

Preparation of Rhenium(VII) Monoimido Alkylidyne Complexes and Metathesis of Acetylenes via Rhenacyclobutadiene Intermediates

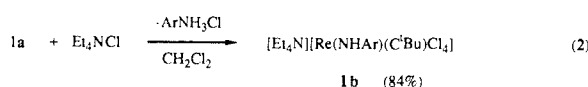
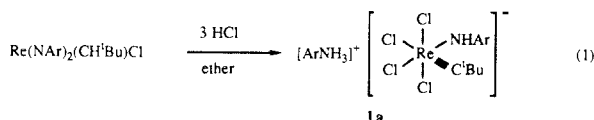
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Received October 21, 1987

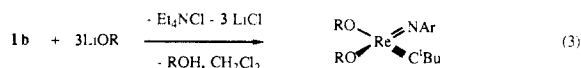
Metathesis of acetylenes by "d⁰" molybdenum and tungsten alkylidyne complexes of the type M(CR)(OR')₃ (R is alkyl, R' is alkyl, fluoroalkyl, or aryl) has been established in the last few years.¹ An interesting question is whether a related rhenium(VII) acetylene metathesis catalyst can be designed, since although acetylene metathesis by rhenium is unknown, rhenium-based catalysts for metathesizing olefins are well-known.² We report here several four-coordinate monoimido bisalkoxide neopentylidyne complexes, the metathesis of several internal acetylenes by one of them, and the X-ray structure of a rhenacyclobutadiene complex.

The reaction between Re(NAr)₂(CH-*t*-Bu)Cl (Ar = 2,6-C₆H₃-*i*-Pr₂)³ and 3 equiv of HCl gives what we propose is **1a** as an insoluble orange powder (96% crude yield; eq 1).⁴ **1a** is soluble



enough in THF-*d*₈ to observe a broad resonance of area 1 that can be assigned to NHAr at 16.75 ppm and a very broad resonance of area 3 at 8.3 ppm that can be assigned to ArNH₃. A more tractable tetraethylammonium salt **1b** can be prepared by cation exchange (eq 2). In the ¹H NMR spectrum of **1b** in CD₂Cl₂ the ArNH resonance at 16.93 ppm is now relatively sharp; the neopentylidyne C_α resonance is found at 315.9 ppm. The reaction shown in eq 1 is believed to be related to that between Re(N-*t*-Bu)₂(CH-*t*-Bu)(CH₂-*t*-Bu) and 3 equiv of HCl to give [Re(C-*t*-Bu)₂(CH-*t*-Bu)(NH₂-*t*-Bu)Cl₂]₂,⁵ the key feature in that case being initial protonation of the imido ligand followed by transfer of the neopentylidene α proton to a nitrogen atom (in an imido or amido ligand).

Addition of 3 equiv of LiOR to **1b** gives the alkylidyne complexes **2a-d** shown in eq 3.⁶ (One equiv of LiOR is required for dehydrohalogenating **1b**.) We were somewhat surprised that these four-coordinate complexes (especially **2c**) do not retain chloride to give complexes of the type [Re(C-*t*-Bu)(NAr)(OR)₂Cl]⁻, since **2a-d** are only 16-electron species (counting the imido electron



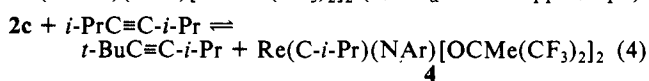
2a: OR = O^{*t*}Bu
2b: OR = OCMe₂(CF₃)
2c: OR = OCMe(CF₃)₂
2d: OR = O-2,6-C₆H₃Pr₂

pair). The high solubility of **2a-d** in pentane suggests that they are monomers, as is their relative, W(CHPh)(NAr)[OCMe(CF₃)₂]₂ (by X-ray studies⁷).

Only **2c** reacts with internal acetylenes readily.⁸ The reaction with 3-hexyne proceeds rapidly at 25 °C to give 1 equiv of *tert*-butylethylacetylene and a dark, orange-brown product **3** that can be isolated in crystalline form in high yield from pentane. An X-ray study⁹ revealed that **3** is a rhenacyclobutadiene complex in which the ReC₃ ring is bent and unsymmetrically bound to the metal (Figure 1). Since N(1), O(3), and C(43) form a trigonal planar arrangement, we can describe the core geometry in **3** as approximately trigonal bipyramidal with the ring spanning axial (C(41)) and equatorial (C(43)) positions. The two Re-C_α bond lengths (Re-C(41) = 1.88 (1) Å; Re-C(43) = 2.09 (1) Å) differ by an amount well beyond 3σ, as do the C_α-C_β bond lengths (C(42)-C(43) = 1.33 (2) Å; C(41)-C(42) = 1.46 (1) Å). The dihedral angle between the C(41)/ReC(43) and C(41)/C(42)/C(43) planes is 34°. These values should be compared with those for a bent tungstacyclobutadiene complex¹⁰ which has W-C_α bond lengths of 1.943 (5) Å and 2.132 (5) Å, C_α-C_β bond lengths of 1.382 (8) Å and 1.485 (7) Å, and a dihedral angle between planes of 58°.

¹³C NMR spectra of **3** at 193 K in toluene-*d*₈ are consistent with it being asymmetric on the NMR time scale. Two resonances at 277.9 and 199.7 ppm can be ascribed to the C_α carbon atoms and a resonance at 141.9 ppm to C_β. At 298 K only a single broad C_α resonance is observed at 241 ppm, while the β carbon resonance is still sharp at 143.9 ppm (cf. 256.2 ppm for C_α and 134.4 ppm for C_β in trigonal bipyramidal W(C₃Et₃)[OCMe(CF₃)₂]₃ in benzene-*d*₆¹¹). We propose that the structure of **3** in solution at low temperatures is essentially the same as that observed in the solid state and that at higher temperatures a "pseudorotational" process interconverts the two α carbon atoms (C(41) and C(43)) and the two alkoxide ligands.¹²

When **2c** is treated with diisopropylacetylene, rhenacycles analogous to **3** are *not* observed at 25 °C, only a mixture of **2c** and what appears to be an analogous isobutylidyne complex, Re(C-*i*-Pr)(NAr)[OCMe(CF₃)₂]₂ (**4**; δ C_α = 300.5 ppm; eq 4).



The relative amounts of **2c** and **4** shift as expected upon addition of more diisopropylacetylene, a result that suggests that they interconvert readily, most likely via rhenacyclobutadiene complexes. Evidently rhenacycles that contain isopropyl or *tert*-butyl substituents can form but are relatively unstable toward loss of an acetylene.

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(3) Horton, A. D.; Schrock, R. R.; Freudenberger, J. H. *Organometallics* 1987, 6, 893.

(4) HCl gas (210 mL, 9.4 mmol) was added via syringe to a stirred ether (250 mL) solution of Re(NAr)₂(CH-*t*-Bu)Cl (2.0 g, 3.12 mmol) at -78 °C. A fine orange precipitate formed after 5 min, and the mixture was then warmed to 25 °C over 1 h. The precipitate was collected by filtration and washed with ether (250 mL); yield 2.24 g (96%). A complete description of the preparation of all compounds reported here can be found in the Supplementary Material along with analytical data (except for **1a** and **4**) and spectroscopic data.

(5) Edwards, D. S.; Biondi, L. V.; Ziller, J. W.; Churchill, M. R.; Schrock, R. R. *Organometallics* 1983, 2, 1505.

(6) Isolated yields 0.14 g/85% **2a**, 1.17 g/80% **2b**, 0.43 g/86% **2c**, 1.7 g/75% **2d**, respectively; δ C_α (CD₂Cl₂) 291.0, 297.6, 304.6, 304.4 ppm, respectively.

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(8) **2b** does not react readily at 25 °C with 20 equiv of 4-nonyne or 1 equiv of phenylacetylene or 1-pentyne.

(9) A crystal was mounted on a glass fiber under a stream of cold nitrogen. Data were collected on a Rigaku AFC6R diffractometer at -70 °C by using Mo Kα radiation. A total of 8189 reflections (+*h*, +*k*, ±*l*) were collected in the range 3° < 2θ < 55° with the 5520 having *I* > 3.00σ(*I*) being used in the structure refinement by full-matrix least-squares techniques (401 variables) by using the TEXSAN crystallographic software package from Molecular Structure Corporation. Final R₁ = 0.070 and R₂ = 0.091. Full details can be found in Supplementary Material.

(10) Churchill, M. R.; Ziller, J. W.; McCullough, L.; Pedersen, S. F.; Schrock, R. R. *Organometallics* 1983, 2, 1046.

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(12) What is probably a related interconversion of α carbon atoms in bent tungstacyclobutadiene complexes of the generic type W(η⁵-C₅H₅)Cl₂(C₃R₃) has been observed.¹⁰ Unfortunately, these processes could not be studied in detail because of the limited solubility of such compounds.

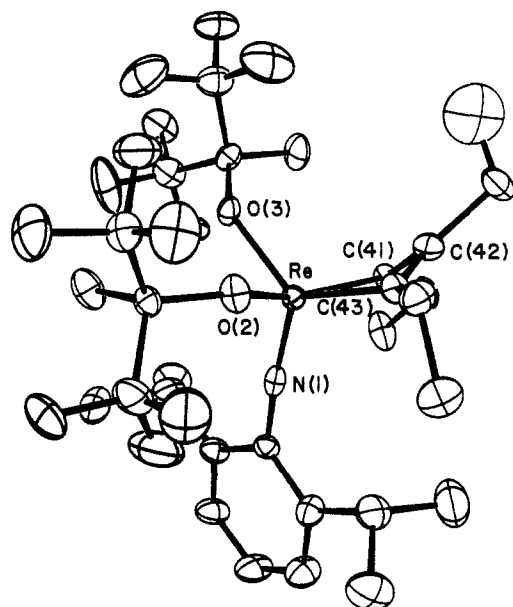


Figure 1. An ORTEP drawing of $\text{Re}(\text{C}_3\text{Et}_3)(\text{N}-2,6\text{-C}_6\text{H}_3\text{-}i\text{-Pr}_2)[\text{OCMe}(\text{CF}_3)_2]_2$ (**3**): $\text{O}(3)\text{-Re-C}(43) = 121.2^\circ$; $\text{O}(3)\text{-Re-N}(1) = 119.1^\circ$; $\text{N}(1)\text{-Re-C}(43) = 119.8^\circ$; $\text{O}(2)\text{-Re-C}(41) = 141.8^\circ$; $\text{O}(2)\text{-Re-O}(3) = 83.2^\circ$; $\text{O}(3)\text{-Re-C}(41) = 105.5^\circ$.

Preliminary studies show that some acetylenes are metathesized in the presence of **2c**, the rate correlating with the size of the alkyl groups in the internal acetylene. 3-Heptyne (20 equiv) in the presence of **2c** in pentane at 25°C is converted into a mixture containing a total of $\sim 25\%$ 3-hexyne and 4-octyne in 24 h; 75% of the initial 3-heptyne remains. 4-Nonyne under the same conditions is converted $\sim 80\%$ of the way to the expected equilibrium mixture in 1 h, while 5-undecyne is converted $\sim 95\%$ to the equilibrium mixture in 0.5 h. We propose (i) that metathesis proceeds via rhenacyclobutadiene complexes analogous to or related to **3** and (ii) that rhenacycles containing the smallest substituents become sinks, i.e., they lose an acetylene most slowly and thereby limit the rate of metathesis.¹³

We believe that **2a**, **2b**, and **2d** do not react with internal acetylenes primarily because the metal is not electrophilic enough, although steric factors might also limit reactivity in the case of **2d**. These results should be compared with other metathesis catalysts in which activity varies dramatically with the nature of the alkoxide (acetylene metathesis by complexes of the type $\text{M}(\text{CR}')(\text{OR})_3$ ($\text{M} = \text{Mo}$ or W) and olefin metathesis by complexes of the type $\text{M}(\text{CH-}t\text{-Bu})(\text{NAr})(\text{OR})_2$ ($\text{M} = \text{W}^{7,14}$ or Mo^{15})).

Acknowledgment. We thank the National Science Foundation for supporting this research (Grant CHE 84-02892) and for a predoctoral fellowship (to I.W.). We also thank the U.S. Department of Energy, Division of University and Industry Programs, for funds to purchase the X-ray diffractometer (Grant DE-FG05-86ER75292).

Supplementary Material Available: A complete description of the preparation of each compound, analytical and spectroscopic data, a full description of the structural study, and a listing of final positional and thermal parameters (8 pages); a listing of final observed and calculated structure factors (38 pages). Ordering information is given on any current masthead page.

(13) (a) Complexes of the type $\text{W}(\text{C}_3\text{R}_3)(\text{O}-2,6\text{-C}_6\text{H}_3\text{-}i\text{-Pr}_2)_3$ ^{13b} and $\text{W}(\text{C}_3\text{R}_3)[\text{OCMe}(\text{CF}_3)_2]_3$ ¹¹ metathesize acetylenes by rate-limiting loss of an acetylene from the tungstacyclobutadiene ring. (b) Churchill, M. R.; Ziller, J. W.; Freudenberg, J. H.; Schrock, R. R. *Organometallics* **1984**, *3*, 1554.

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(15) Murdzek, J. S.; Schrock, R. R. *Organometallics* **1987**, *6*, 1373.

First Demonstration of High Resolution Laser Desorption Mass Spectrometry of High Mass Organic Ions

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Fourier transform mass spectrometry (FTMS)^{1,2} is of great interest as a potential tool for analysis of high mass ions.³ Theory suggests an upper mass limit of at least m/z 375 000 for observations by using a 2.54-cm cubic cell, 8-T spectrometer,³ and Hunt and co-workers have successfully observed horse cytochrome *c* molecular ions (m/z 12 384) by using a 7-T tandem quadrupole Fourier transform mass spectrometer⁴ and a 10 KeV Cs^+ source. Although they could obtain high mass resolution for $(\text{CSI})_{22}\text{Cs}^+$ with m/z 5848.7, they were unable "...to monitor the image current or transient from large oligopeptide ions for more than a few milliseconds at a time...". Such an inability, if general, would place serious constraints on attainable resolution, which, under pressure-limited conditions, is directly proportional to observation time, t (s), and magnetic field, B (T), and inversely proportional to mass, m (amu), (eq 1).⁵ Low-trapping efficiency can result from

$$m/\Delta m = 1.733 \times Bt/m \quad (1)$$

pressure effects (increased collision frequency),⁵ magnetic field inhomogeneity,⁶ space-charge effects,⁷ and short ion lifetimes;⁸ all can decrease t , with corresponding reductions in resolution.

Because of the implications of observation time constraints regarding the applicability of FTMS to high mass organic analysis, it is desirable to evaluate the capabilities of the method in connection with laser desorption sources,^{9,10} which are well-suited for analysis of nonvolatile species. Analysis of polar synthetic polymer mixtures is of interest in this context both because of the intrinsic importance of such materials and because they provide a convenient means of evaluating the possible scope of LD-FTMS.¹¹ Potential applications include the study of structures of biomolecules with masses within the demonstrated range. Figure 1 contains the high mass region of the spectrum of poly(ethylene glycol)-8000, obtained by co-addition of single-scan spectra from 50 individual laser shots;¹² this spectrum, which contains clearly

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(4) Hunt, D. F.; Shabanowitz, J.; Yates, J. R., III; Zhu, N.-Z.; Russell, D. H.; Castro, M. *Proc. Natl. Acad. Sci. U.S.A.* **1987**, *84*, 620-623.

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(11) Brown, R. S.; Weil, D. A.; Wilkins, C. L. *Macromolecules* **1986**, *19*, 1255-1260.

(12) Spectra were recorded with a 7-T Nicolet FTMS-2000 spectrometer, equipped with an autoprobe and a Tachisto 215 CO_2 laser. Samples were deposited from KCl/methanol solutions upon the probe tip; ca. 50 ng of sample were desorbed per laser shot approximately 3 mm outside the source cell. By rotating the probe, a fresh sample surface was exposed after each shot. Ions were transferred to the analyzer cell by grounding the conductance limit for 2 ms, following desorption. For all spectra, trap voltage was 1.6 V, and ions were trapped for 12 s prior to excitation with a 200 V_{pp} sweep from 0 to 100 kHz at 140 Hz/ μs . PEG-8000 was observed in direct mode for 83 ms, observing all ions above m/z 2186; PEG-3350 was observed in heterodyne mode for 8.2 s, observing all ions between m/z 2706 and m/z 4012. For PPG-4000, ions below m/z 5500 and above m/z 6000 were ejected 250 ms after transfer; the spectrum was measured in heterodyne mode for 5.6 s, observing all ions between m/z 4000 and m/z 7000. Data were transformed after one level of zero filling. Resolution was estimated as the ratio of peak position to peak width at half height.