to determine the conformations of all four methyl groups. In the final refinement cycles, hydrogen atoms were included as fixed atom contributions ($U_{iso} = 0.05$ Å^2), while all other atoms were allowed anisotropic thermal motion. The function minimized was $\sum w(|F_o| - |F_c|)^2$ with $w = 4F_o^2/\sigma^2(F_o^2)$ and $\sigma^2(F_o^2) = [\sigma^2(I) + (pF_o^2)^2]/Lp^2$. p was set to 0.07 to give a "flat" analysis of variance. Refinement of the inverse structure did not yield different results. Neutral, isolated atom scattering factors for all non-hydrogen atoms were those of Cromer and Waber.[25] Scattering factors of the H atoms, based on a bonded spherical atom model, were those of Stewart et al.[26] Corrections for anomalous scattering were applied to all atoms.[27] All calculations were carried out on a PDP 11 using SDP-PLUS.[28]

Triisopropylphosphonium Isopropylide, 2. Colorless single crystals were grown from pentane and sealed under an atmosphere of argon at dry ice temperature into a glass capillary. According to diffractometer measurements (Syntex P2_1), it crystallizes in the triclinic space group $P\bar{1}$. Reduced cell calculations[23] did not reveal any higher symmetry nor did axial photographs. Pertinent crystal data as well as a summary of the intensity data collection and refinement procedure are given in Table I. The integrated intensities of the reflections were measured on a computer-controlled four-circle diffractometer (Syntex P2_1), using graphite-monochromated Mo Kα radiation. A multispeed moving-crystal-stationary-counter technique was used where the peak height at the calculated peak position served to determine the final scan speed. A monitor reflection, examined after every 50 reflections, indicated only a random intensity fluctuation. All other details of the data collection followed closely those described for **1b**.

The structure was solved by direct methods which gave all non-H atom positions (MULTAN 80). After refinement of these atoms (anisotropic thermal parameters), all hydrogen atoms could be located in difference Fourier maps. The methine hydrogen atoms (at C2, C3, and C4) were subsequently refined with isotropic thermal parameters, while the methyl groups were treated as rigid bodies, allowing for rotation around the C–CH_3 bonds ($U_{iso} = 0.06$ Å^2 as fixed thermal parameter for the H atoms). The function minimized was $\sum w(|F_o| - |F_c|)^2$ with $w = 1/\sigma^2(F_o)$. "Unobserved" reflections ($F_o < 4.0\sigma(F_o)$) were omitted in all calculations. Programs used were SHELX 76[29] for refinement, XANADU[30] for geometrical calculations, and ORTEP[31] for the molecular plots. All calculations were done on the departmental VAX 780.

Tetraisopropylphosphonium Iodide, 1a. A data set for **1a** was collected as described for **1b** (above, Table I). The tetragonal symmetry of the diffraction pattern (Laue symmetry $4/m$) and the systematic absences ($hkl = 2n + 1$) indicated $I4$ (no. 79), $I\bar{4}$ (no. 82), and $I4/m$ (no. 87) as possible space groups. For $Z = 2$, only $I\bar{4}$ has special positions with site symmetry possible for an ordered $(i\text{-Pr})_4P^+$ cation. With I and P atoms at 0, 0, 0 and 0, 0, 0.5, respectively, R values between 15% and 20% were achieved in $I\bar{4}$. Anisotropic refinement indicated severe displacement of these atoms along the c axis. These special positions do not give sufficient phase information for the structure factor amplitudes, and thus difference Fourier maps did not yield plausible C atom positions. Therefore, the structure solution was not persued further.

Acknowledgment. Our work was generously supported by Deutsche Forschungsgemeinschaft, Fonds der Chemischen Industrie, Hoechst AG and Ciba AG. C.M.F. Frazão is grateful to DAAD, Bonn, for a research fellowship.

Registry No. 1a, 92209-07-9; **1b**, 92209-04-6; **2**, 99829-77-3.

Supplementary Material Available: Additional crystal structure data, tables with H atom parameters, and observed and calculated structure factor amplitudes (38 pages). Ordering information is given on any current masthead page.

---

(25) Cromer, D. T.; Waber, J. T. *Acta Crystallogr.* **1965**, *18*, 104.

(26) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

(27) "International Tables for X-ray Crystallography", Kynoch Press: Birmingham, England, 1974; Vol. 4.

(28) Frenz, B. A. In "Computing in Crystallography"; Schenk, H., Olthof-Hazelkamp, R., van Konigsveld, H., Bassi, G. C., Eds.; Delft University Press: Delft, Holland, 1978.

(29) Sheldrick, G. M. "SHELX 76, Program for Crystal Structure Determination"; University of Cambridge: England, 1976.

(30) Roberts, P.; Sheldrick, G. M. "XANADU"; University of Cambridge: England, 1978.

(31) Johnson, C. K. "ORTEP II, Report ORNL-5138"; Oak Ridge National Laboratory: Oak Ridge, TN, 1976.

Aluminum Alkoxide Chemistry Revisited: Synthesis, Structures, and Characterization of Several Aluminum Alkoxide and Siloxide Complexes

Jeffrey H. Wengrovius,* Mary F. Garbauskas, Elizabeth A. Williams, Rose C. Going, Paul E. Donahue, and Joanne F. Smith

Contribution from the General Electric Company, Corporate Research & Development, Schenectady, New York 12301. *Received May 15, 1985*

Abstract: Several $[Al(OR)_2(\beta\text{-diketonate})]_n$ (OR = alkoxide or siloxide) and $[Al(OR)(\beta\text{-diketonate})_2]_2$ complexes have been prepared and characterized in solution and in the solid state. The unique structures of $[Al(OR)_2(acac)]_n$ compounds (acac = acetylacetone; $n = 1$ for R = $SiPh_3$; $n = 2$ for R = $SiMe_3$, i-Pr, and t-Bu; $n = 3$ for R = i-Pr) contain tetrahedral and octahedral aluminum sites, and n is dependent on the size of the alkoxide or siloxide ligand. The $[Al(OR)(\beta\text{-diketonate})_2]_2$ complexes (for R = i-Pr, β-diketone = acetylacetone, 3,5-heptanedione, and ethyl acetoacetate; for R = Me, β-diketone = ethyl acetoacetate) are dimers containing two octahedral aluminum centers bridged by alkoxide groups. These compounds are thermally unstable in solution and decompose via ligand disproportionation to Al $(\beta\text{-diketonate})_3$ and $[Al(OR)_2(\beta\text{-diketonate})]_n$. The disproportionation of $[Al(O\text{-}i\text{-Pr})(acac)_2]_2$ follows first-order kinetics with a highly positive entropy factor. Dynamic ^1H NMR spectra of $[Al(O\text{-}i\text{-Pr})(acac)_2]_2$ show isomerism between meso and d,l isomers and restricted rotation of the bridging isopropoxide groups at low temperatures.

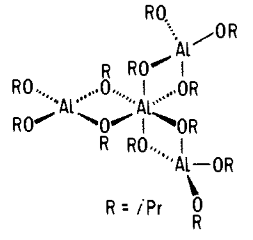
We describe in this report the synthesis and characterization of several Al alkoxide and siloxide β-diketonate complexes. Included in the study are Al compounds of the general formula $[Al(OR)_2(acac)]_n$ (acac = acetylacetone; $n = 1$ for R = $SiPh_3$; $n = 2$ for R = $SiMe_3$, i-Pr, and t-Bu; $n = 3$ for R = i-Pr) and $[Al(OR)(\beta\text{-diketonate})_2]_2$ (for R = i-Pr, β-diketone = acetylacetone, 3,5-heptanedione, and ethyl acetoacetate; for R = Me, β-diketone = ethyl acetoacetate). These compounds have unprecedented structures and reactivity and pose some interesting considerations as to their activity as catalysts and ceramic precursors.

Considerable research has been devoted to understanding the structures of aluminum alkoxide and siloxide complexes.[1] The

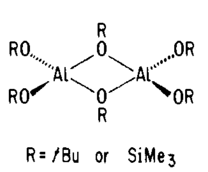
---

(1) Bradley, D. C.; Mehrotra, R. C.; Gaur, D. P. "Metal Alkoxides"; Academic Press: New York, 1978.

general theme of this work is the tendency of Al to maximize its coordination number, resulting in associated molecules containing tetrahedral and octahedral metal centers.[2] Freshly distilled aluminum trisisopropoxide, for example, is proposed to be a trimer, but rearranges to a tetramer after aging for a few weeks at 25 °C.[3] $[\mathrm{Al(O\text{-}\mathit{i}\text{-}Pr)_3}]_4$ is well characterized in solution. ^{1}H NMR[4] and ^{27}Al NMR[5] studies indicate that the molecule contains one central octahedral Al surrounded by three tetrahedral Al sites.

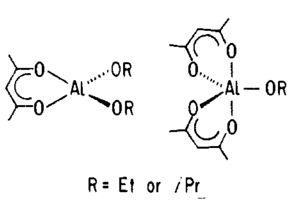


Al complexes with bulkier alkoxide or siloxide ligands, such as *tert*-butoxide[3] and trimethylsiloxide,[6] are tetrahedral dimers. Whereas four- and six-coordinate Al is common, very few five-coordinate Al complexes have been structurally characterized.[7]



In addition to being models for aluminum oxides and aluminosilicates[8], aluminum alkoxide and siloxide compounds have several important applications, including uses as Lewis acid catalysts[1] and aluminosilicate ceramic precursors.[9] Thus, the structures of these complexes are important for understanding their reactivity in these processes. For example, successive substitution of alkoxide or siloxide groups with acetylacetone (acac), ethyl acetoacetate (etac), or other chelating ligands should reduce the Lewis acidity of the resulting complex. Likewise, the Si/Al ratio of an aluminosilicate ceramic should be reduced by substituting a chelate for a siloxide ligand in the ceramic precursor.

Mehrotra and Mehrotra[10] reported in 1961 the synthesis of some acetylacetone and ethyl acetoacetate Al ethoxide and isopropoxide complexes. The structures of these mono- and bis-β-diketonate alkoxide compounds were proposed to contain four- and five-coordinate Al sites, respectively, as depicted for the acetylacetonate complexes below. Our reinvestigation of the Al isopropoxide β-diketonate derivatives, however, indicates that the structures are dimers with tetrahedral and octahedral coordination about the Al metal centers.



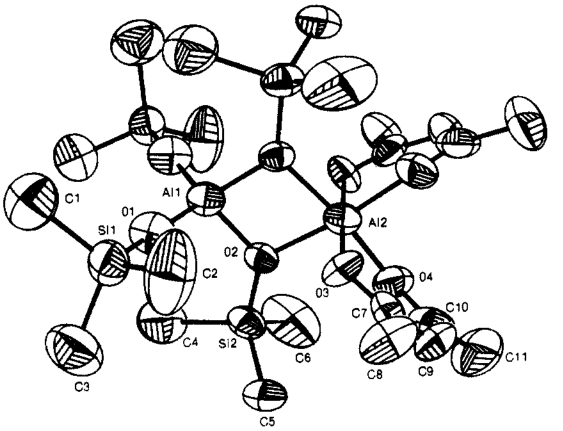


Figure 1. Thermal-ellipsoid (50% probability) plot of $[\mathrm{Al(OSiMe_3)_2(acac)}]_2$.[11]

Results and Discussion

$[\mathrm{Al(OR)_2}(\beta\text{-diketonate})]_2$ Complexes. $[\mathrm{Al(O\text{-}\mathit{i}\text{-}Pr)_2(acac)}]_2$ and $[\mathrm{Al(O\text{-}\mathit{t}\text{-}Bu)_2(acac)}]_2$ can be synthesized as shown in eq 1. We

$$[\mathrm{Al(OR)_3}]_x + x\mathrm{MeC(O)CH_2C(O)Me} \xrightarrow[\text{toluene}]{25\ ^\circ\mathrm{C}} x/2\,[\mathrm{Al(OR)_2(acac)}]_2 + x\,i\text{-PrOH} \qquad (1)$$

R = *i*-Pr (**1**, $x = 4$) and *t*-Bu (**2**, $x = 2$)

observed that substitution of an alkoxide ligand by a β-diketone chelate is rapid and quantitative at 25 °C. Compound **1** is a colorless, volatile liquid which crystallizes slowly at −30 °C, and **2** is a white crystalline solid.

Via a similar synthetic route, Al siloxide complexes can be prepared by the general reaction shown in eq 2. Since the

$$[\mathrm{Al(OSiMe_3)_3}]_2 + 2\beta\text{-diketone} \rightarrow [\mathrm{Al(OSiMe_3)_2}(\beta\text{-diketonate})]_2 + 2\mathrm{Me_3SiOH}$$

$$\beta\text{-diketonate} = \text{acac } (\mathbf{3}) \text{ and etac } (\mathbf{4}) \qquad (2)$$

equilibrium between an Al alkoxide and silanol lies favorably in the direction of the Al siloxide and alcohol, these Al siloxides, **3** and **4**, can also be conveniently prepared by reaction of trimethylsilanol with **1** and **5** (eq 3). Compounds **3** and **4** are white

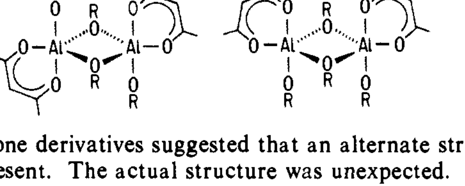
$$\mathbf{1} + 2\mathrm{Me_3SiOH} \xrightarrow{25\ ^\circ\mathrm{C}} \mathbf{3} + 2i\text{-PrOH}$$

$$\underset{\mathbf{5}}{[\mathrm{Al(O\mathit{i}\text{-}Pr)_2(etac)}]_2} + 2\mathrm{Me_3SiOH} \xrightarrow{25\ ^\circ\mathrm{C}} \mathbf{4} + 2i\text{-PrOH} \qquad (3)$$

solids which are less hydrolytically sensitive than their alkoxide counterparts.

^{1}H NMR (**1**–**5**) and ^{29}Si NMR (**3** and **4**) spectra show that each of these molecules has two different alkoxide or siloxide environments. These compounds are rigid in solution at temperatures between −60 and +120 °C. Field desorption mass spectrometry confirms that these complexes are dimers and not monomers as reported by Mehrotra and Mehrotra.[10]

We initially proposed dimer structures consisting of two five-coordinate Al sites with bridging and terminal alkoxide or siloxide groups. However, the absence of geometric isomers for the



acetylacetone derivatives suggested that an alternate structure may be present. The actual structure was unexpected. A single-crystal X-ray diffraction study[11] shows that $[\mathrm{Al(OSiMe_3)_2(acac)}]_2$ (**3**) contains tetrahedral and octahedral Al sites on a twofold axis. As shown in Figure 1, the octahedral Al is bound

---

(2) Bradley, D. C. *Adv. Chem. Ser.* **1959**, *23*, 10.

(3) Mehrotra, R. C., *J. Indian Chem. Soc.* **1953**, *30*, 585.

(4) Oliver, J. G.; Phillips, P. K.; Worrall, I. J. *J. Inorg. Nucl. Chem.* **1969**, *31*, 1609.

(5) Akitt, J. W.; Duncan, R. H. *J. Magn. Reson.* **1974**, *15*, 162.

(6) Schmidbaur, H.; Schmidt, M. *Angew. Chem., Int. Ed. Engl.* **1962**, *6*, 328.

(7) (a) Bonamico, M.; Dessy, G. *J. Chem. Soc. A.* **1968**, 291. (b) Thewalt, U.; Stollmaier, F. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 133. (c) Benn, R.; Rufinska, A.; Lehmkuhl, E. J.; Kruger, C. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 779.

(8) Chisholm, M. H. "Inorganic Chemistry: Toward the 21st Century"; American Chemical Society: Washington, D.C., 1983; Chapter 16.

(9) Williams, A. G.; Interrante, L. V. *Mater. Res. Soc. Symp. Proc.* **1984**, *32*, 151.

(10) Mehrotra, R. K.; Mehrotra, R. C. *Can. J. Chem.* **1961**, *39*, 795.

(11) Garbauskas, M. F.; Wengrovius, J. H.; Going, R. C.; Kasper, J. S. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1984**, *C40*, 1536.

Table I. Selected Bond Lengths (Å) and Bond Angles (deg) for **3**, **6**, **7**, and **10**[a]

$[Al(OSiMe_3)_2(acac)]_2$			
Al(1)–O(2)	1.788 (6)	Al(2)–O(2)	1.948 (6)
Al(2)–O(3)	1.886 (8)	Al(2)–O(4)	1.872 (7)
Al(1)–O(1)	1.700 (8)		
O(1)–Al(1)–O(2)	111.7 (3)	O(2)–Al(2)–O(2a)	78.3 (3)
O(1)–Al(1)–O(1a)	115.8 (5)	O(2)–Al(1)–O(1a)	113.7 (4)
O(2)–Al(1)–O(2a)	86.8 (4)	O(3)–Al(2)–O(4)	91.1 (3)
O(2)–Al(2)–O(3)	92.1 (3)	O(4)–Al(2)–O(2a)	172.6 (3)
O(2)–Al(2)–O(4)	94.4 (2)	O(4)–Al(2)–O(3a)	87.9 (3)
O(3)–Al(2)–O(2a)	89.0 (3)	Al(1)–O(2)–Al(2)	97.4 (3)
O(3)–Al(2)–O(3a)	178.6 (4)		
$[Al(O\text{-}i\text{-}Pr)_2(acac)]_3$			
Al(1)–O(1)	1.872 (7)	Al(1)–O(2)	1.887 (7)
Al(1)–O(3)	1.933 (6)	Al(1)–O(4)	1.980 (7)
Al(1)–O(5)	1.894 (7)	Al(1)–O(6)	1.900 (7)
Al(2)–O(1)	1.873 (7)	Al(2)–O(2)	1.907 (7)
Al(2)–O(9)	1.907 (6)	Al(2)–O(10)	1.890 (8)
Al(2)–O(11)	1.907 (8)	Al(2)–O(12)	1.919 (7)
Al(3)–O(3)	1.766 (7)	Al(3)–O(4)	1.794 (6)
Al(3)–O(7)	1.662 (10)	Al(3)–O(8)	1.716 (7)
O(3)–Al(1)–O(4)	74.4 (3)	O(1)–Al(1)–O(2)	77.5 (3)
O(1)–Al(1)–O(3)	96.0 (3)	O(2)–Al(1)–O(3)	99.5 (3)
O(1)–Al(1)–O(4)	96.6 (3)	O(2)–Al(1)–O(4)	171.2 (2)
O(4)–Al(1)–O(5)	91.4 (3)	O(1)–Al(1)–O(5)	90.9 (3)
O(2)–Al(1)–O(5)	95.2 (3)	O(3)–Al(1)–O(5)	164.9 (3)
Al(3)–Al(1)–O(6)	88.0 (2)	O(1)–Al(1)–O(6)	172.7 (3)
O(2)–Al(1)–O(6)	95.3 (3)	O(3)–Al(1)–O(6)	86.7 (3)
O(4)–Al(1)–O(6)	90.7 (3)	O(5)–Al(1)–O(6)	88.1 (3)
O(1)–Al(2)–O(2)	77.0 (3)	O(1)–Al(2)–O(10)	97.7 (3)
O(1)–Al(2)–O(9)	94.2 (3)	O(2)–Al(2)–O(9)	90.7 (3)
O(2)–Al(2)–O(10)	174.6 (4)	O(9)–Al(2)–O(10)	89.0 (3)
O(10)–Al(2)–O(11)	88.6 (4)	O(1)–Al(2)–O(11)	173.7 (4)
O(2)–Al(2)–O(11)	96.8 (3)	O(9)–Al(2)–O(11)	85.7 (3)
O(1)–Al(2)–O(12)	92.4 (3)	O(2)–Al(2)–O(12)	94.1 (3)
O(9)–Al(2)–O(12)	172.6 (3)	O(10)–Al(2)–O(12)	86.7 (3)
O(11)–Al(12)–O(12)	88.1 (3)	O(3)–Al(3)–O(4)	83.3 (3)
O(4)–Al(3)–O(7)	116.7 (4)	O(3)–Al(3)–O(7)	119.4 (5)
O(3)–Al(3)–O(8)	112.7 (3)	O(4)–Al(3)–O(8)	112.6 (4)
Al(1)–O(1)–Al(2)	103.5 (3)	Al(1)–O(2)–Al(2)	101.6 (4)
Al(1)–O(3)–Al(3)	102.5 (3)	Al(1)–O(4)–Al(3)	99.7 (3)
$Al(OSiPh_3)_2(acac)$			
Al–O(1)	1.797 (4)	Al–O(2)	1.796 (4)
Al–O(3)	1.700 (4)	Al–O(4)	1.680 (4)
O(1)–Al–O(2)	97.7 (2)	O(1)–Al–O(3)	111.1 (2)
O(2)–Al–O(3)	111.1 (2)	O(1)–Al–O(4)	110.0 (2)
O(2)–Al–O(4)	110.2 (2)	O(3)–Al–O(4)	115.3 (2)
$[Al(O\text{-}i\text{-}Pr)(Et_2acac)_2]_2$			
Al–O(1)	1.866 (6)	Al–O(2)	1.927 (6)
Al–O(3)	1.909 (6)	Al–O(4)	1.893 (7)
Al–O(5)	1.911 (6)	Al–O(1a)	1.868 (6)
O(1)–Al–O(2)	173.0 (3)	O(1)–Al–O(3)	93.8 (2)
O(2)–Al–O(3)	88.7 (2)	O(1)–Al–O(4)	96.8 (3)
O(2)–Al–O(4)	89.9 (2)	O(3)–Al–O(4)	87.0 (3)
O(1)–Al–O(5)	94.0 (2)	O(2)–Al–O(5)	84.1 (2)
O(3)–Al–O(5)	171.4 (2)	O(4)–Al–O(5)	88.5 (2)
O(2)–Al–O(1a)	95.9 (3)	O(1)–Al–O(1a)	77.4 (3)
O(4)–Al–O(1a)	174.2 (3)	O(3)–Al–O(1a)	93.5 (2)
Al–O(1)–Ala	102.6 (3)	O(5)–Al–O(1a)	91.8 (2)

[a] We have previously reported the X-ray structures of **3**, **6**, **7**, and **10**.[11,14]

to two acetylacetone chelates and the tetrahedral Al to two trimethylsiloxide ligands; trimethylsiloxide groups bridge the two sites. Selected bond lengths and angles for the crystallographically characterized compounds described in this report are listed in Table I.

^{27}Al NMR at +120 °C confirms that compounds **1**–**5** have the same basic structure. For each complex, a sharp resonance at 0 ppm is assigned to the octahedral Al site, and a broad resonance varying from +49 to +65 ppm is observed for the tetrahedral Al.

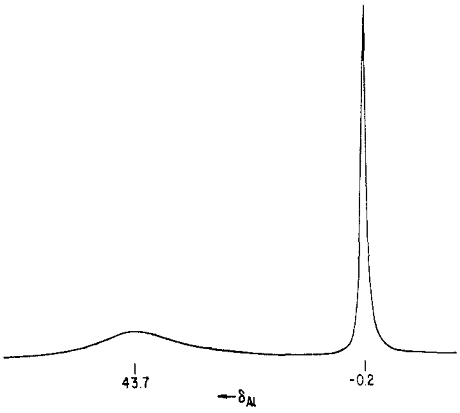


Figure 2. ^{27}Al NMR spectrum of $[Al(O\text{-}t\text{-}Bu)_2(acac)]_2$ at +120 °C.

Table II. ^{27}Al NMR Shifts and Line Widths for Compounds **1**–**12**

compound	temp, °C	shift, δ	line width, Hz	assign[c]
$[Al(O\text{-}i\text{-}Pr)_2(acac)]_2$[a]	+120	+57	1000	t
		+0.4	60	o
$[Al(O\text{-}t\text{-}Bu)_2(acac)]_2$[a]	+120	+44	1200	t
		−0.2	60	o
$[Al(OSiMe_3)_2(acac)]_2$[a]	+120	+55	1200	t
		−0.2	60	o
$[Al(OSiMe_3)_2(etac)]_2$[a]	+120	+59	1400	t
		+1.7	150	o
$[Al(O\text{-}i\text{-}Pr)_2(etac)]_2$[a]	+120	+65	1300	t
		+2.3	170	o
$[Al(O\text{-}i\text{-}Pr)_2(acac)]_3$[a]	+70	+59	1200	t
		+0.5	60	o
$Al(OSiPh_3)_2(acac)$[a]	+120	+53	2300	t
$[Al(O\text{-}i\text{-}Pr)(acac)_2]_2$[b]	+25	+4.1	150	o
$[Al(O\text{-}i\text{-}Pr)(Et_2acac)_2]_2$[b]	+25	+4.7	210	o
$[Al(O\text{-}i\text{-}Pr)(etac)_2]_2$[a]	+25	+3.7	1450	?
	+80	+2.2	480	o
$[Al(OMe)(etac)_2]_2$[a]	+25	+3.2	1000	?

[a] Sample in $C_2D_2Cl_4/C_2H_2Cl_4$. [b] Sample in $CDCl_3$. [c] t = tetrahedral; o = octahedral.

These spectra were run at high temperature, in addition to room temperature, to reduce the line width of the tetrahedral Al.[5] A characteristic ^{27}Al NMR spectrum is shown in Figure 2. ^{27}Al NMR shifts and line widths for all the compounds reported here are shown in Table II.

$[Al(O\text{-}i\text{-}Pr)_2(acac)]_3$. A concentrated solution of $[Al(O\text{-}i\text{-}Pr)_2(acac)]_2$ ages over a period of several weeks at 25 °C. During this time, a white solid crystallizes from solution. This product can be reconverted to **1** on heating at temperatures above 100 °C (eq 4). ^1H NMR, field desorption mass spectrometry, and single-crystal X-ray analyses[11] indicate that this product is a linear trimer whose structure is shown in Figure 3. The two octahedral Al are bound to one and two acetylacetone chelates, respectively. The tetrahedral Al is bound to two terminal isopropoxide ligands, and bridging isopropoxide groups join the metal centers. The isopropoxide ligand described by O(7), C(18), C(19), and C(20) is disordered and, therefore, has been refined isotropically.

$$[Al(O\text{-}i\text{-}Pr)_2(acac)]_2 \underset{\Delta}{\overset{25\ °C}{\rightleftarrows}} [Al(O\text{-}i\text{-}Pr)_2(acac)]_3 \qquad (4)$$

$[Al(OSiPh_3)_2(acac)]$. The observation that the molecular complexity of $[Al(OR)_2(acac)]_n$ complexes depends on the steric bulk of the alkoxide or siloxide group suggested the possibility of the use of a extremely large alkoxide or siloxide to synthesize a monomeric member of this class of compounds. Four equivalents of triphenylsilanol react cleanly with $[Al(O\text{-}i\text{-}Pr)_2(acac)]_2$ to yield compound **7** (eq 5). ^1H NMR, ^{29}Si NMR, and field desorption mass spectrometry of **7** support a monomer whose structure is

$$[Al(O i\text{-}Pr)_2(acac)]_2 + 4Ph_3SiOH \xrightarrow{25\ °C} \underset{\mathbf{7}}{2[Al(OSiPh_3)_2(acac)]} + 4i\text{-}PrOH \qquad (5)$$

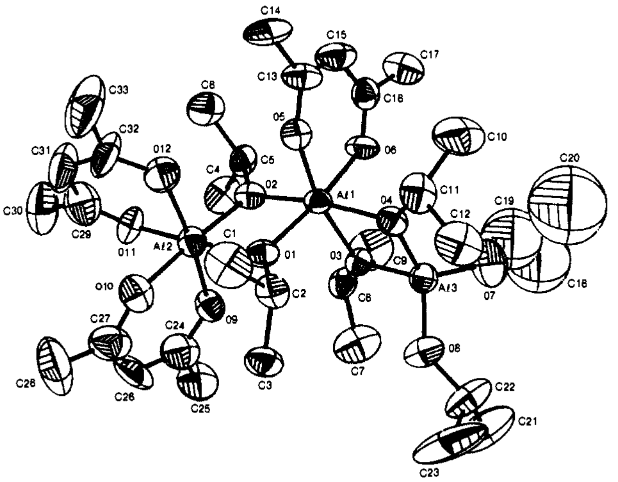


Figure 3. Thermal-ellipsoid (50% probability) plot of $[Al(O\text{-}i\text{-}Pr)_2(acac)]_3$.[11]

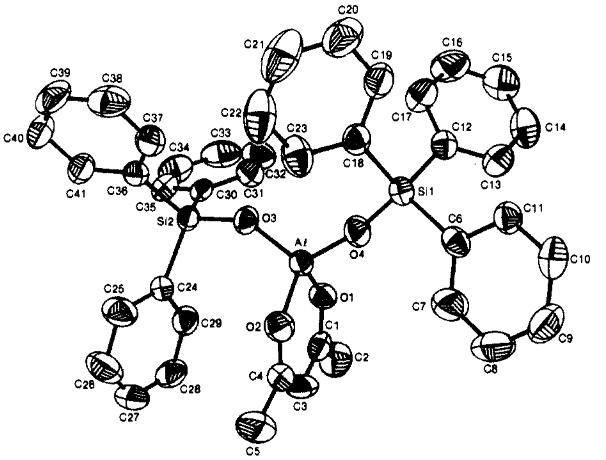


Figure 4. Thermal-ellipsoid (50% probability) plot of $Al(OSiPh_3)_2(acac)$.[11]

confirmed by single-crystal X-ray diffraction (Figure 4).[11]

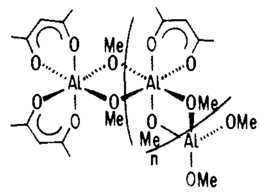
Compounds **1**–**7** show a preference for tetrahedral and octahedral coordination around Al and eschew geometries with a coordination number of five. Although all of these compounds have the same empirical formulas, $[Al(OR)_2(acac)]_n$ and $[Al(OR)_2(etac)]_n$, the molecular formula depends on the size of the alkoxide or siloxide ligand. Thus, when this ligand is a large triphenylsiloxide group, the molecule is a monomer, **7**. With ligands having progressively smaller cone angles, such as trimethylsiloxide and isopropoxide groups, the molecules are dimers **1**–**5** and a trimer **6**, respectively.

The Al–O bond lengths in each molecule are dependent on steric crowding imposed by neighboring ligands. Accordingly, the Al–O bond lengths in the alkoxide and siloxide groups of **3**, **6**, and **7** fall into three general categories: (1) 1.872–1.980 Å found in the bridging isopropoxide and trimethylsiloxide groups bound to the octahedral Al sites in **3** and **6**, (2) 1.766–1.794 Å found in the same bridging alkoxide and siloxide groups bound to the tetrahedral Al sites in **3** and **6**, and (3) 1.662–1.716 Å found in the terminal alkoxide and siloxide groups which occupy tetrahedral positions in **3**, **6**, and **7**. The shorter Al–O bond lengths in the bridging, tetrahedrally coordinated trimethylsiloxide ligands in **3** are nearly identical with similarly coordinated trimethylsiloxide groups (Al–O = 1.79 Å) in $[Al(OSiMe_3)Br_2]_2$.[12] The average Al–O bond lengths (mean value 1.897 Å) and angles (mean value 89.2°) associated with the acetylacetonate ligands in octahedral sites of **3** and **6** are very similar to those found in octahedral aluminum tris(acetylacetonate) (1.892 Å and 91.8°).[13] The O(1)–Al–O(2) bond angle found within the acetylacetonate ligand of tetrahedral **7** is larger (97.7°), and the Al–O bond lengths are shorter (1.797 Å) than their octahedral counterparts (**3** and **6**). All Al–O bond lengths for the octahedral Al sites in **3** and **6** are approximately equal. In all three molecules, distortions in the tetrahedral and octahedral geometries are imposed by steric repulsions between the ligands.

It is unclear why four- and six-coordinate geometries are favored over five-coordinate structures. A possible explanation is that the β-diketone chelates exert a marked preference for spanning tetrahedral and octahedral Al sites and avoid participation in five-coordinate geometries. We cannot rule out the possibility that five-coordinate intermediates are formed in the synthesis of many of these compounds but rapidly rearrange to the observed products. A series of homoleptic complexes would be a more favorable system for studying relative stabilities of various geometries.

The $[Al(OR)_2(acac)]_n$ complexes described here have relatively large alkoxide and siloxide ligands, and, therefore, the molecular complexity is relatively low ($n = 1–3$). Smaller ligands should produce higher molecular complexities. Although we did not examine $[Al(OEt)_2(acac)]_n$, we propose it is at least a trimer and perhaps even a higher molecular weight oligomer. $[Al(OMe)_2(acac)]_n$ can be prepared by the addition of dry methanol to $[Al(O\text{-}i\text{-}Pr)_2(acac)]_2$ (eq 6). Compound **8** immediately precipitates from solution as a white flocculent solid which is insoluble in a wide variety of noncoordinating solvents. We believe it is likely that **8** is a high molecular weight oligomer such as the structure shown below. An alternate structure might have methoxide ligands bridging three Al sites.

$$1 + 2.5MeOH \rightarrow \underset{\mathbf{8}}{[Al(OMe)_2(acac)]_n} + 2i\text{-}PrOH \qquad (6)$$



8

[Al(OR)(β-diketonate)$_2$]$_2$ Complexes. $[Al(OR)(\beta\text{-diketonate})_2]_2$ complexes are synthesized by addition of the requisite amount of β-diketone to the corresponding $[Al(OR)_2(\beta\text{-diketonate})]_n$ complex (eq 7). Compounds **9**–**12** are moisture sensitive white, crystalline solids. Characterization of these complexes, including single-crystal X-ray diffraction analysis of **10**,[14] reveals two interesting phenomena. First, these molecules are thermally sensitive and decompose cleanly to give ligand disproportionation products, and second, these complexes display somewhat complex fluxional ^1H NMR spectra.

$$[Al(OR)_2(\beta\text{-diketone})]_n + n\beta\text{-diketone} \xrightarrow{25\ °C} n/2\,[Al(OR)(\beta\text{-diketonate})_2]_2 + nROH$$
$$\text{for } R = i\text{-Pr},\ \beta\text{-diketone} = \text{acac } (\mathbf{9});\ \text{3,5-heptanedione} = (Et_2acac)\ (\mathbf{10}),\ \text{etac } (\mathbf{11});\ R = Me,\ \beta\text{-diketone} = \text{etac } (\mathbf{12}) \qquad (7)$$

X-ray Structure of $[Al(O\text{-}i\text{-}Pr)(Et_2acac)_2]_2$. The structure of **10** is a centrosymmetric dimer (Figure 5). There are four points of interest concerning this structure: (1) Of the two possible isomers for a symmetric dimer, meso and *d,l*, this molecule crystallizes from pentane at −30 °C in the meso form. (2) The average Al–O bond lengths and angles of $[Al(O\text{-}i\text{-}Pr)(Et_2acac)_2]_2$ are very similar to those in the octahedral sites of $[Al(O\text{-}i\text{-}Pr)_2(acac)]_3$. (3) One of the Al acetylacetonate O bond lengths (Al–O2 = 1.927 (6) Å vs. Al–O4 = 1.893 (7)) is slightly longer than the other equatorial Al acetylacetonate bond. (4) The isoproxide bridges occupy a diastereotopic position.

---

(12) Bonamico, M.; Dessy, G. *J. Chem. Soc. A.* **1967**, 1786.

(13) Hon, P. K.; Pfluger, C. E. *J. Coord. Chem.* **1973**, *3*, 67.

(14) Garbauskas, M. F.; Wengrovius, J. H. *Acta Crystallogr.*, submitted for publication.

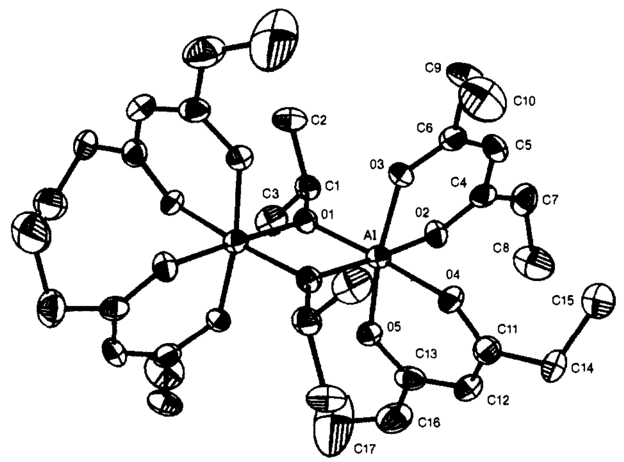


Figure 5. Thermal-ellipsoid (50% probability) plot of [Al(O-*i*-Pr)($Et_2acac)_2]_2$.[14]

Table III. Kinetic Data for the Disproportionation of 9[a]

T, K	[9], M	k_{obsd}, s^{-1}	$t_{1/2}$, min	no. of half-lives	corr coeff
316.9	0.01	5.42×10^{-6}	2130	>2	0.9949
331.4	0.01	2.10×10^{-5}	550	>2	0.9985
345.7	0.01	6.09×10^{-5}	190	>4	0.9978
348.3	0.10	7.85×10^{-5}	147	>3	0.9954
359.3	0.01	2.89×10^{-4}	40	6	0.9911

[a] Arrhenius plot data: E_A = 20.3 kcal/mol, ΔH = 20.5 kcal/mol, and ΔS = 40 eu.

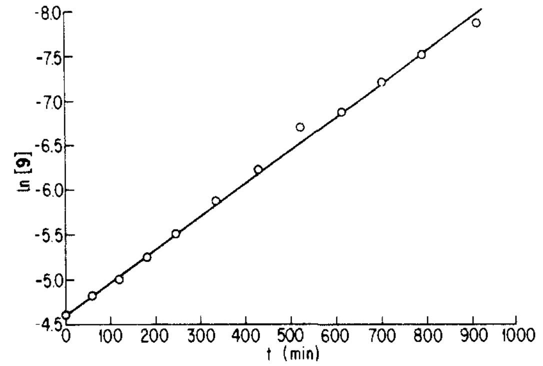


Figure 6. Kinetic plot of the disproportionation of 9 at 72.7 °C ([0.01] in toluene-d_8).

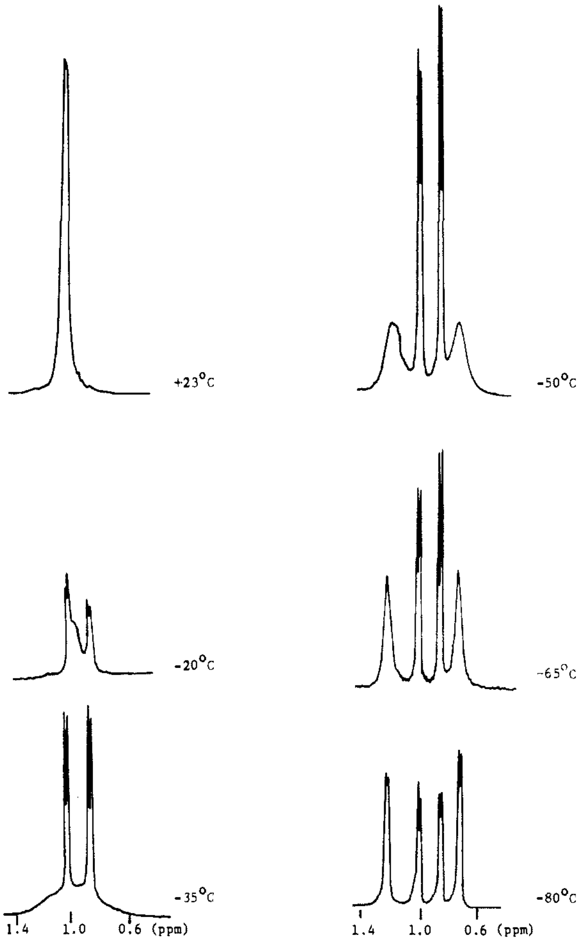


Figure 7. 300-MHz ^1H NMR spectra of the isoproxide methyl resonances of 9 in CD_2Cl_2.

Thermal Stability of [Al(OR)(β-diketonate)$_2$]$_2$ Complexes. Compounds 9–12 are thermally unstable in solution. All decompose via ligand disproportionation (eq 8). The driving force

$$[Al(OR)(\beta\text{-diketonate})_2]_2 \xrightarrow{\Delta} Al(\beta\text{-diketonate})_3 + {}^1/_2[Al(OR)_2(\beta\text{-diketonate})]_2 \quad (8)$$

for these disproportionation reactions may in part be due to the steric crowding about the octahedral aluminum centers. Attempts to prepare similar dimer complexes with even larger bridging alkoxide or siloxide ligands give only the disproportionation products.[15] The reaction of acetylacetone with [Al(O-*t*-Bu)$_2$(acac)]$_2$ at 25 °C, for example, is very slow (several hours) but eventually yields Al(acac)$_3$ and starting material. Similarly, attempts to prepare [Al(OSiMe$_3$)(etac)$_2$]$_2$ by reacting ethyl acetoacetate with [Al(OSiMe$_3$)$_2$(etac)]$_2$ or by reacting trimethylsilanol with [Al(O-*i*-Pr)(etac)$_2$]$_2$ give only disproportionation products. Thus, the size of the bridging alkoxide or siloxide ligand is important in the stability of these dimer complexes. We have found no evidence for the existence of monomeric complexes with the same stoichiometry. Another factor in these disproportionation reactions may be the favorable stability of the resulting Al(β-diketonate)$_3$ complex. Also, we observed that the ethyl acetoacetate chelates are more stable than the β-diketonate complexes.

We have studied in some detail the kinetics of disproportionation of 9 (eq 9). The clean disappearance of 9 and the appearance

$$\underset{9}{[Al(O\text{-}i\text{-}Pr)(acac)_2]_2} \xrightarrow{\Delta} Al(acac)_3 + {}^1/_2 1 \quad (9)$$

of 1 and Al(acac)$_3$ can be monitored by high field ^1H NMR. Disproportionation reactions at several temperatures between 43.9 and 86.3 °C show first-order kinetics over a sufficient number of half-lives (Figure 6 and Table III). Arrhenius treatment of this data indicates a $\Delta H^‡$ of 20 kcal/mol (E_A = 20 kcal/mol) and a high $\Delta S^‡$ of 40 eu. This latter value suggests a product-like transition state which is consistent with a structure in which an acetylacetonate chelate is in the process of an intramolecular transfer from one Al site of the dimer to the other. Another possible mechanism is scission of the dimer to two monomers as the rate-determining step, followed by rapid disproportionation of the monomers to the observed products. This mechanism does not allow for any equilibration between monomer and dimer since the rate of disproportionation is first order over a large concentration range. We also observed that coordinating molecules such as amines, alcohols, or ethers greatly accelerate these disproportionation reactions, Et$_2$O being particularly effective. These coordinating compounds promote disproportionation by stabilization of the transition state.

Fluxionality of [Al(OR)(β-diketonate)$_2$]$_2$ Complexes. We have also examined the fluxionality of [Al(OR)(β-diketonate)$_2$]$_2$ complexes in solution. The variable temperature NMR spectra

---

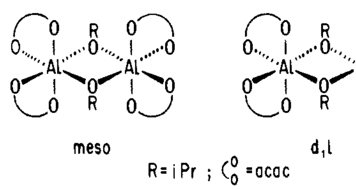
(15) Ercolani, C.; Camilli, A.; Sartori, G. *J. Chem. Soc. A.* **1966**, 603. The reaction between [Al(OSiMe$_3$)X$_2$] (X = Br, Cl) and 4 equiv of Na(acac) is described in this reference. The authors proposed that the products of this reaction, Al(acac)$_3$ and Al(OSiMe$_3$)$_2$(acac), arise from a structural disproportionation of the Al(OSiMe$_3$)(acac)$_2$ intermediate.

Table IV. Free Energy of Activation Parameters Associated with the Fluxional Processes of **9**.

fluxnl proc	solv	T_c,[a] K	ΔG^*, kcal/mol
isomizatn of	CD_2Cl_2	278	13.6
d, *l* and meso isoms	toluene-d_8	303	15.0
rotatn barrier about	CD_2Cl_2	227	10.4
O–C bond of meso isom	toluene-d_8	222	10.2
rotatn barrier about	CD_2Cl_2	216	10.6
O–C bond of *d*, *l* isom	toluene-d_8	199	10.1

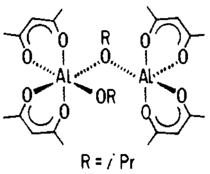
[a] Temperature of NMR probe calibrated with a methanol standard.

of [Al(O-*i*-Pr)(acac)$_2$]$_2$ in CD_2Cl_2 and toluene-d_8 are quite complex. Representative 300-MHz ^{1}H NMR spectra of the isopropoxide methyl resonances of compound **9** in CD_2Cl_2 at various temperatures are shown in Figure 7. At temperatures above +30 °C, the spectra are straightforward; only broad averaged resonances are observed. At lower temperatures, two isomers can be distinguished which we believe are the meso and *d,l* compounds.



The ratio of these isomers changes with temperature; lower temperatures favor the meso compound. At temperatures below −50 °C, the resonances associated with each isomer become even more complex. The observed resonances are consistent with restricted rotation about the C–O bonds of the bridging isopropoxide groups. Table IV summarizes the various free energy of activation parameters associated with these processes. Due to the complexity of the spectra and the short temperature ranges between coalescence of the various dynamic processes, line shape analysis would not be accurate or meaningful.

The mechanism by which the meso and *d,l* isomers interconvert most likely involves bond breaking, since most six-coordinate interconversion processes in which there is no bond-breaking, such as the Bailar twist, would yield the starting isomer in this case. We believe that the Al–O bonds associated with the bridging isopropoxide ligands are the most labile. Thus, at the high-temperature limit, we propose that the meso and *d,l* isomers are rapidly interconverting through a transition state in which one of the Al–O–Al bonds of the bridge is broken. Facile Berry pseudorotation of the five-coordinate half of this transition state and reformation of the Al–O–Al bridge gives the other isomer. Octahedral aluminum tris(β-diketonate) complexes with asymmetric chelate ligands are well-known to be labile toward isomerization and enantiomerization.[16] These reactions involve the rupture of an aluminum acetylacetonate bond. However, we have observed that the meso and *d,l* isomers of **9** interconvert readily on the chemical time scale at temperatures at least as low as −90 °C. Thus, this compound is considerably more labile than the aluminum tris(β-diketonate) complexes which isomerize at temperatures greater than +50 °C. The isomerization through the transition state described above would be expected to be very sensitive to the steric bulk of the bridging alkoxide with bulky ligands facilitating the bond-breaking process. Support for this mechanism, therefore, is found in the large difference between the coalescence temperatures of [Al(OMe)(etac)$_2$]$_2$ ($T_c \simeq$ −20 °C) and [Al(O-*i*-Pr)(etac)$_2$]$_2$ ($T_c \simeq$ −60 °C).



An alternate mechanism for the interconversion of isomers would be dissociation to monomer followed by recombination to produce the other isomer. We do not believe that this is occurring in solution at +25 °C, although we cannot rule out this possibility. ^{27}Al NMR spectra of [Al(OR)(β-diketonate)$_2$]$_2$ complexes show single resonances with narrow line widths at approximately 0 ppm. This is indicative of octahedral coordination[13] of the dimer. Vapor-phase osmometry also indicates that **9** is a dimer in chloroform at +25 °C.

The *d,l* and meso isomers of **9** in CD_2Cl_2 coalesce at +5 °C in the ^{1}H NMR ($\Delta G^* = +13.6$ kcal/mol). The *d,l* isomer can be distinguished from the meso isomer by the presence of diastereotopic isopropoxide methyl protons. The resonances for the *d,l* isomer in CD_2Cl_2 are sharp between 0 °C and −50 °C. The resonances for the meso compound, however, remain broad until bond rotation about the isopropoxide O–C bond is slow (T_c = −45 °C, ΔG^* = 10.4 kcal/mol). Below −57 °C, restricted bond rotation about the O–C bonds of both isomers is observed. Each isomer exhibits four inequivalent acetylacetonate methyl protons, two nonequivalent protons on the central carbons of the acetylacetonate ligands, and diastereotopic isopropoxide methyl protons.

It is also interesting to note that the isopropoxide groups of the meso compound are frozen out in a diastereotopic orientation. Presumably, the same rotomer is present in the solid state of [Al(O-*i*-Pr)(Et$_2$acac)$_2$]$_2$ which crystallizes in the meso form with diastereotopic isopropoxide methyl groups. There is also an interesting difference between the fluxionality of **9** in toluene-d_8 and CD_2Cl_2. The ΔG^* of isomerization of the two isomers is significantly higher in toluene-d_8 (15.0 kcal/mol) than in CD_2Cl_2 (13.6 kcal/mol). This observation is consistent with the ability of CD_2Cl_2 to stabilize the transition state through coordination.

As discussed above, the meso/*d,l* ratio increases as the temperature decreases, indicating that these isomers are still rapidly interconverting on the chemical time scale. The ΔH for the interconversion of the *d,l* isomer to the meso isomer is −0.78 kcal/mol, and the ΔS is 3.5 eu.

We also examined the dynamic NMR spectra of [Al(O-*i*-Pr)(Et$_2$acac)$_2$]$_2$ from +30 to −90 °C. Both meso and *d,l* isomers are observed in addition to restricted bond rotation of the bridging isopropoxide groups at low temperatures. The added complexity of these spectra does not permit determination of accurate coalescence temperatures. However, it appears from the spectra that the dynamic processes occur at approximately the same temperatures as for [Al(O-*i*-Pr)(acac)$_2$]$_2$.

Conclusions

The general properties and structures of the two groups of Al alkoxide (siloxide) β-diketonate complexes reported here are quite different from each other. On one hand, the Al dialkoxide (disiloxide) mono-β-diketonate compounds are thermally stable, have rigid geometries in solution, and have four- and six-coordinate structures whose molecular complexities are dependent on the size of the alkoxide or siloxide ligands. The properties of the aluminum alkoxide bis(β-diketonate) complexes, on the other hand, are influenced by the required six-coordinate dimer structures which are considerably more sterically congested. These compounds are thermally sensitive toward ligand disproportionation and display complex dynamic NMR spectra. Within both groups of these compounds, we could find no evidence for the existence or intermediacy of any five-coordinate Al complexes. Our attempts to prepare and identify similar compounds with intermediate stoichiometries, such as [Al(O-*i*-Pr)$_{1.5}$(acac)$_{1.5}$]$_x$ ($x \geq 2$), gave combinations of the compounds reported here and Al(acac)$_3$.

The chemistry and structures of aluminum alkoxide or siloxide chelate complexes are considerably more complex than once believed. These factors must be considered in their use as catalysts and ceramic precursors and in other applications.

Experimental Section

General Data. All experiments were performed under an argon or nitrogen atmosphere in a Vacuum Atmosphere HE 43-2 drybox or by using standard Schlenk techniques. Reagent grade toluene and pentane

---

(16) Serpone, N.; Bickley, D. G. In "Progress In Inorganic Chemistry"; Edwards, J. O., Ed.; Wiley: New York, 1972; pp 391–566.

were distilled from sodium benzophenone ketyl under nitrogen. Methylene chloride, C_6D_6, $CDCl_3$, CD_2Cl_2, and toluene-d_8 were passed down a column of activated alumina under nitrogen and were stored over activated molecular sieves prior to use. Methanol was distilled from sodium under nitrogen. Ethyl acetoacetate, acetylacetone, and 3,5-heptanedione were degassed and dried over molecular sieves. [Al(O-*i*-Pr)$_3$]$_4$, [Al(O-*t*-Bu)$_3$]$_2$. [Al(O-*i*-Pr)$_2$(etac)]$_2$, and Ph$_3$SiOH were purchased and used as received. [Al(OSiMe$_3$)$_3$]$_2$ was prepared as described by Schmidbaur.[6] Me$_3$SiOH was synthesized by hydrolysis of hexamethyldisilazane in diethyl ether, followed by neutralization with 2 M HCl and distillation.[17]

All NMR spectra were obtained on either a Varian XL-200 or XL-300 spectrometer. ^{1}H NMR spectra were recorded at 200 MHz and 300 MHz, ^{13}C NMR at 75.4 MHz, and ^{29}Si NMR at 59.6 MHz (XL-300). Chemical shifts are given in parts per million (ppm) relative to Me$_4$Si. ^{27}Al NMR spectra were recorded at 52.1 MHz (Varian XL-200) and are referenced to aqueous Al(NO$_3$)$_3$. Typical spectral parameters include a 4000-Hz spectral width, 2.0-s acquisition time, and 6-μs pulse width (45° flip angle) for ^{1}H at 300 MHz; 4000-Hz spectral width, 0.4-s acquisition time, and 12-μs pulse width (45° flip angle) for ^{27}Al at 52.1 MHz; and 20000-Hz spectral width, 0.4-s acquisition time, and 12-μs pulse width (45° flip angle) for ^{13}C at 75.4 MHz. Field desorption (FD) mass spectrometry was performed on a Finnigan MAT 731 instrument.

[Al(O-*i*-Pr)$_2$(acac)]$_2$ (1). Acetylacetone (9.70 g, 97.9 mmol) was slowly added at +25 °C to a stirring solution of [Al(O-*i*-Pr)$_3$]$_4$ (20.0 g, 24.5 mmol) in 50 mL of toluene. Removal of the volatiles yielded a yellow oil which was purified by vacuum distillation (140 °C, 1 mmHg). Compound **1** was obtained as a colorless liquid (19 g, 80%) which slowly crystallized to a white solid upon storage at −30 °C: ^{1}H NMR (C_6D_6) δ 5.24 (s, 1, MeC(O)C*H*C(O)Me′), 4.68 (sep, 1, $^3J_{HH}$ = 6.0 Hz, OC*H*Me$_2$), 4.28 (sep, 1, $^3J_{HH}$ = 6.3 Hz, OC*H*Me$_2$), 1.83 and 1.70 (both a s, both 3, *Me*C(O)CHC(O)*Me′*), 1.67 (d, 3, $^3J_{HH}$ = 6.2 Hz, OCH*Me*Me′), 1.59 (d, 3, $^3J_{HH}$ = 6.0 Hz, OCHMe*Me′*), 1.56 (d, 3, $^3J_{HH}$ = 5.9 Hz, OCH*Me″*Me‴), 1.50 (d, 3, $^3J_{HH}$ = 6.4 Hz, OCHMe″*Me‴*); ^{13}C NMR (C_6D_6) δ 193.2 and 190.3 (Me*C*(O)CH*C*(O)Me′), 101.0 (MeC(O)*C*HC(O)Me′), 66.2 and 63.2 (O*C*HMe$_2$), 28.3, 25.44, and 25.38 (OCH*Me*$_2$), 26.6 and 26.2 (*Me*C(O)CHC(O)*Me′*). Anal. Calcd for $C_{22}H_{42}Al_2O_8$: C, 54.09; H, 8.67. Found: C, 53.70; H, 8.76.

[Al(O-*t*-Bu)$_2$(acac)]$_2$ (2). Compound **2** was prepared from [Al(O-*t*-Bu)$_3$]$_2$ (5.0 g, 10.1 mmol) and acetylacetone (2.03 g, 20.3 mmol) by using the same reaction scheme as used for **1**. It was recrystallized from pentane yielding a white solid (5.25 g, 95%): ^{1}H NMR (C_6D_6) δ 5.31 (s, 1, MeC(O)C*H*C(O)Me′), 1.86 and 1.72 (both a s, both 3, *Me*C(O)CHC(O)*Me′*), 1.72 and 1.69 (both a s, both 9, OC*Me*$_3$); ^{13}C NMR (C_6D_6) δ 192.6 and 189.6 (Me*C*(O)CH*C*(O)Me′), 101.1 (MeC(O)*C*HC(O)Me′), 73.4 and 68.5 (O*C*Me$_3$), 34.4 and 31.4 (OC*Me*$_3$), 26.4 and 26.2 (*Me*C(O)CHC(O)*Me′*); mass spectrum (FD) *m/e* 544 (M$^+$), 529 (M$^+$ − Me), 471 (M$^+$ − O-*t*-Bu). Anal. Calcd for $C_{26}H_{50}Al_2O_8$: C, 57.34; H, 9.25. Found: C, 56.98; H, 9.36.

[Al(OSiMe$_3$)$_2$(acac)]$_2$ (3). Me$_3$SiOH (0.74 g, 8.22 mmol) was added rapidly to a solution of **1** (1.00 g. 2.06 mmol) in 5 mL of pentane. Removal of the volatiles and recrystallization from pentane gave **3** as a white solid (1.12 g, 90%). Compound **3** was also prepared in high yield by the reaction of 2 equiv of acetylacetone with [Al(OSiMe$_3$)$_3$]$_2$: ^{1}H NMR (C_6D_6) δ 5.25 (s, 1, MeC(O)C*H*C(O)Me′), 1.88 and 1.65 (both a s, both 3, *Me*C(O)CHC(O)*Me′*), 0.47 and 0.45 (both a s, both 9, OSi*Me*$_3$); ^{13}C NMR ($CDCl_3$) δ 192.8 and 190.0 (Me*C*(O)CH*C*(O)Me′), 101.1 (MeC(O)*C*HC(O)Me′), 26.5 and 26.1 (*Me*C(O)CHC(O)*Me′*), 2.8 and 1.4 (OSi*Me*$_3$); ^{29}Si NMR (C_6D_6) δ 13.7 (bridging OSiMe$_3$), −1.7 (terminal OSiMe$_3$);[18] mass spectrum (FD) *m/e* 608 (M$^+$). Anal. Calcd for $C_{22}H_{50}Al_2O_8Si_4$: C, 43.39; H, 8.28. Found: C, 43.08, H, 7.98.

[Al(OSiMe$_3$)$_2$(etac)]$_2$ (4). Compound **4** was prepared from **5** (5.0 g, 9.11 mmol) and Me$_3$SiOH (3.29 g, 36.4 mmol) by using the same reaction scheme as used for **3**. It was vacuum distilled (130 °C, >0.1 mmHg) yielding a slightly pink noncrystalline solid (5.48 g, 90%). Several isomers are observed in the NMR spectra: ^{1}H NMR (C_6D_6) δ 5.17–5.11 (MeC(O)C*H*C(O)OEt), 4.55–3.91 (MeC(O)CHC(O)OC*H*$_2$CH$_3$), 1.91–1.68 (*Me*C(O)CHC(O)OEt), 1.26–0.97 (MeC(O)CHC(O)OCH$_2$C*H*$_3$), 0.47–0.40 (OSi*Me*$_3$); ^{13}C NMR ($CDCl_3$) δ 189.4–186.4 (Me*C*(O)CHC(O)OEt), 174.4–174.2 (MeC(O)CH*C*(O)OEt), 86.4–84.9 (MeC(O)*C*HC(O)OEt), 60.9–60.5 (MeC(O)CHC(O)O*C*H$_2$CH$_3$), 26.1–25.7 (*Me*C(O)CHC(O)OEt), 14.5–14.2 (MeC(O)CHC(O)OCH$_2$*C*H$_3$), 2.9–1.4 (OSi*Me*$_3$); ^{29}Si NMR (C_6D_6) δ 14.0–12.9 (bridging OSiMe$_3$), −1.4 to −2.3 (terminal OSiMe$_3$); mass spectrum (FD) *m/e* 668 (M$^+$). Anal. Calcd for $C_{24}H_{54}Al_2O_{10}Si_4$: . C, 43.09; H, 8.14. Found: C, 42.71; H, 8.22.

[Al(O-*i*-Pr)$_2$(acac)]$_3$ (6). A solution of **1** (1.0 g, 2.05 mmol) in 1 mL of $CDCl_3$ was aged for 6 weeks at 25 °C. During this time, **6** crystallized from solution as a white solid (0.85 g, 85%). It was recrystallized from CH$_2$Cl$_2$/pentane solution at −30 °C: ^{1}H NMR ($CDCl_3$) δ 5.48, 5.40, and 5.36 (each a s, each 1, MeC(O)C*H*C(O)Me′), 4.90, 4.22, and 4.08 (each a sep, 1, 2, 3, average $^3J_{HH}$ = 6.1 Hz, OC*H*Me$_2$), 1.94, 1.91, 1.88, 1.77, and 1.76 (each a s, 6, 3, 3, 3, 3, *Me*C(O)CHC(O)*Me′*), 1.37, 1.31, 1.23, 1.18, 1.13, 0.86, and 0.77 (each a d, 3, 3, 3, 3, 18, 3, 3, $^3J_{HH}$ = 6.2, 6.2, 6.4. 6.7, 6.1, 6.2, and 6.4 Hz, OCH*Me*$_2$); ^{13}C NMR ($CDCl_3$) δ 190.7, 190.5, and 188.9 (Me*C*(O)CH*C*(O)Me′), 100.7, 100.1, and 99.7 (MeC(O)*C*HC(O)Me′), 64.1, 63.9, and 63.4 (O*C*HMe$_2$), 26.9, 26.4, 26.2, 25.5, 23.8, 23.6, and 23.2 (OCH*Me*$_2$ and *Me*C(O)CHC(O)*Me′*); mass spectrum (FD) *m/e* 675 (M$^+$ − O-*i*-Pr) and 635 (M$^+$ − acac). Anal. Calcd for $C_{33}H_{63}Al_3O_{12}$: C, 54.09; H, 8.67. Found: C, 53.77; H, 8.76.

Al(OSiPh$_3$)$_2$(acac) (7). Ph$_3$SiOH (2.27 g, 8.22 mmol) was added rapidly to a solution of **1** (1.00 g, 2.05 mmol) in 5 mL of CH$_2$Cl$_2$. After all of the Ph$_3$SiOH had dissolved, the volatiles were removed in vacuo. The resulting white solid was recrystallized from CH$_2$Cl$_2$/pentane solution at −30 °C yielding **7** (2.22 g, 80%): ^{1}H NMR (C_6D_6) δ 7.93 (m, 6, Ph H), 7.25 (m, 9, Ph H), 4.78 (s, 1, MeC(O)C*H*C(O)Me), 1.35 (s, 6, *Me*C(O)CHC(O)*Me*); ^{13}C NMR ($CDCl_3$) δ 195.8 (Me*C*(O)CH*C*(O)Me), 138.1 (C_{ipso}), 134.9 (C_m), 128.9 (C_p), 127.3 (C_o), 104.1 (MeC(O)*C*HC(O)Me), 26.4 (*Me*C(O)CHC(O)*Me*); ^{29}Si NMR ($CDCl_3$) δ −24.2; mass spectrum (FD) *m/e* 679 (M$^+$). Anal. Calcd for $C_{41}H_{37}AlO_4Si_2$: C, 72.75; H, 5.51. Found: C, 72.55; H, 5.74.

[Al(OMe)$_2$(acac)]$_n$ (8). MeOH (0.33 g, 10.3 mmol) was added to a solution of **1** (1.0 g, 2.05 mmol) in 10 mL of pentane. A white flocculent precipitate formed in minutes. This product was collected by filtration and dried in vacuo (0.75 g, 97%). Further purification and characterization of **8** was not possible due to its insolubility. Anal. Calcd for $C_7H_{13}AlO_4$: C, 44.69; H, 6.96. Found: C, 44.76; H, 7.38.

[Al(O-*i*-Pr)(acac)$_2$]$_2$ (9). Acetylacetone (0.82 g, 8.22 mmol) was added carefully to a solution of **1** (2.0 g, 4.11 mmol) in 20 mL of pentane over a period of 0.5 h at 25 °C. Compound **9** precipitated from solution as formed and was collected by filtration and dried in vacuo (1.99 g, 86%). This product was purified by recrystallization from CH$_2$Cl$_2$/pentane solution at −30 °C. Two isomers of **9** are observed in solution at low temperatures by ^{1}H and ^{13}C NMR: ^{1}H NMR of meso isomer (−90 °C, CD_2Cl_2) δ 5.53 and 5.42 (both a s, both 1, MeC(O)C*H*C(O)Me′ and Me″C(O)C*H*C(O)Me‴), 3.91 (sep, 1, $^3J_{HH}$ = 5.9 Hz, OC*H*MeMe′), 2.07, 1.96, 1.93, and 1.81 (each a s, each 3, *Me*C(O)CHC(O)*Me′* and *Me″*C(O)CHC(O)*Me‴*), 1.27 and 0.68 (both a d, both 3, both $^3J_{HH}$ = 5.9 Hz, OCH*MeMe′*); ^{1}H NMR of the *d*,*l* isomer (−90 °C, CD_2Cl_2) δ 5.57 and 5.48 (both a s, both 1, MeC(O)C*H*C(O)Me′ and Me‴C(O)C*H*C(O)Me‴), 3.82 (sep, 1, $^3J_{HH}$ = 6.4 Hz, OC*H*MeMe′), 2.08, 1.97, 1.93, and 1.79 (each a s, each 3, *Me*C(O)CHC(O)*Me′* and *Me″*C(O)CHC(O)*Me‴*), 1.00 and 0.84 (both a d, both 3, both $^3J_{HH}$ = 6.4 Hz, OCH*MeMe′*); ^{13}C NMR of both isomers (−80 °C, CD_2Cl_2) δ 192.3, 191.9, 190.5, 190.0, 188.2, and 187.8 (Me*C*(O)CH*C*(O)Me′), 100.5, 100.3, 99.9, and 99.1 (MeC(O)*C*HC(O)Me′), 63.2 and 63.0 (O*C*HMe$_2$), 26.8, 26.7, 26.2, and 26.0 (*Me*C(O)CHC(O)*Me′*), 24.0, 22.7, and 22.0 (OCH*Me*$_2$); mass spectrum (FD) *m/e* 568 (M$^+$), 509 (M$^+$ − O-*i*-Pr), 499 (M$^+$ − acac); mol wt (VPO) g/mol 510 (568 calcd). Anal. Calcd for $C_{26}H_{42}Al_2O_{10}$: C, 54.92; H, 7.45. Found: C, 54.91; H, 7.66.

[Al(O-*i*-Pr)(Et$_2$acac)$_2$]$_2$ (10). 3,5-Heptanedione (2.51 g, 19.6 mmol) was added slowly to a solution of [Al(O-*i*-Pr)$_3$]$_4$ (2.00 g, 2.45 mmol) in 25 mL of CH$_2$Cl$_2$. The reaction volatiles were removed in vacuo, and the resulting oily solid was recrystallized from pentane at −30 °C yielding white crystalline **10** (1.30 g, 39%): ^{1}H NMR of *d*,*l* and meso isomers (−30 °C, CD_2Cl_2) δ 5.38 and 5.35 (s, 2, EtC(O)C*H*C(O)Et), 4.01 (sep, 1, $^3J_{HH}$ = 6.5 Hz, OC*H*Me$_2$), 2.18, 2.17, and 2.04 (q, 8, $^3J_{HH}$ = 7.5 Hz, H$_3$CC*H*$_2$C(O)CHC(O)C*H*$_2$CH$_3$), 1.14, 1.10, and 0.95 (t, 12, $^3J_{HH}$ = 7.5 Hz, *H*$_3$CCH$_2$C(O)CHC(O)CH$_2$C*H*$_3$), 1.04 and 0.84 (d, 6, $^3J_{HH}$ = 6.5 Hz, OCH*Me*$_2$); ^{13}C NMR of *d*,*l* and meso isomers (−30 °C, CD_2Cl_2) δ 194.7, 194.6, and 191.6 (Et*C*(O)CH*C*(O)Et), 97.0 and 96.8 (EtC(O)*C*HC(O)Et), 62.5 (O*C*HMe$_2$), 32.9, 32.8, and 32.2 (H$_3$C*C*H$_2$C(O)CHC(O)*C*H$_2$CH$_3$), 23.7 and 23.2 (OCH*Me*$_2$), 10.2, 10.1, and 10.0 (H$_3$*C*CH$_2$C(O)CHC(O)CH$_2$*C*H$_3$); mass spectrum (FD) *m/e* 621 (M$^+$ − O-*i*-Pr), 553 (M$^+$ − Et$_2$acac). Anal. Calcd for $C_{34}H_{58}Al_2O_{10}$: C, 59.99; H, 8.59. Found: C, 59.98; H, 8.56.

[Al(O-*i*-Pr)(etac)$_2$]$_2$ (11). Compound **11** was prepared from ethyl acetoacetate (0.95 g, 7.29 mmol) and **5** (2.00 g, 3.65 mmol) by using the same reaction scheme as used for **9**. The product is a colorless oil which slowly crystallized to a white solid at 25 °C (2.42 g, 96%): ^{1}H NMR (C_6D_6) δ 5.30 (s, 2, MeC(O)C*H*C(O)OEt), 4.73 (br m, 1, OC*H*Me$_2$), 4.29 (br m, 4, MeC(O)CHC(O)OC*H*$_2$CH$_3$), 1.89 (s, 6, *Me*C(O)CHC(O)OEt), 1.60 (br m, 6, OCH*Me*$_2$), 1.17 (t, 6, $^3J_{HH}$ = 7.0 Hz, MeC(O)CHC(O)OCH$_2$C*H*$_3$); ^{13}C NMR (C_6D_6) δ 187.0 (Me*C*(O)CHC-

---

(17) White, M. A.; Schwabacher, D. W., unpublished results.

(18) Assignment of the ^{29}Si NMR resonances for **3** and **4** are based on comparison with the ^{29}Si NMR of [Al(OSiMe$_3$)$_3$]$_2$ which shows peaks at +23.0 and +2.0 ppm in a 1:2 ratio corresponding to the bridging and terminal siloxide ligands, respectively.

(O)OEt), 174.3 (MeC(O)CH*C*(O)OEt), 85.4 (MeC(O)*C*HC(O)OEt), 64.2 (O*C*HMe$_2$), 60.2 (MeC(O)CHC(O)O*C*H$_2$CH$_3$), 26.3 (*Me*C(O)-CHC(O)OEt), 24.3 (OCHMe$_2$), 14.7 (MeC(O)CHC(O)OCH$_2$*C*H$_3$). Anal. Calcd for $C_{30}H_{50}Al_2O_{14}$: C, 52.32; H, 7.32. Found: C, 52.24; H, 7.42.

[Al(OMe)(etac)$_2$]$_2$ (12). Compound **12** was prepared from "[Al(OMe)$_2$(etac)]$_x$" and ethyl acetoacetate. "[Al(OMe)$_2$(etac)]$_x$" was prepared by the addition of MeOH (20 g, 0.624 mol) to **5** (62.9 g, 0.115 mol). After having been stirred for 1 h, the volatiles were removed in vacuo. This procedure was repeated with 10 g of MeOH. This reaction mixture was then dissolved in 100 mL of pentane, and ethyl acetoacetate (29.8 g, 0.229 mol) was slowly added. After having been stirred for 12 h, a copious amount of a white solid precipitated from the solution. This product was collected by filtration and dried in vacuo (66 g, 91%). Compound **12** was recrystallized from CH_2Cl_2/pentane solution at −30 °C: ^{1}H NMR ($CDCl_3$) 4.89 (s, 2, MeC(O)C*H*C(O)OEt), 4.11 (br m, 4, MeC(O)CHC(O)OC*H*$_2$CH$_3$), 3.13 (s, 3, OCH$_3$), 1.90 (s, 6, *Me*C-(O)CHC(O)OEt), 1.24 (br t, 6, $^3J_{HH}$ = 7.0 Hz, MeC(O)CHC(O)-OCH$_2$C*H*$_3$); ^{13}C NMR (C_6D_6) 187.0 (Me*C*(O)CH(O)OEt), 174.6 (MeC(O)CH*C*(O)OEt, 85.3 (MeC(O)*C*HC(O)OEt), 60.4 (MeC(O)-CHC(O)O*C*H$_2$CH$_3$), 49.6 (OCH$_3$), 26.2 (*Me*C(O)CHC(O)OEt), 14.5 (MeC(O)CHC(O)OCH$_2$*C*H$_3$); mass spectrum (FD) *m/e* 632 (M$^+$), 503 (M$^+$ − etac). Anal. Calcd for $C_{26}H_{42}Al_2O_{14}$: C, 49.37; H, 6.69. Found: C, 49.37; H, 6.29.

Kinetics of Ligand Disproportionation of 9. Stock solutions (0.01 M and 0.1 M) of **9** were prepared in toluene-d_8. The disproportionation reaction was monitored by 200-MHz ^{1}H NMR. The MeC(O)C*H*C-(O)Me resonance of **9** can be clearly distinguished from those of the products, **1** and Al(acac)$_3$. The kinetics were determined by the relative integration of the respective resonances. After several minutes were allowed for temperature equilibration in the NMR probe, at least 10 spectra were recorded over a period of 2–4 half-lives. After each kinetic run, the temperature of the NMR probe was calibrated with use of an ethylene glycol standard. The k_{obsd}, $t_{1/2}$, correlation coefficient for each run, and the Arrhenius plot data are listed in Table III. The kinetic plot of the reaction at 72.7 °C is shown in Figure 6. The error of these kinetics is estimated to be ±5% based on the precision of the integration technique.

Acknowledgment. We thank Steve Dorn for obtaining the mass spectral data and gratefully acknowledge Drs. Ken Smith and Dave Gross for helpful discussions.

Study of the Formation of a σ,π-Vinyl Ligand by Hydrogen Atom Transfer from a Coordinated Dimethylamide to a Perpendicularly Bonded Ethyne Ligand. Preparation and Characterization of $(PMe_2Ph)Cl_2W(\mu\text{-}NMe_2)(\mu\text{-}\eta^1,\eta^2\text{-}CHCH_2)(\mu\text{-}\eta^2,\eta^1\text{-}CH_2NMe)WCl(NMe_2)(PMe_2Ph)$

Kazi J. Ahmed, Malcolm H. Chisholm,* Kirsten Folting, and John C. Huffman

Contribution from the Department of Chemistry and Molecular Structure Center, Indiana University, Bloomington, Indiana 47405. *Received August 19, 1985*

Abstract: Addition of ethyne (1 equiv) to hydrocarbon solutions of $W_2Cl_3(NMe_2)_3L_2$ yields μ-perpendicular alkyne adducts $W_2Cl_3(NMe_2)_3L_2(\mu\text{-}C_2H_2)$ where L = PMe_2Ph, I, and PMe_3, Ia. Compound Ia may also be obtained by the displacement of PMe_2Ph from I upon addition of PMe_3 (>2 equiv). The molecular structure of Ia, deduced from a single-crystal X-ray analysis, shows the presence of one μ-Cl, one μ-NMe_2, and the μ-C_2H_2 ligand. Each tungsten is also coordinated to three terminal ligands, NMe_2, Cl, and PMe_3, such that if the μ-C_2H_2 ligand is viewed to occupy a single coordination site, then the dinuclear compound can be considered to contain a central confacial bioctahedral core. ^{1}H and ^{13}C NMR data for I and Ia are entirely reconcilable with the structure found in the solid state for Ia. Of note are the small values of $J_{^{13}C-^{13}C}$, ca. 18 Hz in the labeled μ-*C_2H_2 containing compounds (*C represent 92.5 g-atom % ^{13}C) and the large chemical shift difference between the two types of μ-C nuclei, ca. 40 ppm. The compounds I and Ia react in benzene or toluene at and above room temperature to give compounds II and IIa, respectively, which contain a $W_2(\mu\text{-}C_2H_3)(\mu\text{-}CH_2NMe)$ core. The compounds II and IIa can be considered to have a $(W-W)^{10+}$ core supported by a bridging σ,π-vinyl(3−) and a bridging imine(2−) ligand. The structural characterization of II, by a single-crystal study, provides the first example of a μ-CH_2NMe ligand. The conversions of I to II and Ia to IIa have been followed by ^{1}H NMR spectroscopy as a function of time and temperature. A double-labeling experiment shows that transfer of an H atom to the μ-C_2H_2 carbon atom involves an intramolecular process. The rate of reaction is independent of added phosphine and shows a large primary kinetic isotope effect, k_H/k_D, of ca. 6 at +60 °C and a small but positive secondary isotope effect, k_H/k_D, of ca. 1.4 when the reaction rates are followed involving $N(CH_3)_2/N(CD_3)_2$ and μ-C_2H_2/μ-C_2D_2 labeled compounds, respectively. The entropy of activation is of medium magnitude and negative. Taken together, the data conform to a model in which C–H bond breaking (NMe_2) and forming (μ-C_2H_2) are of approximately equal importance in the transition state. A direct tranference of the H atom via a five-membered ring is thus favored over a reaction pathway involving initial β-hydrogen atom transfer to a metal atom. These reactions are compared to related findings reported in the literature. Crystal data are as follows: for (i) $W_2Cl_3(NMe_2)_3(PMe_3)_2(\mu\text{-}C_2H_2)\cdot{}^1/_2C_7H_8$ at −162 °C, a = 18.069 (7) Å, b = 14.108 (4) Å, c = 11.204 (3) Å, β = 106.09 (2)°, Z = 4, d_{calcd} = 2.01 g cm^{-3}, and space group $P2_1/a$; for (ii) $W_2(NMe_2)_2Cl_3(\mu\text{-}CH_2NMe)(\mu\text{-}C_2H_3)(PMe_2Ph)_2\cdot{}^1/_2C_7H_8$ at −160 °C, a = 16.929 (7) Å, b = 17.766 (8) Å, c = 11.108 (4) Å, α = 103.31 (2)°, β = 91.76 (2)°, γ = 78.59 (2)°, Z = 4, d_{calcd} = 2.01 g cm^{-3}, and space group $P\bar{1}$.

Previous studies of the reactions between alkynes and ditungsten hexaalkoxides have revealed a rich and varied chemistry.[1] The principle reactions discovered thus far include metathesis-like alkylidyne formation, alkyne adduct formation, carbon–carbon bond forming reactions, and the formation of alkylidyne-capped cluster compounds. There is also evidence for a kinetically facile equilibrium involving $W_2(\mu\text{-}C_2R_2)$- and W≡CR-containing compounds. The position of the equilibrium appears very sensitive to the nature of the alkoxide ligands and the substituent, R, on the alkyne.

We have been interested in how changes in the ligands bonded to tungsten would influence the reactivity of the W≡W bond toward alkynes. With that view, we have started to investigate

---

[1] Chisholm, M. H.; Hoffman, D. M.; Huffman, J. C. *Chem. Soc. Rev.* **1985**, *14*, 69 and references cited therein.

0002-7863/86/1508-0989$01.50/0