected bond lengths (Å) and angles (°) for compound **1**

Ag—O(1)	2.258(6)	Ag(A)—O(1A)	2.261(7)
Ag—O(2)	2.271(6)	Ag(A)—O(2A)	2.296(8)
Ag—O(3)	2.496(6)	Ag(A)—O(3A)	2.459(7)
Ag—C(6)	2.337(10)	Ag(A)—C(6A)	2.318(10)
Ag—C(7)	2.307(9)	Ag(A)—C(7A)	2.317(11)
C(6)—C(7)	1.342(13)	C(6A)—C(7A)	1.29(2)
C(9)—C(10)	1.285(14)	C(9A)—C(10A)	1.26(2)
O(1)—Ag—O(2)	82.8(2)	O(1A)—Ag(A)—O(2A)	81.2(2)
O(1)—Ag—O(3)	109.0(2)	O(1A)—Ag(A)—O(3A)	114.9(3)
O(1)—Ag—C(6)	124.8(3)	O(1A)—Ag(A)—C(6A)	150.5(4)
O(1)—Ag—C(7)	158.3(3)	O(1A)—Ag(A)—C(7A)	120.8(3)
O(2)—Ag—O(3)	104.2(3)	O(2A)—Ag(A)—O(3A)	107.8(3)
O(2)—Ag—C(6)	151.8(3)	O(2A)—Ag(A)—C(6A)	124.4(4)
O(2)—Ag—C(7)	118.5(3)	O(2A)—Ag(A)—C(7A)	156.9(4)
O(3)—Ag—C(6)	74.2(3)	O(3A)—Ag(A)—C(6A)	73.9(3)
O(3)—Ag—C(7)	71.7(3)	O(3A)—Ag(A)—C(7A)	71.2(3)
C(6)—Ag—C(7)	33.6(3)	C(6A)—Ag(A)—C(7A)	32.4(4)
Ag—O(3)—C(12)	102.9(5)	Ag(A)—O(3A)—C(12A)	104.4(5)
Ag—O(3)—C(13)	130.3(5)	Ag(A)—O(3A)—C(13A)	133.6(5)
Ag—C(6)—C(7)	72.0(6)	Ag(A)—C(6A)—C(7A)	73.7(7)
Ag—C(7)—C(6)	74.5(6)	Ag(A)—C(7A)—C(6A)	73.8(7)

Table 4. Selected bond lengths (Å) and angles (°) for compound **2**.

Ag(1a)—O(1a)	2.294(9)	Ag(2a)—O(1a)	2.464(9)
Ag(1a)—C(6a)	2.417(13)	Ag(2a)—O(2a)	2.328(13)
Ag(1a)—O(3a)	2.420(14)	Ag(2a)—C(8a)	2.48(2)
C(6a)—C(6b)	1.36(3)	C(8a)—C(8b)	1.32(3)
O(1a)—Ag(1a)—O(1b)	82.0(5)	O(1a)—Ag(2a)—O(2a)	74.7(4)
O(1a)—Ag(1a)—C(6a)	119.1(4)	O(1a)—Ag(2a)—O(1b)	75.3(4)
O(1a)—Ag(1a)—C(6b)	148.9(4)	O(1a)—Ag(2a)—O(2b)	127.0(5)
O(1a)—Ag(1a)—O(3a)	118.9(4)	O(1a)—Ag(2a)—C(8a)	92.6(4)
O(3a)—Ag(1a)—C(6a)	72.9(5)	O(1a)—Ag(2a)—C(8b)	111.7(5)
C(6a)—Ag(1a)—C(6b)	32.8(6)	O(2a)—Ag(2a)—O(2b)	90.3(7)
Ag(1a)—O(1a)—Ag(2a)	100.3(3)	O(2a)—Ag(2a)—C(8a)	112.3(6)
Ag(1a)—O(1a)—C(1a)	137.7(8)	O(2a)—Ag(2a)—C(8b)	139.1(5)
Ag(2a)—O(1a)—C(1a)	122.0(8)	C(8a)—Ag(2a)—C(8b)	30.8(8)
Ag(2a)—O(2a)—C(3a)	125.5(13)	Ag(1a)—C(6a)—C(6b)	73.6(3)
Ag(1a)—O(3a)—C(9a)	105.3(12)	Ag(2a)—C(8a)—C(8b)	74.6(4)
Ag(1a)—O(3a)—C(10a)	133.1(12)		

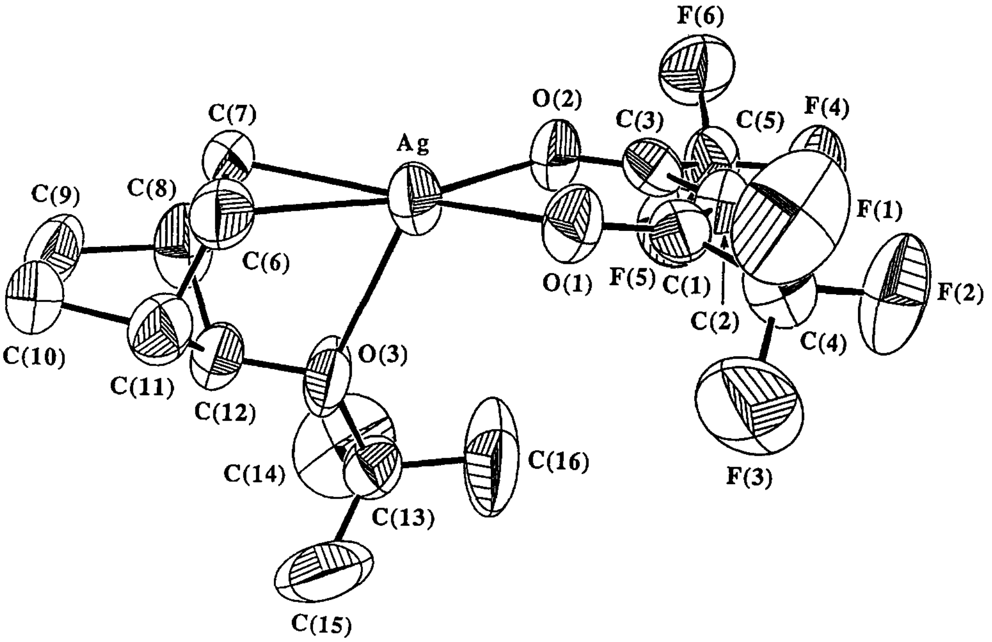

Fig. 1. ORTEP diagram of the molecular structure of compound **1**.

Compound **2** exists as an infinitely polymeric species (Fig. 2) and consists of binuclear units bridged by μ-7-Bu^{t}O-NBD groups in the solid state. The molecule possesses a mirror plane which contains Ag, O(3a) and C(10a) atoms and is perpendicular to C═C double bonds. There are two types of silver atoms in the molecule: Ag(1a) is tetrahedrally coordinated with two oxygen atoms of different hfac ligands, a C═C double bond and an oxygen atom of 7-Bu^t-O-NBD; the coordination geometry about Ag(2a) is a distorted square pyramid, which consists of four O atoms of two chelating hfac ligands and another C═C double bond of 7-Bu^t-O-NBD. The hfac ligand exhibits a μ-η-O,η^2-*O*,*O′* coordination mode, which also observed previously in the structures of {[(hfac)Ag]$_2$NBD}$_2$ [9c], [(hfac)Ag]$_2$(H$_2$O) [9c], {[(hfac)Ag]$_2$(Pr^n-C≡CPr^n)}$_2$ [9d] and [(hfac)Ag]$_4$(SEt$_2$) [11]. The 7-Bu^t-O-NBD group bridges two silver centers by coordination of C(6a)═C(6b) and O(3a) to Ag(1a) and by coordination of C(8a)═C(8b) to Ag(2a). The interactions between Ag centers and C═C [Ag(1a)—C(6a) = 2.42 Å, Ag(2a)—C(8a) = 2.48 Å] in compound **2** are weaker than those in compound **1** [Ag—C$_{(av)}$ = 2.32 Å]. It is likely due to the steric crowdness. Both C═C bond distances (1.36 and 1.32 Å) in compound **2** are similar to the coordinated C═C bond distance and longer than the noncoordinated one in compound **1**.

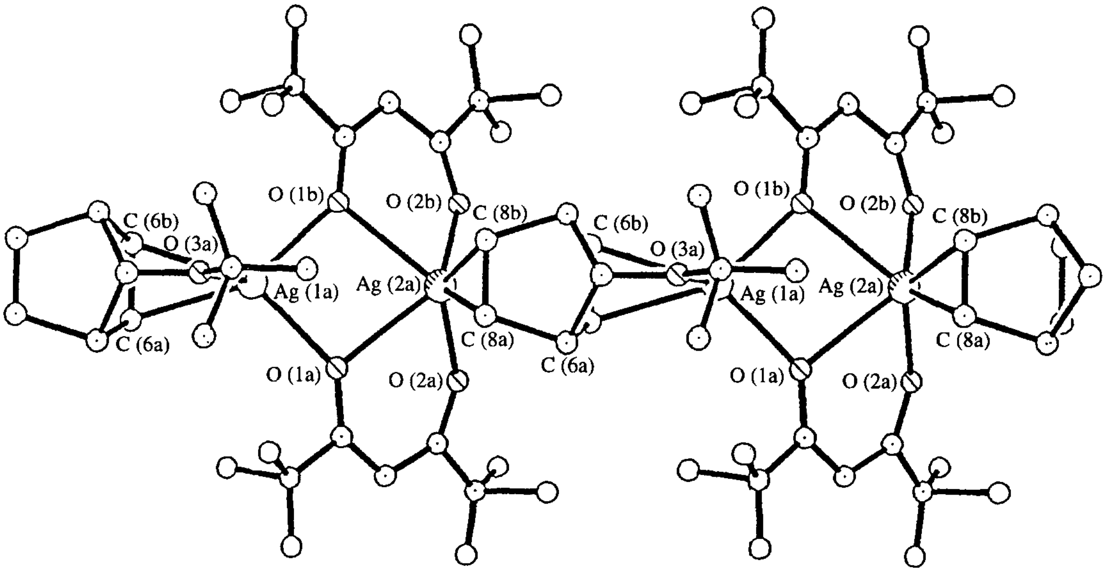

Fig. 2. Crystal structure of compound **2** emphasizing the one-dimensional polymeric structure.

In summary, we have prepared a series of silver-alkene complexes of the general formula $[(\beta\text{-diketonato})\text{Ag}]_n(7\text{-Bu}^t\text{-O-NBD})$ ($n = 1$ or 2). All compounds were characterized by analytical and spectroscopic methods. Structural properties of two compounds were determined by single-crystal X-ray diffraction analyses. Due to the thermal unstability, these compounds are not suitable for chemical vapor deposition.

Supplementary material available. Crystallographic data for compounds **1** and **2**, including tables of crystal data, atomic coordinates, bond distances and angles, anisotropic displacement parameters (33 pages). Ordering information is given on any current masthead page.

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