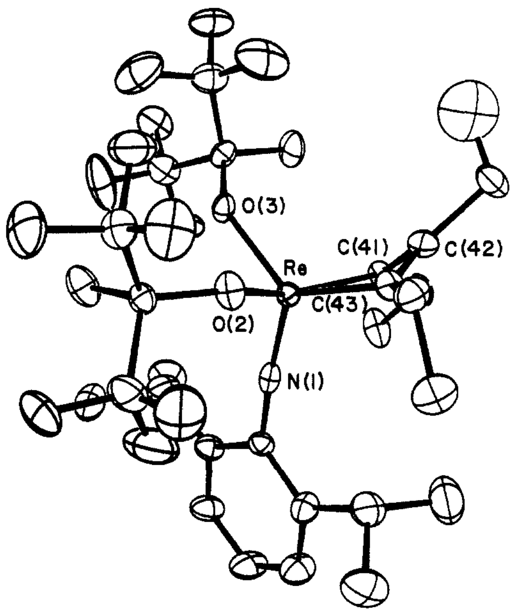

Figure 1. An ORTEP drawing of $Re(C_3Et_3)(N\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)[OCMe(CF_3)_2]_2$ (**3**): O(3)-Re-C(43) = 121.2°; O(3)-Re-N(1) = 119.1°; N(1)-Re-C(43) = 119.8°; O(2)-Re-C(41) = 141.8°; O(2)-Re-O(3) = 83.2°; O(3)-Re-C(41) = 105.5°.

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 ~25% 3-hexyne and 4-octyne in 24 h; 75% of the initial 3-heptyne remains. 4-Nonyne under the same conditions is converted ~80% of the way to the expected equilibrium mixture in 1 h, while 5-undecyne is converted ~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 $M(CR')(OR)_3$[1] (M = Mo or W) and olefin metathesis by complexes of the type $M(CH\text{-}t\text{-}Bu)(NAr)(OR)_2$ (M = W[7,14] or Mo[15])).

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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.

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[13] (a) Complexes of the type $W(C_3R_3)(O\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)_3$[13b] and $W(C_3R_3)[OCMe(CF_3)_2]_3$[11] metathesize acetylenes by rate-limiting loss of an acetylene from the tungstacyclobutadiene ring. (b) Churchill, M. R.; Ziller, J. W.; Freudenberger, J. H.; Schrock, R. R. *Organometallics* **1984**, *3*, 1554.

[14] Schrock, R. R.; Feldman, J.; Grubbs, R. H.; Cannizzo, L. *Macromolecules* **1987**, *20*, 1169.

[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 spectrometer[4] and a 10 KeV Cs^+ source. Although they could obtain high mass resolution for $(CSI)_{22}Cs^+$ 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

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

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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[1] Laude, D. A.; Johlman, C. L.; Brown, R. S.; Weil, D. A.; Wilkins, C. L. *Mass Spectrom. Rev.* **1986**, *5*, 107-166.

[2] Gross, M. L.; Rempel, D. L. *Science (Washington, D. C.)* **1984**, *226*, 261-268.

[3] Russell, D. H. *Mass Spectrom. Rev.* **1986**, *5*, 167-189.

[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.

[5] Marshall, A. G.; Comisarow, M. B.; Parisod, G. *J. Chem. Phys.* **1979**, *71*, 4434-4444.

[6] Laukien, F. H. *Int. J. Mass Spectrom. Ion Proc.* **1986**, *73*, 81-107.

[7] Ledford, E. G.; Rempel, D. L.; Gross, M. L. *Anal. Chem.* **1984**, *56*, 2744-2748.

[8] Brown, R. S.; Wilkins, C. L. *J. Am. Chem. Soc.* **1986**, *108*, 2447-2448.

[9] Cody, R. B.; Burnier, R. C.; Reents, W. D., Jr.; Carlin, T. J.; McCrery, D. A.; Lengal, R. K.; Freiser, B. S. *Int. J. Mass Spectrometrom. Ion Phys.* **1980**, *33*, 37-43.

[10] McCrery, D. A.; Ledford, E. B., Jr.; Gross, M. L. *Anal. Chem.* **1982**, 1435-1437.

[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.

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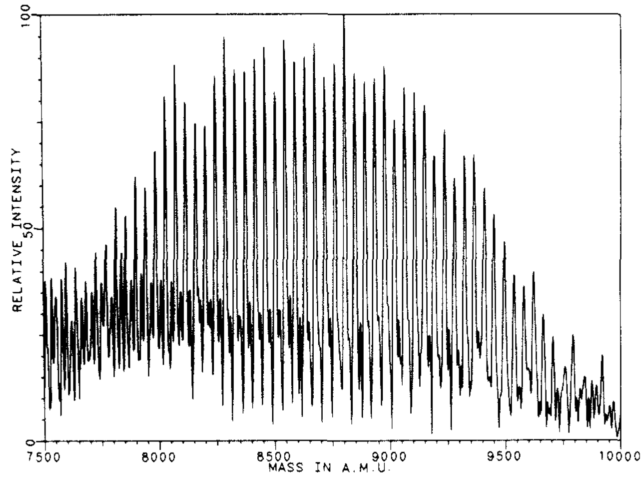

Figure 1. High mass region of laser desorption Fourier transform mass spectrum of poly(ethylene glycol)-8000. Lower mass cutoff m/z 2186.

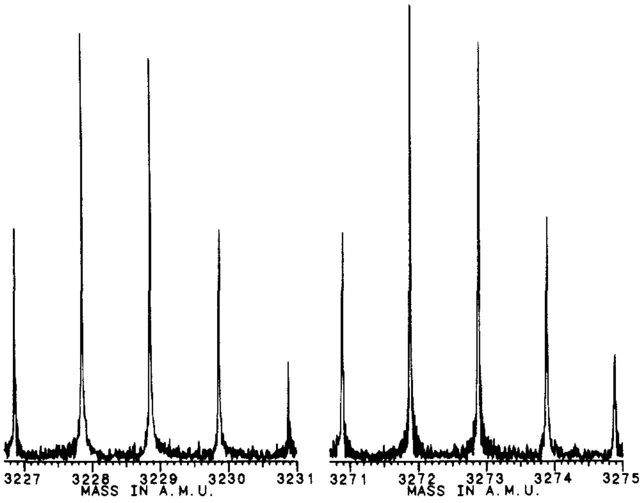

Figure 2. A portion of the high resolution laser desorption Fourier transform mass spectrum of poly(ethylene glycol)-3350 between m/z 2706 and m/z 4012.

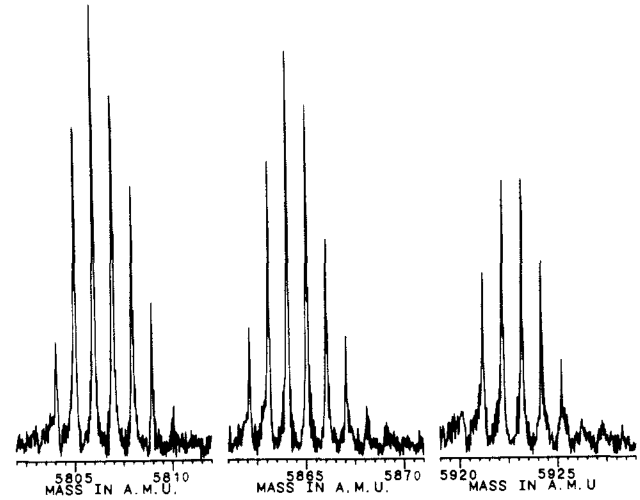

Figure 3. A portion of the high resolution laser desorption Fourier transform mass spectrum of poly(propylene glycol)-4000 between m/z 5500 and m/z 6000. Ions outside that range were ejected.

identifiable potassium-attached oligomer ions up to m/z 9700 is the highest mass range LD-FTMS spectrum yet obtained. Figures 2 and 3 are selected high mass regions of spectra of poly(ethylene glycol)-3350 and poly(propylene glycol)-4000, respectively, demonstrating both unprecedented organic high mass resolution (Figure 2—160 000 at m/z 3200, unapodized, for PEG-3350) (Figure 3—resolution 60 000 at m/z 5922, unapodized, for PPG-4000) and accuracy, with mass measurement accuracy of 8.59 ppm (σ = 6.3 ppm) for the 48 ions with m/z between 5500 and 6000.

In view of these results, obtained under conditions where space-charge effects were limited and by using a 7-T Fourier transform mass spectrometer of significantly lower magnetic field homogeneity (100 ppm over a 6.3 cc vol, drift rate ca. 6.5 ppm/h) than that employed by others, it appears that factors other than the masses involved, space-charge effects, or field inhomogeneity may be limiting in tandem instrument measurements. Not only are the present results fully consistent with expectations based upon the use of a 7-T magnetic field (rather than 3 T, used for our previous LD-FTMS studies) but also demonstrate that high mass laser-desorbed ions can be trapped for nearly 20 s, providing encouraging evidence of the potential of the method for accurate high resolution mass analysis of such species.

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"Tailored" Organometallics as Precursors for the Chemical Vapor Deposition of High-Purity Palladium and Platinum Thin Films

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The fabrication of electronic devices by chemical vapor deposition is a rapidly expanding area of great current interest. Metal-organic chemical vapor deposition (MOCVD) routes to the preparation of semiconductor thin films, such as GaAs from $GaMe_3$ and AsH_3, are becoming increasingly attractive, due largely to the high growth rates, high purity, high crystal quality, and ease of process control that are characteristic of the MOCVD method.[1] However, despite the intensive study of the synthesis of main-group materials by MOCVD, relatively few studies of the deposition of thin films that contain transition metals have been reported,[2] largely because suitably volatile and reactive molecular CVD precursors are scarce. For example, palladium films are of interest as a potential replacement for gold as an electrical contact material in integrated circuits.[3] This interest arises from its high electrical conductivity, its resistance to oxidation, and its economic advantages over gold. While palladium films have been made by electroplating,[4] vacuum sputtering,[5] and laser direct-write metallization,[6] no CVD methods have been reported to date, despite the advantages offered by this technique. Here we report the synthesis of high-quality Pd and Pt films by

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[1] (a) Dupuis, R. D. *Science (Washington, D.C.)* **1984**, *226*, 623–629. (b) Moss, R. H. *Chem. Brit.* **1983**, 733–737.

[2] For example see: (a) Girolami, G. S.; Jensen, J. A.; Pollina, D. M.; Williams, W. S.; Kaloyeros, A. E.; Allocca, C. M. *J. Am. Chem. Soc.* **1987**, *109*, 1579–1580. (b) Jensen, J. A.; Gozum, J. E.; Pollina, D. M.; Girolami, G. S. *J. Am. Chem. Soc.* **1988**, *110*, 1643–1644. (c) Kaloyeros, A. E.; Williams, W. S.; Allocca, C. M.; Pollina, D. M.; Girolami, G. S. *Adv. Ceram. Mater.* **1987**, *2*, 257–263. (d) Trent, D. E.; Paris, B.; Krause, H. H. *Inorg. Chem.* **1964**, *3*, 1057–1058. (e) Truex, T. J.; Saillant, R. B.; Monroe, F. M. *J. Electrochem. Soc.* **1975**, *122*, 1396–1400. (f) Czekaj, C. L.; Geoffroy, G. L. *Inorg. Chem.* **1988**, *27*, 8–10.

[3] McCaskie, J. E. *Plat. Electron. Ind., Symp., 5th* **1975**, 5–27.

[4] Lowenheim, F. A. *Modern Electroplating*; Wiley: New York, 1974.

[5] (a) Schlenk, W.; Bauer, E. *Surf. Sci.* **1980**, *93*, 9–32. (b) Egelhoff, W. F.; Tibbetts, G. G. *Phys. Rev. B: Condens. Matter.* **1979**, *19*, 5028–5035. (c) Erlings, J. G.; Weerheijm, H. *J. Vac. Sci. Technol.* **1980**, *17*, 851–853.

[6] (a) Gross, M. E.; Appelbaum, A.; Gallagher, P. K. *J. Appl. Phys.* **1987**, *61*, 1628–1632. (b) Harriott, L. R.; Cummings, K. D.; Gross, M. E.; Brown, W. L. *Appl. Phys. Lett.* **1986**, *49*, 1661–1662.

0002-7863/88/1510-2688$01.50/0