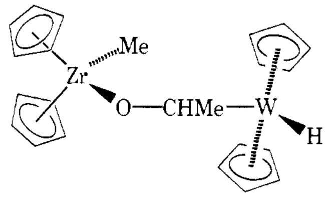
sequently II is a major product; Cp_2MoCO is formed in only 10% yield. Consistent with this observation, if Cp_2MoD_2 is employed with $Cp_2ZrCl[\eta^2\text{-}C(O)CH_3]$, a significant amount of $Cp_2ZrCl(OCHDCH_3)$ accompanies the $Cp_2ZrCl(OCD_2CH_3)$. We have established that a formal hydrogenated analogue of II, $[(\eta^5\text{-}C_5H_5)MoH]_2[\mu\text{-}(\eta^1\text{:}\eta^5\text{-}C_5H_4)]_2$,[10] is not a viable intermediate in the hydrogen transfer to the acyl since it is unaffected by I under the reaction conditions.[11]

We have attempted to probe the generality of this reaction, and also to intercept a possible intermediate, by employing Cp_2ReH as a hydride source. This monohydride reacts smoothly with I at 25 °C in C_6D_6, yielding a product which shows no proton resonance in the hydride region.[12] The former acetyl methyl group appears as a doublet due to coupling to a single vicinal proton. The presence, in the recrystallized product, of two equally intense cyclopentadienyl singlets (at 60 MHz), one each in regions characteristic of Cp_2Zr and Cp_2Re units, is consistent with a dimer of formula $Cp_2ZrCH_3(OCHMe)ReCp_2$.[13] The presence of a chiral center in the -OCHMe- bridge leaves both C_5H_5 rings on rhenium equivalent[16] regardless of which metal is bound to the chiral carbon; similarly, both linkage isomers require diastereotopic inequivalence of the ring protons on zirconium. The 220-MHz ^1H NMR spectrum of $Cp_2ZrCH_3(OCHMe)ReCp_2$ (in C_6D_6) shows that the Cp_2Zr signal at δ 5.83 is in fact a doublet with a separation of 0.0016 ppm (0.35 Hz). In view of this small anisochrony, we prefer the Zr-OCHMe-Re structure.

Finally, we have been able to exploit the decreased rates typically found for third transition series metals in order to directly observe the primary product in acyl hydrogenation by Cp_2MH_2 species. Compound I reacts with Cp_2WH_2 in C_6D_6 at 25 °C to produce a bimetallic complex exhibiting a methyl doublet characteristic of the $-OC(H)CH_3-$ unit.[17] This doublet is collapsed when Cp_2WD_2 is employed as the reductant. This complex is a monohydride, and the Cp rings on tungsten exhibit diastereotopic inequivalence. Structure III is consistent with all of these observations. This complex has a limited lifetime (minutes) at 25 °C. The products of this subsequent reaction are currently under study.



III

We[1c] and others[1a,18] have proposed the concept of Lewis acid activation of possible Fischer-Tropsch intermediates. Acyl I was selected for this study because the dihapto binding of the acetyl group provides such activation in a sterically compact manner. The significance of this mode of activation is clearly indicated since the acetyl stretching frequency persists when refluxing heptane solutions of $CpFe(CO)_2[C(O)Me]$ or $Co[C(O)Me](acacen)$ are treated with Cp_2MoH_2.

This work, as well as that reported earlier,[2] demonstrates that this bimolecular approach constitutes a viable alternative to metal clusters as a strategy for ligand activation and hydrogenation. It is also clear that it is exceptionally easy to generalize the bimolecular approach to heterobimetallic[19] systems, while the production of heterometallic clusters MM′M″ . . . constitutes a formidable synthetic challenge.

Acknowledgment. This work was supported in part by NSF Grant No. CHE 77-10059. We thank Galen Stucky, James Welter, Jay Labinger, and M. L. H. Green for useful advice and information.

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(5) ^1H NMR (C_6D_6): δ 5.78 (s, 10 H), 3.83 (q, 2 H), 1.00 (t, 3 H), 0.32 (s, 3 H). This product has been synthesized independently by the reaction of Cp_2ZrMe_2 with EtOH.

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(7) Thomas, J. L. *J. Am. Chem. Soc.* **1975,** *97,* 5943. ^1H NMR (CD_3CN): δ 4.43 (s). IR: ν (CN) 1780 cm^{-1} (in CD_3CN). We have synthesized this compound independently by photolysis of Cp_2MoCO in CD_3CN.

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(9) (a) By carbonylation of $Cp_2Zr(CH_3)Cl$.[9b] ^1H NMR (C_6D_6): δ 5.48 (s, 10 H), 2.25 (s, 3 H). IR: ν(C═O) 1556 cm^{-1} (Nujol). $Cp_2Zr(OEt)Cl$[9c] ^1H NMR (C_6D_6): δ 5.97 (s, 10 H), 3.85 (q, 2 H), 0.98 (t, 3 H). (b) Wailes, P. C.; Weigold, H.; Bell, A. P. *J. Organomet. Chem.* **1972,** *34,* 155. (c) Gray, D.; Brubaker, C. H. *Inorg. Chem.* **1971,** *10,* 2143.

(10) (a) The fulvalenide dimer $(CpMoH)_2(C_{10}H_8)$,[10b] which forms from $[(\eta^5\text{-}C_5H_5)MoH)]_2[\mu\text{-}(\eta^1\text{:}\eta^5\text{-}C_5H_4)]_2$ in a thermal reaction, is neither formed in the reactions described here, nor is it capable of hydrogen transfer to I. (b) Cooper, N. J.; Green, M. L. H.; Couldwell, C.; Prout, K. *J. Chem. Soc., Chem. Commun.* **1977,** 145.

(11) These reactions represent the mildest conditions yet reported for dehydrogenation of Cp_2MoH_2. In view of the relatively low ionization potential of Cp_2MoH_2, an electron transfer to the ZrC(O)Me moiety may initiate this rapid reaction of an 18-electron molybdenum complex.

(12) ^1H NMR (C_6D_6): δ 5.83 (s, 10 H), 3.95 (s, 10 H), 1.83 (d, 3 H), 0.30 (s, 3 H). The weak signal due to the proton on the tertiary carbon has been located (by spin decoupling) at δ 5.7. IR ν(C–O): 1030 cm^{-1}.

(13) While compounds of this type have been reported,[1b,14,15] in every case they have been formed from zirconium hydrides; an important aspect of the work reported here is the demonstration that later transition metal hydrides can also effect this hydrogen transfer.

(14) Fachinetti, G.; Floriani, C.; Roselli, A.; Pucci, S. *J. Chem. Soc., Chem. Commun.* **1978,** 269.

(15) Gell, K. I.; Schwartz, J. *J. Organomet. Chem.* **1978,** *162,* C11.

(16) Rapid rotation about the Re–CH(Me)O bond is assumed.

(17) ^1H NMR (C_6D_6): δ 5.83 (s, 10 H), 4.27 (s, 5 H), 4.20 (s, 5 H), 1.65 (d, 3 H), 0.20 (s, 3 H), −10.8 (br s, 1 H), 5.40 (q, 1 H).

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(19) We define a reaction system which begins by mixing soluble complexes of two different metals M and M′ as being heterobimetallic and bimolecular.

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Received October 22, 1979

Conformations and Rotation Barriers in 1,8-Bis(trimethylelement)naphthalenes

Sir:

The availability[1-3] of naphthalenes substituted in the peri positions by different $(CH_3)_3Z$ groups (Z = group 4a element) presents an exceptional opportunity to investigate the effects of severe internal strain on static and dynamic stereochemistry as a function of Z. Comparison[4] of the X-ray structures of 1,3,6,8-tetra-*tert*-butylnaphthalene (**1**), 1,8-bis(trimethylgermyl)naphthalene (**2**), and 1,8-bis(trimethylstannyl)naphthalene (**3**) has revealed that nonbonded repulsion between the bulky $(CH_3)_3Z$ groups in the 1,8 positions warps the naphthalene framework and imparts C_2 symmetry to all three molecules, with skeletal distortions decreasing in the order **1** ≫ **2** > **3**.[5] Surprisingly, however, this familial resemblance does not extend to the conformations of the $(CH_3)_3Z$ groups, which exhibit the same pattern for **2** and **3** but a distinctly different one for **1** (Figure 1).[4] If, as suggested by empirical force-field (EFF) calculations,[4] the ground-state conforma-

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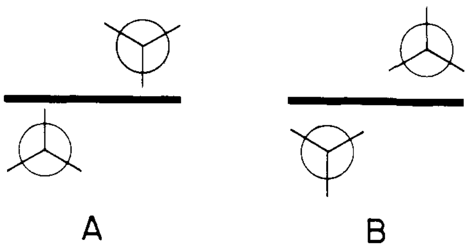

Figure 1. A schematic representation of idealized conformations of $(CH_3)_3Z$ groups in 1,8-bis(trimethylelement)naphthalenes, viewed down the C(9)-C(10) bond axis: A, **2** (Z = Ge) and **3** (Z = Sn); B, **1** (Z = C). The heavy horizontal line symbolizes the projection of the average plane of the naphthalene ring.

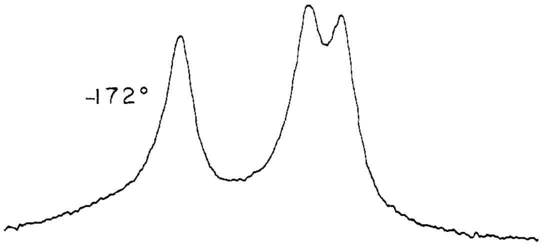

Figure 2. ^1H NMR spectrum (350.25 MHz, methyl region) of **2** in a 2:1 mixture of CHF_2Cl and CF_2Cl_2 at −172 °C.

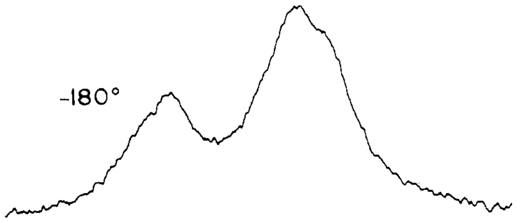

Figure 3. ^1H NMR spectrum (383.74 MHz, methyl region) of **3** in a 2:1 mixture of CHF_2Cl and CF_2Cl_2 at −180 °C.

tions of **1**, **2**, and **3** in solution resemble those in the solid state (i.e., if the conformational differences are not merely induced by lattice forces), it can be predicted[4] that the effect of the naphthalene ring on the chemical shifts of the three diastereotopic methyl groups in **2** and **3** at the slow exchange limit will differ markedly from that in **1**. We now report, first, an experimental verification of this prediction, and, second, the determination, by dynamic NMR, of the energy requirement for torsion about the $(CH_3)_3Z$-C bonds in **2** and **3**.

The ^1H NMR spectrum of **2** near the slow exchange limit (Figure 2) features three singlets in the methyl region, two of which are closely spaced (0.11 ppm) while the third is 0.41 ppm downfield from the center peak. For **3** we were able to resolve only the widely separated (0.43 ppm) chemical shifts, and thus the spectrum appears as a 2:1 doublet with the high intensity component at high field (Figure 3).[6] The downfield singlet in **2** and **3** is evidently due to the methyl groups which point toward the average plane of the naphthalene ring in conformation A (Figure 1).[4] In contradistinction, the chemical shifts of the methyl protons in **1** and other substituted 1,8-di-*tert*-butylnaphthalenes exhibit the reverse pattern, corresponding to conformation B (Figure 1), with the downfield and upfield singlets separated from the center singlet by 0.26-0.38 and 0.79-0.80 ppm, respectively.[1b] The different ground-state conformations (Figure 1) are therefore inherent molecular properties. It seems likely that the significantly greater crowding and internal strain in **1**, as compared with **2** and **3** (to judge by the skeletal deformations[5]), lies at the root of this distinction.

As determined by line shape analysis of the ^1H NMR spectra,[7] the rate constant for $(CH_3)_3Z$ group rotation is 140 s^{-1} for **2** at −160 °C and for **3** at −175 °C; $\Delta G^{\ddagger} = 5.4_5$ and 4.7 kcal/mol for **2** and **3**, respectively. For 1,8-di-*tert*-butylnaphthalenes, the corresponding barriers are ~6.5 kcal/mol at ca. −140 °C.[1b] It therefore seems reasonable to expect that the as yet unknown[2b] 1,8-bis(trimethylsilyl)naphthalene will exhibit a $(CH_3)_3Si$-C rotation barrier of ~6.0 kcal/mol, which is precisely the barrier recently predicted by Hutchings and Watt, using an EFF approach.[8] However, the same calculations[8] also predict a trend in $(CH_3)_3Z$-C rotation barriers of 4.7, 6.0, and 6.9 kcal/mol for Z = C, Si, and Sn, respectively, which is the reverse of the trend observed for $\Delta G^{\ddagger}$ (6.5, 5.5, and 4.7 kcal/mol for Z = C, Ge, and Sn, respectively). The source of this discrepancy remains to be discovered.

Acknowledgments. We thank the National Science Foundation (CHE77-07665 and CHE78-23858) for support of this work.

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(5) The extent of skeletal distortion may be gauged by the artificial torsion angle Z(1)-C(1)-C(8)-Z(2) (68.6, 54.3, and 53.1° for Z = C, Ge, and Sn, respectively), by the average values of Z(1)-C(1)-C(4) and Z(2)-C(8)-C(5) (150.9, 155.8, and 156.3° for Z = C, Ge, and Sn, respectively), by the average values of C(1)-C(9)-C(10)-C(4) and C(8)-C(9)-C(10)-C(5) (19.3, 11.2, and 9.3° for Z = C, Ge, and Sn, respectively), and by the spread in the C(1)-C(9)-C(8) angle (129.9, 126.1, and 125.6° for Z = C, Ge, and Sn, respectively).

(6) The barrier for methyl exchange is lower in **3** than in **2** and as a result different temperatures are required for slow exchange conditions in the two compounds. The viscosity of the solvent increases rapidly as the temperature is lowered and this leads to increased dipole-dipole relaxation and broader lines in **3** compared with **2**. It is remarkable that compounds of molecular weights of the order of 400 give resolved NMR spectra at temperatures near −180 °C. The success achieved with **2** and **3** can be attributed to the very high spectrometer frequency used to measure the NMR spectra and presumably also to the presence of internal rotation in the methyl groups. This internal rotation can give rise to nonexponential relaxation and non-Lorentzian line shapes: Matson, G. B. *J. Chem. Phys.* **1976,** *65* 4147. Werbelow, L. G.; Grant, D. M. *J. Magn. Reson.* **1978,** *29,* 603. However, the broad base on the peaks in Figure 2 is at least partly instrumental in origin.

(7) Chemical shifts of **2** and **3** in CF_2Cl_2-$CHFCl_2$ show negligible temperature dependence, i.e., <2 Hz in the range −50 to −100 °C for **2** and in the range −100 to −140 °C for **3**, as measured relative to the Freon 21 doublet.

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Received October 15, 1979

Preparation and Reactions of New Dioxygen Complexes of Rhodium

Sir:

Traditionally, dioxygen complexes of transition metals have been prepared by the oxidative addition of molecular oxygen to the low valent metal complexes stabilized by phosphine or isonitrile ligands.[1] We recently reported a new preparative method of dioxygen complexes of palladium using superoxide ion as a dioxygen source.[2] Extension of the work has led to the formation of dioxygen complexes of various transition metals having olefinic ligands or π-allyl ligands.[3] Dioxygen complexes of rhodium thus prepared have only π-coordinated ligands

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