The solid-state molecular structure of the complex cation is shown in Figure 1. The central Ga_3O moiety consists of a planar, oxo-centered triangular arrangement of gallium(III) atoms; see Figure 2. The average Ga–Ga–Ga, Ga–Ga–O(B), and Ga–O(B)–Ga angles (see Figure 1) are within experimental error of the angles of an equilateral triangle. The μ_3-O atom is equidistant from the three gallium atoms; the average Ga–O(B) distance is 1.874 (3) Å.[5] Each edge of the Ga_3O core is bridged by two $C_6H_5CO_2^-$ ligands; the three axial positions are occupied by 4-methylpyridine molecules. Thus, each gallium(III) center possesses a slightly distorted octahedral coordination sphere.

The peripheral Ga–O distances range from 1.959 (5) to 2.006 (9) Å, with an average distance of 1.985 (6) Å. The observed distances are comparable to the average Ga–O distances found in other octahedrally-coordinated gallium(III) compounds.[6] The six bridging benzoato groups are equivalent as demonstrated by ^1H and ^{13}C NMR spectroscopy.[7] Within the benzoate groups, the average bond distances and angles are in accord with values reported for related complexes.[8]

As evidenced by Figure 1, there is a distinct difference in the orientation of the three axial 4-methylpyridine ligands around the Ga_3O core. Two of the 4-methylpyridine planes are approximately parallel to the Ga_3O plane; the dihedral angle is 10°. The plane of the third 4-methylpyridine is perpendicular to the plane; the dihedral angle is 90.1°.

Variable-temperature ^1H NMR studies of **1** indicate a rapid interconversion between the two orientations of the axial 4-methylpyridine ligands. At 34 °C, the ^1H NMR spectrum of **1** in solution is consistent with the solid-state structure shown in Figure 1.[7] Two sets of signals, in a 1:2 ratio, are observed for each of the three types of protons in the 4-methylpyridine ligands.[9] Increasing the temperature to 50 °C results in coalescence for each 4-methylpyridine (methyl and α and β ring: 2.63, 9.06, and 7.54 ppm, respectively) proton signal. Finally, as the probe is returned to ambient conditions, the original ^1H NMR spectrum is obtained.

The infrared spectrum[10] of **1**, between 800 and 4000 cm^{-1}, is dominated by bands attributable to the organic constituents of the cation.[11] We tentatively assign the strong bands at 1602, 1556, and 1420 cm^{-1} to bridging benzoate groups.[8a] Several IR bands below 800 cm^{-1} may be assigned by analogy to other $[M_3(\mu_3\text{-}O)(\mu\text{-}O_2CR)_6L_3]^+$ complexes.[11] These include an asymmetric stretch at 655 cm^{-1} of the central M_3O unit and the ν_d mode at 500 and 479 cm^{-1} of the MO_4 units. The band at 550 cm^{-1} occurs in almost all trimeric carboxylates and is assigned to a carboxylate mode.[1b,11]

In conclusion, we have observed a new reactivity pattern for Ga_2Cl_4. This simple one-step reaction demonstrates the accessibility of main group carboxylates of the general formula, $[M_3(\mu_3\text{-}O)(\mu\text{-}O_2CR)_6L_3]^+$, and constitutes a starting point in the discovery of related complexes. Investigations into the syntheses, characterization, and applications of related main group carboxylates are currently underway.

Acknowledgment. M.T.A. (Postdoctoral Fellowship, National Research Council/NASA Lewis Research Center), S.A.D. (NASA grant NCC3-162), and A.F.H. (Director's Discretionary Fund) acknowledge support from NASA Lewis Research Center. We thank Dr. David G. Hehemann and Mr. Frederick K. Oplinger of Cleveland State University for the NMR studies of **1**.

Supplementary Material Available: Tables of positional parameters, thermal parameters, and bond distances and angles (21 pages); tables of observed and calculated structure factors (17 pages). Ordering information is given on any current masthead page. Similar information is also available from A.F.H. at NASA Lewis Research Center.

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[5] Individual Ga–O(B) and Ga···Ga bond distances: Ga(1)–O(B) 1.890 (9), Ga(2)–O(B) 1.866 (9), Ga(3)–O(B) 1.867 (9), Ga(1)–Ga(2) 3.228 (2), Ga(2)–Ga(3) 3.259 (2), and Ga(3)–Ga(1) 3.251 (2) Å.

[6] (a) Hausen, H. D.; Sille, K.; Weidlein, J.; Schwarz, W. *J. Organomet. Chem.* **1978**, *160*, 411–419. (b) Bulc, N.; Golic, L.; Siftar, J. *Acta Crystallogr.* **1984**, *C40*, 1829–1831. (c) Riley, P. E.; Pecoraro, V. L.; Carrano, C. J.; Raymond, K. N. *Inorg. Chem.* **1983**, *22*, 3096–3103.

[7] NMR data in $CDCl_3$: ^1H δ (ppm) 2.35 (s, 3 H, Me′), 2.67 (s, 6 H, Me), 7.12 (d, 2 H, β'), 7.35 (t, 12 H, meta), 7.48 (t, 6 H, para), 7.61 (d, 4 H, β), 7.84 (d, 12 H, ortho), 8.47 (d, 2 H, α'), 9.09 (d, 4 H, α); ^{13}C δ (ppm) 21.1, 21.7, 124.8, 125.4, 128.4, 130, 132.9, 133, 148.1, 149, 153, 173.5. The unique 4-methylpyridine ligand is indicated by (′).

[8] (a) Gorun, S. M.; Papaefthymiou, G. C.; Frankel, R. B.; Lippard, S. J. *J. Am. Chem. Soc.* **1987**, *109*, 3337–3348. (b) Vincent, J. B.; Christmas, C.; Huffman, J. C.; Christou, G.; Chang, H.-R.; Hendrickson, D. N. *J. Chem. Soc., Chem. Commun.* **1987**, 236–237.

[9] The ^1H NMR spectrum of $[Co_3(\mu_3\text{-}O)(\mu\text{-}O_2CCH_3)_5(OH)(py)_3]PF_6$ shows similar behavior; see: Sumner, C. E., Jr.; Steinmetz, G. R. *J. Am. Chem. Soc.* **1985**, *107*, 6124–6126.

[10] Infrared data (KBr, cm^{-1}): 3067 (m), 1664 (s), 1625 (vs, br), 1602 (vs, br), 1575 (vs), 1556 (s), 1551 (s), 1546 (s), 1536 (m), 1509 (m), 1495 (s), 1420 (vs, br), 1340 (m), 1329 (m), 1315 (m), 1309 (m), 1233 (m), 1215 (m), 1178 (s), 1070 (s), 1026 (s), 724 (vs), 688 (s), 683 (vs), 655 (vs), 550 (m), 500 (s), 479 (vs).

[11] (a) Johnson, M. K.; Powell, D. B.; Cannon, R. D. *Spectrochim. Acta* **1981**, *37A*, 995–1006. (b) Monti, L.; Cannon, R. D. *Ibid.* **1985**, *41A*, 643–646. (c) Meesuk, L.; Jayasooriya, V. A.; Cannon, R. D. *J. Am. Chem. Soc.* **1987**, *109*, 2009–2016.

Observation of β-Kinetic and β-Equilibrium Isotope Effects in Organometallic Oxidative Addition Reactions

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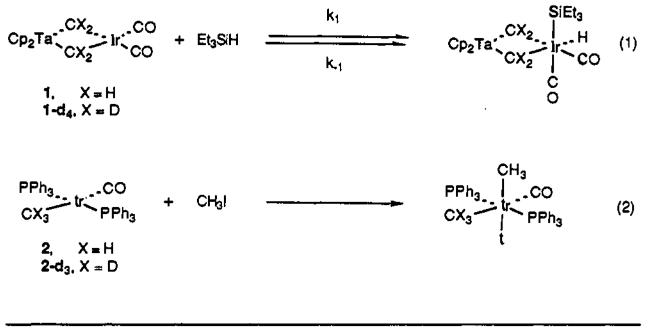
Received September 9, 1991

Secondary β-deuterium isotope effects have long been an important tool in the study of organic reaction mechanisms. Normal effects ($k_H/k_D > 1$) have been used to obtain evidence for hyperconjugation,[1a] and inverse effects ($k_H/k_D < 1$) have provided evidence for the steric[2] and inductive[3] influence of deuterium on the rates of organic transformations.[4] Both steric and inductive effects have been proposed to result from the shorter average length of a C–D bond (1.107 Å) relative to a C–H bond (1.112 Å).[5]

In contrast to their widespread use in organic chemistry, the employment of β-deuterium isotope effects to study transition-metal organometallic reactions has been essentially nonexistent.[6] We report an application of this technique to investigate both the rate and equilibrium of an organometallic transformation. The result of this work is an apparently general electron-donating effect of β-deuterium on oxidative addition reactions.

Scheme I



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[1] Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*, 3rd ed.; Harper & Row: New York, 1987; (a) p 240, (b) p 257.

[2] Carter, R. E.; Melander, L. *Ad. Phys. Org. Chem.* **1973**, *10*, 1.

[3] Halevi, E. A. *Prog. Phys. Org. Chem.* **1963**, *1*, 109.

[4] Collins, C. J., Bowman, N. S., Eds. *Isotope Effects in Chemical Reactions*; Van Nostrand: New York, 1970.

[5] Obtained from electron diffraction studies on C_2H_6 and C_2D_6. Kuchitsu, K. *J. Chem. Phys.* **1968**, *49*, 4456.

[6] One report of such an effect for a transition-metal compound is for the reaction $H_2O + [Co(NX_3)_5Cl]^{2+} \rightarrow [Co(NX_3)_5(H_2O)]^{3+} + Cl^-$ (X = H, D), for which $k_{11}/k_D = 1.47$ in H_2O and $k_H/k_D = 1.19$ in D_2O. See: Pearson, R. G.; Stellwagen, N. C.; Basolo, F. *J. Am. Chem. Soc.* **1960**, *82*, 1077.

0002-7863/92/1514-787$03.00/0

Table I. Comparison of Secondary Kinetic Isotope Effects for the Oxidative Addition Reactions at 0 °C

system	k_H (M^{-1} s^{-1})	k_D (M^{-1} s^{-1})	k_H/k_D
1/Et_3SiH in THF	2.79 ± 0.04		
1-d_4/Et_3SiH in THF[a]		3.15 ± 0.08	0.886
1/Et_3SiD in THF	2.66 ± 0.08		
1-d_4/Et_3SiD in THF		3.05 ± 0.08	0.872
1/Et_3SiH in toluene	3.72 ± 0.07		
1-d_4/Et_3SiH in toluene		4.25 ± 0.07	0.875
1/Et_3SiD in toluene	3.30 ± 0.18		
1-d_4/Et_3SiD in toluene		3.77 ± 0.18	0.875
1/Ph_3SiH in THF[b]	1.32 ± 0.07		
1-d_4/Ph_3SiH in THF[b]		1.47 ± 0.10	0.898
1/CH_3I in THF	$9.88 \pm 0.53 \times 10^{-2}$		
1-d_4/CH_3I in THF		$11.00 \pm 0.37 \times 10^{-2}$	0.898
2/CH_3I in THF	$2.26 \pm 0.05 \times 10^{-1}$		
2-d_3/CH_3I in THF		$2.45 \pm 0.06 \times 10^{-1}$	0.922

[a] Exchange into the methylene positions occurs much more slowly than oxidative addition at 0 °C. [b] 10 °C.

We first detected a β-deuterium isotope effect in the oxidative addition of silanes to the tantalum/iridium complex **1** (eq 1, Scheme I). In order to evaluate the contributions from the Si–H(D) and μ-$CH(D)_2$ groups, the rate constants for oxidative addition of $Et_3SiH(D)$ to both **1** and **1**-d_4 (bridging methylene groups deuterated) were measured (Table I).[7] As can be seen, the Si–H(D) bond contributes only a small primary isotope effect to k_1 ($k_H/k_D = 1.13$). Interestingly, an *inverse* effect of 0.875 is caused by isotopic substitution at the bridging methylenes.

The silane oxidative addition illustrated in eq 1 is reversible. This provided an opportunity to measure the isotope effect on the equilibrium constant $K_{eq} = k_1/k_{-1}$ associated with the oxidative addition/reductive elimination process. The combined primary and secondary equilibrium isotope effect $K_{eq(H)}/K_{eq(D)}$ (defined here as K_H/K_D) is 0.54 at 0 °C.[8] A value of 0.78 for the contribution to $K_{H/D}$ from the primary isotope effect can be estimated[9] from the Ir–H(D) and Si–H(D) stretching and bending vibrations in the IR spectrum.[1b,10] From this value and the magnitude of the overall $K_{H/D}$ we calculate 0.70 for the secondary equilibrium isotope effect. Interestingly, this is larger than the kinetic effect. From the values obtained for K_{eq} and k_1, the isotope effects on k_{-1} (the reductive elimination) can be calculated: the Ir–H(D) bond contributes a small primary isotope effect of 1.45, and the bridging methylenes a secondary isotope effect of 1.25. Thus, the β-effects are inverse for oxidative addition and normal for reductive elimination.

Table II. ν(CO) for Oxidative Addition Products of $Cp_2Ta(CH_2)_2Ir(CO)_2$ in THF

compound	ν(CO), cm^{-1}
$Cp_2Ta(CH_2)_2Ir(CO)_2$	1946, 2008
$Cp_2Ta(CH_2)_2Ir(CO)_2(Me)(I)$	2023, 2067
$Cp_2Ta(CH_2)_2Ir(CO)_2(SiEt_3)(H)$	1958, 2025
$Cp_2Ta(CH_2)_2Ir(CO)_2(SiPh_3)(H)$	1973, 2035

To determine whether the β-effect is caused by inductive or steric factors, the size of the substrates added to **1** and **1-d$_4$** was varied. The isotope effects measured for oxidative addition of both MeI and Ph_3SiH were identical to that obtained for Et_3SiH (see Table I). This seems most consistent with an inductive effect. The ν(CO) values for **1** and the oxidative addition products formed with triethylsilane and methyl iodide (Table II) are also consistent with this conclusion. The carbonyl stretching frequencies are substantially higher for the Ir(III) complexes, indicating that the iridium center in the product carries a higher charge than that in the starting material. By inference the transition state has an intermediate charge density, accounting for the fact that the forward kinetic effect is smaller than the equilibrium effect.[11]

To test the generality of the isotope effect, the rates for the oxidative addition of MeI to the classically studied oxidative addition substrate[12] $Ir(CO)(PPh_3)_2(CX_3)$, **2** (X = H, D), were measured (see Table I). A value of k_H/k_D of 0.922 in THF was obtained, which gives $(0.922)^{1/3} = 0.973$ for the effect due to a single deuterium. This is remarkably similar to the effect observed in the Ta/Ir system [$(0.889)^{1/4} = 0.971$ per deuterium atom].

The present work establishes the existence of secondary β-isotope effects in an organometallic oxidative addition reaction and suggests that the observation may be general. Our results indicate that the effects are due to the inductive rather than the steric properties of deuterium.[13] Oxidative addition causes an increase in the formal oxidation state at the metal center, lowering its charge density, and the magnitude and direction of the effect caused by β-deuterium substitution are consistent with this interpretation. We hope that this work will encourage further studies of β-deuterium isotope effects in organometallic reactions and development of their use in examining the mechanisms of these transformations.

Acknowledgment. We thank the National Science Foundation for partial financial support of this work (Grant No. CHE8722801) and Johnson-Matthey-Aesar for a gift of iridium chloride. We also thank Dr. Andrew Streitwieser for helpful discussions on differentiating steric and inductive contributions to the secondary isotope effect and Dr. Kevin R. Kyle for assistance in using kinetic analysis software.

Supplementary Material Available: Representative plots of ln (c/c_0) vs *t*, a table containing all measured rate constants, and calculation of the contribution of the primary isotope effect to $K_{H/D}$ (18 pages). This supplementary material is provided with the archival edition of the journal, which is available in many libraries. Alternatively, ordering information is given on any current masthead page.

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(7) Measured by UV–vis spectroscopy in the specified solvent. Each value represents an average of four runs. For THF, each run was monitored at two wavelengths, one in the UV region and one in the visible. For toluene, only the visible region was monitored. In general, standard deviations were calculated from the average of the rate constants determined from ln (c/c_0) vs time plots. However, in several cases nonlinear least-squares fits to the simple concentration vs time exponential decay curves were carried out. In all cases examined, the rate constants calculated in these two different ways were identical to within 1 standard deviation.

(8) Measured by ^1H NMR spectrometry in toluene-d_8.

(9) At the longer times needed to reach equilibrium, these determinations were complicated because of deuterium transfer between the hydride and methylene positions, providing pathways for exchange of deuterium between three types of positions (Si–H, Ir–H, and β-CH). This exchange was slow enough to allow measurement of k_H and k_D for the forward (oxidative addition) reaction, but K_{eq} for the mixed systems **1**/Et_3SiD and **1**-d_4/Et_3SiH could not be measured directly without interference from the competing hydride/methylene exchange.

(10) IR (THF-d_8): Ir–H, 2095; Ir–D, 1600; Si–H, 1978; Si–D, 1494 cm^{-1}. The degenerate bending vibration for the Si–H bond was estimated to be 860 cm^{-1} (Imai, Y.; Aida, K. *Bull Chem. Soc. Jpn.* **1981**, *54*, 925) on the basis of a full vibrational study of Me_3SiH. The Ir–H bend was assumed to be approximately degenerate and set at a value of 1020 cm^{-1} on the basis of the IR spectra of three different silane oxidative addition products.

(11) Another sensitive probe of charge density at a metal center is its effect on J_{Pt-P} for the system (dppe)PtX_2 (Appleton, T. G.; Bennett, M. A. *Inorg. Chem.* **1978**, *17*, 738). We have found that the value of J_{Pt-P} (898.2 Hz) for X = CH_3 is greater than J_{Pt-P} (893.4 Hz) for X = CD_3. This supports our conclusion that CH_3 is more electron withdrawing toward metals than CD_3.

(12) (a) Burk, M. J.; McGrath, M. P.; Wheeler, R.; Crabtree, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 5034. (b) Churchill, M. R.; Fettinger, J. C.; Janik, T. S.; Rees, W. M.; Thompson, J. S.; Tomaszewski, S.; Atwood, J. D. *J. Organomet. Chem.* **1987**, *323*, 233.

(13) A referee has suggested the interesting possibility that C–H hyperconjugative interaction with an unoccupied 6p orbital at the coordinatively unsaturated iridium center might stabilize the square-planar Ir(I) complex. A lessening of the hyperconjugative interaction in the transition state and octahedral Ir(III) product could produce an inverse isotope effect in the oxidative addition reaction. We cannot rule out this possibility, but we share the referee's concern about whether the overlap and energy match between the methylene C–H and iridium 6p orbitals would be sufficient to create this effect.