

Steric Separation of Nucleophile and Lewis Acid Providing Dramatically Accelerated Reaction. High-Speed Polymerization of Methyl Methacrylate with Enolate–Aluminum Porphyrin/Sterically Crowded Organoaluminum Systems

Masakatsu Kuroki, Tsuyoshi Watanabe, Takuzo Aida, and Shohei Inoue*

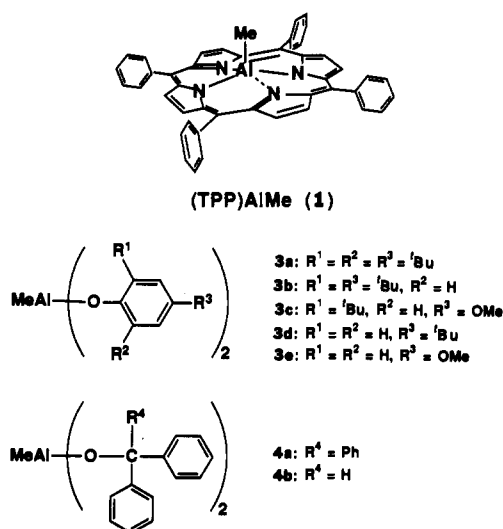
Department of Synthetic Chemistry
Faculty of Engineering, University of Tokyo
Hongo, Bunkyo-ku, Tokyo 113, Japan

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It has been recognized that nucleophilic reactions can be promoted by Lewis acids via coordinative activation of substrates and eventually provide high chemo- and stereoselectivities.¹ However, the reactions are usually accompanied by undesired attack of nucleophiles to Lewis acidic centers. Therefore, rigorous optimization of the reaction conditions, such as stoichiometry of reagents, choice of solvents, and reaction temperature, is a prerequisite.

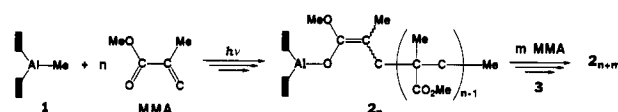
We report herein a novel, Lewis acid assisted, extremely rapid Michael addition of an enolate complex to an α,β -unsaturated ester, where the unfavorable reaction between nucleophile and Lewis acid is sterically suppressed. This was developed in the addition polymerization of methyl methacrylate (MMA) via an enolate complex of aluminum tetraphenylporphyrin (**2**, Scheme 1)² as the nucleophilic growing species in the presence of bulky organoaluminum compounds (**3a–c**, **4a**)^{1c,3} as Lewis acids.

For example, to a 100-mL round-bottomed flask fitted with a three-way stopcock, containing a CH_2Cl_2 solution (8 mL) of (TPP)AlMe (**1**, 0.2 mmol)⁴ under dry nitrogen, was added MMA (43.4 mmol), and the mixture was irradiated with visible light ($\lambda > 420 \text{ nm}$) at 35 °C to convert **1** to the enolate species (**2**).²



After a 2.5-h irradiation, the polymerization proceeded to attain only 6.1% conversion, indicating that the addition of **2** to MMA is very slow [$1.5 \times 10^{-3} \text{ mol s}^{-1} (\text{mol of } \mathbf{2})^{-1}$]. On the other hand, when 3 equiv of **3b** with respect to **2** was added at room temperature to the above reaction mixture under diffuse light, a

Scheme 1



strikingly vigorous reaction took place with heat evolution to attain 100% conversion within only 3 s [$68 \text{ mol s}^{-1} (\text{mol of } \mathbf{2})^{-1}$]. This corresponds to the acceleration of reaction by a factor of 45 300. In contrast, **3b** by itself did not bring about the polymerization of MMA under similar conditions.

Of much interest is the cleanness of the reaction with the **2/3b** system, as shown by the uniformity of the molecular weight of the produced polymer with the ratio of weight- and number-average molecular weights (M_w/M_n) being 1.09. The observed M_n value of the polymer (25 500) was in good agreement with the value (21 700)⁵ expected when every molecule of **2** produces one polymer molecule. When the initial mole ratio of MMA to **2** ($[\text{MMA}]_0/[\mathbf{2}]_0$) was changed in the range 200–500, the polymer with the degree of polymerization close to $[\text{MMA}]_0/[\mathbf{2}]_0$ ($M_w/M_n \sim 1.1$) was formed at 100% conversion. On the other hand, when the mole ratio $[\mathbf{3b}]_0/[\mathbf{2}]_0$ was decreased from 3.0 to 1.0 and then to 0.2, the degree of acceleration became less pronounced, while the number of polymer molecules produced⁶ remained almost unchanged and virtually equal to that of **2**. The polymer formed with the **2/3b** system has no phenoxy group originating from **3b**, as indicated by gel permeation chromatography (GPC) monitored at 253 nm. Accelerated polymerizations also took place when **3a**, **3c**, and **4a** were used in place of **3b**.

It is also interesting to note that the reaction of **2** with **3a** hardly took place in C_6D_6 at 25 °C, as observed by ^1H NMR examination of an equimolar mixture of **2** and **3a** over a period of 24 h, where possible products via ligand exchange, (TPP)AlMe (**1**) and (TPP)AlOPh, were not detected at all. This observation indicates a large steric barrier for the access of the bulky nucleophile (**2**) to the sterically crowded Lewis acidic center of **3a**. In conformity with this observation, in the two-stage polymerization of MMA with the **2/3a** (1/1) system ($[\text{MMA}]_0/[\mathbf{2}]_0$: 50 and 200 for the first and second stages, respectively), the second-stage polymerization also took place rapidly with heat evolution and was completed within 60 s even when the polymerization mixture after the first stage was allowed to stand at 25 °C for 4 h in the absence of the monomer. The GPC profile showed a clear increase in the molecular weight of the polymer, retaining the narrow molecular weight distribution (M_n : 7000 [$M_w/M_n = 1.12$] \rightarrow 47 600 [1.05]).

In contrast with **3a–c** and **4a**, when sterically less crowded organoaluminum compounds such as **3d**, **3e**, **4b**, and trimethylaluminum (Me_3Al) were used, the accelerated polymerizations did not occur. The ^1H NMR spectrum of the mixture of **2** and Me_3Al (1/1) in C_6D_6 at 25 °C showed the occurrence of a rapid ligand exchange, which was completed within 25 min, generating (TPP)AlMe (**1**) and a dimethylaluminum enolate.⁸

The highly reactive **2/bulky** organoaluminum systems have a potential utility to synthesize ultrahigh molecular weight polymers. For example, in the presence of **3b** (6 equiv), 6000 equiv of MMA with respect to **2** was consumed within only 6 min, affording the polymer with the M_n value of 596 000. The highly accelerated polymerization of MMA thus achieved is a consequence of the coordinative activation of MMA by the bulky Lewis acids, as evidenced by the clear downfield shifts for the ^1H NMR signals of MMA in the presence of **3b**.⁹

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(5) M_n (expected) = (molecular weight of MMA)($[\text{MMA}]_0/[\mathbf{1}]_0$)(conversion/100).

(6) Number of polymer molecules = polymer yield (g)/ M_n (gel permeation chromatography).

(7) **2** in C_6D_6 shows a characteristic signal at δ 0.53–0.61 due to the methoxy group of the terminal enolate unit [(TPP)AlOC(OCH₃)=C(C-H₃)CH₂].

(8) No polymerization of MMA took place with **1** under diffuse light (see ref 2). Polymerization of MMA with a dialkylaluminum enolate [$\text{Et}_2\text{AlOC}(\text{O}^i\text{Bu})=\text{CMe}_2$] proceeded very slowly to give the polymer with a much broader molecular weight distribution ($M_w/M_n = 5.6$).

In conclusion, a novel, Lewis acid assisted Michael reaction was realized by the combined use of a bulky nucleophile [enolate-aluminum porphyrin (2)] and sterically crowded Lewis acids (3a-c, 4a), where the reaction was dramatically rapid and clean owing to the steric suppression of the undesired attack of the nucleophile to the Lewis acidic center.

(9) ^1H NMR at 25 °C [CD_2Cl_2 , CH_2Cl_2 (δ 5.30) as internal standard] for MMA: δ 6.00 and 5.49 ($=\text{CH}_2$), 3.66 (OCH_3), 1.86 (CH_3). For MMA/3b (1/1): δ 6.41 and 5.81 ($=\text{CH}_2$), 3.92 (OCH_3), 1.98 (CH_3).

The Syntheses, Structures, and Reactivity of Monomeric Tungsten(IV) and Tungsten(VI) Bis(sulfido) Complexes: Facile Elimination of H_2 from H_2S

Daniel Rabinovich and Gerard Parkin*

Department of Chemistry, Columbia University
New York, New York 10027

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Complexes containing metal-ligand multiple bonds,^{1,2} e.g., $\text{L}_n\text{M}=\text{E}$ (E = O, S; NR, PR; CR_2 , SiR_2) and $\text{L}_n\text{M}\equiv\text{E}$ (E = N, P; CR), are of considerable interest both in terms of their bonding and reactivity. Furthermore, research in this area has been prompted as a consequence of the roles that such groups may play in important processes such as oxidation, hydrodesulfurization, hydrodenitrification, and nitrogen fixation. Although the most common class of metal-ligand multiple bond encountered is the metal-oxo, surprisingly few studies have been reported on the closely related terminal metal-sulfido systems. In part this is a result of the lack of suitable synthetic methods for terminal sulfido complexes and also the tendency for sulfido ligands to bridge two or more metal centers.³ Here we report the syntheses, structures, and reactivity of some tungsten bis(sulfido) complexes that are stabilized by trimethylphosphine coligands.

The purple bis(sulfido) complex $\text{trans-W}(\text{PMe}_3)_4(\text{S})_2$ is readily obtained by the reaction of $\text{W}(\text{PMe}_3)_4(\eta^2\text{-CH}_2\text{PMe}_2)\text{H}^4$ with H_2S in benzene at room temperature (Scheme I).^{5,6} Although sulfido and imido ligands are isoelectronic, it is interesting to contrast the formation of the six-coordinate 18-electron bis(sulfido) complex $\text{trans-W}(\text{PMe}_3)_4(\text{S})_2$ with that of the related bis(imido) system reported by Schrock, for which the four-coordinate tetrahedral derivative $\text{W}(\text{PMe}_2\text{Ph})_2(\text{NAr})_2$ (Ar = 2,6- $\text{C}_6\text{H}_3\text{Pr}^t_2$) was isolated.⁷

The facile elimination of hydrogen from H_2S giving $\text{W}(\text{PMe}_3)_4(\text{S})_2$ is of considerable interest in view of the proposal that hydrogenation of organic substrates during hydrodesulfurization may involve hydrogen transfer from a -SH group.⁸ Thus, we

have demonstrated that the elimination of dihydrogen from H_2S proceeds via the initial formation of the proposed hydrido-hydrosulfido intermediate $\text{W}(\text{PMe}_3)_4(\text{H})_2(\text{SH})_2$, which may be isolated if the reaction is carried out in pentane. Although complete characterization of $\text{W}(\text{PMe}_3)_4(\text{H})_2(\text{SH})_2$ is precluded by its instability in solution (vide infra), evidence for its formulation is provided by the observation of both $\nu_{\text{W-H}}$ and $\nu_{\text{S-H}}$ at 1860 and 2545 cm^{-1} , respectively, in the solid-state (KBr pellet) IR spectrum.⁹ Solutions of yellow $\text{W}(\text{PMe}_3)_4(\text{H})_2(\text{SH})_2$ immediately eliminate hydrogen at room temperature giving purple $\text{W}(\text{PMe}_3)_4(\text{S})_2$. The stoichiometry of this reaction has been confirmed by carrying out the reaction in the presence of $\text{W}(\text{PMe}_3)_4\text{H}_2(\eta^2\text{-OC}_6\text{H}_4)$, a hydrogen trap (eq 1).¹⁰ In this regard,

$$\text{W}(\text{PMe}_3)_4(\text{H})_2(\text{SH})_2 + 2\text{W}(\text{PMe}_3)_4\text{H}_2(\eta^2\text{-OC}_6\text{H}_4) \rightarrow \text{W}(\text{PMe}_3)_4(\text{S})_2 + 2\text{W}(\text{PMe}_3)_4\text{H}_3(\text{OC}_6\text{H}_5) \quad (1)$$

the reactions of other transition-metal complexes with H_2S have been the subject of previous investigations. Whereas the formation of a bridging sulfido complex accompanied by elimination of H_2 has been observed,¹¹ the facile elimination of H_2 and formation of a terminal sulfido complex at a single metal center has not previously been reported to our knowledge.¹²

Dissociation of the trimethylphosphine ligands from $\text{W}(\text{PMe}_3)_4(\text{S})_2$ is facile, as evidenced by the rapid formation of the red-brown isocyanide derivatives $\text{trans,trans,trans-W}(\text{PMe}_3)_2(\text{CNR})_2(\text{S})_2$ [R = Pr^t, Bu^t, *c*- C_6H_{11}].⁶ The complexes $\text{W}(\text{PMe}_3)_4(\text{S})_2$ and $\text{W}(\text{PMe}_3)_2(\text{CNR})_2(\text{S})_2$ represent rare examples of 18-electron complexes containing terminal sulfido ligands, and, as such, the electronic nature of the tungsten center inhibits lone-pair donation so that the bond order in these complexes is aptly described as two (i.e., $\text{W}=\text{S}$ versus $\text{W}\equiv\text{S}^+$).¹³ Support for this formalism is provided by the observation of particularly low $\nu_{\text{W-S}}$ stretching frequencies in the range 385-393 cm^{-1} .¹⁴ Furthermore, the molecular structure of the derivative $\text{W}(\text{PMe}_3)_2(\text{CNBu}^t)_2(\text{S})_2$ has been determined,¹⁵ and the $\text{W}=\text{S}$ bond

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(9) IR assignments have been confirmed by deuterium labeling: $\nu_{\text{W-D}} = 1337 \text{ cm}^{-1}$ ($\nu_{\text{H}}/\nu_{\text{D}} = 1.39$) and $\nu_{\text{S-D}} = 1850 \text{ cm}^{-1}$ ($\nu_{\text{H}}/\nu_{\text{D}} = 1.38$). Further support for the formulation of the intermediate as $\text{W}(\text{PMe}_3)_4(\text{H})_2(\text{SH})_2$ is provided by the observation that oxidative addition of other reagents HX (X = H, SiH_3 , Cl) to $\text{W}(\text{PMe}_3)_4(\eta^2\text{-CH}_2\text{PMe}_2)\text{H}$ gives similar products $\text{W}(\text{PMe}_3)_4(\text{H})_2(\text{X})_2$; ref 4 and Rabinovich, D.; Parkin, G., unpublished results.

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(13) The 18-electron sulfido complexes $\text{W}(\text{PMe}_3)_4(\text{S})_2$ and $\text{W}(\text{PMe}_3)_2(\text{CNBu}^t)_2(\text{S})_2$ can be seen to be closely related to oxo complexes of the type $[\text{OsL}_4(\text{O})_2]^{2+}$ (see ref 1).

(14) $\nu_{\text{W-S}}$ stretching frequencies and $\text{W}=\text{S}$ bond lengths are typically in the ranges 450-570 cm^{-1} and 2.06-2.18 Å, respectively. (a) Chisholm, M. H.; Huffman, J. C.; Pasterczyk, J. W. *Polyhedron* 1987, 6, 1551-1557, and references therein. (b) Müller, A. *Polyhedron* 1986, 5, 323-340, and references therein.

(15) Crystal data for $\text{W}(\text{PMe}_3)_2(\text{CNBu}^t)_2(\text{S})_2$: monoclinic, $P2_1/n$ (no. 14), $a = 11.003$ (2) Å, $b = 10.513$ (3) Å, $c = 11.947$ (3) Å, $\beta = 109.87$ (2)°, $V = 1299.6$ (6) Å³, $Z = 2$, ρ_{calc} = 1.57 g cm^{-3} , μ (Mo K α) = 49.9 cm^{-1} , λ (Mo K α) = 0.710 73 Å (graphite monochromator); 2978 unique reflections with $3^\circ < 2\theta < 55^\circ$ were collected of which 2032 reflections with $F > 6\sigma(F)$ were used in refinement; $R = 0.0302$, $R_w = 0.0389$, GOF = 2.108.

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(5) A solution of $\text{W}(\text{PMe}_3)_4(\eta^2\text{-CH}_2\text{PMe}_2)\text{H}$ (1.0 g, 1.8 mmol) in pentane (ca. 30 mL) was treated with H_2S (1 atm) resulting in the rapid formation of yellow microcrystalline $\text{W}(\text{PMe}_3)_4(\text{H})_2(\text{SH})_2$, which was isolated by filtration at -78 °C. The isolated $\text{W}(\text{PMe}_3)_4(\text{H})_2(\text{SH})_2$ was redissolved in benzene to give a red-purple solution, accompanied by the evolution of H_2 . The solution was filtered, and the solvent was removed in vacuo to give purple $\text{W}(\text{PMe}_3)_4(\text{S})_2$ (0.63 g, 63%). NMR data for $\text{W}(\text{PMe}_3)_4(\text{S})_2$ (in C_6D_6): ^1H δ 1.67, virtual triplet, $J_{\text{P-H}} = 2.7 \text{ Hz}$; $^{13}\text{C}\{^1\text{H}\}$ δ 25.1, multiplet, $J_{\text{P-C}} = 13 \text{ Hz}$; $^{31}\text{P}\{^1\text{H}\}$ (relative to H_3PO_4) δ -44.3, s, $J_{\text{W-P}} = 268 \text{ Hz}$; IR data (KBr pellet): $\nu_{\text{W-S}} = 390 \text{ cm}^{-1}$. Anal. Calcd for $\text{C}_{12}\text{H}_{36}\text{S}_2\text{W}$: C, 26.1; H, 6.6. Found: C, 26.1; H, 6.4.

(6) All new compounds have been characterized analytically and spectroscopically (see supplementary material).

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