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Unusual Activation of 1,1-Diphenyl-2-propyn-1-ol Mediated by the Os(η^5-C_5H_5) Unit

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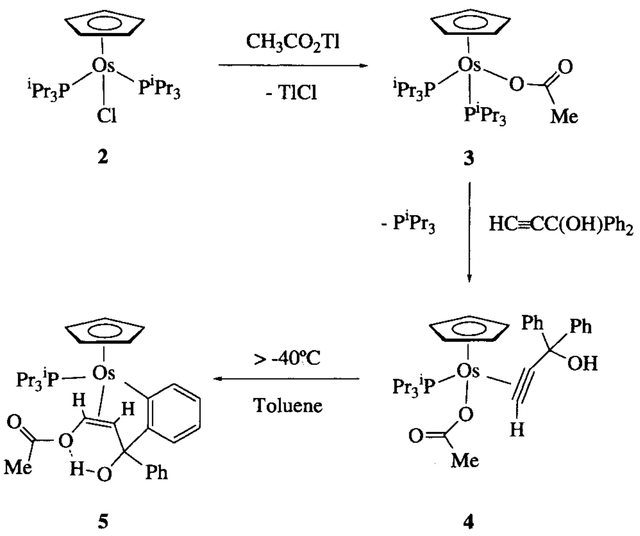
*Summary: Os(η^5-C_5H_5)Cl(P^iPr_3)$_2$ (**2**) reacts with thallium acetate in CH_2Cl_2 to give Os(η^5-C_5H_5){κ^1-OC(O)CH_3}(P^iPr_3)$_2$ (**3**). Reaction of the latter with 1,1-diphenyl-2-propyn-1-ol affords the π-alkyne derivative Os(η^5-C_5H_5){κ^1-OC(O)CH_3}{η^2-HC≡CC(OH)Ph_2}(P^iPr_3) (**4**). In solution, complex **4** is unstable above −40 °C and rapidly changes into the 2-{(Z)-3-acetoxy-1-hydroxy-1-phenyl-2-propenyl}aryl complex Os(η^5-C_5H_5)-{C_6H_4[C(OH)(Ph)CH═CHOC(O)CH_3]}(P^iPr_3) (**5**), whose structure was determined by X-ray diffraction analysis.*

In comparison with related iron and ruthenium complexes, the chemistry of the Os(η^5-C_5H_5) unit is not well-understood[1] due to the lack of convenient synthetic precursors[2] and the kinetic stability of $CpOsL_3$ compounds.[3] Recently, we reported the preparation of the labile cyclopentadienylosmium synthetic precursors Os(η^5-C_5H_5)Cl(CO)(P^iPr_3)[4] (**1**) and Os(η^5-C_5H_5)Cl(P^iPr_3)$_2$[5] (**2**). This communication reports a novel Os(η^5-C_5H_5)-mediated acetato-plus-1,1-diphenyl-2-propyn-1-ol coupling reaction leading to a 2-{(*Z*)-3-acetoxy-1-hydroxy-1-phenyl-2-propenyl}aryl complex, which is of interest because the aryl ligand is the result of the *trans* anti-Markovnikov addition of acetic acid to the carbon−carbon triple bond of 1,1-diphenyl-2-propyn-1-ol and because its formation involves the C−H activation of an *ortho* C−H bond of one of the two phenyl groups of the prop-2-yn-1-ol in the presence of weaker H−C(sp) and H−O bonds.

The acetato complex Os(η^5-C_5H_5){κ^1-OC(O)CH_3}-(P^iPr_3)$_2$ (**3**) was prepared in 88% yield by reaction of **2** with thallium acetate in dichloromethane as solvent[6] (Scheme 1).

Scheme 1



Although complex **3** is soluble in pentane and its solutions are stable for a matter of days, a P^iPr_3 ligand was easily displaced by 1,1-diphenyl-2-propyn-1-ol to afford the π-alkyne derivative Os(η^5-C_5H_5){κ^1-OC(O)CH_3}{η^2-HC≡CC(OH)Ph_2}(P^iPr_3) (**4**), which was isolated as an orange solid in 50% yield.[7] The proposed π-coordination of the alkynol is supported by the IR spectrum, which shows the C≡C stretching frequency at 1797 cm^{-1}, shifted 320 cm^{-1} to lower wavenumbers in comparison with the free alkynol (2117 cm^{-1}).[8]

In the solid state, complex **4** is stable for 2 days if kept under argon at −20 °C. However, in solution, at temperatures higher than −40 °C,[9] it rapidly evolves into the 2-{(*Z*)-3-acetoxy-1-hydroxy-1-phenyl-2-propenyl}aryl complex Os(η^5-C_5H_5){C_6H_4[C(OH)(Ph)CH═CHOC(O)CH_3]}(P^iPr_3) (**5**).

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(6) Experimental procedure for the preparation of **3**: a solution of **2** (140 mg, 0.23 mmol) in 15 mL of dichloromethane was treated with thallium acetate (62 mg, 0.24 mmol). After the mixture was stirred for 1 h at room temperature, the suspension was filtered. The resulting solution was concentrated to dryness, and the residue was extracted with 20 mL of pentane. After filtration through Kieselguhr, the solution was concentrated until a yellow solid began to precipitate and the suspension was stored at −78 °C for 1 h. The yellow solid obtained was separated by decantation and dried in vacuo. Yield: 128 mg (88%). IR (Nujol): ν(OCO) 1622 cm^{-1}. ^1H NMR (300 MHz, C_6D_6, 293 K): δ 5.03 (s, 5 H, Cp), 2.32 (m, 6 H, PC*H*), 2.17 (s, 3 H, *Me*CO_2), 1.10 (dd, 18 H, ^3J(HH) = 7.1 Hz, ^3J(PH) = 11.6 Hz, PC*Me*), 1.06 (dd, 18 H, ^3J(HH) = 7.4 Hz, ^3J(HH) = 12.2 Hz, PC*Me*). $^{31}P\{^1H\}$ NMR (121.42 MHz, C_6D_6, 293 K): δ 6.4 (s). $^{13}C\{^1H\}$ NMR (75.42 MHz, C_6D_6, 293 K): δ 177.8 (s, Me*C*O_2), 68.0 (s, Cp), 29.2 (second-order system, P*C*H), 23.3 (s, *Me*CO_2), 20.8 (s, PC*Me*), 20.7 (s, PC*Me*). Anal. Calcd for $C_{25}H_{50}O_2OsP_2$: C, 47.30; H, 7.94. Found: C, 46.98; H, 8.13.

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The crystal structure of **5**[10] (Figure 1), which was obtained as a colorless crystalline solid in 61% yield, verifies the formation of the 2-{(*Z*)-3-acetoxy-1-hydroxy-1-phenyl-2-propenyl}aryl ligand. This group acts as a bidentate ligand and is bonded to the osmium atom by the aromatic carbon atom C(5) and by the C(1)−C(2) olefinic bond. The Os−C(5) bond distance of 2.108(11) Å is in agreement with values previously reported for Os−C(aryl) bond lengths (mean 2.09(3) Å).[11] The osmium−olefin coordination exhibits Os−C distances of 2.183(9) Å (Os−C(1)) and 2.142(10) Å (Os−C(2)), which agree well with those found in other osmium−olefin complexes (between 2.15 and 2.28 Å).[12] Similarly, the olefinic bond distance C(1)−C(2) (1.389(14) Å) is within the range reported for transition-metal olefin complexes (between 1.340 and 1.445 Å).[13] The angles C(3)−C(2)−C(1) (133.27(85)°) and O(3)−C(1)−C(2) (116.79(92)°) support sp^2 hybridization at C(1) and C(2).

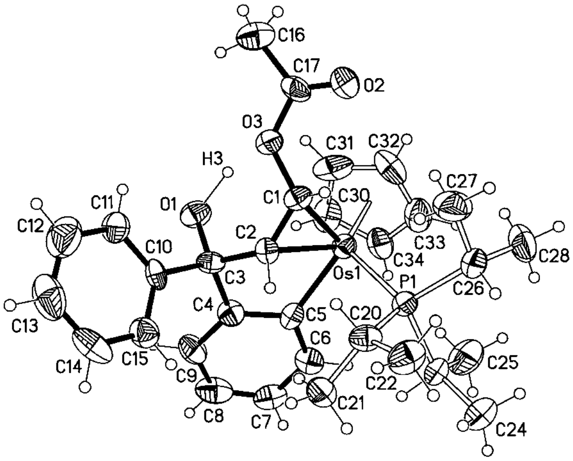

Figure 1. Molecular diagram of complex **5**. Selected distances (Å) and angles (deg): Os−C(5), 2.108(11); Os−C(2), 2.142(10); Os−C(1), 2.183(9); C(1)−C(2), 1.389(14); C(1)−O(3), 1.439(11); C(2)−C(3), 1.522(14); C(3)−O(1), 1.456(11); C(17)−O(2), 1.187(13); C(17)−O(3), 1.342(13); O(1)−H(3), 1.228(8); C(3)−C(2)−C(1), 133.27(85); O(3)−C(1)−C(2), 116.79(92).

Although reaction intermediates have not been isolated, it has been proposed that the catalytic addition of carboxylic acids to prop-2-yn-1-ols in the presence of transition-metal compounds requires the initial π-coordination of the alkynol to the metallic center, with subsequent attack of the carboxylato group at the coordinated carbon−carbon triple bond of the alkyne.[14] In this communication, we report evidence in favor of this proposal by isolating complexes which are examples of species proposed as intermediates in these catalytic transformations.

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Supporting Information Available: Tables of positional and displacement parameters, crystallographic data, and bond lengths and angles (7 pages). Ordering information is given on any current masthead page.

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(7) Experimental procedure for the preparation of **4**: a solution of **3** (110 mg, 0.17 mmol) in 10 mL of pentane was treated with 1,1-diphenyl-2-propyn-1-ol (50 mg, 0.24 mmol). After the mixture was stirred for 15 min at room temperature, the resulting orange solid was separated by decantation, washed with pentane, and dried *in vacuo*. Yield: 58 mg (50%). IR (Nujol): ν(C≡C) 1797, ν(OCO) 1576 cm^{-1}. ^1H NMR (300 MHz, CD_2Cl_2, 233 K): δ 7.58 (d, 4 H, $^3J(HH) = 7.8$ Hz, *o*-Ph), 7.29 (t, 4 H, $^3J(HH) = 7.3$ Hz, *m*-Ph), 7.20 (t, 2 H, $^3J(HH) = 6.6$ Hz, *p*-Ph), 6.53 (very br s, 1 H, O*H*), 5.40 (s, 5 H, Cp), 2.68 (m, 3 H, PC*H*), 1.42 (s, 3 H, O_2CMe), 1.25 (dd, 18 H, $^3J(HH) = 6.9$ Hz, $^3J(PH) = 13.2$ Hz, PC*Me*); the ≡CH proton was not observed. $^{31}P\{^1H\}$ NMR (121.42 MHz, CD_2Cl_2, 233 K): δ 17.8 (br s). Anal. Calcd for $C_{31}H_{41}O_3OsP$: C, 54.53; H, 6.05. Found: C, 54.91; H, 6.41.

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(9) Experimental procedure for the preparation of **5**: a solution of **3** (108 mg, 0.17 mmol) in 15 mL of toluene was treated with 1,1-diphenyl-2-propyn-1-ol (51 mg, 0.24 mmol). After it was stirred for 2 h at room temperature, the solution was filtered and concentrated to dryness. Addition of 5 mL of pentane afforded the precipitation of a white solid, which was separated by decantation, washed with pentane, and dried *in vacuo*. Yield: 71 mg (61%). IR (Nujol): ν(CO) 1729, ν(C=C) 1572 cm^{-1}. ^1H NMR (300 MHz, C_6D_6, 293 K, plus COSY): δ 8.14 (d, 2 H, $^3J(HH) = 7.2$ Hz, *o*-Ph), 7.54 (d, 1 H, $^3J(HH) = 7.2$ Hz, C_6H_4), 7.44 (t, 2 H, $^3J(HH) = 7.7$ Hz, *m*-Ph), 7.39 (dd, 1 H, $^3J(PH) = 4.2$ Hz, $^3J(HH) = 6.3$ Hz, =C*H*), 7.23 (t, 1 H, $^3J(HH) = 7.1$ Hz, *p*-Ph), 6.97 (m, 3 H, C_6H_4), 4.79 (s, 5 H, Cp), 4.54 (t, 1 H, $^3J(PH) = {}^3J(HH) = 6.2$ Hz, =C*H*), 3.10 (br s, 1 H, O*H*), 1.92 (m, 3 H, PC*H*), 1.61 (s, 3 H, *Me*CO_2), 0.84 (dd, 9 H, $^3J(HH) = 7.4$ Hz, $^3J(PH) = 12.8$ Hz, PC*Me*), 0.81 (dd, 9 H, $^3J(HH) = 7.5$ Hz, $^3J(PH) = 11.7$ Hz, PC*Me*). $^{31}P\{^1H\}$ NMR (121.42 MHz, C_6D_6, 293 K): δ 2.6 (s). $^{13}C\{^1H\}$ NMR (75.42 MHz, C_6D_6, 293 K, plus DEPT): δ 169.8 and 168.8 (both s, Me*C*O_2 and C_6H_4), 149.2 (s, *ipso*-Ph), 143.0 (+, s, Ph or C_6H_4), 139.6 (d, $^2J(PC) = 8.8$ Hz, Os-*C*), 128.2 (+, s, Ph or C_6H_4), 127.3 (+, d, $J(PC) = 4.2$ Hz, C_6H_4), 126.7, 126.2, 126.0, and 121.7 (+, all s, Ph and C_6H_4), 88.9 (s, *C*OH), 83.4 (+, d, $^2J(PC) = 2.3$ Hz, Cp), 74.3 (+, s, =*C*H), 59.5 (+, s, =*C*H), 26.4 (+, d, $^1J(PC) = 24.9$ Hz, P*C*H), 20.3 (+, s, *Me*CO_2), 20.0 (+, s, PC*Me*), 19.4 (+, d, $^2J(PC) = 1.8$ Hz, PC*Me*). Anal. Calcd for $C_{31}H_{41}O_3OsP$: C, 54.53; H, 6.05. Found: C, 54.61; H, 5.93.

(10) Complex **5** is monoclinic, space group $P2_1/c$, with $a = 9.3619(8)$ Å, $b = 21.464(2)$ Å, $c = 14.699(2)$ Å, $\beta = 107.652(2)°$, $V = 2814.6(4)$ $Å^3$, and $Z = 4$. A quadrant of 6110 data was collected at room temperature with a Siemens CCD diffractometer (sealed tube 2.4 kW, $\lambda = 0.710\ 73$ Å) *via* two runs of 0.3° ω scans at different φ values, over a 2θ range of 1.7−23.3°. An empirical absorption correction from ψ scans was applied to the data ($\mu = 4.617\ mm^{-1}$ for Mo Kα radiation). Structural solution by direct methods and least-squares refinement (based on F^2) was performed with SHELXTL. The refinement on 3188 unique data converged at $R1(F) = 0.056$, $wR2(F^2) = 0.10$ for all data and $R1(F) = 0.0448$, $wR2(F^2) = 0.095$ for 2735 observed data ($I > 2\sigma(I)$).

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