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Preliminary communication

FORMATION OF FOUR-MEMBERED OsC_2P METALLAHETEROCYCLES VIA CATIONIC HYDRIDO- AND DEUTERIDO-METHYLENE INTERMEDIATES: AN UNPRECEDENTED EXAMPLE OF INTRAMOLECULAR C–H-ACTIVATION

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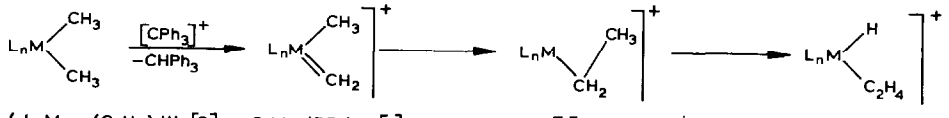
Summary

Treatment of the hydrido(methyl)- and deuterido(methyl)-osmium complexes $[C_6H_6OsX(CH_3)PPr^i_3]$ (**3**, X = H; **3'**, X = D) with $[CPh_3]PF_6$ gives the metallaheterocycles $[C_6H_6(CH_2X)H\overline{OsCH_2CH(CH_3)}PPr^i_2]PF_6$ (**4**,**4'**) probably via cationic $OsX(=CH_2)$ and $Os(CH_2X)$ species as intermediates, the latter of which activates a C–H bond of a methyl group of a Pr^i substituent to form the four-membered ring. In the presence of CO, the coordinatively unsaturated intermediate $[C_6H_6OsCH_3(PPr^i_3)]^+$ can be stabilized as the carbonyl(methyl)osmium cation $[C_6H_6OsCH_3(CO)PPr^i_3]^+$. On deprotonation of **4** the neutral complex $[C_6H_4(CH_3)OsCH_2CH(CH_3)PPr^i_2]$ (**6**) is obtained.

It has recently been shown [1], that hydrido metal complexes HML_n react with carbenium ions such as $[CPh_3]^+$ by hydride abstraction to form coordinatively unsaturated species $[ML_n]^+$. In some cases, reaction of the corresponding methyl-metal compounds CH_3ML_n with $[CPh_3]^+$ proceed analogously, with cleavage of the methyl–metal bond [2]. The trityl cation can, however, also abstract a hydride ion from a coordinated methyl group to form an intermediate methylene species which is stabilized either by inter- or intra-molecular addition of a nucleophile. A striking example of an intramolecular process is the formation of ethylene hydridometal cations $[L_nMH(C_2H_4)]^+$ from the corresponding dimethyl metal complexes $L_nM(CH_3)_2$ and $[CPh_3]PF_6$, for which the following mechanism has been proposed:



(L_nM = $(C_5H_5)_2W$ [3] , $C_6Me_6(PR_3)Ru$ [4] , $C_6H_6(PMe_3)Os$ [5] , $C_5H_5(PPr^i_3)Ir$ [5])

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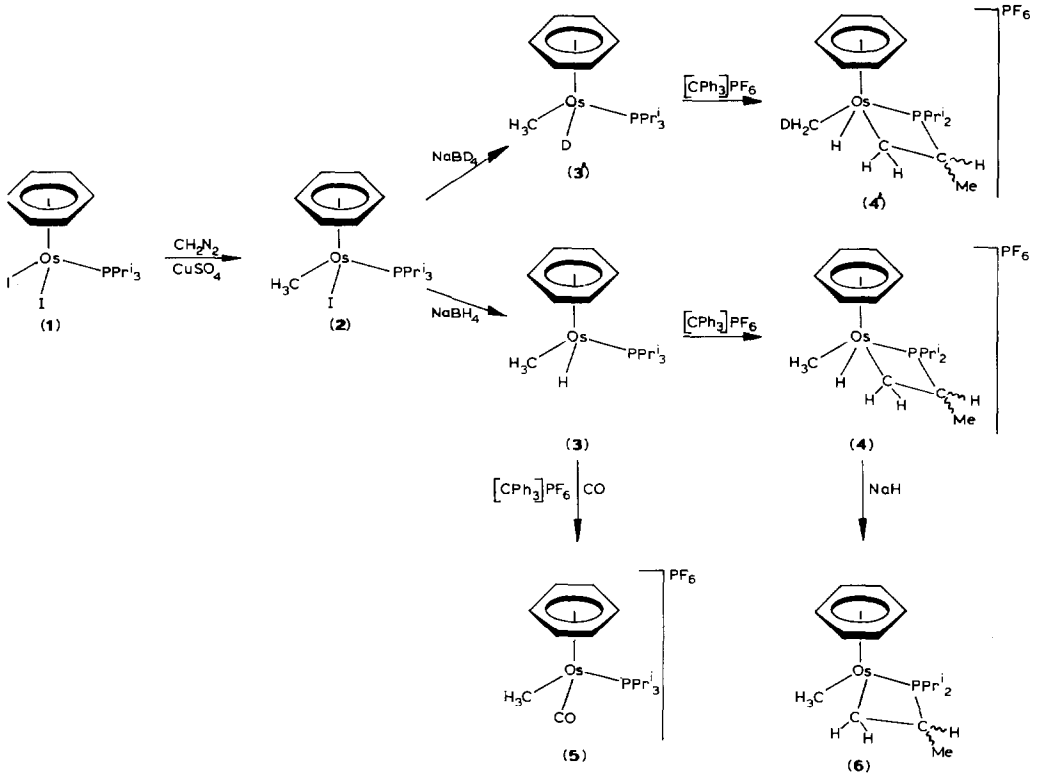
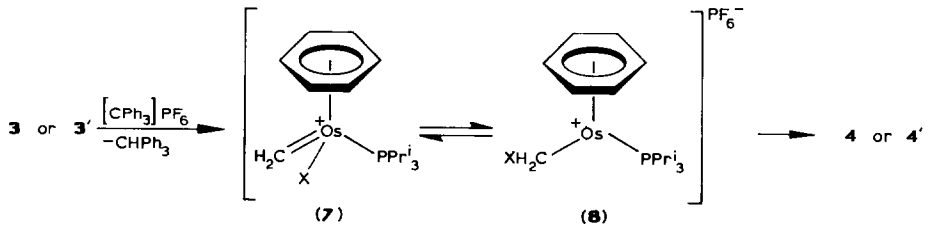


SCHEME 1

In pursuing our general interest in the reactivity of electron-rich half-sandwich type compounds towards electrophiles [6], we have now prepared hydrido(methyl) and deuterido(methyl) analogues of the above-mentioned dimethylosmium derivative and investigated their reactions with $[CPh_3]PF_6$. The first step of the synthesis of **3** and **3'**, the conversion of **1** [7] into **2** by use of diazomethane and catalytic amounts of $CuSO_4$ in ether at 0°C (see Scheme 1), follows the route which was recently developed for methylrhodium complexes [8]. Treatment of **2** with $NaBH_4$ in ethanol/hexane at −78°C leads to almost quantitative formation of **3**, which is surprisingly stable and does not undergo a loss of CH_4 even on warming. With $NaBD_4$ the corresponding deuterido compound **3'** is formed.

The reaction of **3** with an equimolar amount of $[CPh_3]PF_6$ in dichloromethane also proceeds under mild conditions, and after addition of ether gives a cream-coloured precipitate which analyses for **4**. The deuterido derivative **4'** can be prepared in the same way. In both reactions, the only other product is triphenylmethane, which was identified by mass spectrometry. It is also important to note that in CD_2Cl_2 **3** reacts with $[CPh_3]PF_6$ to produce **4** and CPh_3H, indicating that the solvent is not involved in the ring-forming process.

The notable features of the ^1H NMR spectroscopic data (see Experimental) of both complexes, **4** and **4'**, are (1) the high-field signal of the metal-bound hydrogen atom, (2) the two signals separated by ca. 1 ppm of the two diastereotopic



SCHEME 2. X = H or D.

Os-CH_2-protons, and (3) the five different signals of the five methyl groups belonging to the isopropyl substituents and the $CH(CH_3)$ fragment of the metallacycle. The general pattern of the ^1H NMR spectrum of the neutral compound **6**, obtained on deprotonation of **4** with NaH in THF, is quite similar, except that no hydride signal is observed. The ^{13}C NMR spectrum of **6** confirms the proposed structure.

The mechanism of formation of the OsC_2P metallaheterocycle is outlined in Scheme 2. There is no doubt that the trityl cation selectively attacks the coordinated methyl group and not the hydride ligand of **3** (or deuteride ligand of **3'**). As a consequence, the hydrido methylene (or deuterido methylene) intermediate **7** is formed, which although it is an 18-electron species, is in equilibrium with the corresponding methyl derivative (**8**). This coordinatively unsaturated compound smoothly undergoes an intramolecular oxidative addition with a C–H bond of one of the isopropyl groups to produce the metallaheterocycle **4** or **4'**. In the presence of CO, **8** can be stabilized as the PF_6 salt of the carbonyl methylosmium cation **5**. There is a precedent for such an equilibrium between a hydrido methylene and the isomeric methyl derivative, namely that observed by Cooper and Green [9] in the reaction of $[(C_5H_5)_2WCH_3(C_2H_4)]^+$ with PMe_2Ph in which the products obtained come either from the $[(C_5H_5)_2WCH_3]^+$ or the $[(C_5H_5)_2WH(=CH_2)]^+$ cation.

To the best of our knowledge the present results provide the first example of reaction of a cationic species of the general type $[C_nR_nM(L)X]^+$ with a C–H bond by oxidative addition. The role of neutral 16-electron fragments $[C_nR_nM(L)]$ such as $[C_5Me_5Ir(PMe_3)]$ [10], $[C_5Me_5Ir(CO)]$ [11], $[C_5Me_5Rh(PMe_3)]$ [12] or $[C_6H_6M(PR_3)]$ (M = Ru, Os) [7,13] in C–H activation is well established, but there is, as yet, no real evidence that a related coordinatively unsaturated cation, formally produced by addition of an electrophile X^+ to the 16-electron fragment $[C_nR_nM(L)]$, can participate in such a process. There is good reason to believe [14] that by varying the ligands (i.e., changing the coordination sphere of the cation $[C_nR_nM(L)X]^+$) not only an intramolecular but also an intermolecular C–H bond activation can occur.

Experimental

Preparation of $C_6H_6OsCH_3(PPr^i_3)I$ (2). A suspension of 191.3 mg (0.34 mmol) of **1** in 7.5 ml of ether was treated at 0°C with 7.5 ml of a 0.5 molar solution of CH_2N_2 in ether. After addition of 10 mg $CuSO_4$ gas evolution was observed, and this was accompanied by a color change from yellow to orange. The solution was stirred for 1 h at 0°C, then slowly warmed to room temperature and evaporated to dryness. The residue was dissolved in 10 ml benzene, then the solution was filtered and the concentrated filtrate chromatographed on Al_2O_3 (activity grade III) with

benzene. The solvent was removed and the orange-yellow solid was repeatedly washed with cold hexane and dried in vacuo. Yield 151 mg (78%). Found: C, 33.89; H, 5.55; I, 22.50; mol.-wt. 572 (MS, calc. for ^{192}Os). $C_{16}H_{30}IOsP$ calcd.: C, 33.69; H, 5.30; I, 22.25%; mol.-wt. 570.50.

Preparation of $C_6H_6OsH(CH_3)PPr^i_3$ (3). A solution of 170 mg (0.30 mmol) of **2** in 6 ml of ethanol/hexane (1/1) was treated at −78°C with an excess of $NaBH_4$ (ca. 50 mg) and the mixture then slowly warmed to room temperature and was stirred for 1.5 h. The solvent was removed and the residue extracted with benzene. The extract was evaporated to leave a yellow oil. Yield 89 mg (67%). Found: C, 42.77; H, 6.97; Os, 42.55. $C_{16}H_{31}OsP$ calcd.: C, 43.22; H, 7.03; Os, 42.78%. The highest peak in the mass spectrum (*m/e* 430) corresponds to $M^+ - CH_4$.

The deuterido complex **3'** was prepared similarly, starting from **2** and $NaBD_4$ in ethanol. Yield 83%.

Preparation of $[C_6H_6(CH)_3H\overline{OsCH_2CHMePPr^i_2}]PF_6$ (4). A solution of **3** in ether was treated at −78°C with an equimolar amount of $[CPh_3]PF_6$ in CH_2Cl_2. After slow warming to room temperature (ca. 1 h) and further stirring for 1 h the solution was concentrated in vacuo and ether was added. The cream-colored precipitate was filtered off and the solution was evaporated to dryness. The colorless solid obtained after column chromatography (Al_2O_3, activity grade III, benzene/hexane) was identified (MS) as CPh_3H. The precipitate was also purified by chromatography (Al_2O_3, activity grade I, acetone) to give **4**. Yield 82 mg (48%). Found: C, 32.22; H, 4.68. $C_{16}H_{30}F_6OsP_2$ calcd.: C, 32.65; H, 5.14%.

Complex **4'** was prepared similarly, starting from **3'** and $[CPh_3]PF_6$. Yield 45%.

Preparation of $[C_6H_6OsCH_3(CO)PPr^i_3]PF_6$ (5). The procedure described for **4**, but involving ether saturated with CO, gave a yellow microcrystalline solid. Yield 162 mg (71%). Found: C, 33.40; H, 4.79; Os, 30.90. $C_{17}H_{30}F_6OOsP_2$ calcd.: C, 33.12; H, 4.90; Os, 30.84%.

Preparation of $C_6H_6(CH_3)\overline{OsCH_2CHMePPr^i_2}$ (6). A suspension of 163.2 mg (0.28 mmol) of **4** in 4 ml THF was treated at room temperature with an excess of NaH. A smooth gas evolution occurred and a light brown precipitate was formed. After 1 h stirring the solvent was removed and the solid residue was extracted with hexane. The extract was filtered and then evaporated to leave a yellow, very air-sensitive oil. It was characterized by IR and ^1H and ^{31}P NMR spectroscopy. Yield 78%.

Selected spectroscopic data. IR in KBr, ν in cm^{-1}; δ in ppm, J in Hz. **2**: ^1H NMR (C_6D_6) 4.90 [6H, d, J(H–P) 0.4, C_6H_6], 2.03 [3H, d, J(H–P) 6.0, $OsCH_3$]; ^{31}P NMR (C_6D_6) −10.70(s), **3**: ^1H NMR (C_6H_6) 4.84 [6H, d, J(H–P) 0.4, C_6H_6], 0.96 [3H, dd, J(H–P) 5.6, J(H–H) 1.7, $OsCH_3$], −10.11 [1H, d, J(H–P) 42.0, OsH]; ^{31}P NMR ($C_6D_{11}CD_3$) 25.78(s), doublet in off-resonance. **3'**: ^1H NMR (C_6H_6) 4.80 [6H, bs, C_6H_6], 0.90 [3H, d, J(H–P) 5.7, $OsCH_3$]; ^{31}P NMR (C_6D_6) 25.94(t). **4**: ^1H NMR (CD_3NO_2) 6.15 [6H, bs, C_6H_6], 3.59 [1H, dd, J(H–P) 30.4, J(H–H) 2.0, one H of $OsCH_2$], 2.66 [1H, ddd, J(H–P) 6.6, J(H–H) 4.9, J(H–H) 2.0, one H of $OsCH_2$], 2.13 [3H, d, J(H–P) 8.1, $OsCH_3$], 1.26 [3H, dd, J(H–P) 13.3, J(H–H) 7.3, CH_3 of $CH(CH_3)$ ring fragment], −12.87 [1H, dd, J(H–P) 23.2, J(H–H) 4.9, OsH]; ^{31}P NMR (acetone-d_6) 30.83(s), doublet in off-resonance; IR 1980 [ν(Os–H)]. **4'**: ^{31}P NMR (CD_3NO_3) 31.24(s); IR 1978 [ν(Os–H)]. **5**: ^1H NMR (CD_3NO_2) 6.43 [6H, bs, C_6H_6], 0.88 [3H, d, J(H–P) 4.2, $OsCH_3$]; ^{31}P NMR (CD_3NO_2) 19.07(s); IR 1976 [ν(CO)]. **6**: ^1H NMR (C_6H_6) 5.04 [6H, bs, C_6H_6], 2.17

[3H, d, J(H–P) 7.5, $OsCH_3$], 1.97 [1H, dd, J(H–P) 37.7, J(H–H) 2.0, one H of $OsCH_2$], 1.69 [1H, m, H of $CH(CH_3)$ ring fragment], 1.57 [1H, dd, J(H–P) 22.9, J(H–H) 2.0, one H of $OsCH_2$], 1.01 [3H, dd, J(H–P) 12.1, J(H–H) 6.9, CH_3 of $CH(CH_3)$ ring fragment]; ^{31}P NMR (C_6D_6) 3.31(s); ^{13}C NMR (C_6D_6) 69.77 [s, d in off-resonance, C_6H_6], 29.79 and 29.43 [s, d in off-resonance, CH of isopropyl groups], 6 signals between 23.47 and 20.02 [s, q in off-resonance, CH_3 of isopropyl groups, of $CH(CH_3)$ ring fragment, and of $OsCH_3$], 16.22 [s, d in off-resonance, CH of $CH(CH_3)$ ring fragment], 8.04 (s, t in off-resonance, $OsCH_2$].

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