NMR data for **3** were identical with those of Arg except for a signal of the C-1 carboxyl carbon, while the α-proton[17] showed a correlation with an sp^3 carbon at δ 97.4 in the HMBC spectrum. This carbon appeared at δ 196.9 in DMSO-d_6, thus suggesting conversion from a hydrated to a simple carbonyl. Therefore, it is reasonable to place this carbon next to an amide carbon (δ 174.7) which showed no correlation peaks in the HMBC spectrum. Thus, this new amino acid has structure **3**. The structure of **4** was deduced from ^1H and ^{13}C NMR data. The presence of a formyl group (δ_H 8.08, δ_C 166.7 d) attached to the α-amino group of Dpr was revealed by the HMBC data. Connecting the five amino acids (Pro, Phe, Dpr, **3**, and **4**) by five amide bonds resulted in a molecular weight of 749, corresponding to the weight of the hydrated carbonyl, while the FABMS weight of 731 is that of the dehydrated carbonyl. Ready hemiketal formation explains the mass spectral data for the species with added alcoholic solvents.

Partial sequencing from the HMBC spectrum (D_2O) was deduced by cross peaks between the α-proton of **3** and the carbonyl of Pro, and between the β-protons of Dpr and the carbonyl of **4**, but no further information was obtained from NMR spectra measured in D_2O. Since NMR spectra recorded in DMSO[18] revealed well-resolved signals, final sequencing was determined from the NOESY spectrum,[19] which led to gross structure **1**.

To our surprise, cyclotheonamide B (**2**) obtained from the 1989 collection lacked the formyl proton in the ^1H NMR spectrum, which was replaced by a sharp methyl singlet at δ 2.00, indicating the presence of an *N*-acetyl Dpr residue. From our experience with **1**, we decided to measure NMR spectra of **2** in 90% H_2O–D_2O solution, which afforded valuable information. The COSY and the TOCSY (HOHAHA)[20] spectra of **2** revealed the same amino acid residues as in **1**. An HMBC spectrum disclosed the crucial amide protons and hence all connections of the five residues.[21] Though the NOESY spectrum in 90% H_2O disclosed merely sequential information, the ROESY spectrum[22] yielded a number of informative cross peaks, which allowed us to confirm the sequential assignment obtained by the HMBC spectrum.

The stereochemistries of Pro, Phe, and Dpr were determined to be L, D, and L, respectively, by chiral GC on a Chirasil Val III (Alltech) column.[23] The configuration of **4** was determined by degradation of **1** with $KMnO_4$–$NaIO_4$ followed by chiral GC analysis, which resulted in D-Asp, thus suggesting the 4*R* stereochemistry of **4**. Incidentally, Asp is not released from Phe by these conditions. Elucidation of the stereochemistry of **3** is in progress.

The amino acids **3** and **4** appear to be new.[24] β and γ amino acid residues seem to be characteristic of highly bioactive peptides from marine organisms.[25]

Acknowledgment. We thank Professor Paul J. Scheuer, University of Hawaii, for reading this manuscript. Thanks are also due to Ms. Sakiko Nagaoka, Yamanouchi Pharmaceutical Co., Ltd., Central Laboratories, for enzyme inhibition tests.

Supplementary Material Available: HMBC and NOESY spectra for **1** and HMBC, TOCSY, and ROESY spectra for **2** (5 pages). Ordering information is given on any current masthead page.

(16) ^{13}C NMR data for **1** in D_2O: Phe residue 173.8 (CO), 57.0 (α), 41.8 (β), 138.2 (1), 132.2 (2, 6), 131.3 (3, 5), 130.0 (4); **4** residue 170.5 (CO), 125.5 (α), 146.3 (β), 55.5 (γ), 40.5 (δ), 132.4 (1), 133.4 (2, 6), 118.5 (3, 5), 157.4 (4); Dpr residue 173.1 (CO), 51.7 (α), 42.3 (β), 166.7 (CHO); Pro residue 176.2 (CO), 63.5 (α), 33.1 (β), 27.5 (γ), 51.6 (δ); **3** residue 174.7 (amide), 97.4 [$C(OH)_2$], 57.4 (α), 26.1 (β), 27.3 (γ), 43.7 (δ), 159.7 (guanidine). ^1H NMR data for **1** in D_2O: Phe residue 4.61 (dd, 4.9, 6.1; α), 2.77 (dd, 4.9, 13.6; β), 2.85 (dd, 6.1, 13.6; β'), 7.23 (2 H, m; 2, 6), 6.91 (2 H, t, 8.0; 3, 5), 7.25 (t, 8.0; 4); **4** residue 5.92 (td, 1.9, 15.6; α), 6.80 (td, 2.6, 15.6; β), 4.57 (m; γ), 2.50 (dd, 10.1, 14.2; δ), 2.98 (dd, 4.9, 14.2; δ'), 7.19 (2 H, d, 7.8; 2, 6), 6.66 (2 H, d, 7.8; 3, 5); Dpr residue 4.85 (m; α), 2.95 (m; β), 4.24 (ddd, 4.1, 10.1, 12.9; β'), 8.08 (s; CHO); Pro residue 4.52 (dd, 5.9, 5.9; α), 1.90 (m; β), 2.30 (m; β'), 1.86 (m; γ), 2.00 (m; γ'), 3.49 (m; δ), 3.76 (ddd, 6.7, 6.7, 10.2; δ'); **3** residue 4.00 (m; α), 1.55 (m; β), 1.93 (m, β'), 1.53 (m; γ), 1.66 (m; γ'), 3.17 (2 H, m; $\delta\delta'$).

(17) For convenience in comparison with Arg, the methine carbon of **3** is designated as the α-carbon.

(18) Cyclotheonamide A decomposed during measurement of NMR spectra in DMSO-d_6: 10% of **1** was recovered by HPLC. Due to the instability in DMSO-d_6 solution, an HMBC spectrum of good quality was not obtained in this solvent.

(19) The following NOESY sequential cross peaks were observed: Phe-α, 4-NH; 4-α, Dpr-β-NH; Dpr-α, Pro-δ; Pro-α, 3-NH; 3-α, Phe-NH.

(20) (a) Braunshweiler, L.; Ernst, R. R. *J. Magn. Reson.* **1983**, *53*, 521–528. (b) Davis, D. G.; Bax, A. *J. Am. Chem. Soc.* **1985**, *107*, 7197–7198.

(21) The following HMBC sequential cross peaks were observed: Phe-CO, 4-NH; 4-CO, Dpr-β; Dpr-CO, Pro-α; Pro-CO, 3-NH; 3-amide, Phe-α.

(22) Bothner-By, A. A.; Stephens, R. L.; Lee, J.; Warren, C. D.; Jeanloz, R. W. *J. Am. Chem. Soc.* **1984**, *106*, 811–813. Selected ROESY sequential cross peaks: Phe-α, 4-NH; 4-α, Dpr-β-NH; Dpr-α, Pro-δ; Pro-α, 3-NH; 3-α, Phe-NH.

(23) Since the Dpr residue is epimerized during standard acidic hydrolysis as shown in our study on theonellamide F,[5] milder conditions (2 N HCl, 108 °C, 2 h) were used for the stereochemical analysis.

(24) (a) Barrett, G. C., Ed. *Chemistry and Biochemistry of the Amino Acids*; Chapman and Hall: London and New York, 1985. (b) Davies, J. S., Ed. *Amino Acids and Peptides*; Chapman and Hall: London and New York, 1985.

(25) Ireland, C. M.; Molinski, T. F.; Roll, D. M.; Zabriskie, T. M.; McKee, T. C. In *Bioorganic Marine Chemistry*; Scheuer, P. J., Ed.; Springer-Verlag: Berlin, 1989; Vol. 3, p 1.

Chelatoselective Fluorescence Perturbation in Anthrylazamacrocycle Conjugate Probes. Electrophilic Aromatic Cadmiation[1]

Michael E. Huston,[2] Carl Engleman, and Anthony W. Czarnik*

Department of Chemistry, The Ohio State University Columbus, Ohio 43210

Received May 14, 1990

Fluorescence methods offer many potential advantages in ion quantitation: sensitivity, ease of automation, and straightforward application to fiber optics based remote sensing techniques. While fluorimetric methods for the determination of some metal ions in aqueous solution exist using intrinsic probes,[3] selective methods for the determination of Zn(II) and Cd(II) do not. We have recently reported that anthrylazamacrocycle conjugate probes yield large (20–190-fold) changes in fluorescence upon metal ion complexation in aqueous solution;[4] the very large association constants between several transition metals (e.g., Pb(II), Cu(II), Zn(II), Cd(II), Hg(II)) and azamacrocycles[5] make the sequestration (and therefore quantitation) of small amounts of such ions possible. Only Zn(II) and Cd(II) bind anthrylazamacrocycles with net chelation-enhanced fluorescence (CHEF); however, assigning an enhancement to one metal or the other has not been possible heretofore. We now report that the complexation of Cd(II) and (anthrylmethyl)pentacyclen (**3**) *uniquely* demonstrates a perturbation of the fluorophore emission spectrum; the resulting ion discrimination can be utilized directly for simultaneous Zn(II)/Cd(II) analysis.

Normalized emission spectra for the complexes of Zn(II) and Cd(II) perchlorates with four homologous anthrylazamacrocycles[4] are shown in Figure 1. In each case an anthracenic fluorescence spectrum is observed. However, the Cd(II)–**3** complex displays an additional broad, red-shifted band yielding the composite spectrum with λ_{max} 446 nm. A typical anthracenic emission is observed for Zn(II) and Cd(II) complexes of (9′-anthryl-

(1) Presented at the 1989 International Chemical Congress of Pacific Basin Societies in Honolulu, HI, Dec 1989.

(2) Recipient of Ohio State University and Amoco graduate fellowships.

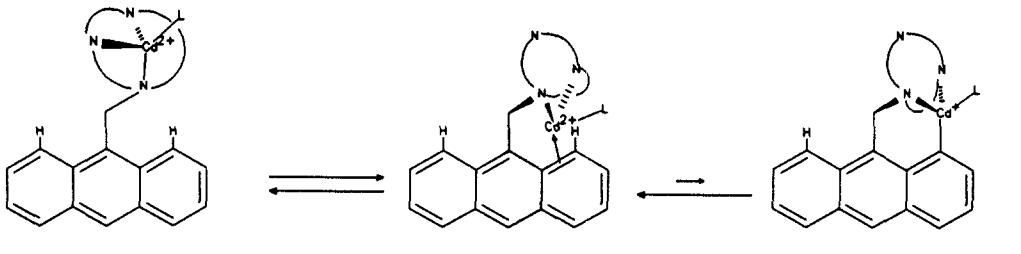
(3) (a) Schwarzenbach, G.; Flaschka, H. *Complexometric Titrations* (translated by H. Irving); Metheum: 1969. (b) West, T. S. *Complexometry with EDTA and Related Reagents*; BDH: 1969. (c) *Indicators*; Bishop, E., Ed.; Pergamon: 1972. (d) Guilbault, G. G. *Practical Fluorescence*, Marcel Dekkar, Inc., New York, 1973; Chapter 6.

(4) Akkaya, E. U.; Huston, M. E.; Czarnik, A. W. *J. Am. Chem. Soc.* **1990**, *112*, 3590.

(5) (a) Kodama, M.; Kimura, E. *J. Chem. Soc., Dalton Trans.* **1978**, 1081. (b) Kodama, M.; Kimura, E.; Yamaguchi, S. *J. Chem. Soc., Dalton Trans.* **1980**, 2536. (c) Hancock, R. D.; Bhavan, R.; Wagner, C. A.; Hosken, G. D. *S. Afr. J. Chem.* **1986**, *39*, 238.

0002-7863/90/1512-7054$02.50/0

Scheme I



no Ar-Cd(II) complex Ar-Cd(II) π-complex Ar-Cd(II) σ-complex

5 6 7

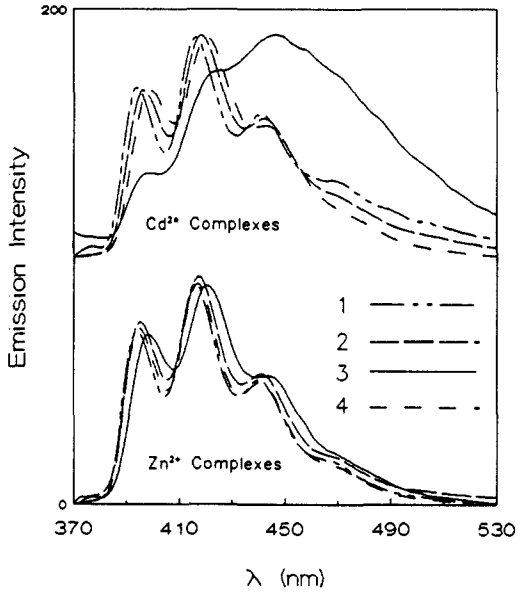


Figure 1. Normalized fluorescence spectra of 10 μM solutions of **1**, **2**, **3**, and **4** containing $Cd(ClO_4)_2$ (above) and $Zn(ClO_4)_2$ (below) in 0.1 M pH 10 CAPS buffer. Excitation was at 335 ± 3 nm.

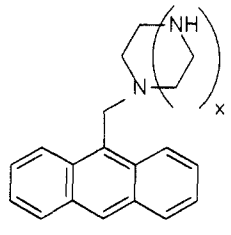
methyl)-1,4,7,10,13-pentaazatridecane,[6] a linear analogue of **3**. The unique fluorescence behavior of the Cd(II)–**3** complex along with the large binding constants of Zn(II) and Cd(II) to pentacyclen[5a,b] allow for the simultaneous determination of each metal ion in aqueous solution. When the total Zn(II) and Cd(II) concentration is less than that of the probe (10 μM), the concentrations of Zn(II) and Cd(II) can be expressed as in eqs 1 and 2.[7]

$$[Zn(II)] = 0.54I_{398} - 0.62I_{516} - 1.2 \quad (1)$$

$$[Cd(II)] = 1.1I_{516} - 0.037I_{398} - 0.11 \quad (2)$$

In addition to a fluorescence pertubation, the Cd(II)–**3** combination also uniquely yields a perturbation in the UV spectrum. A difference spectrum obtained by subtracting a fractional amount of an uncomplexed **3** spectrum from the perturbed spectrum[8] is the mirror image of a fluorescence difference spectrum obtained by similar means.[9] Moreover, excitation at 400 nm (where **1**–**4** are weakly absorbing but where moderate absorption is seen in the difference spectrum) gives rise to an emission spectrum with shape and λ_{max} (456 nm) identical with those of the fluorescence difference spectrum. Thus, evidence points to the existence of two equilibrating ground-state species as the physical basis for the chelatoselective emission. Bouas-Laurant has very recently reported a related observation in methanol where a red-shifted small atypical CHEF was observed for a Tl(I) π-complex.[10]

The ^{1}H NMR spectrum of the Cd(II)–**3** complex in D_2O solution reveals the presence of more than one chelate in solution, and H-10 is clearly represented by major and minor singlets (ratio = 6:4). All aromatic peaks are noticeably broadened with respect to a spectrum of **3** taken in the absence of Cd(II) or in the presence of Zn(II). Stepwise heating of the solution (300–360 K) leads to a gradual coalescing of the aromatic resonances. The spectra of all other permutations of **1**–**4** with Zn(II) and Cd(II) show only



1, x=2; 2, x=3; 3, x=4; 4, x=5

one species, qualitatively similar to that of the Zn(II)–**3** complex. *Most interestingly, the Cd(II)–3 complex uniquely experiences deuterium exchange* ($k = 1.5 \times 10^{-3}$ s^{-1} *at 343 K and pD 8*), *occurring only at the 1- and 8-positions.*

The observed fluorescence, UV, and ^{1}H NMR perturbations of the Cd(II)–**3** complex are observed only in water; in methanol, ethanol, and acetonitrile, only unperturbed anthracenic spectra are observed.

These observations are most consistent with the equilibria shown in Scheme I. (1) The Cd(II)–**3** complex uniquely populates a conformer in which an anthracene–Cd(II) π–d orbital interaction is enforced (**6**). (2) The π-complex leads to a higher energy σ-complex (**7**) that results in deuterium exchange. (3) Solvation strongly influences the position of the conformational equilibrium (i.e., **5** $\rightleftarrows$ **6**); the complete selectivity for water vs methanol argues for stringent external ligand steric requirements in **6**. Aryl-cadmium species are well-known, but previously restricted to anhydrous environments.[11] In fact, cadmium's position above

(6) (9′-Anthrylmethyl)-1,4,7,10,13-pentaazatridecane was synthesized and fully characterized by S. A. VanArman of this research group using synthetic methods analgous to those used for the preparation of the anthrylazamacrocycles (ref 4). Starting materials were purchased from Aldrich Chemical Company, Inc., 940 West Saint Paul Ave., Milwaukee, WI.

(7) In eqs 1 and 2, Zn(II) and Cd(II) concentrations are expressed in units of μM. The coefficients shown are based on standard curves generated on a specific fluorimeter. The subscript of *I* (fluorescence intensity) refers to the monitored wavelength in nanometers.

(8) The UV spectrum of uncomplexed **3** at pH 10 was shifted by +2 nm and then uniformly multiplied by the scaling factor 0.4. The adjusted spectrum was then subtracted from the Cd(II)–**3** complex UV spectrum to obtain the difference spectrum. UV spectra were acquired by using a HP 8452 diode array spectrophotometer. Data storage and manipulation were conducted by using HP 89531A UV/vis operating software, MS-DOS version, and Lotus 1-2-3.

(9) The fluorescence difference spectrum was obtained by scaling the anthracenic fluorescence spectrum of **3** in pH 3, 0.1 M chloroacetate buffer so that the fluorescence intensity at 398 nm was equivalent to the intensity of the Cd(II)–**3** complex at pH 10, and then subtracting the adjusted spectrum from the Cd(II)–**3** complex spectrum.

(10) Fages, F.; Desvergne, J.-P.; Bouas-Laurent, H.; Marsau, P.; Lehn, J.-M.; Kotzyba-Hibert, F.; Albrecht-Gary, A.-M.; Al-Joubbeh, M. *J. Am. Chem. Soc.* **1989**, *111*, 8672. An analogous ground-state species was also reported for the Ag(I) π-complex; however, it is nonemissive.

(11) (a) Atwood, J. L.; Berry, D. E.; Stobart, S. R.; Zorworotko, M. *J. Inorg. Chem.* **1983**, *2*, 3480. (b) Osman, A.; Steevensz, R. G.; Tuck, D. G.; Meinema, H. A.; Noltes, J. G. *Can. J. Chem.* **1984**, *62*, 1698.

mercury in the periodic table portends activity as an electrophile toward aromatics.[12] Conclusions regarding the structural basis of chelatoselective fluorescence perturbation suggest variations on the incorporation of such "nonclassical" selectivity into future fluoroionophores.

Acknowledgment. We gratefully acknowledge support for this work from The Ohio State University and from Amoco. Shared resources, including the use of a Perkin-Elmer LS-5 fluorimeter, were made available by Prof. M. Platz of this department. FT-NMR spectra were obtained by using equipment funded in part by NIH Grant No. 1 S10 RR01458-01A1. A.W.C. thanks the A. P. Sloan and the Camille and Henry Dreyfus Foundations for support in the form of fellowships and Eli Lilly and Company and Merck for support in the form of granteeships.

(12) The observation of aqueous electrophilic cadmiation raises interesting possibilities for the undetermined mechanism of cadmium toxicity.

Rhenium Oxo–Methylidene and Oxo–Methylidyne Compounds and Evidence for Facile Methylidene Proton Exchange

David M. Hoffman* and Derk A. Wierda

Department of Chemistry, Harvard University
12 Oxford Street, Cambridge, Massachusetts 02138

Received April 12, 1990

Rhenium oxo–alkylidene species, in some form, are probably the active catalysts in several olefin metathesis catalyst systems,[1-4] but to our knowledge there is only one example of a well-characterized rhenium oxo–alkylidene complex.[5] We report here the synthesis of two new dinuclear rhenium oxo–methylidene compounds, and for one of these we demonstrate facile methylidene proton exchange. Such a process may be relevant to deactivation of oxo-based metathesis catalysts. Additionally, we report the preparation of an unusual anionic rhenium oxo–methylidyne complex.

The d^2 oxo–methyl complex $ReOMe_3(PMe_3)$,[6] prepared in situ from $ReOMe_2Cl(PMe_3)_2$ and 0.5 equiv of $ZnMe_2$, decomposed rapidly in pentane at room temperature (6 h) to give methane and the oxo–methylidene compound $Re_2(\mu\text{-}CH_2)(\mu\text{-}O)(O)Me_4(PMe_3)_2$ (**1**; Figure 1).[7] Compound **1** was isolated as a blue crystalline solid from pentane at −20 °C in 77% yield. By ^1H NMR the decomposition was nearly quantitative, and 1 equiv of methane was produced for every molecule of **1**.

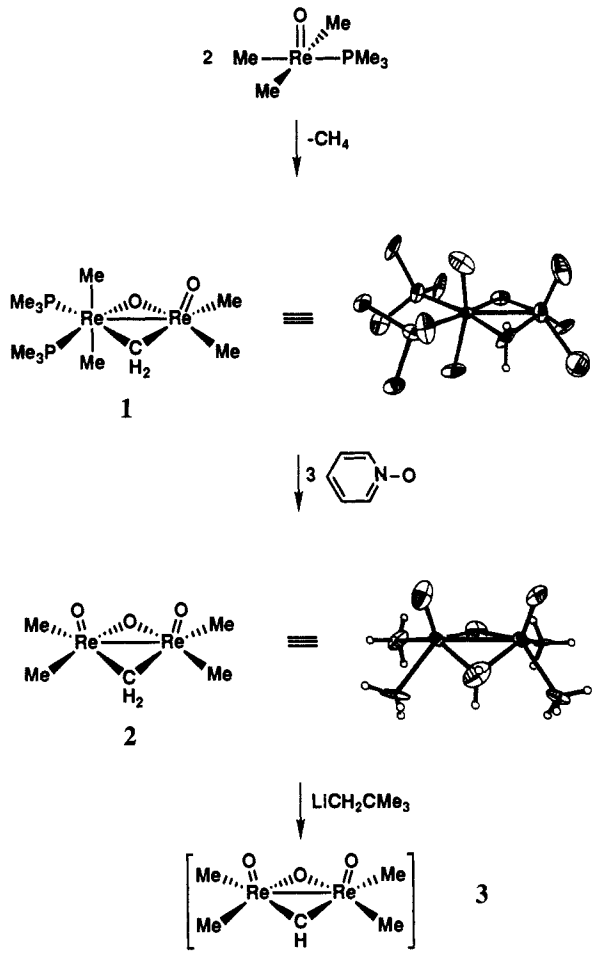


Figure 1. Reaction scheme described in the text. ORTEP plots (50% probability levels) of $Re_2(\mu\text{-}CH_2)(\mu\text{-}O)(O)Me_4(PMe_3)_2$ (**1**) and $Re_2(\mu\text{-}CH_2)(\mu\text{-}O)O_2Me_4$ (**2**) are presented at the right of their respective stick drawings.

An X-ray crystallographic study (ORTEP, Figure 1)[8,9] revealed that **1** has square-pyramidal and octahedral rhenium centers. The Re–Re distance of 2.548 (2) Å is consistent with a single bond.[2a,10] Extended Hückel calculations[11] indicate that **1** has a covalent

(1) A general reference: Ivin, K. J. *Olefin Metathesis*; Academic Press: London, 1983. Review of organometallic rhenium–oxo compounds used in catalysis: Herrmann, W. A. *J. Organomet. Chem.* **1990**, *382*, 1.

(2) (a) Herrmann, W. A.; Kuchler, J. G.; Felixberger, J. K.; Herdtweck, E.; Wagner, W. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 394; *Angew. Chem.* **1988**, *100*, 420. (b) Rybak, W. K.; Ziolkowski, J. J. *J. Mol. Catal.* **1987**, *42*, 347.

(3) A well-defined rhenium catalyst has been reported: Toreki, R.; Schrock, R. R. *J. Am. Chem. Soc.* **1990**, *112*, 2448.

(4) For other rhenium alkylidene and alkylidyne chemistry, see: (a) Edwards, D. S.; Biondi, L. V.; Ziller, J. W.; Churchill, M. R.; Schrock, R. R. *Organometallics* **1983**, *2*, 1505. (b) Horton, A. D.; Schrock, R. R.; Freudenberger, J. H. *Organometallics* **1987**, *6*, 893. (c) Schrock, R. R.; Weinstock, I. A.; Horton, A. D.; Liu, A. H.; Schofield, M. H. *J. Am. Chem. Soc.* **1988**, *110*, 2686. (d) Horton, A. D.; Schrock, R. R. *Polyhedron* **1988**, *7*, 1841. (e) Felixberger, J. K.; Kiprof, P.; Herdtweck, E.; Herrmann, W. A.; Jakobi, R.; Gütlich, P. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 334; *Angew. Chem.* **1989**, *101*, 346. (f) Savage, P. D.; Wilkinson, G.; Motevalli, M.; Hursthouse, M. B. *Polyhedron* **1987**, *6*, 1599.

(5) Cai, S.; Hoffman, D. M.; Wierda, D. A. *J. Chem. Soc., Chem. Commun.* **1988**, 1489–1490.

(6) Hoffman, D. M.; Wierda, D. A. *Polyhedron* **1989**, *8*, 959–967.

(7) Amounts used in a typical preparation: $ReOMe_2Cl(PMe_3)_2$ (1.00 g, 2.39 mmol); $ZnMe_2$ (0.144 mL, 1.19 mmol); pentane (50 mL).

(8) Anal. Calcd for $Re_2P_2O_2C_{11}H_{32}$: C, 20.92; H, 5.11. Found: C, 20.49; H, 4.77. ^1H NMR (C_6D_6): δ 10.34 (ddd, 1, J_{HH} = 6.9 Hz, J_{PH} = 4.2 Hz, J_{PH} = 2.2 Hz, $\mu\text{-}CH_aH_b$ cis with respect to Re=O), 8.31 (dd, 1, J_{HH} = 6.9 Hz, J_{PH} = 3.2 Hz, $\mu\text{-}CH_aH_b$ trans with respect to Re=O). ^{13}C NMR (C_6D_6): δ 138.3 (dddd, 1, J_{CP}(trans) = 34 Hz, J_{CP}(cis) = 12 Hz, J_{CH} = 134 Hz, J_{CH} = 146 Hz, $\mu\text{-}CH_2$). IR (Nujol, CsI, cm^{-1}): ν(Re=O) 988 s (ν(Re=^{18}O) 938). Crystal data for $Re_2P_2O_2C_{11}H_{32}$ at −88 (1) °C: blue blocks, 0.20 × 0.25 × 0.30 mm, monoclinic, space group *Cc*, a = 15.386 (5) Å, b = 10.295 (4) Å, c = 23.753 (9) Å, β = 92.86 (3)°, d_{calcd} = 2.23 g cm^{-3}, Z = 8, μ = 132.1 cm^{-1}. X-ray diffraction data were collected on a Nicolet R3m/V diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å) in the θ–2θ scan mode. A linear decay correction based on the intensity changes of the check reflections (to correct for an ca. 9% average decrease in intensity after 120 h of exposure), a semiempirical absorption correction (XEMP), and Lorentz and polarization corrections were applied to the data. The absolute configuration was confirmed by inversion of configuration and by refinement of the η parameter (η = 0.98 (5)). A total of 10 820 reflections were collected in the range $4° < 2\theta < 48°$ ($\pm h,k,\pm l$); 5911 were unique reflections (R_{int} = 0.0518), and 4741 with $F_o > 6\sigma(F_o)$ were used in the structure solution. $R(F)$ = 0.0437; $R_w(F)$ = 0.0444. Structure factors from the following: *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV.

(9) NOE difference and selective heteronuclear decoupling NMR experiments were used to assign resonances and coupling constants; see: Derome, A. E. In *Modern NMR Techniques for Chemistry Research*; Baldwin, J. E., Ed.; Organic Chemistry Series; Pergamon Press: New York, 1987; Vol. 6.

(10) Cai, S.; Hoffman, D. M.; Huffman, J. C.; Wierda, D. A.; Woo, H.-G. *Inorg. Chem.* **1987**, *26*, 3693. Huggins, J. M.; Whitt, D. R.; Lebioda, L. *J. Organomet. Chem.* **1986**, *312*, C15.

(11) Hoffmann, R. *J. Chem. Phys.* **1963**, *39*, 1397–1412. Weighted H_{ij}'s were used: Ammeter, J. H.; Burgi, H. B.; Thibeault, J. C.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 3686. Parameters for Re were taken from the following: Shaik, S.; Hoffmann, R.; Fisel, C. R.; Summerville, R. H. *J. Am. Chem. Soc.* **1980**, *102*, 4555.

0002-7863/90/1512-7056$02.50/0