$^1/_2$ mol of Na_2O_2 and the green mixed valence PF_6^- salts $\mathbf{2^+}$–$\mathbf{4^+}$, and then with another $^1/_2$ mol of O_2, giving the dicationic precursor PF_6^- salts $\mathbf{2^{2+}}$–$\mathbf{4^{2+}}$ (the presence of $Na^+PF_6^-$ inhibits the cage nucleophilic reactivity of $O_2^{\bullet -}$ on the sandwiches[17]).

In conclusion, this first series of bimetallic Cp*Fe complexes of polyaromatics provides electron reservoir complexes, stable in three oxidation states, in which the ligand structures control the coupling and the number of electrons transferred in a redox step.[18]

Acknowledgment. The experimental assistance of N. Ardoin, I. Rusig, Dr. W. Bowyer, and J.-G. Melin is acknowledged.

Supplementary Material Available: Spectroscopic, CV, and analytical data for $(\mathbf{2}$-$\mathbf{4})^{2+/+/0}$ and $\mathbf{5}^{2+}$ and tables of atomic positional and thermal parameters, bond lengths and angles, and general temperature factor expressions (6 pages); tables of calculated and observed structure factors (4 pages). Ordering information is given on any current masthead page.

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Intermolecular Vinylic C–H Bond Activation by a Doubly Bonded Organoditantalum Complex

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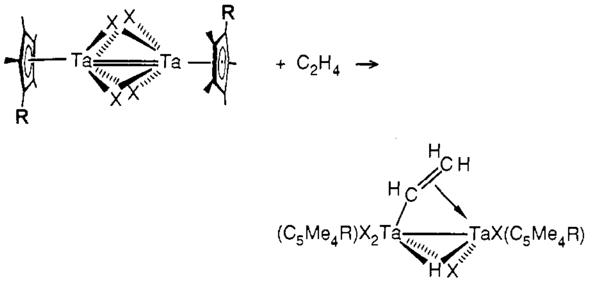
Intermolecular C–H bond activation of hydrocarbons, in particular alkanes, by organotransition-metal species is a reaction of fundamental modelling importance[1] for future efforts at hydrocarbon functionalization. Examples of hydrocarbon oxidative addition and of alkyl/hydrocarbon exchange have been reported with organometallic complexes of the late transition metals,[2] metals from groups 6[3] and 7,[4] and the lanthanides/actinides,[5] but there are no examples of intermolecular alkane or vinylic C–H bond activation with metals from groups 4 and 5. Intermolecular vinylic C–H bond activation is an underrepresented area in hydrocarbon C–H bond activation by organometallics, with few mononuclear[6] and dinuclear,[7] as opposed to polynuclear, examples. The kinetic and thermodynamic differences[8] between C–H activation involving the low-valent late metal and the high-valent lanthanide/actinide complexes suggest that intervening metal complexes, such as intermediate valent group 5 species, may exhibit optimal properties in C–H activation; the propensity for electronic unsaturation in complexes of these metals may lead to successful functionalization studies. Intramolecular ligand metalations[9] and arene H/D exchange reactions[10] with Nb and Ta complexes have been reported, and in principle intermolecular vinylic and alkane C–H bond reactivity should be feasible. We wish to report the first examples[11] of isolable *inter*molecular vinylic C–H activation by an early transition-metal (groups 4 and 5) organometallic and by a metal–metal multiply bonded complex.[12]

The reaction of the tantalum–tantalum doubly bonded complex $(\eta$-$C_5Me_4R)_2Ta_2(\mu$-$X)_4$[13] (**1a**, R = Me, X = Cl; **1b**, R = Me, X = Br; **1c**, R = Et, X = Cl; **1d**, R = Et, X = Br), prepared by the reductive dimerization of $(\eta$-$C_5Me_4R)TaX_4$, with ethylene (50 psi, 25 °C, 1 h) in ether leads to formation of the ditantalum vinyl hydride **2** (eq 1) in 75–85% isolated yield on the basis of analytical and spectroscopic data.[14] The 360 MHz ^1H NMR spectrum of the crystalline organoditantalum compound (Figure 1) exhibits an ABMX pattern for the vinyl hydride resonances. The IR spectrum shows an absorption at 1480 cm^{-1} which is tentatively assigned to a bridging hydride mode (in the absence of labeling



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[14] **2b**: Mass spectrum (30 eV, direct inlet) *m/e* 980, Br_4 pattern; ^1H NMR (δ, 25 °C, C_6D_6) 9.31 (m, 1, Ta–CH_x, $^3J_{H_XH_m}$ = 6.6 Hz, $^3J_{H_xH_a}$ = 8.7 Hz, $^3J_{H_xH_b}$ = 11.7 Hz), 4.36 (d of t, 1, Ta–H_m–Ta, $^4J_{H_mH_a}$ = 2.2 Hz, $^4J_{H_mH_b}$ = 2.0 Hz), 3.07 and 2.92 (m, 2, CH_aH_b, $^2J_{H_aH_b}$ = 7.3 Hz), 2.32 and 2.09 (s, 30, Cp*, Cp*′); ^{13}C NMR (δ, 25 °C, C_6D_6, gated {^1H}) 214.7 (d, $^1J_{CH}$ = 144 Hz, Ta–CH), 124.5 and 120.2 (Cp*, Cp*′), 98.4 (dd, $^1J_{CH}$ = 142 Hz, $^1J_{CH}$ = 162 Hz, CH_aH_b), 13.6 and 12.3 (Me and Me′, $^1J_{CH}$ = 129 Hz). Anal. Calcd ($Ta_2C_{22}H_{34}Br_4$): C, 26.96; H, 3.50; Br, 32.61. Found (combustion with WO_3/V_2O_5): C, 26.49; H, 3.50; Br, 32.12. **2a**: ^1H NMR (δ, 25 °C, C_6D_6) 8.62 (m, 1, Ta–CH_x), 4.71 (d of t, 1, Ta–H_m–Ta), 3.27 and 3.14 (m, 2, CH_aH_b), 2.23 and 2.01 (s, 30, Cp*, Cp*′).

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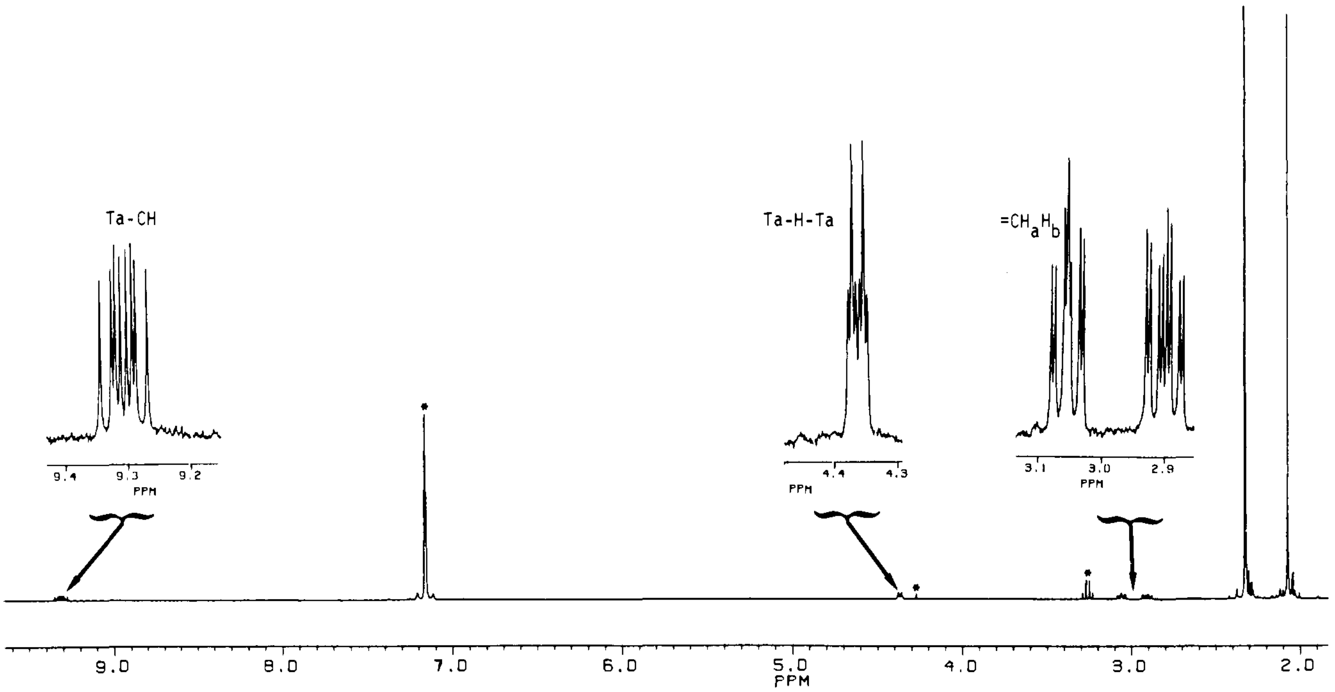
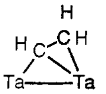
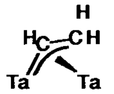


Figure 1. 360 MHz ^{1}H NMR spectrum of (η-C$_5$Me$_5$)$_2$Ta$_2$Br$_4$(μ-H)(μ-CH=CH$_2$) in C$_6$D$_6$ at 25 °C. (* = organic solvent impurities, C$_6$D$_5$H).

studies with C_2D_4). The gated {^{1}H}^{13}C NMR spectrum is unusual because of the low $^1J_{CH}$ values for two of the three vinyl protons (142 and 144 Hz, versus 162 Hz for the other CH$_A$H$_B$ proton). A metal-substituted metallacyclopropane **2i** should result in a lowering of all three $^1J_{CH}$ values to the 140-Hz range observed in a mononuclear tantallacyclopropane.[15] Agostic interactions could also lower the two coupling constants, but T_1 measurements[16] appear to rule this out. Another possible explanation for the disparate $^1J_{CH}$ values is a tantalum-substituted tantalum–allyl structure **2ii**, since metal–allyl complexes can exhibit different geminal C–H coupling constants.[17] A molecular structure determination of **2** at −50 °C should settle this question; data collected at room temperature on **2b** suggests that the complex contains one μ-bromide, but the data is dominated by the heavy atom contributions and was not sufficiently accurate for locating carbon positions. Low-temperature (−100 °C) data collection has been unsuccessful because of crystal damage during cooling.



2i



2ii

Present evidence is consistent with intermolecular reaction between **1** and ethylene. Reaction of C_2H_4 with an equimolar mixture of **1b** and **1d** yields only **2b** and **2d**; none of the cross product (C$_5$Me$_5$)(C$_5$Me$_4$Et)Ta$_2$Br$_4$(H)(CH=CH$_2$), **2e**, can be detected by ^{1}H NMR. This rules out any appreciable reaction of a mononuclear fragment such as (C$_5$Me$_4$R)TaX$_2$(solvent) (**3**), derived from dissociation of **1**, with C_2H_4 followed by coupling of the mononuclear vinyl hydride with **3** to give **2e**. In situ NMR studies of the reaction show the presence of catalytically produced 1-butene;[18] reaction of isolated **2** with excess C_2H_4 does not yield 1-butene, so the ditantalum vinyl hydride **2** is not an intermediate in the dimerization side reaction. The reaction of **1** with propylene under mild conditions leads to (C$_5$Me$_4$R)$_2$Ta$_2$X$_4$(H)(CH=CHMe)[19] in ~50% yield and 2,3-dimethyl-1-butene (from catalytic propylene dimerization), with present evidence ruling out allylic C–H activation. Reactions of **1** with 1-butene and 1-pentene give similar organoditantalum products, derived from terminal vinylic C–H activation, with less olefin dimerization.

A plausible route to olefin dimers such as 1-butene (from C_2H_4) and 2,3-dimethyl-1-butene (from C_3H_6) involves reaction of mononuclear **3**, from preequilibrium dissociation of **1**, with 2 equiv of olefin to form a tantalacyclopentane[20] catalytic intermediate. The kinetics of the C–H activation reaction, complicated by the parallel olefin dimerization reaction and by slow decomposition of **1** in solution, will be reported later. The rate of C–H activation of C_2H_4 by the bromide dimer **1b** is qualitatively faster than by the chloride analogue **1a**, and faster rates are seen in polar solvents such as tetrahydrofuran.

The reactions of other olefins with **1** proceed more slowly (>24 h) to yield mononuclear olefin complexes. The reaction of *p*-methylstyrene or butadiene with **1b** or **1d** forms the mononuclear η^2-methylstyrene complex (C$_5$Me$_4$R)TaBr$_2$(CH$_2$=CHC$_6$H$_4$-*p*-Me) and the tantalacyclopent-3-ene complex (C$_5$Me$_4$R)TaBr$_2$(σ^2,η^2-CH$_2$CH=CHCH$_2$), respectively; chloride analogues of both have been reported via alternate routes.[21,22]

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(19) ^{1}H NMR data for (η-C$_5$Me$_4$Et)$_2$Ta$_2$Br$_4$(H)(CH=CHMe) (δ, C$_6$D$_6$, 25 °C) 8.82 (m, 1, TaCH), 4.29 (d, 1, Ta–H–Ta), 3.64 (m, 1, CHMe), 2.79 (m, 2, CH_aH_bMe), 2.64 (m, 2, C′$H'_aH'_b$Me′), 2.48 (d, 3, CHMe), 2.45, 2.43, 2.36, 2.35, 2.21, 2.20, 2.12, and 2.11 (s, 24, ring methyls), 0.94 (t, 3, CH$_2$$Me$), and 0.80 (t, 3, C′H′$_2$$Me'$).

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system were purchased in part with funds from the National Science Foundation (CHE82-01836 and CHE85-07623, respectively). We thank Calvin J. Curtis of Solar Energy Research Institute and Malcohm H. Chisholm of Indiana University for communication of unpublished results.

^{37}Cl/^{35}Cl Isotope Effects on the ^{1}H NMR Spectra of Some Chloromethane Derivatives. Practical Consequences

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In Gombler's notation,[1] $^n\Delta A(^{m'/m}X)$ is the shift in the nuclear magnetic resonance frequency of A arising from substitution of ^mX by $^{m'}X$ ($m' > m$) n bonds from A. In general, $^{m'}X$ causes increased screening of A (lower frequency, negative shifts); isotope shifts are largest when $n = 1$, are proportional to the chemical shift range of A, are related to the fractional change in mass upon isotope replacement, and are roughly additive.[2,3] In view of these characteristics, it is perhaps expected that relatively few $^n\Delta A$ values are available for $^{37/35}$Cl. $^1\Delta A$ has been reported for ^{31}P in[4] PCl_3, ^{195}Pt in[5] $[PtCl_6]^{2-}$, and ^{19}F in[6] CCl_3F. $^1\Delta^{13}C$ in some chlorine derivatives of hydrocarbons is -0.1 Hz at 25 MHz, or -4 ppb (parts per billion).[7] To our knowledge, no $\Delta^1H(^{37/35}Cl)$ measurements have been reported.

Figure 1 displays ^{1}H NMR spectra at 300 MHz for CH_3Cl, CH_2Cl_2, and $CHCl_3$. The $^2\Delta^1H$ values are small but significant. From the figure and its caption it is clear that $^2\Delta^1H$ ranges from -0.04 to -0.08 Hz, that is, from -0.13 to -0.26 ppb. To within experimental error the isotope shifts are additive within a molecule (CH_2Cl_2 and $CHCl_3$) and appear to be very slightly larger in acetone-d_6 than in CS_2 solution.

The observed isotope shifts have some practical consequences. The ^{1}H NMR spectrum of, for example, 1,1-dichloroethane at 300 MHz displays no evidence for $^3\Delta^1H$ but, in the methine region, the outer peaks of the quartet demonstrate a $^2\Delta^1H$ of -0.066 (1) Hz, the same as seen for CH_2Cl_2 in the same solvent, CS_2. In a 2.5 mol % acetone-d_6 solution, $^2\Delta^1H$ is -0.065 (4) Hz for the ethane derivative. The inner peaks of the quartet are a jumble because isotope shifts are superimposed on second-order splittings of similar magnitude. Consequently, precise spectral parameters are only attainable if the ^{37}Cl/^{35}Cl isotope effects are built into an analysis.

Figure 2 shows the ^{1}H NMR spectrum of the methine proton of benzyl chloride together with computed spectra that do and do not take the isotope shifts into account.

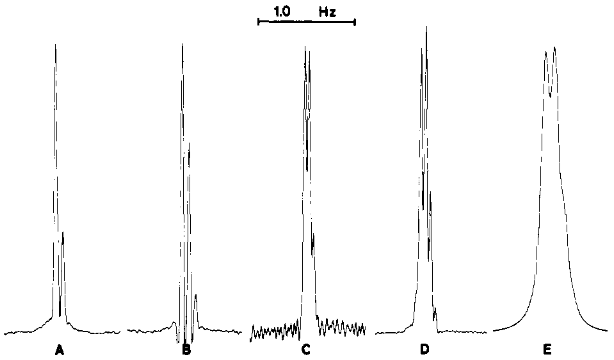

Figure 1. In A, the ^{1}H NMR spectrum of a ca. 2 mol % solution of CH_3Cl in CS_2, containing also 10 mol % of C_6D_{12} and 0.5 mol % TMS, is shown at a spectrometer frequency of 300.135 MHz (Bruker AM300) and a probe temperature of 297 K. The digital resolution was 0.006 Hz/point and a line broadening of -0.12 and a gaussian broadening of 0.60 was used. The peak widths at half-height are less than 0.04 Hz. The natural abundance of ^{35}Cl is 75.5% and that of ^{37}Cl is 24.5%, implying relative areas of 1.00:0.32 for the isotopically shifted peaks. Apparently the resolution enhancement procedures have not markedly distorted the relative heights of the peaks, which have the same width to within experimental error. The shift to low frequency (increased screening) for the $CH_3{}^{37}Cl$ molecules is 0.07_0 Hz or 0.23 ppb. An almost identical spectrum appears for a ca. 2 mol % solution in acetone-d_6, with a shift of 0.07_8 Hz. In B, the ^{1}H NMR spectrum of CH_2Cl_2 as a 1 mol % solution in acetone-d_6 is shown, some distortion of peak intensities arising from the resolution enhancement procedures. The three peaks have theoretical intensities of 1.00:0.65:11, quite close to the observed heights of 1.00:0.65:0.12. The isotope shifts appear to be additive, the two values both being 0.07_0 Hz in magnitude. In C, the ^{1}H NMR spectrum of a 1 mol % solution of $CHCl_3$ in the CS_2/C_6D_{12}/TMS mixture is shown. Only three of four peaks are apparent, the intensity ratios being predicted as 1.00:0.97:0.32:0.03. The isotope shifts are again additive, amounting to 0.04_4 Hz. In D the test sample for the spectrometer (10% $CHCl_3$ in acetone-d_6) has its ^{1}H NMR spectrum shown. All four peaks are visible at the cost of peak distortions. The three shifts are 0.05_1 Hz each. Another sample, 1 mol % in acetone-d_6, gave 0.04_8 Hz for the isotope shifts. The ^{1}H NMR spectrum of the $H^{13}CCl_3$ molecules in the test sample was noisy and, to within experimental error, no evidence was found for a ^{13}C isotope effect on the ^{37}Cl/^{35}Cl isotope effect on the proton screening constant or of a ^{37}Cl/^{35}Cl isotope effect on ^1J(C,H). ^1J(C,H) is 214.92_8 Hz for the $H^{13}C^{35}Cl_3$ molecule and 214.93_0 Hz for the $H^{13}C^{35}Cl_2{}^{37}Cl$ molecule.[11] $^1\Delta^1H(^{13/12}C)$ is -0.80_3 Hz or -2.6_8 ppb in both molecules. In E the ^{1}H NMR spectrum of the test sample is simulated at 600 MHz with a line width of 0.1 Hz for each of the four peaks.

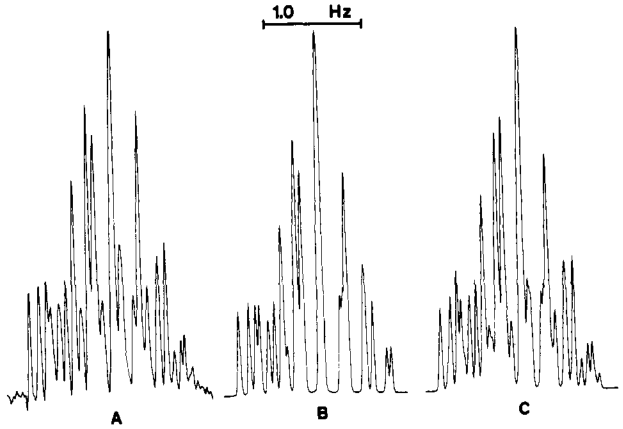

Figure 2. The ^{1}H NMR spectrum at 300 MHz of the methine proton in benzyl chloride is shown, together with theoretical spectra computed without (B) and with (C) the presence of a $^2\Delta^1H(^{37/35}Cl)$ of -0.07_6 Hz. The spectral parameters were obtained from a complete analysis of the seven-spin ^{1}H NMR spectrum for a 2.5 mol % solution in acetone-d_6. In CS_2 solution a $^2\Delta^1H$ of -0.05_9 Hz appears to be present. The line widths of the computed spectra are 0.03 Hz.

Because chloroform is often used as a line shape standard for spectrometer specification,[8] it may be noted that its ^{1}H NMR spectrum consists of a number of peaks (Figure 1). At 500 MHz, now a common frequency in NMR, and at 600 MHz, not yet common, the ^{1}H NMR spectrum will display a characteristic asymmetry if the isotope shifts are not resolved, but reasonably good resolution (0.1 Hz) is nevertheless attained (see the theoretical spectrum in Figure 1). It is also apparent that $^1\Delta^{13}$C-

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