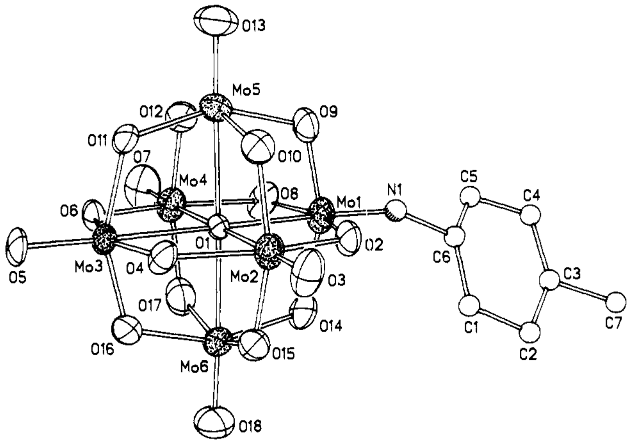


Figure 1. ORTEP drawing of the structure of the $[Mo_5O_{18}(MoNC_6H_4CH_3)]^{2-}$ anion. Selected bond lengths (Å) and bond angles (deg): Mo(1)–N(1) = 1.661 (18), Mo(1)–O(1) = 2.202 (11), Mo(1)–O(2) = 1.982 (12), Mo(1)–O(8) = 1.930 (11), Mo(1)–O(9) = 1.931 (12), Mo(1)–O(14) = 1.997 (12), Mo(2)–O(1) = 2.340 (10), Mo(3)–O(1) = 2.306 (11), Mo(4)–O(1) = 2.359 (10), Mo(5)–O(1) = 2.360 (9), Mo(6)–O(1) = 2.344 (9); Mo(1)–N(1)–C(6) = 154.2 (16), N(1)–Mo(1)–O(2) = 99.0 (7), N(1)–Mo(1)–O(8) = 104.6 (7), N(1)–Mo(1)–O(9) = 103.8 (7), N(1)–Mo(1)–O(14) = 99.6 (7), N(1)–Mo(1)–O(1) = 176.9 (6).

have proven to be problematic.[8] In DMF solution, cyclic voltammetry of complex **1** reveals two one-electron reductions at –0.52 V and –1.09 V (vs SCE); corresponding values for $[Mo_6O_{19}]^{2-}$ are –0.39 V and –1.12 V.

The structure of the anion of **1** is depicted in Figure 1.[9] The gross structure resembles that of its $[Mo_6O_{19}]^{2-}$ parent,[10] with a *p*-tolylimido group replacing a terminal oxo ligand. The bond lengths of the five terminal oxo ligands do not vary appreciably, ranging from 1.673 (15) to 1.700 (14) Å. The Mo(1)–O(1) distance of 2.202 (11) Å is significantly shorter than other Mo–O(1) distances, which average 2.342 (10) Å; an analogous contraction has been noted in the structure of the hydrazido(2–) system $[Mo_5O_{18}(MoNNMePh)]^{2-}$.[5a] Considerable variations are seen in the bond lengths involving the doubly bridging oxygens, which range from 1.849 (15) to 1.997 (12) Å. Klemperer[4] has correlated similar bond-length alternations in the $[(\eta^5\text{-}C_5H_5)Ti(Mo_5O_{18})]^{3-}$ anion with the ^{17}O NMR spectrum of that species; we will address these points in our full paper. The molybdenum–imido linkage appears to be both slightly shorter [1.661 (18) Å] and less obtuse [154.2 (16)°] than expected, but the relatively low precision of the structural data precludes a detailed analysis.

This study has demonstrated that, despite the exceedingly low surface charge density of the $[Mo_6O_{19}]^{2-}$ species,[11] direct functionalization can be accomplished in a straightforward manner under mild conditions. Our isolation of an imido derivative of a polyoxometalate system lends further credence to the proposal[3] that similar species are key surface intermediates in ammoxidation chemistry. In subsequent contributions, we will demonstrate that the reaction chemistry presented here can be extended to encompass a variety of polyoxometalate systems, including multiply substituted derivatives of **1**.

Acknowledgment. E.A.M. thanks the National Science Foundation for support.

Supplementary Material Available: Tables of atomic coordinates and isotropic thermal parameters, bond lengths, bond angles, anisotropic thermal parameters, and H atom coordinates and isotropic thermal parameters for **1** (8 pages); listing of observed and calculated structure factors for **1** (21 pages). Ordering information is given on any current masthead page.

---

[8] Nugent, W. A.; Mayer, J. M. *Metal–Ligand Multiple Bonds*; Wiley: New York, 1988; pp 123–125.

[9] Crystal data for $C_{39}H_{79}N_3O_{18}Mo_6$ (**1**): orange crystals, monoclinic, $P2_1/c$, $a = 12.774$ (4) Å, $b = 22.502$ (9) Å, $c = 19.716$ (7) Å, $\beta = 106.33°$, $V = 5439$ (4) Å^3, $Z = 4$. Of 7579 reflections collected ($T = 294$ K, $2\theta_{max} = 45°$), 3718 were independent and observed ($4\sigma F_o$). Except for C and N atoms, all non-hydrogen atoms were anisotropically refined. H atom contributions were idealized. $R = 7.48\%$ and $R_w = 8.90\%$. Disorder within the butyl and tolyl groups accounts for the high R factor and distortions in these groups.

[10] Allcock, H. R.; Bissell, E. C.; Shawl, E. T. *Inorg. Chem.* **1973**, *12*, 2963.

[11] Barzca, L.; Pope, M. T. *J. Phys. Chem.* **1975**, *79*, 92.

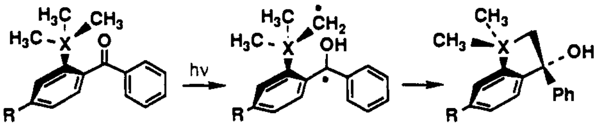
Activation Parameters for Triplet δ-Hydrogen Abstraction by *o*-*tert*-Butylbenzophenones: No Tunneling but an Entropy-Controlled Inductive Effect in the Isoelectronic Anilinium Ion

Peter J. Wagner,* Qunjian Cao, and Raul Pabon

Chemistry Department, Michigan State University
East Lansing, Michigan 48824

Received August 15, 1991
Revised Manuscript Received October 7, 1991

We recently reported that *o*-benzoyltrimethylanilinium ion as its BF_4 salt (OTMABP)[1] mimics *o*-*tert*-butylbenzophenone (OTBBP)[2] in undergoing facile photoinduced cyclization to indanol derivatives. We have now measured the activation parameters for δ-hydrogen abstraction in the triplet states of these two ketones as well as in 2,4-di-*tert*-butylbenzophenone with fully deuterated *tert*-butyl groups. We find no evidence for tunneling but do note that the inductive deceleration caused by the positive nitrogen atom in OTMABP is due entirely to a lower entropy of activation.



OTBBP : R = H, X = C OTMABP : R = H, X = N$^+$ 24tBBP : R = t-Bu, X = C

The triplet decay of OTMABP was studied as a function of temperature in methanol for comparison to the similar study done on OTBBP.[2] Triplet lifetimes were measured by monitoring decay of the T–T absorption at 625 nm following excitation of <0.01 M solutions by a nitrogen laser (337 nm). Figure 1 compares plots of log (k_H/T) vs $1/T$ for the two compounds. Since there are no known decay processes of triplet ketones with rate constants within an order of magnitude of the decay rates measured, we can safely assume that the only significant mode of triplet decay at all temperatures is hydrogen abstraction. The high cyclization quantum yields for both compounds[1,2] at room temperature validate this premise. Quenching studies had indicated that triplet OTMABP is only 1/30 as reactive as triplet OTBBP.[1] The flash studies verify this finding and furthermore indicate that the two compounds have identical activation energies and enthalpies, within experimental error. The factor of 30 difference in reactivity is entirely due to a more negative entropy of activation for the ketone containing the positive nitrogen.

It is commonly assumed that inductive effects on reactivity involve primarily changes in activation enthalpies. Such a situation is entirely reasonable for ionic reactions with large activation energies. However, a hydrogen atom transfer has a low activation energy and is a neutral reaction, since the reactant and product have the same charge. Nonetheless, significant inductive effects on reactivity are well-known in radical reactions and are thought to reflect charge transfer specifically in the transition state (TS).[3]

---

[1] Wagner, P. J.; Cao, Q. *Tetrahedron Lett.* **1991**, *32*, 3915.

[2] Wagner, P. J.; Giri, B. P.; Scaiano, J. C.; Ward, D. L.; Gabe, E.; Lee, F. L. *J. Am. Chem. Soc.* **1985**, *107*, 5483.

[3] Walling, C. *Free Radicals in Solution*; John Wiley & Sons: New York, 1957. Pryor, W. *Free Radicals*; McGraw-Hill: New York, 1966. Breslow, R. *Organic Reaction Mechanisms*; W. A. Benjamin: New York, 1969; pp 235–42.

0002-7863/92/1514-346$03.00/0

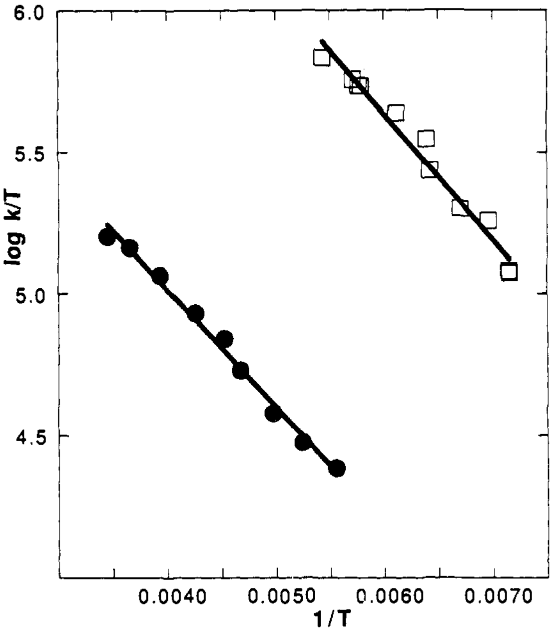


Figure 1. Temperature dependence of triplet decay rates in 4:1 methanol/ethanol. (□) OTBBP: $\Delta S^{\ddagger} = -9.23$ eu, $\Delta H^{\ddagger} = 2.06$ kcal/mol ($r = 0.986$); $\log A = 10.96 \pm 0.3$; $E_a = 2.37 \pm 0.3$ kcal/mol. (●) OTMABP: $\Delta S^{\ddagger} = -16.84$ eu, $\Delta H^{\ddagger} = 1.90$ kcal/mol ($r = 0.995$); $\log A = 9.46 \pm 0.2$; $E_a = 2.35 \pm 0.2$ kcal/mol.

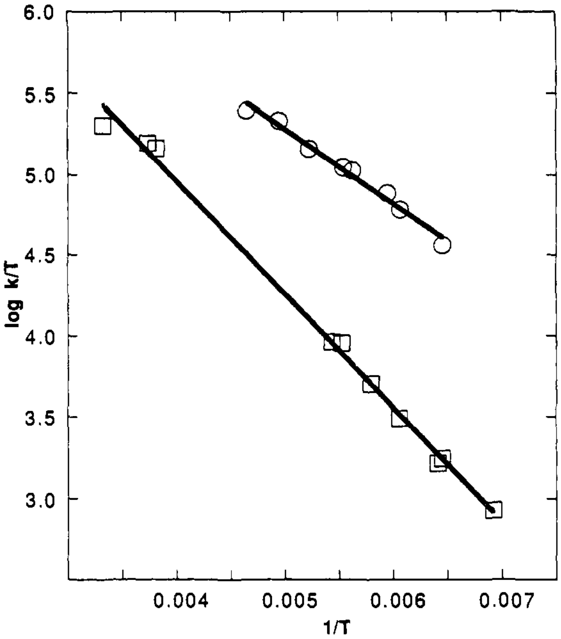


Figure 2. Temperature dependence of triplet decay rates in 4:1 ethanol/methanol. (○) 24tBBP-d_0: $\log A = 10.44 \pm 0.2$; $E_a = 2.62 \pm 0.2$ kcal/mol; $\Delta S^{\ddagger} = -12.6$ eu; $\Delta H^{\ddagger} = 2.11$ kcal/mol ($r = 0.992$). (□) 24tBBP-d_{18}: $\log A = 10.51 \pm 0.2$; $E_a = 3.62 \pm 0.2$ kcal/mol; $\Delta S^{\ddagger} = -11.9$ eu; $\Delta H^{\ddagger} = 3.21$ kcal/mol ($r = 0.998$).

In this picture the enthalpy of the TS is lowered by mixing with a charge-separated state. The 30-fold deactivation of triplet OTMABP relative to OTBBP by the positive nitrogen is not at all surprising, since triplet ketones, like alkoxy radicals, are strongly electron deficient and react more slowly with C–H bonds near electron-withdrawing groups.[4,5] However, the fact that the inductive effect is entirely entropic clearly was unanticipated and requires explanation.

To understand this unusual inductive effect, it was necessary to establish the possible importance of tunneling, which could explain why the activation energy for OTBBP itself is lower than the expected 5–6 kcal/mol for attack at an unactivated methyl group.[6] Therefore we prepared 2,4-di-*tert*-butylbenzophenone (24tBBP) with fully protonated as well as fully deuterated *tert*-butyl groups.[7] Both ketones undergo very efficient solution-phase photocyclization.[8] Figure 2 compares their triplet decay rates in 4:1 methanol/ethanol, determined as above, from 160 to 290 K. The standard deviation of the measurements corresponds to ±0.9 eu. *The activation parameters respond to deuteration in a fully classical way.* Both ketones have the same $\Delta S^{\ddagger}$ value while $\Delta H^{\ddagger}$ is 1.1 kcal/mol higher for the deuterated compound, exactly half the difference between the *tert*-butyl C–H (2964 cm^{-1}) and C–D (2223 cm^{-1}) stretching frequencies. Thus the activation energy responds fully to the change in zero-point energy of the C–H bond being broken. On the usual assumption that tunneling is unimportant in the deuterated species at high temperatures, we conclude that there is no significant tunneling in the protonated ketone, otherwise even lower values of the activation parameters would obtain. The lack of tunneling at high temperatures removes it as an explanation for the entropy-driven inductive effect in OTMABP. (We do intend to study our system at much lower temperatures, since Grellmann recently reported that intramolecular hydrogen abstraction in triplet *o*-alkyl ketones involves a strong tunneling component, which becomes most evident at temperatures below 160 K.[9])

The difference in $\Delta S^{\ddagger}$ is not due to any significant geometric differences between the two reactants. We have compared the X-ray structure of the OTMABP salt to that of OTBBP.[2] Despite slight distortions caused by the counterion, which may disappear in solution, the two have nearly identical structures, with very similar bond angles and distances.[10] Orientations of the reactive hydrogens with respect to the carbonyl are identical in both; and H–O distances are actually somewhat shorter in OTMABP *but inside van der Waals radii in both.* Consideration of this strained molecular geometry and the very low $\Delta H^{\ddagger}$ value indicates that these molecules require very little nuclear motion to reach their TSs. The cause for the low $\Delta H^{\ddagger}$ value in both compounds probably is relief of nonbonded repulsion as a "too-close" hydrogen begins to bond to oxygen. Since the ground states of both can achieve essentially the same minimum-energy geometry, and triplet excitation involves primarily C–O stretching, it seems reasonable that they can both attain TSs of very similar geometry and enthalpy. In fact, isoelectronic molecules with minimal conformational flexibility, such as these, are ideally suited for isolating inductive effects on reactivity. The minimal motion required and the lack of any change in charge distribution during reaction also make it very unlikely that the different $\Delta S^{\ddagger}$ values are due to differential solvation of the two ketones.

Other examples of entropy-controlled relative reactivity have been reported for low activation energy bimolecular reactions[12] and explained on the basis of TSs at various positions along the reaction coordinate, with $\Delta S^{\ddagger}$ decreasing as the TS becomes less

---

[4] Wagner, P. J. *Acc. Chem. Res.* **1971**, *4*, 168.

[5] Wagner, P. J.; Kemppainen, A. E. *J. Am. Chem. Soc.* **1972**, *94*, 7495.

[6] Encinas, M. V.; Lissi, E. A.; Lemp, E.; Zanocco, A.; Scaiano, J. C. *J. Am. Chem. Soc.* **1983**, *105*, 1856.

[7] Both compounds were prepared by low-temperature Friedel–Crafts acylation of *p*-di-*tert*-butylbenzene made from regular or fully deuterated *tert*-butyl alcohol. They were purified by repeated recrystallization and were fully characterized spectroscopically and by X-ray crystallography.

[8] Wagner, P. J.; Giri, B. P.; Pabon, R.; Singh, S. B. *J. Am. Chem. Soc.* **1987**, *109*, 8104.

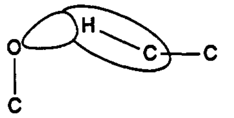
[9] Al-Soufi, W.; Eychmuller, A.; Grellmann, K. H. *J. Phys. Chem.* **1991**, *95*, 2022.

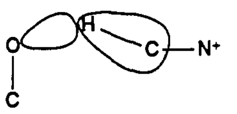
[10] In each compound there are two methyl hydrogen atoms within bonding distance of the oxygen: H_A makes an angle ω of 32° in both; for H_B, ω is 90° for both, where ω is the dihedral angle that the hydrogen makes with the nodal plane of the carbonyl π system.[11] $d(H_A–O)$ and $d(H_B–O)$ are 2.47 and 2.67 Å for OTBBP and 2.27 and 2.63 Å for OTMABP. The only significant structural differences are as follows: the N–CH$_3$(a) bond is 1.63 Å vs 1.54 Å for the corresponding C–CH$_3$ bond in OTBBP; the phenyl–CO bond is 1.49 Å in OTBBP and 1.43 Å in OTMABP. Complete X-ray data for OTMABP will be provided in the full paper.

[11] Scheffer, J. R. *Org. Photochem.* **1987**, *8*, 249.

[12] Scaiano, J. C.; Wintgens, V.; Haider, K.; Berson, J. A. *J. Am. Chem. Soc.* **1989**, *111*, 8732. Houk, K. N.; Rondau, N. G.; Mareda, J. *Tetrahedron* **1985**, *44*, 1555.

reactant-like. A similar effect could occur here. We suggest that the decrease in activation entropy reflects a decreased probability that the electron-deficient oxygen atom will encounter electron density on the hydrogen atom in OTMABP at the molecular geometry corresponding to the TS for OTBBP. In order to achieve comparable overlap, the methyl group of OTMABP must move closer to the oxygen, with an expected decrease in entropy and increase in enthalpy. In such a sterically crowded system there are two possible explanations for the two molecules having the same $\Delta H^{\ddagger}$: either their TSs have essentially the same geometry and $\Delta S^{\ddagger}$ reflects electron density, or the enthalpy increase caused by extra motion of a methyl toward oxygen in OTMABP is offset by relief of nonbonded interactions elsewhere.





We are unaware of other studies that separate the inductive effects on rate constants of radical-like hydrogen transfer into enthalpy and entropy contributions. Consequently we are studying other, similar systems in order to establish how general this phenomenon of entropy control may be. In this regard it is noteworthy that 24tBBP is less reactive than OTBBP, showing the expected small inductive deactivation by a *p*-alkyl group,[13] and *the difference is almost entirely in their entropies of activation.*

Acknowledgment. This work was supported with the help of NSF Grant No. CHE-88-05502. We thank Dr. Tito Scaiano of Ottawa University, until recently at the National Research Council of Canada, for his enthusiastic cooperation in making his flash kinetics apparatus available.

Registry No. OTMABP·BF$_3$, 136579-87-8; OTBBP, 22679-53-4; 2,4-*t*-BBP, 111959-99-0; D$_2$, 7782-39-0.

---

(13) Wagner, P. J.; Truman, R. J.; Scaiano, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 7093.

Characterization of Complexes between Esters and Lithium Hexamethyldisilazide

Paul G. Williard* and Qi-Yong Liu

Department of Chemistry, Brown University
Providence, Rhode Island 02912

Lubomír Lochmann

Institute of Macromolecular Chemistry
Czechoslovak Academy of Sciences
162 06 Prague 6, Czechoslovakia

Received January 16, 1991

Proton transfer, i.e., enolization, proceeds readily under preparatively useful conditions upon reaction of lithium hexamethyldisilazide (LiHMDS) (**1**) with most ketone substrates. It has been noted by Heathcock et al. that LiHMDS fails to react with enolizable ester and amide substrates under the same conditions, i.e., THF solution at ∼−78 °C.[1] Yet there exist a few examples in which LiHMDS has been utilized to enolize esters.[2]

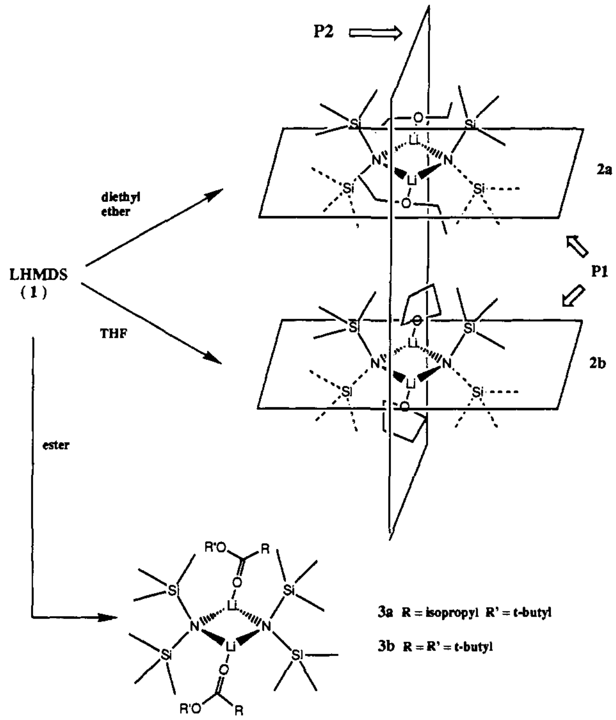


Figure 1. Coordination geometry of the LiHMDS dimer solvated with diethyl ether (**2a**) and with tetrahydrofuran (**2b**) (from their crystal structures) and expected geometry of the ester complexes (**3**).

While we do not propose to offer the explanation for these contradictory reports of the kinetic competence of LiHMDS to enolize esters, we now present evidence for the existence of stabile complexes between LiHMDS and ester substrates both in solution and in the solid state.[3]

Evidence for an intermediate adduct between sodium hexamethyldisilazide (NaHMDS) and carboxylic esters in solution was previously reported by one of us.[4] This adduct was characterized by a carbonyl absorption in the IR spectrum that is lowered relative to free ester by about 20–40 cm^{-1} due to coordination with an organometallic compound.[5] The intensity of the coordinated ester carbonyl band was shown to decrease with time proportional to the intensity increase of both the ester enolate band (at 1665 cm^{-1}) and the HMDS free amine band (at 3370 cm^{-1}). We now have similar IR evidence that adducts are formed between LiHMDS and the three esters *tert*-butyl pivalate, methyl pivalate, and *tert*-butyl isobutyrate in benzene solution. An adduct is not completely formed between LiHMDS and *tert*-butyl pivalate since both free ester (1723 cm^{-1}, strong, roughly 40%) and coordinated ester (1686 cm^{-1}, strong, roughly 60%) bands are observed. Analogous bands (1732 cm^{-1}, weak inflex, and 1702 cm^{-1}, very strong) appear in the methyl pivalate spectrum. The IR spectrum of the LiHMDS/*tert*-butyl isobutyrate mixture shows only two relevant bands (1728 cm^{-1}, weak, and 1685 cm^{-1}, very strong). The upper band is attributed to free ester, and the lower band in this latter spectrum is close to that of the pure lithium enolate (1671 cm^{-1} in Nujol). Only a relatively weak HMDS absorption corresponding to a maximum of roughly 25% enoli-

---

(1) Heathcock, C. H.; Buse, C. T.; Kleschich, W. A.; Pirrung, M. C.; Sohn, J. E.; Lampe, J. *J. Org. Chem.* **1980**, *45*, 1066.

(2) (a) Gamboni, R.; Tamm, C. *Helv. Chim. Acta* **1986**, *69*, 615. (b) Gennari, C.; Bernardi, A.; Colombo, L.; Scolastico, C. *J. Am. Chem. Soc.* **1985**, *107*(20), 5812. (c) Ireland, R. E.; Daub, J. P. *J. Org. Chem.* **1981**, *46*, 479.

(3) For recent discussions of aggregates of a variety of lithium amide bases in solution, see: (a) Galiano-Roth, A. S.; Kim, Y.-J.; Gilchrist, J. H.; Harrison, A. T.; Fuller, D. J. *J. Am. Chem. Soc.* **1991**, *113*, 5053. (b) Hall, P.; Gilchrist, J. H.; Collum, D. B. *J. Am. Chem. Soc.*, manuscript in press. (c) Hall, P.; Gilchrist, J. H.; Harrison, A. T.; Fuller, D. J.; Collum, D. B. *J. Am. Chem. Soc.*, manuscript in press. (d) Romesberg, F. E.; Gilchrist, J. H.; Harrison, A. T.; Fuller, D. J.; Collum, D. B. *J. Am. Chem. Soc.* **1991**, *113*, 5751. (e) Gilchrist, J. H.; Collum, D. B. *J. Am. Chem. Soc.*, manuscript in press.

(4) Lochmann, L.; Trekoval, J. *J. Organomet. Chem.* **1975**, *99*, 329.

(5) (a) Pasynkiewicz, S.; Starowieyski, K. *Roczniki Chem.* **1967**, *41*, 1139. (b) Lappert, M. F. *J. Chem. Soc.* **1961**, 817; **1962**, 542; **1965**, 5826. (c) Lochmann, L.; Sorm, M. *Collect. Czech. Chem. Commun.* **1973**, *38*, 3449.

0002-7863/92/1514-348$03.00/0