

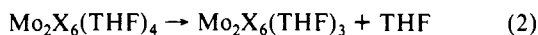
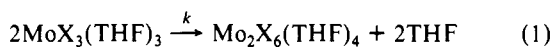
extent and because these peaks probably overlap with the β -H resonances of I and with the α -H resonances of III and IV. The stereoisomerism suggested for the confacial bioctahedral structure is analogous to that reported for the $[\text{Mo}_2\text{X}_7(\text{PMe}_2)_2]^-$ ($\text{X} = \text{Cl}, \text{I}$) ions.^{21,22}

The following points are also worthy of note. There is no extra peak in the NMR spectrum that could be assigned to a mononuclear facial isomer. Therefore, the $\text{MoX}_3(\text{THF})_3$ compounds are present *in solution* as meridional isomers exclusively. Integration establishes that the amounts of free THF and THF of compounds III and IV that are produced are equivalent to each other and correspond to 1.5 mol per mole of $\text{MoCl}_3(\text{THF})_3$ consumed. However, extrapolation of the data to zero time shows that the starting materials were already contaminated by free THF (for $\text{X} = \text{Cl}, \text{Br}$) and face-sharing dimers (for $\text{X} = \text{Cl}$).

An important point emerges from the latter observation. Most of the recommended procedures for the synthesis of $\text{MoCl}_3(\text{THF})_3$ involve the use of CH_2Cl_2 as solvent or cosolvent for the synthesis or separation procedure.^{1b,6,7} The product has been described before as orange, brownish-orange, pink, pinkish-purple, and even blue-purple.^{1b,2c,6,7,9} We propose that these different colors are the result of variable amounts of dinuclear impurities. According to our study, the product can be expected to be a mixture of $\text{MoCl}_3(\text{THF})_3$ and $\text{Mo}_2\text{Cl}_6(\text{THF})_3$, containing perhaps minor amounts of $\text{Mo}_2\text{Cl}_6(\text{THF})_4$ and free THF. Wedd and co-workers^{1b} reported that $\text{MoCl}_3(\text{THF})_3$ loses THF in benzene to afford a pinkish-red, diamagnetic solid, which they formulated as $\text{Mo}_3\text{Cl}_6(\text{THF})_5$ on the basis of analytical data. A subsequent investigation by electronic spectroscopy suggested that association to $\text{Mo}_2\text{Cl}_6(\text{THF})_3$ occurs instead.²⁵ The conversion of III and IV back to $\text{MoCl}_3(\text{THF})_3$ in THF is very slow (less than 20% conversion over 48 h at room temperature).

The above NMR data can be interpreted in terms of the two-step process illustrated in Scheme I. A preliminary kinetic analysis for the bromide system indicates a second-order decay of the monomer concentration, for a k value of $0.431 \pm 0.005 \text{ M}^{-1} \text{ min}^{-1}$ at 30 °C. The data for the chloride system are less accurate.

Scheme I



but the two halide systems take approximately the same time to transform to the final dinuclear product. More kinetic studies are planned for the near future.

Similar equilibria might take place with different ligand systems. For instance, the acetonitrile derivatives $\text{MoCl}_3(\text{MeCN})_3 \cdot \text{MeCN}$,⁸ $\text{MoCl}_3(\text{MeCN})_3$,⁹ and $\text{Mo}_2\text{Cl}_6(\text{MeCN})_3$ ²⁶ have all been described. We are planning to reinvestigate these compounds as well as others and to study the monomer/dimer interconversion by paramagnetic ¹H NMR.

Acknowledgment. We are grateful to the University of Maryland, College Park (UMCP), Department of Chemistry and Biochemistry, the UMCP General Research Board, the Camille and Henry Dreyfus Foundation (for a Distinguished New Faculty Award to R.P.), and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support. H.D.M. thanks the UMCP office of Undergraduate Studies for a Senior Summer Fellowship.

Supplementary Material Available: A figure showing the linear relationship between the inverse concentration of $\text{MoBr}_3(\text{THF})_3$ and time (1 page). Ordering information is given on any current masthead page.

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(27) **Note Added in Proof:** While this manuscript was in press, the solid-state structure of *mer*- $\text{MoCl}_3(\text{THF})_3$ has appeared: Hofacker, P.; Frieberl, C.; Dehnicke, K.; Bäuml, P.; Hiller, W.; Strähle, J. *Z. Naturforsch.* 1989, 44B, 1161.

A Well-Defined Rhenium(VII) Olefin Metathesis Catalyst

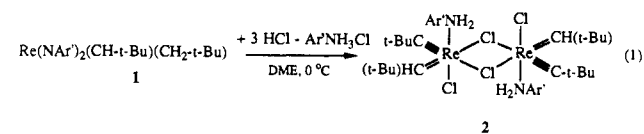
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Received October 20, 1989

Molybdenum, tungsten, and rhenium are the three most active metals in classical olefin metathesis systems.¹ Molybdenum(VI)² and tungsten(VI)³ alkylidene complexes of the type $\text{M}(\text{CHR}')(\text{NAr})(\text{OR})_2$ ($\text{Ar} = 2,6\text{-C}_6\text{H}_3\text{-}i\text{-Pr}_2$) have been shown to be well-behaved olefin metathesis catalysts with an activity that can be controlled through the choice of OR. Although several rhenium alkylidene complexes have been reported,⁴ none has shown any confirmable metathesis activity, even toward strained cyclic olefins such as norbornene. Since $\text{Re}\equiv\text{CR}''$ and $\text{M}=\text{NR}''$ ($\text{M} = \text{Mo}$ or W) can be regarded as isoelectronic units, plausible candidates as olefin metathesis catalysts are complexes of the type $\text{Re}(\text{CHR}')(\text{CR}'')(\text{OR})_2$. We report here that such a complex in which $\text{OR} = \text{OCMe}(\text{CF}_3)_2$ is a well-behaved olefin metathesis catalyst.

Treatment of orange $\text{Re}(\text{NAr}')_2(\text{CH-}t\text{-Bu})(\text{CH}_2\text{-}t\text{-Bu})$ (**1**) ($\text{Ar}' = 2,6\text{-C}_6\text{H}_3\text{Me}_2$)^{4c} with excess HCl in dimethoxyethane at 0 °C affords $[\text{Re}(\text{C-}t\text{-Bu})(\text{CH-}t\text{-Bu})(\text{H}_2\text{NAr}')\text{Cl}_2]_2$ (**2**, eq 1) in 80% yield.⁵ Two isomers of **2** are observed in solution. The structure



of what we presume to be the major isomer has been determined by an X-ray study, details of which will be published in the full report. The structure is that shown in eq 1 in which the alkylidene

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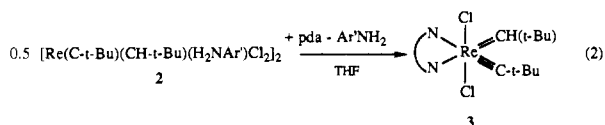
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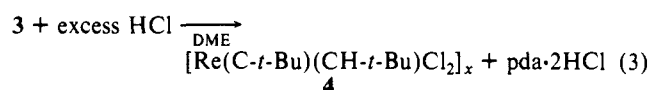
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(5) A solution of $\text{Re}(\text{NAr}')_2(\text{CH-}t\text{-Bu})(\text{CH}_2\text{-}t\text{-Bu})$ (4.64 g, 8.2 mmol) in dimethoxyethane (100 mL) was cooled to 0 °C and treated with HCl (590 mL, 26 mmol). The orange solution immediately darkened, and a white precipitate formed. After stirring of the solution at 25 °C for 2.5 h, the solvent was removed in vacuo, leaving a beige powder, which was extracted away from insoluble $\text{Ar}'\text{NH}_2\text{Cl}$ with benzene and filtered through a pad of Celite. The filtrate was then reduced to dryness in vacuo and washed with pentane, to yield a faintly orange powder (3.4 g, 80%): ¹H NMR (C_6D_6) (major isomer) δ 14.49 (s, 2, *CH-t-Bu*), 6.7–6.5 (m, 6, H_{ar}), 6.7 and 6.3 (d, 2, NH_2), 2.37 and 2.17 (s, 6, 2,6- $\text{C}_6\text{H}_3\text{Me}_2$), 1.39 and 1.01 (s, 18, CMe_3); ¹³C NMR (THF-*d*₆, major isomer) δ 292.1 (*C-t-Bu*), 286.3 (*CH-t-Bu*, $J_{\text{CH}} = 130 \text{ Hz}$), 144.2 (C_{ipso}), 128.7 (C_{meta}), 123.7 (C_{ortho}), 119.5 (C_{para}), 53.4 and 46.8 (CMe_3), 31.5 and 28.5 (CMe_3). Anal. Calcd for $\text{C}_{36}\text{H}_{60}\text{Cl}_4\text{N}_2\text{Re}_2$: C, 41.77; H, 5.84; N, 2.71. Found: C, 42.11; H, 6.00; N, 2.50.

ligand lies in the C/Re/C plane and the *tert*-butyl group of the neopentylidene ligand points toward the neopentylidene ligand (syn orientation). Reaction of **2** with 2 equiv of phenylenediamine (pda) in tetrahydrofuran or methylene chloride at room temperature yields $\text{Re}(\text{C-}t\text{-Bu})(\text{CH-}t\text{-Bu})(\text{pda})\text{Cl}_2$ (**3**, eq 2) in 95% yield.⁶ One possible configuration (based on NMR data) is that



shown in eq 2. **3** reacts with excess HCl gas in dimethoxyethane at room temperature to yield $[\text{Re}(\text{C-}t\text{-Bu})(\text{CH-}t\text{-Bu})\text{Cl}_2]_x$ (**4**, eq 3) in 85% yield.⁷ **4** is believed to be a polymer in the solid state, but it is soluble in dimethoxyethane and therefore easily separated from virtually insoluble $\text{pda} \cdot 2\text{HCl}$.



Addition of 2 equiv of potassium hexafluoro-*tert*-butoxide to **4** suspended in dichloromethane at 25 °C affords $\text{Re}(\text{C-}t\text{-Bu})(\text{CH-}t\text{-Bu})[\text{OCMe}(\text{CF}_3)_2]_2$ (**5**) quantitatively as an orange oil.⁸ Although **5** decomposes slowly when isolated, it appears to be stable indefinitely in solution at concentrations of ~10 mM. It is presumably a pseudotetrahedral species in which the *tert*-butyl group of the neopentylidene ligand points toward the neopentylidene ligand (syn orientation).^{2b,3a}

Ten equivalents of *cis*-3-hexene reacts with **5** in C_6D_6 in 7 h at 25 °C to give a product quantitatively versus an internal standard whose ¹H and ¹³C NMR spectra⁹ are consistent with it being two isomers of $\text{Re}(\text{C-}t\text{-Bu})(\text{CHEt})[\text{OCMe}(\text{CF}_3)_2]_2$. It is important to note that the neopentylidene ligand is unaltered, a fact that suggests that proton transfer from an alkylidene ligand to the neopentylidene ligand is slow and that the neopentylidene ligand therefore is an ancillary ligand in this reaction. We propose that the isomers of $\text{Re}(\text{C-}t\text{-Bu})(\text{CHEt})[\text{OCMe}(\text{CF}_3)_2]_2$ are syn and anti alkylidene rotamers, the anti rotamer being that in which the ethyl group of the propylidene ligand points away from the neopentylidene ligand. Complexes of the type $\text{M}(\text{CHR}')(\text{NAr})(\text{OR})_2$ (M = Mo^{2b} or W¹⁰) are also believed to form rotamers.

Compound **5** is an effective catalyst for the metathesis of internal and functionalized olefins. The activity of **5** is limited by its relatively slow reaction with olefin, but the rate of metathesis

increases appreciably when a smaller alkylidene ligand is formed. For example, **5** metathesized 100 equiv of *cis*-2-pentene in benzene to an equilibrium mixture (1:2:1) of 2-butenes, 2-pentenenes, and 3-hexenes in 2.5 h at 25 °C. Another 100 equiv of *cis*-2-pentene was then added and was equilibrated in less than 30 min.

Methyl oleate reacts slowly with **5**. Methyl oleate (5 equiv) in C_6D_6 converted 40% of **5** to two new alkylidene complexes in 12 h, according to proton NMR spectra. A reaction involving 50 equiv of methyl oleate with **5** in dichloromethane required 12 h to reach equilibrium [1:2:1 mixture of $\text{Me}(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{Me}$, $\text{Me}(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{CO}_2\text{Me}$, and $\text{MeO}_2\text{C}(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{CO}_2\text{Me}$]. After 24 h, another 50 equiv of methyl oleate was added to this solution, and equilibrium was reached in 7.5 h. When **5** was first treated with 10 equiv of *cis*-3-hexene for several hours and then 50 equiv of methyl oleate was added, equilibrium was reached in 3 h. An additional 100 equiv of methyl oleate added to this mixture was equilibrated in 6 h.

To our knowledge, this is the first time that olefin metathesis by rhenium alkylidene complexes has been proven.¹¹ Until now, only heterogeneous Re metathesis catalysts had been prepared, and the oxidation state of the metal was not known.¹ We currently are studying modification of the ligands in this system, polymerization of cyclic olefins and acetylenes, metathesis of functionalized olefins, and pathways of catalyst deactivation.

Acknowledgment. R.R.S. thanks the National Science Foundation for support through Grant CHE 88-22508.

(11) (a) Some metathesis activity, presumably homogeneous, starting with a characterized alkylidene complex has been observed before,^{11b} although the nature of the active species could not be determined. (b) Edwards, D. S. Ph.D. Thesis, MIT, 1983.

Stepwise Mechanism of Formal 1,5-Sigmatropic Rearrangement of Dimethyl 3,3-Dialkyl-3H-pyrazole-4,5-dicarboxylates

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Received August 30, 1989

(6) 1,2-Phenylenediamine (0.31 g, 2.9 mmol) was added to $[\text{Re}(\text{C-}t\text{-Bu})(\text{CH-}t\text{-Bu})(\text{H}_2\text{NAr})\text{Cl}_2]_2$ (1.5 g, 1.45 mmol) in 40 mL of THF. The orange solution rapidly darkened, and after 25 min, the solvent was removed in vacuo. The resulting pale orange solid was washed with pentane and then twice reprecipitated from 10 mL of THF with pentane, to give 1.39 g of product (95%): ¹H NMR (CD_2Cl_2) δ 13.52 (s, 1, *CH-}t\text{-Bu}*), 7.31 (m, 4, H_{ar}), 4.74 (br s, 4, NH_2), 1.38 and 1.32 (s, 9, *C-}t\text{-Bu}*); ¹³C NMR (CD_2Cl_2) δ 295.6 (*C-}t\text{-Bu}*), 292.0 (*CH-}t\text{-Bu}*, $J_{\text{CH}} = 118$ Hz), 138.1 ($\text{C}_{1,2}$), 130.1, 129.0, 128.4, and 127.5 ($\text{C}_{3,6}$), 52.9 and 47.0 (CMe_3), 31.2 and 28.1 (CMe_3).

(7) Addition of HCl(g) (98 mL, 4.4 mmol) via syringe to a dimethoxyethane solution of **3** (1.0 g, 1.98 mmol) yielded a white precipitate immediately. After 20 min, the precipitate was removed by filtration and the orange filtrate reduced to dryness in vacuo. The resulting solid was washed with pentane, to afford a pale orange powder (0.67 g, 85%), which is insoluble in all but strongly coordinating solvents: ¹H NMR ($\text{THF-}d_6$) δ 13.26 (s, 1, *CH-}t\text{-Bu}*), 1.35 and 1.26 (s, 9, *C-}t\text{-Bu}*); ¹³C NMR ($\text{THF-}d_6$) δ 293.9 (*C-}t\text{-Bu}*), 285.8 (*CH-}t\text{-Bu}*, $J_{\text{CH}} = 125$ Hz), 53.59 and 46.66 (CMe_3), 31.4 and 28.4 (CMe_3). Anal. Calcd for $\text{C}_{10}\text{H}_{19}\text{Cl}_2\text{Re}$: C, 30.30; H, 4.83. Found: C, 30.21; H, 4.84.

(8) ¹H NMR (C_6D_6): δ 11.05 (s, 1, *CH-}t\text{-Bu}*), 1.15 and 1.13 (s, 9, *C-}t\text{-Bu}*), 1.11 [s, 6, $\text{OC}(\text{CF}_3)_2\text{Me}$]. ¹³C: δ 295.8 (*C-}t\text{-Bu}*), 248.8 (*CH-}t\text{-Bu}*, $J_{\text{CH}} = 127$ Hz), 54.8 and 45.3 (*C-}t\text{-Bu}*), 31.9 and 29.9 (CMe_3). Related bisalkoxide derivatives in which $\text{OR} = \text{O-}t\text{-Bu}$,^{4a} $\text{O-2,6-C}_6\text{H}_3\text{-}i\text{-Pr}_2$, $\text{O-2,6-C}_6\text{H}_3\text{Me}_2$, and $\text{OCMe}_2(\text{CF}_3)$ have also been prepared. They will be discussed in later publications.

(9) ¹H NMR (C_6D_6 , major, minor): δ 11.36, 12.42 (t, 1, *CHEt*, $J_{\text{HH}} = 6, 9$ Hz), 4.03, 3.71 (dq, 2, *CHCH}_2\text{Me}*). ¹³C (CD_2Cl_2): δ 299.7, 303.2 (*C-}t\text{-Bu}*), 245.2, 245.0 (*CHEt*, $J_{\text{CH}} \sim 126$ Hz), 55.9, 33.1 (CMe_3), 35.4, 48.2 (*CHCH}_2\text{Me}*).

(10) Bazan, G.; Crowe, W.; DiMare, M.; Robbins, J., unpublished results.

Intramolecular migrations of atoms or groups from an sp^3 carbon to a proximate sp^2 atom of a five-membered, four- π -electron ring are well recognized. Probably the most familiar of such rearrangements is the migration of a hydrogen atom around the cyclopentadiene ring¹ that rapidly interconverts 5-alkylcyclopentadienes with their 1-alkyl and 2-alkyl isomers, Scheme I. Similar H migrations are common in acyclic conjugated diene systems,²⁻⁴ and there are examples also of analogous migrations of alkyl,^{2,3,5} aryl,^{2,3,6} acyl,^{2,7} vinyl,³ alkynyl,⁸ and cyano⁸ groups.

* Author to whom correspondence may be addressed.

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