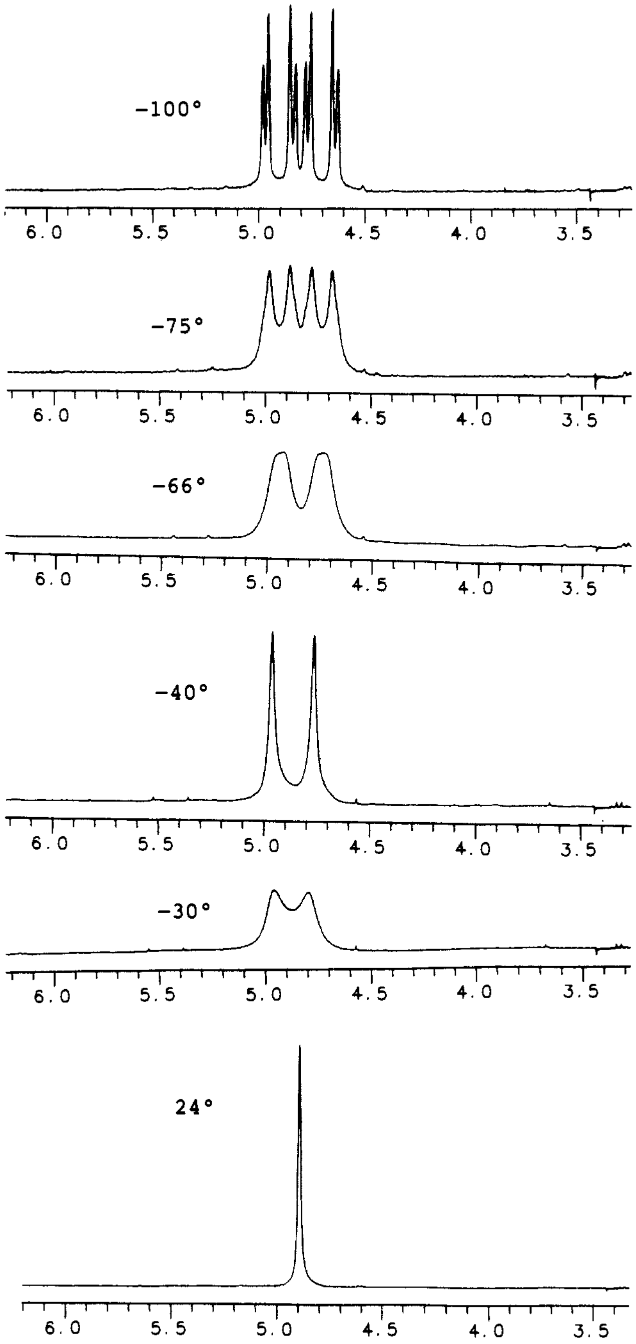

Figure 3. NMR signals measured at 300 MHz in $CCl_3F/C_6D_5CD_3$ (4:1) for the fluoromethylene protons of **3** at various temperatures (scale in δ units).

exchange became slow. Subsequent transformation of the doublet into a doublet of quartets confirmed the message conveyed by the other methylene protons, viz. that conformational mobility had been lost. This result also confirmed that the apparent equivalence of the fluoromethylene protons in **1** had been fortuitous. At the slow exchange limit, $\Delta\delta$ for the fluoromethylene protons of **3** was 0.13 ppm, $J_{HH} = 7.8$, $J_{HF} = 60.1$ Hz. Computer simulation[22] of the lineshape changes in the region of the initial decoalescence yielded the rate constant $k = 88 \pm 4$ s^{-1} at -66 °C, $\Delta G^{\ddagger} = 10.1$ (3) kcal/mol for rotation–inversion in **3**.

The barriers found for **1** and **3** are thus identical within experimental error. These remarkably high barriers are not attributable solely to negative hyperconjugation, as there should be contributions from dipole–dipole repulsion and torsional strain as well.[23] If the Pople group's Fourier analysis of the barrier in α-fluoromethylamine[9] is assumed to be correct for **1** and **3**, half of the barrier height we have observed (5 kcal/mol) can be ascribed to negative hyperconjugation.

Acknowledgment. We thank C. H. Bushweller for the use of his modification of the Kleier–Binsch DNMR3 program. This research was supported by the Air Force Office of Scientific Research and the National Science Foundation.

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[20] Bushweller, C. H.; Fleischmann, S. H.; Grady, G. L.; McGoff, P.; Rithner, C. D.; Whalon, M. R.; Brennan, J. G.; Marcantonio, R. P.; Domingue, R. P. *J. Am. Chem. Soc.* **1982**, *104*, 6224–36.

[21] Ab initio calculations[18] have indicated that trifluoromethyl can engage in negative hyperconjugation, albeit somewhat less effectively than fluoro. A similar study, clearly at odds with our findings, concluded that the two substituents are comparably potent (Stamper, J. G.; Taylor, R. *J. Chem. Res.* (*S*) **1980**, 128; (*M*), **1980**, 1930–9).

[22] The DNMR3 program of D. A. Kleier and G. Binsch was used as modified by Bushweller's group (Bushweller, C. H.; Bhat, G.; Letendre, L. J.; Brunelle, J. A.; Bilofsky, H. S.; Ruben, H.; Templeton, D. H.; Zalkin, A. *J. Am. Chem. Soc.* **1975**, *97*, 65).

[23] Note that *inversion makes no contribution to the rotation–inversion barrier height*, as the nitrogen is pyramidal in both the antiperiplanar and perpendicular conformations.

Reactions of MCl_5 (M = Nb or Ta) with Excess PhLi: Structural Characterization of Bisbenzyne/Polyphenyl Derivatives of Niobium and Tantalum

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Reactions between transition-metal halides and an excess of an aryllithium reagent have long been known to give unexpected products with an interesting variety of oxidation states, coordination numbers, and bonding types.[2] A recent example involves the structural characterization of the unusual complex $[Li_4FePh_4{\cdot}4Et_2O]$ in which the lithium ions are thought to play a vital role in stabilization through a coordinative interaction with the transition metal.[3] Earlier work by Kurras[4] and Sarry[5] in the group 5 transition elements had indicated that low valent species such as $[MPh_2(LiPh)_4{\cdot}3.5Et_2O]$ were present in metal halide/excess LiPh reaction mixtures. However, more recent work, based upon ^1H and ^7Li NMR, has indicated the unexpected presence of benzyne complexes in these solutions.[6] Rapid progress in this area has often been hindered by the difficulty in obtaining X-ray data even though many structures are known for closely related complexes that involve various π-acid ligands.[7] Here we provide the first X-ray structural evidence for the presence of benzyne groups in two compounds which are derived from the treatment of $NbCl_5$ or $TaCl_5$ with an excess of PhLi in THF.

The complexes $[Nb(\eta^2\text{-}C_6H_4)_2Ph_3(LiPh{\cdot}THF)(LiTHF)_4]{\cdot}0.5THF0.5C_6H_{14}$, **1**, and $[Ta(\eta^2\text{-}C_6H_4)_2Ph_4(LiTHF)_2]_2[Li_4Cl_2(THF)_{10}]$, **2**, were synthesized as described.[8] Their X-ray crystal

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[1] Fellow of the A.P. Sloan Foundation 1985–1987.

[2] Taube, R. *Comments Inorg. Chem.* **1984**, *3*, 69.

[3] Bazhenova, T. A.; Lobkovskaya, R. M.; Shibaeva, R. P.; Shilov, A. E.; Shilova, A. K.; Gruselle, M.; Levy, G.; Tchoubar, B. *J. Organomet. Chem.* **1983**, *244*, 265.

[4] Kurras, E. *Angew. Chem.* **1960**, *72*, 635.

[5] Sarry, B.; Schön, M. *J. Organomet. Chem.* **1968**, *13*, 9.

[6] Sarry, B.; Schaeffernicht, R. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1981**, *36B*, 1238.

[7] An example of such a compound is $[(\{(LiPh)_3(Et_2O)_{1-1.5}Ni\}_2N_2)_2]$, see: Jonas, K. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 997. See, also: Krüger, C.; Tsay, Y. H. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 998. Jonas, K.; Brauer, D. J.; Krüger, C.; Roberts, P. J.; Tsay, Y. H. *J. Am. Chem. Soc.* **1976**, *98*, 74. For recent reviews which include many such compounds, see: Setzer, W. N.; Schleyer, P. v. R. *Adv. Organomet. Chem.* **1985**, *24*, 353. Jonas, K. *Adv. Organomet. Chem.* **1981**, *19*, 97.

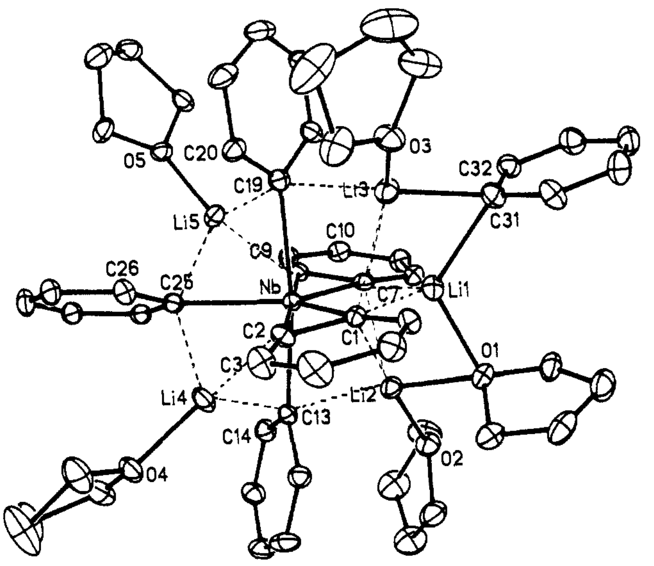

Figure 1. Computer-generated drawing of **1**. Hydrogens and disordered lattice THF/hexane omitted for clarity. Selected bond distances (Å) and angles (deg) are as follows: Nb–C(1) = 2.185 (5), Nb–C(2) = 2.166 (6), Nb–C(7) = 2.210 (5), Nb–C(8) = 2.215 (5), Nb–C(13) = 2.327 (6), Nb–C(19) = 2.380 (6), Nb–C(25) = 2.323 (5), C(1)–C(2) = 1.419 (7), C(7)–C(8) = 1.410 (7), Li(1)–C(1) = 2.258 (11), Li(1)–C(7) = 2.264 (10), Li(1)–O(1) = 2.022 (11), Li(1)–C(31) = 2.170 (12), Li(2)–C(7) = 2.208 (11), Li(2)–C(13) = 2.263 (11), Li(2)–O(1) = 2.152 (10), Li(2)–O(2) = 1.965 (11), Li(3)–C(1) = 2.438 (12), Li(3)–C(19) = 2.347 (11), Li(3)–O(3) = 1.934 (12), Li(3)–C(31) = 2.187 (13), Li(4)–C(2) = 2.232 (12), Li(4)–C(13) = 2.306 (12), Li(4)–C(25) = 2.239 (12), Li(5)–C(8) = 2.181 (11), Li(5)–C(19) = 2.278 (11), Li(5)–C(25) = 2.267 (11), C(1)–Nb–C(2) = 38.1 (2), C(1)–Nb–C(7) = 105.9 (2), C(1)–Nb–C(8) = 142.6 (2), C(1)–Nb–C(13) = 97.8 (2), C(1)–Nb–C(19) = 92.7 (2), C(7)–Nb–C(13) = 89.4 (2), C(7)–Nb–C(19) = 89.9 (2), C(13)–Nb–C(19) = 169.2 (2), C(13)–Nb–C(25) = 86.1 (2), C(19)–Nb–C(25) = 85.7 (2).

structures[9] are illustrated in Figures 1 and 2 (anion only). In **1**, the niobium (formally Nb(III)) is surrounded, in a roughly trigonal bipyramidal way, by two benzynes and a phenyl group that are equatorially bonded as well as two axially bound phenyls. Five lithium ions involving five solvating THF's and a further phenyl group, bridging Li(1) and Li(3), comprise a secondary coordination sphere. There are numerous interactions between the lithiums and various carbons of the benzyne and phenyl ligands. Some of these involve lengths similar to the Li-C distances in $(PhLi{\cdot}Et_2O)_4$.[10] The Nb–C(Ph) distances average ca. 2.34 Å, whereas Nb–C(benzyne) ranges from ca. 2.17 to 2.22 Å.

The tantalum-centered anion in **2** involves tantalum(V) coordinated, in a distorted octahedral fashion, to two mutually *cis*-benzyne groups and four phenyl groups. Two THF solvated Li^+ ions cap adjacent triangular faces involving the *cis*-benzyne groups as a common edge. The cation $[Li_4Cl_2(THF)_{10}]^{2+}$, or its ether-solvated analogue, has been observed at least twice in other systems[11] and can no longer be considered a curiosity. The Ta–C(Ph), ca. 2.36 Å, and Ta–C(benzyne), ca. 2.22 Å, distances are marginally longer than those found in **1**. This is not surprising in view of the similar sizes of Nb and Ta and higher (6 versus 5) coordination number of the metal in **2**.

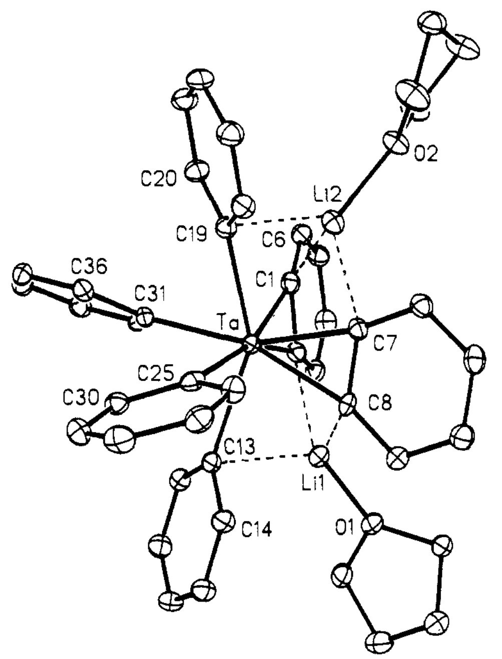

Figure 2. Computer-generated drawing of the anion of **2**. Hydrogens omitted for clarity. Selected bond distances (Å) and angle (deg) are as follows: Ta–C(1) = 2.208 (5), Ta–C(2) = 2.228 (6), Ta–C(7) = 2.218 (5), Ta–C(8) = 2.214 (4), Ta–C(13) = 2.384 (6), Ta–C(19) = 2.393 (6), Ta–C(25) = 2.320 (6), Ta–C(31) = 2.339 (4), Ta--Li(1) = 2.740 (9), Ta--Li(2) = 2.739 (10), C(1)–C(2) = 1.384 (8), C(7)–C(8) = 1.402 (8), Li(1)–C(2) = 2.213 (11), Li(1)–C(8) = 2.211 (12), Li(1)–C(13) = 2.169 (9), Li(1)–O(1) = 1.903 (9), Li(2)–C(1) = 2.229 (13), Li(2)–C(7) = 2.240 (11), Li(2)–C(19) = 2.197 (9), Li(2)–O(2) = 1.909 (11), C(1)–Ta–C(2) = 36.3 (2), C(7)–Ta–C(8) = 36.9 (2), C(1)–Ta–C(7) = 88.8 (2), C(2)–Ta–C(8) = 87.7 (2), C(1)–Ta–C(19) = 85.6 (2), C(1)–Ta–Ca(13) = 117.9 (2), C(1)–Ta–C(25) = 163.7 (2), C(1)–Ta–C(31) = 81.6 (2), C(8)–Ta–C(13) = 81.8 (2), C(8)–Ta–C(19) = 116.1 (2), C(8)–Ta–C(25) = 85.9 (2), C(8)–Ta–C(31) = 162.9 (2), C(13)–Ta–C(19) = 147.1 (2), C(13)–Ta–C(25) = 75.5 (2), C(13)–Ta–C(31) = 81.3 (2), C(19)–Ta–C(25) = 78.5 (2), C(19)–Ta–C(31) = 79.9 (2), C(25)–Ta–C(31) = 92.1 (2).

The structures of both **1** and **2** have a number of distinct features. For example, they are the first structurally characterized mononuclear transition-metal complexes involving two benzyne ligands.[12] Also, the important role which the solvated lithium ions play in the stabilization of each structure is apparent from the many interactions with ligand carbon atoms. Other important features relate to the differences between the C–C benzyne distances in **1** and **2** and those seen in the three other structurally characterized mononuclear benzyne complexes previously reported.[12] The most closely related compounds to **1** and **2** are $Ta(\eta^5\text{-}C_5Me_5)(\eta^2\text{-}C_6H_4)Me_2$, **3**,[12a] and $Zr(\eta^5\text{-}C_5H_5)_2(\eta^2\text{-}C_6H_4)PMe_3$, **4**.[12b] In both of these complexes the η^2-C-C distance involving the benzyne ligand is 1.364 (8) Å, whereas in **1** the

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[8] The routes employed were modifications of those in ref 6. The major differences was the use of THF rather than ether solvent. For example, $NbCl_5$ (0.527 g, 1.95 mmol) was added slowly to a stirred solution of phenyllithium (1.64 g, 19.5 mmol) in THF (60 mL and cooled in a dry ice/acetone bath. The dark green mixture was allowed to warm to ambient temperature overnight. The resultant dark blue solution was filtered, and the volume was reduced to ~10 mL by evaporation under reduced pressure. Hexane (15 mL) was added giving some precipated solids which were removed by filtration. Slow cooling (over 40 h) in a −25 °C freezer gave the product **1** as dark blue (almost black) crystals in ca. 10% yield. **2** was synthesized in a similar manner. Initially, the solution was bright green but this became very dark red on warming. Reduction of the volume to 10 mL, addition of hexane (10 mL), and filtration afforded upon cooling a low yield (5%) of yellow crystals of **2**.

[9] Crystal data with Mo Kα (λ = 0.71069 Å) radiation at 130 K: **1**, $C_{61}H_{79}O_{5.5}NbLi_5$, a = 15.379 (8) Å, b = 18.015 (7) Å, c = 20.974 (8) Å, β = 96.59 (4)°, Z = 4, monoclinic, space group $P2_1/a$, R = 0.073; **2**, $C_{128}H_{168}O_{14}Cl_2Li_8Ta_2$, a = 11.786 (5) Å, b = 14.339 (6) Å, c = 19.453 (9) Å, α = 78.97 (3)°, β = 99.29 (4)°, c = 73.65 (3)°, Z = 1, triclinic, space group, $P\bar{1}$, R = 0.049.

[10] Hope, H.; Power, P. P. *J. Am. Chem. Soc.* **1983**, *105*, 5320.

[11] Hope, H.; Oram, D.; Power, P. P. *J. Am. Chem. Soc.* **1984**, *106*, 1149 describes $[Li_4Cl_2(OEt_2)_{10}]^{2+}$. The cation $[Li_4Cl_2(THF)_{10}]^{2+}$ has also been seen in $[Li_4Cl_2(THF)_{10}]^{2+}[O\{Fe(NPh_2)_3\}_3]^{2-}$: Olmstead, M. M.; Power, P. P., unpublished work.

[12] Three mononuclear benzyne complexes have been structurally characterized. The first was $[Ta(\eta^5\text{-}C_5Me_5)(\eta^2\text{-}C_6H_4)Me_2]$ in the following: (a) McLain, S. J.; Schrock, R. R., Sharp, P. R.; Churchill, M. R.; Youngs, W. J. *J. Am. Chem. Soc.* **1979**, *101*, 263. See, also: (b) Bennett et al. (Bennett, M. A.; Hambley, T. W.; Roberts, N. K.; Robertson, G. B. *Organometallics* **1985**, *4*, 1992) for the structure of $[Ni(\eta^2\text{-}C_6H_4)(Cy_2PCH_2CH_2PCy_2)]$ and (c) Buchwald et al. (Buchwald, S. L.; Watson, B. T.; Huffman, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 7411) for the structure of $[Zr(\eta^5\text{-}C_5H_5)_2(\eta^2\text{-}C_6H_4)PMe_3]$.

corresponding lengths are 1.419 (7) and 1.410 (7) Å. In **2** they are 1.402 (8) and 1.384 (8) Å. The remaining benzyne ring C–C distances in **1** range from 1.416 (7) to 1.388 (8) Å and from 1.404 (9) to 1.380 (9) Å in **2**. Thus, all the benzyne bond lengths are relatively long and show, to some degree, an alternating pattern similar to the D_{3h} symmetry first noted by Schrock.[12a] The longer benzyne C–C bonds may be due to a number of factors. First, the group 5 metal centers in **2** and, especially, **1** are probably more electron rich than **3** or **4**. This can be attributed to the good σ-donor and poor π-acid properties of the phenyl coligands. The Nb and Ta metals are thus able to donate electron density more readily into antibonding benzyne orbitals giving the longer C–C distances seen throughout the benzyne ligands in **1** and **2**. Secondly, the many interactions between the Li^+ ions and the ligands serve to reduce bonding electron density in the benzynes even further.

It is also notable that the average benzyne C–C bond length in **1** is slightly longer than in **2**, 1.403 versus 1.396 Å. This is consistent with a more electron-rich center in the niobium compound as a result of its lower oxidation state. Further evidence for greater electron density is seen in the greater number of associated Li^+ ions; five for niobium versus two for tantalum.

Finally, we note that the complex **2** is very close to the structures for $[Ta(\eta^2\text{-}C_6H_4)_2Ph_4(Li{\cdot}OEt_2)_3]$ proposed on the basis of ^1H and ^7Li NMR data.[6] The major difference involves the number of complexes Li^+ ions. However, we believe that this difference is merely a consequence of the greater lattice energy obtained by crystallization as the ionic **2**. Apparently, two Li^+ ions suffice to stabilize the structure obtained. Attempts to remove the complexes Li^+ ions from either **1** or **2** to test their dependence on Li^+ for stability did not afford any material suitable for X-ray crystallography.

Acknowledgment. We thank the Petroleum Research Fund for financial support.

Supplementary Material Available: Summary of data collection and refinement and tables of atom coordinates, thermal parameters, bond distances and angles, and hydrogen coordinates (22 pages). Ordering information is given on any current masthead page.

Asymmetric Dihydroxylation via Ligand-Accelerated Catalysis†

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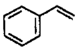
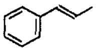
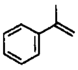
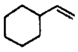
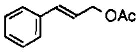
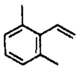
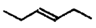
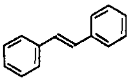
The addition of osmium tetroxide to olefins may be both the most selective and reliable of known organic transformations.[1] The added utility of stereospecifically imbedding two hydroxyl groups in a hydrocarbon framework (cis vicinal dihydroxylation) accounts for osmium tetroxide's popularity in organic synthesis, but osmium's expense and toxicity call for a catalytic solution.[1c,2]

Table I[a]

entry	olefin	ligand, % ee,[b] confgn of diol[c] sign of $[\alpha]^{25}_D$	time (h)
1		**1**, 62, *R*-(−) **1**, 60, *R*-(−) **2**, 53.6, *S*-(+)	3[d] 7[e] 7[e]
2		**1**, 65, *R*,*R*-(−) **2**, 55.4, *S*,*S*-(+)	5[d] 12[e]
3		**1**, 33, *R*-(−)	1.5[d]
4		**1**, 46, *R*-(+)	1[d]
5		**1**, 76, *R*,*R*-(+)	7[d]
6		**1**, 65, (−)	3[d]
7		**1**, 20, *R*,*R*-(+)	17[d]
8		**1**, 88, *R*,*R*-(+) **1**, 85, *R*,*R*-(+) **2**, 78.5, *S*,*S*-(−)	7[d] 15[e] 17[e]

[a] All reactions were performed essentially as described for the molar scale process with stilbene. Specific notes and exceptions: (1) 1–5 mmol of olefin; (2) in small (ca. 7 mL) screw-cap vials (avoid rubber septa); (3) a temperature of 0 °C was maintained by storing the vials in an ice-bath for the duration of the reaction; (4) either 1 or 2 M in olefin as indicated (i.e., *d* or *e*). In all cases the isolated yield of the diol was 80–95%. [b] The enantiomeric excesses were determined by HPLC separation of the mono MTPA ester (entry 3), bis MTPA esters (entries 1, 2, 4–7), or the bis acetates (entry 8) in all cases by using a chiral Pirkle column (type 1A, preparative version) and eluting with *i*-PrOH/hexane. [c] The absolute configurations of the diols were established as described in ref 5. For case 6, the correlation is not yet accomplished. Rotations were measured in EtOH except entry 5 which was taken in $CHCl_3$. [d] [olefin] = 1 M and [Os] = 4 × 10^{-3} M. [e] [olefin] = 2 M and [Os] = 4 × 10^{-3} M.

We report a new catalytic process achieving substantially improved rates and turnover numbers[2] as well as useful levels of asymmetric induction.

Knowing that certain tertiary amines accelerate the stoichiometric reaction between OsO_4 and olefins,[1a,b] in the late seventies we developed an asymmetric osmylation of olefins by using cinchona alkaloid derivatives as the chiral ligands;[3] improvements and variations followed.[4,5] Our stoichiometric procedure[3] becomes a highly effective catalytic process (Scheme I) with the apparently trivial act of combining it with the well-known Upjohn, N-oxide-based, catalytic method.[2a] Table I and the experimental details given for the molar-scale asymmetric dihydroxylation of (*E*)-stilbene[6] illustrate the procedure's simplicity and effectiveness.

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† Dedicated to Professor Hans Wynberg on the occasion of his 65th birthday.

(1) (a) Criegee, R. *Justus Liebigs Ann. Chem.* **1936**, *522*, 75. (b) Criegee, R.; Marchand, B.; Wannowius, H. *Justus Liebigs Ann. Chem.* **1942**, *550*, 99. (c) Schröder, M. *Chem. Rev.* **1980**, *80*, 187–213.

(2) (a) VanRheenen, V.; Kelly, R. C.; Cha, D. F. *Tetrahedron Lett.* **1976**, 1973. (b) Sharpless, K. B.; Akashi, K. *J. Am. Chem. Soc.* **1976**, *98*, 1986. (c) Akashi, K.; Palermo, R. E.; Sharpless, K. B. *J. Org. Chem.* **1978**, *43*, 2063. (d) Ray, R.; Matteson, D. S. *Tetrahedron Lett.* **1980**, *21*, 449. (e) Myers, R. S.; Michaelson, R. C.; Austin, R. G., U.S. Patents 4496778 and 4496779 and others cited therein.

(3) Hentges, S. G.; Sharpless, K. B. *J. Am. Chem. Soc.* **1980**, *102*, 4263.

(4) The 4-chlorobenzoyl derivatives **1** and **2** are not previously described.[3] For comparison, **1** was tried with stilbene under the original[3] stoichiometric conditions (in toluene at room temperature) and yielded (*R*,*R*)-*threo*-hydrobenzoin of 99% ee. Upon reexamination, however, all the enantiomeric excesses reported in ref 3 are low (unpublished results of present authors, see also ref 5c). The acetate analogue of **1**, for example, affords the *R*,*R*-diol from stilbene in 94% ee not in 83% ee as recorded in ref 3. Alkaloid **1** is the best of 20 related derivatives examined. The structure given for dihydroquinine acetate in ref 3 is wrong: the configuration at carbon-9 should be *R* not *S*.

(5) Stoichiometric, asymmetric osmylations involving external chiral amine ligands reported by other groups: (a) Yamada, T.; Narasaka, K. *Chem. Lett.* **1986**, 131. (b) Tokles, M.; Snyder, J. K. *Tetrahedron Lett.* **1986**, *27*, 3951. (c) Annunziata, R.; Cinquini, M.; Cozzi, F.; Raimondi, L.; Stefanelli, S. *Tetrahedron Lett.* **1987**, *28*, 3139. (d) Tomioka, K.; Nakajima, M.; Koga, K. *J. Am. Chem. Soc.* **1987**, *109*, 6213. Asymmetric osmylations involving internal chiral ligands: (e) Johnson, C. R.; Barbachyn, M. R. *J. Am. Chem. Soc.* **1984**, *106*, 2459. (f) Hauser, F. M.; Ellenberger, S. R.; Clardy, J. C.; Bass, L. S. *J. Am. Chem. Soc.* **1984**, *106*, 2458. (g) Hassine, B. B.; Gorsane, M.; Pecher, J.; Martin, R. H. *Bull. Soc. Chim. Belg.* **1985**, *94*, 759. Catalytic asymmetric osmylation: (h) Kokubo, T.; Sugimoto, T.; Uchida, T.; Tanimoto, S.; Okano, M. *J. Chem. Soc., Chem. Commun.* **1983**, *769*.

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