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Triple C−H Activation of a Cycloalkyl Ketone Using an Osmium−Hexahydride Complex

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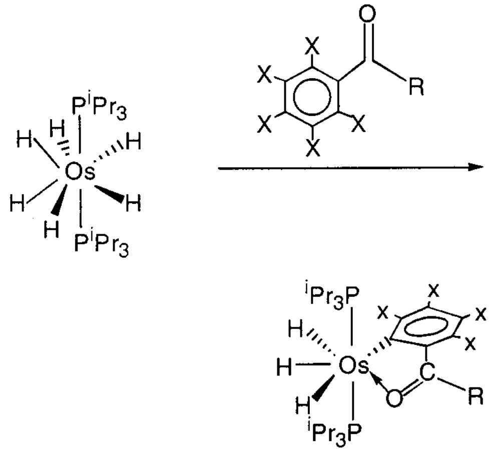
Summary: The hexahydride $OsH_6(P^iPr_3)_2$ reacts with cyclohexylmethyl ketone to give the trihydride $OsH_3\{C_6H_8C(O)CH_3\}(P^iPr_3)_2$, which has been characterized by X-ray diffraction analysis. In solution, the hydride ligands of this complex undergo two different thermally activated exchange processes. Two of them also show weak quantum exchange coupling.

The activation of C−H bonds by transition-metal compounds is a type of reaction of general interest due to its connection with the functionalization of nonactivated organic molecules.[1] An example is the Murai reaction,[2] which allows the catalytic alkylation of aromatic ketones,[3] esters,[4] and imines,[5] and the copolymerization of aromatic ketones and α,ω-divinylsilanes.[6] Experimental evidence and theoretical calculations suggest that the above-mentioned processes involve the selective ortho-CH activation of the aromatic ring of the organic molecule, by the d^8 derivative $Ru(CO)(PPh_3)_3$.[7]

The Murai reaction is limited to aromatic compounds. In this context, it should be noted that the arene-CH activation is easier than the alkane-CH activation. Although the arene-CH bond is between 8 and 14 kcal mol^{-1} stronger than the alkane-CH bond, the activation of the first one is kinetically and thermodynamically favored. The kinetic advantage of the arene activation appears to be due to its prior π-coordination, while the thermodynamic preference has been largely attributed to a metal−carbon bond much stronger for aryl than for alkyl.[8]

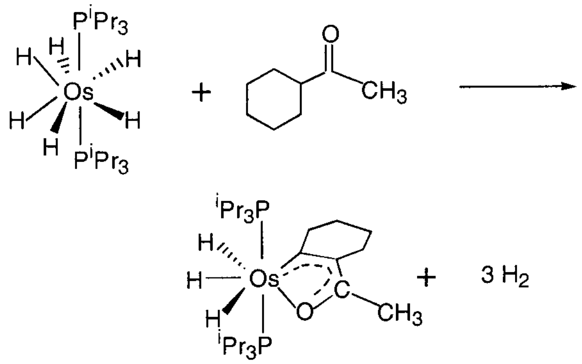
Although the C−H activation reactions with high-valent metal complexes are rare, and in general, the formation of organometallic intermediates is only suspected,[1] Chaudret and co-workers have observed that the d^6 complex $RuH_2(\eta^2\text{-}H_2)_2(PCy_3)_2$ is also an active catalyst precursor for the Murai reaction.[9] In agreement with Chaudret's observations, we have recently shown that the d^2 hexahydride compound $OsH_6(P^iPr_3)_2$ activates the ortho-CH and -CF bonds of aromatic ketones to afford $OsH_3\{C_6X_4C(O)R\}(P^iPr_3)_2$ (eq 1), which are reminiscent of the intermediates proposed in the Murai reaction.[10]



X = H, F

(1)

We now show that the hexahydride $OsH_6(P^iPr_3)_2$ activates not only aromatic ketones but also cycloalkyl ketones. Thus, under reflux, the treatment of its toluene solutions with 1.2 equiv of cyclohexylmethyl ketone affords after 5 h brown solutions, from which the trihydride $OsH_3\{C_6H_8C(O)CH_3\}(P^iPr_3)_2$ is obtained by addition of methanol, as an orange solid in 62% yield (eq 2). In contrast to the aromatic ketones, the activation of the cycloalkyl ketone is three times as great. During the reaction, the cyclohexyl group of the cyclohexyl-



(2)

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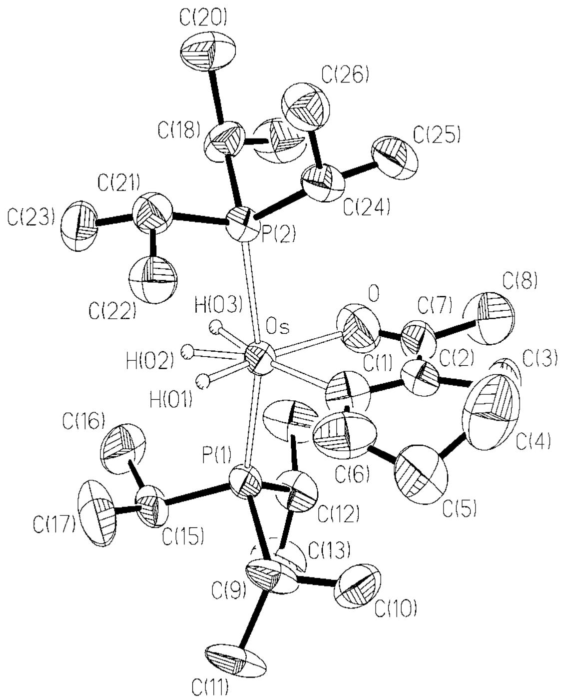
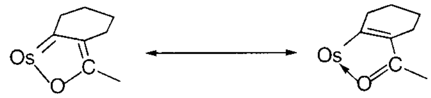


Figure 1. Molecular diagram of the complex $OsH_3\{C_6H_8C(O)CH_3\}(P^iPr_3)_2$. Selected bond distances (Å) and angles (deg): Os−C(1) = 2.071(9), Os−O(2) = 2.157(6), C(1)−C(2) = 1.369(10), C(1)−C(6) = 1.392(11), C(2)−C(7) = 1.494(13), O−C(7) = 1.216(9); Os−C(1)−C(2) = 116.5(7), Os−C(1)−C(6) = 128.0(7), Os−O−C(7) = 117.6(7), C(1)−C(2)−C(7) = 113.4(7), C(2)−C(7)−O = 116.8(9).

Scheme 1



methyl ketone undergoes the cleavage of both C−H bonds of one of the two CH_2 groups β-disposed to the carbonyl and the activation of the C−H bond of the α-CH group.

Figure 1 shows a drawing of the new compound. The coordination geometry around the osmium atom can be rationalized as a distorted pentagonal bipyramid with the two phosphorus atoms of the triisopropylphosphine ligands occupying axial positions (P(1)−Os−P(2) = 165.81(6)°). The osmium sphere is completed by the hydride ligands and the metalated ketone, which acts with a bite angle of 75.6(3)°. The five-membered metallacycle is almost planar (maximum deviation 0.027(5) Å, C(1)).

The $^{13}C\{^1H\}$ NMR spectrum of $OsH_3\{C_6H_8C(O)CH_3\}(P^iPr_3)_2$ suggests that for an adequate description of the bonding situation in this compound, the resonance form shown in Scheme 1 should be taken into account. Thus, the resonance due to the OsC carbon atom appears at 255.9 ppm, shifted about 40 ppm to higher field in comparison with the shift of a typical Os−carbene[11] and more than 60 ppm to lower field with regard to the chemical shift observed for the OsC_α resonances in six-coordinate osmium−alkenyl compounds.[12] The chemical shift of the OsC resonance of $OsH_3\{C_6H_8C(O)CH_3\}(P^iPr_3)_2$ agrees well with those corresponding to the related resonances of the complexes $Os\{CHCHC(O)Ph\}Cl(CO)(P^iPr_3)_2$ (230.13 ppm)[13] and $OsH\{CHCHC(O)CH_3\}(CO)(P^iPr_3)_2$ (250.8 ppm),[14] where a similar bonding situation has been proposed to exist.

The $^{31}P\{^1H\}$ NMR spectrum of the new trihydride, in toluene-d_8, is consistent with the structure shown in Figure 1. In agreement with the mutually trans disposition of the phosphine ligands, it contains a singlet at 31.2 ppm, which is temperature-invariant between 183 and 373 K.

In contrast to the $^{31}P\{^1H\}$ NMR spectrum, the ^1H NMR spectrum is temperature-dependent. At 373 K, the spectrum shows in the hydride region a single resonance. This observation is consistent with the operation of two thermally activated site exchange processes, which proceed at rates sufficient to lead to the single hydride resonance. At 293 K, the first decoalescence occurs, and at 253 K the second one takes place. At this temperature, an $ABCX_2$ spin system ($X = {}^{31}P$) is observed, which becomes well-resolved at 223 K. The $^1H\{^{31}P\}$ spectra (Figure 2) are simplified to the expected ABC spin system. At 223 K, this spin system is defined by $\delta_A = -4.96$, $\delta_B = -12.45$, $\delta_C = -13.15$, $J_{AB} = 12$ Hz, $J_{AC} = 0$ Hz, and $J_{BC} = 9$ Hz. Between 223 and 193 K, the values of the chemical shifts of A, B, and C sites, as well as those of J_{AC} and J_{BC}, show no significant temperature dependence. However, the magnitude of the observed J_{AB} value is sensitive to the temperature, decreasing from 12 to 7 Hz as the temperature decreases from 223 to 193 K. This can be explained in terms of a weak quantum exchange coupling between H_A and H_B.

The T_1 values of the hydrogen nuclei of the OsH_3 unit were determined over the temperature range 248−218 K. T_1(min) values of 152 ± 7 ms for H_A, 84 ± 3 ms for H_B and 102 ± 3 for H_C were obtained at 238 K and 300 MHz. They support the trihydride character of $OsH_3\{C_6H_8C(O)CH_3\}(P^iPr_3)_2$ and suggest that the central atom of the OsH_3 unit is H_B. To assign the positions of H_A and H_C, we carried out a ROESY ^1H NMR experiment at 213 K. This experiment (Figure 3) indicates that H_A is the hydride ligand located cis to the metalated ring. Thus, H_C is the hydride situated cis to the carbonyl group.

Line-shape analysis of the spectra of Figure 2 allows the calculation of the rate constants for the thermal exchange processes at different temperatures. The activation parameters obtained from the corresponding Eyring analysis are $\Delta H^\ddagger = 11.2 \pm 0.4$ kcal mol^{-1} and

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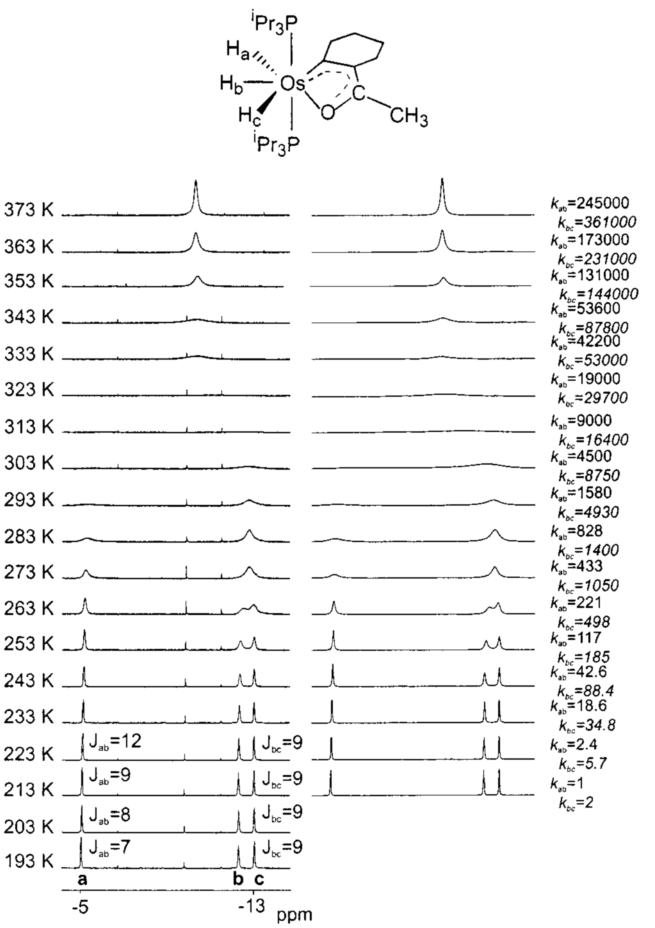

Figure 2. (left) Variable-temperature $^1H\{^{31}P\}$ NMR spectra (300 MHz) in CD_2Cl_2 in the high-field region of $OsH_3\{C_6H_8C(O)CH_3\}(P^iPr_3)_2$. J_{ab} and J_{bc} are given in Hz. (right) Simulated spectra and rate constants (s^{-1}) for the intramolecular hydrogen site exchange.

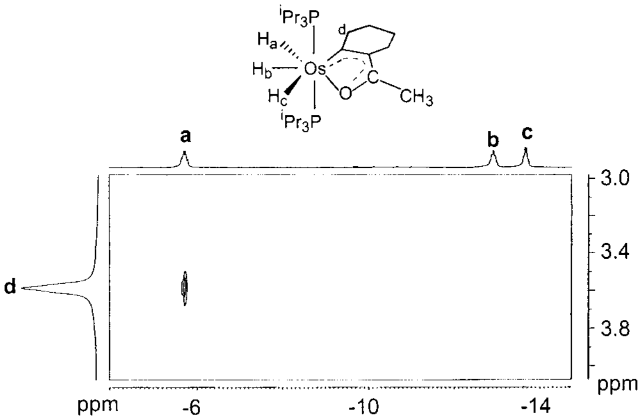

Figure 3. Partial view of the ROESY ^1H NMR spectrum at 300 K in CD_2Cl_2 of $OsH_3\{C_6H_8C(O)CH_3\}(P^iPr_3)_2$.

$\Delta S^\ddagger = -3.3 \pm 1$ cal mol^{-1} K^{-1} for the H_B/H_C exchange and $\Delta H^\ddagger = 11.7 \pm 0.2$ kcal mol^{-1} and $\Delta S^\ddagger = -2.8 \pm 0.5$ cal mol^{-1} K^{-1} for the H_A/H_B exchange. The values for the entropy of activation, close to zero, are in agreement with an intramolecular process, whereas the values for the enthalpy of activation lie in the range reported for thermal exchange processes in related osmium−trihydride complexes.[10,15]

In conclusion, the hexahydride $OsH_6(P^iPr_3)_2$ is capable of producing the triple C−H bond activation of the cyclohexyl group of cyclohexylmethyl ketone to afford the trihydride derivative $OsH_3\{C_6H_8C(O)CH_3\}(P^iPr_3)_2$. In solution, the hydride ligands of the OsH_3 unit of this complex undergo two different thermally activated exchange processes, and two of them show weak quantum exchange coupling. The formation of $OsH_3\{C_6H_8C(O)CH_3\}(P^iPr_3)_2$ suggests that cycloalkyl ketones should be able to afford alkylcycloalkenyl ketones by Murai's method.

Experimental Section

All reactions were carried out with rigorous exclusion of air using Schlenk-tube techniques. Solvents were dried by the usual procedures and distilled under argon prior to use. The starting material $OsH_6(P^iPr_3)_2$, was prepared by the published method.[16]

In the NMR spectra, chemical shifts are expressed in ppm downfield from Me_4Si (^1H and ^{13}C) and 85% H_3PO_4 (^{31}P). Coupling constants, J, are given in hertz.

Kinetic Analysis. Complete line-shape analysis of the $^1H\{^{31}P\}$ NMR spectra of the complex $OsH_3\{C_6H_8C(O)CH_3\}(P^iPr_3)_2$ was achieved using the program gNMR v3.6 for Macintosh (Cherwell Scientific Publishing Limited). The rate constants for various temperatures were obtained by fitting calculated to experimental spectra by full line shape iterations. The transverse relaxation time T_2 was estimated at the lowest interval of temperatures using the resonances corresponding to the hydride ligands. The activation parameters $\Delta H^\ddagger$ and $\Delta S^\ddagger$ were calculated by a least-squares fit of $\ln(k/T)$ vs $1/T$ (Eyring equation). Error analysis assumed a 10% error in the rate constant and 1 K in the temperature. Errors were computed by published methods.[17]

Preparation of $OsH_3\{C_6H_8C(O)CH_3\}(P^iPr_3)_2$. A colorless solution of $OsH_6(P^iPr_3)_2$ (90 mg, 0.174 mmol) in 10 mL of toluene was treated with cyclohexylmethyl ketone (29 μL, 0.21 mmol) and heated under reflux for 5 h. The brown solution was filtered through Celite and dried in vacuo. Methanol was added to afford an orange solid, which was washed with methanol at −78 °C and dried in vacuo. Yield: 68.9 mg (62%). Anal. Calcd for $C_{26}H_{56}OOsP_2$: C, 49.03; H, 8.86. Found: C, 48.64; H, 8.93. IR (KBr, cm^{-1}): ν(OsH) 2139 (m), 1929 (s); ν(CO) 1692 (s). ^1H NMR (300 MHz, C_6D_6, 293 K): δ 3.93 (t, J(H−H) = 6.0 Hz, 2H, CH_2); 2.33 (t, J(H−H) = 6.0 Hz, 2H, CH_2); 2.12 (t, J(P−H) = 1.8 Hz, 3H, CH_3); 1.8−1.6 (m, 4H, CH_2); 1.88 (m, 6H, PCH); 1.13 and 1.11 (both dvt, N = 12.3 Hz, J(H−H) = 6.9 Hz, 18H, PCHCH_3); −5.95 (br, 1H, OsH); −12.82 (br, 2H, OsH). $^{13}C\{^1H\}$ NMR (75.42 MHz, C_6D_6, 293 K): δ 255.9 (t, J(P−C) = 4.2 Hz, Os−C); 198.8 (t, J(P−C) = 2.3 Hz, C=O); 132.4 (s, C_{ipso}); 51.1, 27.9, 26.3, and 23.6 (all s, CH_2); 23.8 (s, CH_3); 27.7 (vt, N = 24.9 Hz, PCH); 19.9 and 19.7 (both s, PCHCH$_3$). $^{31}P\{^1H\}$ NMR (121.42 MHz, C_6D_6, 293 K): δ 31.2 (s). MS (FAB$^+$): m/z 636 (M^+ − H). T_1(min) (ms, OsH_3,

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300 MHz, C_7D_8, 238 K): 152 ± 7 (−4.96 ppm, 1H), 84 ± 3 (−12.45 ppm, 1H), 102 ± 3 (−13.15 ppm, 1H).

Crystal Data for $\mathbf{\overline{OsH_3\{C_6H_8C(O}})CH_3\}(P^iPr_3)_2}$: $C_{26}H_{56}OOsP_2$ (M_w = 636.85); monoclinic, space group $P2_1/c$; a = 20.2832(15) Å, b = 8.6559(6) Å, c = 18.1252(13) Å, β = 112.226(2)° at 173.0(2) K; V = 2945.8(4) Å^3; Z = 4. Irregular crystals were mounted on a Bruker Smart APEX CCD diffractometer equipped with a normal-focus 2.4 kW sealed-tube X-ray source (molybdenum radiation, λ = 0.710 73 Å) operating at 50 kV and 35 mA. Data were collected over a hemisphere by a combination of three sets. The cell parameters were determined and refined by a least-squares fit of all collected reflections. Each frame exposure time was 10 s, covering 0.3° in ω ($2 \leq 2\theta \leq 60°$, 19 151 reflections, 7007 unique (merging R factor 0.1063). The first 100 frames were collected at the end of the data collection to monitor crystal decay. The absorption correction was made using SADABS.[18] The structure was solved by Patterson and Fourier methods using SHELXS.[19] Full-matrix least-squares refinement was carried out using SHELXL97,[19] minimizing $w(F_o^2 - F_c^2)^2$. Weighted R factors (R_w) and goodness of fit (S) are based on F^2; conventional R factors are based on F.

The presence of a residual peak of about 1.9 e/Å very close to the C(1) carbon atom gives rise to unreasonable anisotropic thermal parameters and bond distances. To try to solve this problem, reflections of two different crystals of different preparations were collected, and different absorption correction methods were used, but no results were obtained. Finally, an isotropic refinement of C(1) was used. The rest of the non-hydrogen carbon atoms were anisotropically refined. The hydrogen atoms were observed or calculated and refined riding on bonded carbon atoms. The hydride ligands were observed in the difference Fourier maps and refined as isotropic atoms with the same distance to the osmium atom. Final R1($F^2 > 2\sigma(F^2)$) = 0.0530, wR2(all data) = 0.0975, and S^c(all data) = 0.840.[19]

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Supporting Information Available: Tables of atomic coordinates and equivalent isotropic displacement coefficients, anisotropic thermal parameters, experimental details of the X-ray studies, and bond distances and angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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