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(14) The amidophosphorane intermediate **3a** is only 2.4-kcal/mol higher energy than **3b** and 1.67-kcal/mol higher energy than **3b′**.
(15) Fellow of the Alfred P. Sloan Foundation, 1975–1979.

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Reaction of Group 6 Organoimido Complexes with Organozinc. Reductive Elimination across a Metal–Nitrogen Multiple Bond

Sir:

Sharpless and co-workers have suggested that the addition of bis(alkylimido)osmium complexes to olefins proceeds via migration of an organic ligand to an electron deficient imido nitrogen atom.[1] The industrially important ammoxidation of propylene to acrylonitrile may similarly involve transfer of an allyl moiety to $^{VI}Mo{=}NH$.[2] Unfortunately appropriate model compounds for studying this type of process[3] have not been available: no complex containing both imido and hydrocarbyl ligands [nor any organomolybdenum(VI) species whatsoever] has been reported. We now report that such complexes have been prepared and present preliminary evidence that the proposed rearrangements do occur.

Treatment of $(^tBuN)_2W(O^tBu)_2$ or $(^tBuN)_2Mo(OSiMe_3)_2$[4] with dimethylzinc in hexane, followed by cooling to −40 °C in the latter case,[5] follows eq 1. Red-orange crystals of Ia (60%) or violet crystals of Ib (52% after recrystallization) were collected by filtration.[6] The color of solutions of compounds I discharged to pale yellow upon addition of potential donor ligands (PMe_3, pyridine, $AlMe_3$, O_2) with a concomitant upfield shift of the methyl NMR resonances.[7]

$$2(^tBuN)_2M(OR)_2 + 4Me_2Zn \rightarrow [(^tBuN)_2M(CH_3)_2]_2 + 4MeZnOR \quad (1)$$

$$\text{Ia, M} = \text{W}$$
$$\text{b, M} = \text{Mo}$$

The X-ray crystal structure[8,9] of Ib (Figure 1) shows it to contain the first example[10] of an unsymmetrically bridging imido ligand. The dimer is situated on a crystallographic center of symmetry and each molybdenum exhibits distorted trigonal bipyramidal coordination. The three Mo–N bond lengths in Ib [Mo–N(1) = 1.730 (2), Mo–N(2) = 1.819 (2), Mo′–N(2) = 2.322 (2) Å] roughly correspond to those expected[10] for triple-, double-, and single-bonded nitrogen, respectively. However, Mo–N(1) is ~0.02 Å longer[10] than is anticipated for a Mo–N triple bond and the Mo–N–C bond angle also deviates somewhat from linearity [Mo–N(1)–C(11) = 167.4 (1)°].

When diphenylzinc was added to a solution of $(^tBuN)_2Cr(OSiMe_3)_2$ in hexane, $PhZnOSiMe_3$ precipitated as expected but no complex analogous to Ib could be isolated. Instead, upon hydrolysis, organic products[11] including biphenyl and *N-tert*-butylaniline were identified by GLC as summarized in Table I. Thus, under conditions where diphenylzinc is added dropwise *to* the chromium complex at 80 °C, up to 70% *tert*-butylaniline is observed. It is noteworthy that the ratio of *tert*-butylaniline to biphenyl in the product decreases when (1) the reagents are added in inverse order, (2) the reaction is carried out at reduced temperature, (3) the reaction is carried out in the presence of added pyridine, or (4) complex Ib is substituted for the chromium complex in this reaction.

Table I. Yield of *N-tert*-Butylaniline and Biphenyl from Reaction of 1 mmol of $(Me_3SiO)_2Cr(N^tBu)_2$ with Diphenylzinc

Ph_2Zn, mmol	temp, °C	addition[a]	additive	$PhNH^tBu$[b]	Ph–Ph[c]
2.0	80	normal		0.704	0.293
2.0	25	normal		0.334	0.377
2.0	80	inverse		0.258	0.638
2.0	80	normal	pyridine[d]	0.174	0.660
2.0	−78	inverse		0.038	0.687
1.0	80	normal		0.699	0.096
2.0	80	normal	Mo[e]	0.015	0.352

[a] In normal addition the Ph_2Zn in 10 mL of toluene was added to the Cr complex in 10 mL of toluene. [b] Yield of *N-tert*-butylaniline in millimole (by GLC). [c] Yield of biphenyl in millimole (by GLC). [d] The Cr complex was dissolved in 9 mL of toluene and 1 mL of pyridine. [e] Compound Ib was substituted for the Cr complex.

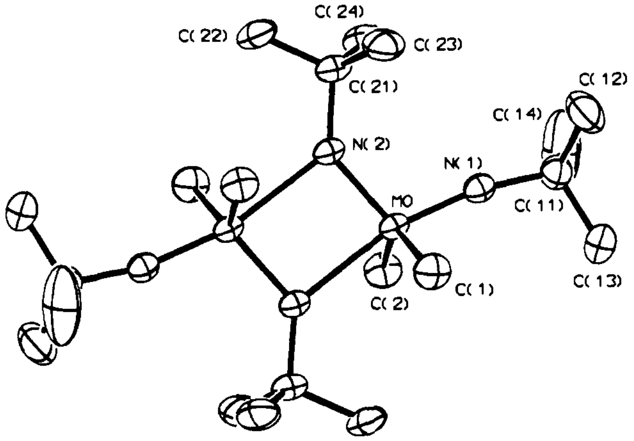
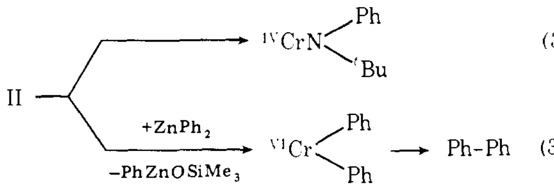


Figure 1. Structure of bis(μ-*N-tert*-butylimido)-(*N-tert*-butylimido)-tetramethyldimolybdenum.

The observation of different products depending on the order of addition of the reactants requires formation of at least one intermediate. In light of the facile substitution of compounds I, a reasonable intermediate is a monophenyl substituted derivative such as II.[12] Intermediate II may then undergo phenyl migration to the electron-deficient imido nitrogen affording a chromium(IV) amide (eq 3a). Alternatively, II can react with a second equivalent of zinc reagent to afford a diphenyl derivative which subsequently reductively eliminates biphenyl (eq 3b). In accord with this model, factors 1–4 noted above can be expected in each case to increase the likelihood that II will survive to undergo reaction 3b.[13]

$$(^tBuN)_2Cr(OSiMe_3)_2 + Ph_2Zn \longrightarrow \underset{\text{II}}{(^tBuN)_2Cr(OSiMe_3)Ph} + PhZnOSiMe_3 \quad (2)$$



(3a)

(3b)

Supplementary Material Available: Final positional parameters (as fractional coordinates), table of thermal parameters, and structure factor amplitudes (observed and calculated) of $C_{20}H_{48}Mo_2N_4$ (21 pages). Ordering information is given on any current masthead page.

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(4) For the preparation of starting materials see: Nugent, W. A.; Harlow, R. L., *Inorg. Chem.*, in press.

(5) Additional Ia could be obtained by cooling the solution but was contaminated with white needles of ^{t}BuOZnMe.

(6) Ia: mp 131 °C dec; ^{1}H NMR (C_7D_8) δ 0.98 (s, 12 H, Me), 1.40 (s, 36 H, ^{t}Bu) [methyl resonance exhibited characteristic satellites due to 14.4% ^{183}W ($S = \frac{1}{2}$), $J = 7$ Hz]. Anal. Calcd for $C_{20}H_{48}N_4W_2$: C, 33.72; H, 6.79; N, 7.86. Found: C, 33.89; H, 6.78; N, 7.83. Ib: mp 102 °C dec; ^{1}H NMR (C_7D_8) δ 1.02 (s, 12 H, Me), 1.39 (s, 36 H, ^{t}Bu). Anal. Calcd for $C_{20}H_{48}N_4Mo_2$: C, 44.78; H, 9.02; N, 10.44. Found: C, 45.16; H, 8.81; N, 10.93.

(7) For instance, on adding 1 equiv of pyridine to Ib, the methyl resonance was shifted to δ 0.59 and the *tert*-butyl resonance to 1.48; cf. previous note.

(8) Crystal Data: $C_{20}H_{48}Mo_2N_4$; M 536.52; monoclinic; space group $P2_1/n$; at −95 °C, a = 12.941 (4), $b = 9.487$ (2), $c = 11.226$ (2) Å; $\beta = 103.36$ (2)°; Z = 2; $D_c = 1.329$ g cm^{-3}; Mo Kα radiation ($\lambda = 0.71069$ μ; $\mu = 5.1$ cm^{-1}). Data were collected on a Syntex P3 diffractometer (4° < 2θ < 55°) *using the ω-scan technique. The structure was solved by the Patterson* heavy-atom method and refined by the full-matrix least-squares technique. The refinement of 214 variables (anisotropic thermal parameters for Mo, N, and C, isotropic thermal parameters for H) using 2494 reflections for which $I > 2.0\sigma(I)$ yielded a conventional R index of 0.024. The largest peak in the final difference Fourier (0.37 eÅ^{-3}) was close to the Mo atom.

(9) (a) Additional important bond lengths are Mo–C(1), 2.177 (2); Mo–C(2) 2.181 (2); N(1)–C(11), 1.457 (3); N(2)–C(21), 1.487 (2); C(11)–C(av), 1.518 (4); C(21)–C(av), 1.526 (3) Å. Additional important bond angles are N(1)–Mo–N(2), 108.61 (7); N(1)–Mo–N(2)′, 166.90 (6); N(1)–Mo–C(1), 92.17 (9); N(1)–Mo–C(2), 92.37 (8); N(2)–Mo–N(2)′, 84.48 (6); N(2)–Mo–C(1), 110.44 (9); N(2)–Mo–C(2), 110.11 (8); N(2)′–Mo–C(1), 82.47 (8); N(2)′–Mo–C(2), 83.24 (8); C(1)–Mo–C(2), 135.21 (10); Mo–N(2)–Mo′, 95.52 (6); Mo–N(2)–C(21), 134.7 (1); Mo′–N(2)–C(21), 129.8 (1); N(1)–C(11)–C(av), 108.7 (2); C–C(11)–C(av), 110.2 (3); N–C(21)–C(av), 109.5 (2); C–C(21)–C(av), 109.5 (2)°. (b) A referee has inquired about the relatively large thermal ellipsoid of C(14). This effect possibly reflects the absence of any close intermolecular contacts with C(14). In contrast, C(13) has a C–H contact of 3.07 Å and C(12) has two contacts of 3.17 Å each. However, the C(11)–C(methyl) distances are all in the range 1.513 (4)–1.526 (4) Å with identical esd's.

(10) Nugent, W. A.; Haymore, B. L. *Coord. Chem. Rev.* **1980,** *31*, 123–175.

(11) The remaining organic products after hydrolysis in each case were benzene, *tert*-butylamine, trimethylsilanol, and hexamethyldisiloxane. These were identified, as were biphenyl and *N-tert*-butylaniline, by GC–mass spectroscopy. Authentic *N-tert*-butylaniline was purified by spinning-band distillation (119 °C, 45 Torr) after preparation according to Hickenbottom, W. J. *J. Chem. Soc.* **1933**, 946–951.

(12) II represents the simplest formulation for a species in which a trimethylsiloxo ligand has been replaced by a phenyl group. We cannot at this time exclude other formulations such as "ate" complexes or binuclear (Cr, Cr, or Cr, Zn) species. We are continuing our investigation into the mechanism of this reaction.

(13) Brominolysis studies appear to confirm the greater stability of the phenylmolybdenum species derived from Ib. Thus 1 mmol of Ib in hexane was treated with 2 mmol of diphenylzinc. After the resultant $PhZnOSiMe_3$ was filtered off (0.78 mmol recovered), addition of excess bromine afforded 1.5 mmol of bromobenzene, determined by GLC.

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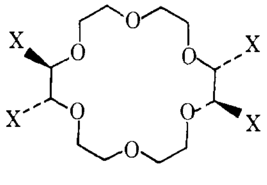
Photophysical Investigations of Chiral Recognition in Crown Ethers

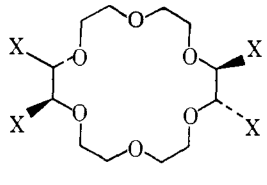
Sir:

The present communication reports the first use of photophysical techniques for the elucidation of chiral recognition in crown ethers.[1-10] Fluorescence quenching, energy transfer, and excimer formation have provided information on the complexation of achiral and chiral guests, on the conformation of functionalized crown ethers and on the effects of solvents and guests on given conformations.

1,2,10,11-(S,S,S,S)-(−)-Tetracarbo(N,N)dimethylamido-3,6,9,12,15,18-hexaoxocyclooctadecane (L-crown-amide, $\mathbf{1}_\mathrm{L}$) or its enantiomer, 1,2,10,11-(R,R,R,R)-(+)-tetracarbo-(N,N)dimethylamide-3,6,9,12,15,18-hexaoxocyclooctadecane (D-crown-amide, $\mathbf{1}_\mathrm{D}$),[11] were used as starting materials for the synthesis of optically active fluorescent crown ethers. $\mathbf{1}_\mathrm{L}$ and $\mathbf{1}_\mathrm{D}$ were converted into their acids, $\mathbf{2}_\mathrm{L}$ and $\mathbf{2}_\mathrm{D}$. The acids provided the acid chlorides, $\mathbf{3}_\mathrm{L}$ and $\mathbf{3}_\mathrm{D}$, which, in turn, allowed the preparation of L-crown-D-Trp ($\mathbf{4}_\mathrm{LD}$), L-crown-L-Trp ($\mathbf{4}_\mathrm{LL}$), D-crown-D-Trp ($\mathbf{4}_\mathrm{DD}$), D-crown-L-Trp ($\mathbf{4}_\mathrm{DL}$),[12] L-crown-pyr ($\mathbf{5}_\mathrm{L}$), and D-crown-pyr ($\mathbf{5}_\mathrm{D}$).[13]



$\mathbf{1}_\mathrm{L}$, X = $CON(CH_3)_2$
$\mathbf{2}_\mathrm{L}$, X = CO_2H
$\mathbf{3}_\mathrm{L}$, X = COCl
$\mathbf{4}_\mathrm{LD}$, X = $\text{D-CONH}\underset{\text{CO}_2\text{Me}}{\underset{|}{\text{C}}}\text{HCH}_2\text{(3-indole)}$
$\mathbf{4}_\mathrm{LL}$, X = $\text{L-CONH}\underset{\text{CO}_2\text{Me}}{\underset{|}{\text{C}}}\text{HCH}_2\text{(3-indole)}$
$\mathbf{5}_\mathrm{L}$, X = CONH-1-pyrene



$\mathbf{1}_\mathrm{D}$, X = $CON(CH_3)_2$
$\mathbf{2}_\mathrm{D}$, X = CO_2H
$\mathbf{3}_\mathrm{D}$, X = COCl
$\mathbf{4}_\mathrm{DD}$, X = $\text{D-CONH}\underset{\text{CO}_2\text{Me}}{\underset{|}{\text{C}}}\text{HCH}_2\text{(3-indole)}$
$\mathbf{4}_\mathrm{DL}$, X = $\text{L-CONH}\underset{\text{CO}_2\text{Me}}{\underset{|}{\text{C}}}\text{HCH}_2\text{(3-indole)}$
$\mathbf{5}_\mathrm{D}$, X = CONH-1-pyrene

Absorption spectra of all isomeric crown ether tryptophans were identical in methanol.[14] Small, but noticeable, differences were observed, however, between the emission intensities of the diastereomers: $\Phi_{4_\mathrm{DL}} = 0.200 \pm 0.008$, $\Phi_{4_\mathrm{LL}} = 0.180 \pm 0.008$.[15] Addition of $TbCl_3$ decreased the fluorescence yields. Stern-Volmer plots for 5.0×10^{-5} M D-crown-L-Trp and L-crown-L-Trp in MeOH were linear up to $\sim 5.0 \times 10^{-5}$ M $TbCl_3$, after which they leveled off. This data implies the quenching of the excited states by Tb^{3+} ions bound in the cavities of the crown ethers. Treatment of fluorescence intensities in the absence and in the presence of different amounts of $TbCl_3$[16] leads to binding constants of K(Tb^{3+}/D-crown-L-Trp) = $(2.90 \pm 0.21) \times 10^4$ M^{-1} and K(Tb^{3+}/L-crown-L-Trp) = $(2.76 \pm 0.12) \times 10^4$ M^{-1}. These values are of the same magnitude as determined for metal ion-crown ether complexes.[17] Complexing an achiral guest into crown ethers is seen to be unaffected by the chirality of the host. Cavity diameters are apparently the same for D-crown-L-Trp and L-crown-L-Trp. Only modest chiral recognitions have been observed using glycine-L-phenylalanine (Gly-L-Phe) and glycine-D-phenylalanine (Gly-D-Phe). Treatment of fluorescence intensities of D-crown-L-Trp (5.0×10^{-5} M in MeOH) in the absence and in the presence of different amounts of chiral guests[16] leads to K(Gly-L-Phe/D-crown-L-Trp) = $(1.3 \times 0.1) \times 10^4$ M^{-1} and K(Gly-D-Phe/D-crown-L-Trp) = $(1.9 \pm 0.1) \times 10^4$ M^{-1}.

Substantial chiral discriminations are seen, however, in the efficiencies of energy transfer from the tryptophan side arms

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