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Double C−H Activation on Osmium and Ruthenium Centers: Carbene vs Olefin Products

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Summary: Cyclometalation of bis(di-tert-butylphosphino)pentane (D^{t}BPP) and subsequent product dehydrogenation take place in reactions of D^{t}BPP with $[OsCl_6]^{2-}$ and $[RuCl_2(p\text{-cymene})]_2$ to give the M(IV) dihydrides, $MH_2Cl[CH(C_2H_4PBu^t{}_2)_2]$, and the (alkylidene)osmium and (olefin)ruthenium complexes $OsHCl[{=}C(C_2H_4PBu^t{}_2)_2]$ and $RuHCl[Bu^t{}_2PCH_2CH_2((E)\text{-}CH{=}CH)CH_2PBu^t{}_2]$.

Bulky diphosphine ligands often generate unusual metal chemistry.[1] "Pincer" complexes of cyclometalated 1,3-bis((di-*tert*-butylphosphino)methyl)benzene have demonstrated exceptional thermal stability along with high reactivity and found important applications in synthesis and catalysis.[1] Considerable interest in C−H bond activation and alkane dehydrogenation prompted us to study reactions of a related diphosphine, 1,5-bis(di-*tert*-butylphosphino)pentane (D^{t}BPP),[2] with ruthenium and osmium halides. We now report the observation of dehydrogenation of the alkane chain of D^{t}BPP on Ru and Os centers and the isolation of novel group 8 metal carbene and olefin complexes.

When $[Et_4N]_2OsCl_6$[3] was heated with D^{t}BPP[2b,f] under H_2, the cyclometalated complex $OsH_2Cl[CH(C_2H_4PBu^t{}_2)_2]$ (**1**) was obtained[4] in good yield (Scheme 1). Thermal dehydrogenation of **1** afforded the carbene $OsHCl[{=}C(C_2H_4PBu^t{}_2)_2]$ (**2**).[5]

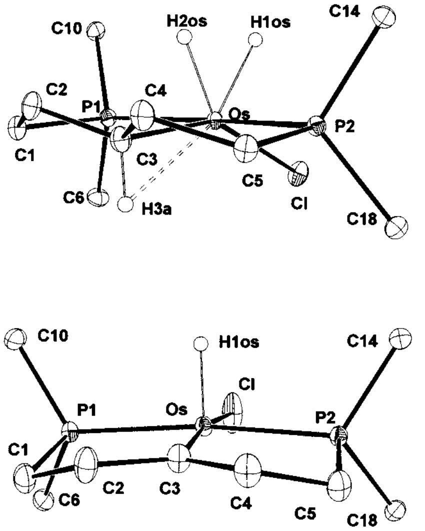
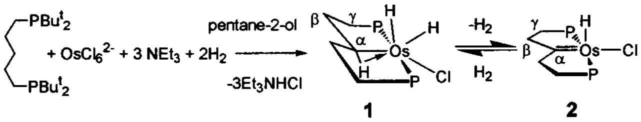


Figure 1. Partial structures of **1** and **2** with the ellipsoids set at 30% probability level. Key parameters (distances in Å and angles in deg) are as follows. **1**: Os−C3 = 2.089(3), Os−Cl = 2.4168(7), C3−H3a = 1.00(3); P1−Os−P2 = 166.45(3), C3−Os−Cl = 149.2(1), H1os−Os−H2os = 60.2(14), C3−Os−H2os = 68.4(11), H1os−Os−Cl = 82.3(9), C2−C3−Os = 116.8(2). **2**: Os−C3 = 1.911(3), Os−Cl = 2.4388(9); P1−Os−P2 = 166.94(3), C3−Os−Cl = 170.6(1), C2−C3−Os = 124.8(2).

Scheme 1



The identity of **1** follows from the NMR spectra and was confirmed by a crystal structure determination (Figure 1).[6] The inequivalent hydrides at δ −23.8 (H_a) and −18.8 (H_b) exchange sites above −40 °C and coalesce at 38 °C ($\Delta G^{\ddagger} = 13.2$ kcal/mol[7]). T_1(min) times for H_a in **1** and in the OsHD isotopomer[8] of **1** are 109 and 257 ms, respectively (−80 °C, 300 MHz). This corresponds to a $H_a \cdots H_b$ distance of 1.68 Å.[9] The proton α-CH resonance of **1** is shifted upfield to δ 0.31. In the carbon spectrum, the α-CH resonance is deshielded (δ

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(2) (a) Crocker, C.; Errington, R. J.; McDonald, W. S.; Odell, K. J.; Shaw, B. L. *Chem. Commun.* **1979**, 498. (b) Al-Salem, N. A.; Empsall, H. D.; Markham, R.; Shaw, B. L.; Weeks, B. *J. Chem. Soc., Dalton Trans.* **1979**, 1972. (c) Crocker, C.; Errington, R. J.; Markham, R.; Moulton, C. J.; Odell, K. J.; Shaw, B. L. *J. Am. Chem. Soc.* **1980**, *102*, 4373. (d) Crocker, C.; Errington, R. J.; Markham, R.; Moulton, C. J.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1982**, 387. (e) Crocker, C.; Empsall, H. D.; Errington, R. J.; Hyde, E. M.; McDonald, W. S.; Markham, R.; Norton, M. C.; Shaw, B. L.; Weeks, B. *J. Chem. Soc., Dalton Trans.* **1982**, 1217. (f) Timmer, K.; Thewissen, D. H. M. W.; Marsman, J. W. *Recl. Trav. Chim. Pays-Bas* **1988**, *107*, 248. (g) McLoughlin, M. A.; Flesher, R. J.; Kaska, W. C. *Organometallics* **1994**, *13*, 3816.

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(4) A mixture of $[Et_4N]_2OsCl_6$ (2.8 g, 4.22 mmol), D^{t}BPP (1.67 g, 4.63 mmol), and triethylamine (1.28 g, 12.65 mmol) in 15 mL of pentan-2-ol was stirred under H_2 for 72 h at 140 °C. A solid crystallized upon slow cooling. The product was filtered, washed with 3 × 5 mL of methanol, and dried in vacuo for 1 h. Yield: 2.00 g (81%) of a moderately air-sensitive solid containing **1** and 13% of **2**. Anal. Calcd for $C_{21}H_{47}ClOsP_2$ (587.24): C, 42.95; H, 8.07. Found: C, 42.95; H, 8.22. IR (Nujol and KBr): ν(OsH) 2207, 2225 cm^{-1}; ν(η^2-CH) 2633 cm^{-1}. ^{1}H NMR (−40 °C, CD_2Cl_2): δ −23.81 (dt, $^3J_{HH} = 18.3$ Hz, $^2J_{HP} = 10.3$ Hz, 1H, Os*H*), −18.80 (m, $^3J_{HH} = 6.0$ Hz, $^2J_{HP} = 10.3$ Hz, 1H, Os*H*). ^{1}H{^{31}P} NMR (−40 °C, CD_2Cl_2): δ 0.31 (m, 1H, α-C*H*), 1.17 (s, 18H, Bu^t), 1.27 (s, 18H, Bu^t), 1.23 (m, 2H, β-CH_2), 1.51 (ddd, $^2J_{HH} = 14.7$ Hz, $^3J_{HH} = 13.1$, 7.2 Hz, 2H, γ-CH_2), 2.12 (dd, $^2J_{HH} = 14.7$ Hz, $^3J_{HH} = 6.1$ Hz, 2H, γ-CH_2), 2.33 (ddd, $^2J_{HH} = 13.5$ Hz, $^3J_{HH} = 7.2$, 2.2 Hz, 2H, β-CH_2). ^{13}C{^{1}H} NMR (20 °C, CD_2Cl_2): δ 26.1 (vt, $^vJ = 11.2$ Hz, γ-*C*H_2), 29.4, 29.8 (vt, $^vJ = 2.7$ Hz, *C*H_3), 35.3 (vt, $^vJ = 10.1$ Hz, P*C*), 39.5 (vt, $^vJ = 9.0$ Hz, P*C*), 47.2 (vt, $^vJ = 6.6$ Hz, β-*C*H_2), 84.45 (t, $^2J_{CP} = 3.4$ Hz, α-*C*H). ^{31}P{^{1}H} NMR (20 °C, CD_2Cl_2): δ 80.5 (s, $^1J_{POs} = 202$ Hz).

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84.4) and shows a reduced $^1J_{C-H}$ coupling of 106 Hz, similar to $^1J_{C-H} = 104$ Hz for (η^2-CH)Ir in $IrH_2[CH(C_2H_4PBu^t_2)_2]$.[2g] We similarly assign an agostic structure to **1**. The IR spectrum of **1** shows an absorption at 2633 cm^{-1} due to the agostic ν_{C-H}. The Os−C3−H3a angle is reduced to 90.7(18)° in the crystal structure. This (η^2-CH)Os bonding is weak, and the Os−H3a distance is long, 2.33(3) Å.

NMR spectra of the hydrido carbene **2** show the characteristic resonances of OsH at δ −26.08 and Os=C at δ 280.5. The formation of **2** was also confirmed by a crystal structure determination (Figure 1).[10] The molecular geometry of **2** is square pyramidal. The Os=C distance is 1.911(3) Å: that is, shorter than the corresponding 1.997(5) Å bond in the related iridium carbene $IrCl[{=}C(C_2H_4PBu^t_2)_2]$.[2e]

To prepare Ru analogues, we reacted D^{t}BPP with $[RuCl_2(p\text{-cymene})]_2$ and obtained the two isomers **3** and **4** in a 1.5:98.5 ratio.[11] Limited NMR information available for **3** is consistent with the monohydride carbene structure shown in Scheme 2. The hydride resonance is observed at δ −21.16 (t, $^2J_{HP} = 17.9$), and the hydride-coupled ^{31}P NMR spectrum shows a doublet at δ 95.1.

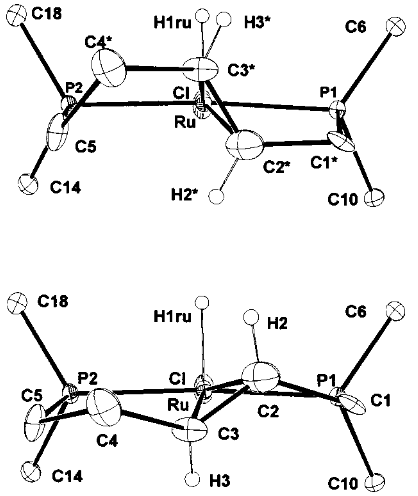
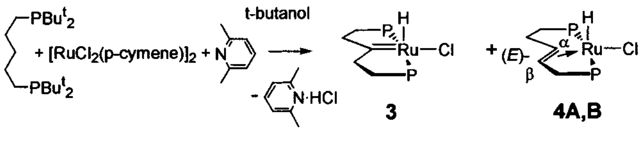


Figure 2. Partial structures of **4A** (bottom) and **4B** (top) with the ellipsoids set at the 30% probability level. Key parameters (distances in Å and angles in deg): Ru−C3 = 2.213(4), Ru−C3* = 2.132(8), Ru−C2 = 2.312(5), Ru−C2* = 2.140(10), C2−C3 = 1.404(6), C2*−C3* = 1.401(13), Ru−Cl1 = 2.4028(7), P1−Ru−P2 = 171.53(2), C3−Ru−Cl1 = 162.9(1), C3*−Ru−Cl1 = 166.8(2).

Scheme 2



In CD_2Cl_2, the major product **4** itself is a 1:1 mixture of isomers of $RuHCl[^tBu_2PCH_2CH_2((E)\text{-}CH{=}CH)CH_2PBu^t_2]$ (**4A**,**B**). Single-crystal X-ray analysis established the presence of **4A**,**B** in a 2:1 ratio in the solid state (Figure 2).[12] The two molecular structures differ only by the configuration of the *trans*-pent-2-ene chain: the α-CH−RuH fragment is anti in **4A** and syn in **4B**. The Ru−C distances vary greatly in **4A**,**B** (from 2.132 to 2.312 Å); however, the C=C bond lengths are the same at 1.401−1.404 Å. NMR data[11] for **4** are in full agreement with the X-ray structures and show no formation of a *Z* isomer in solution.[13]

Complexes **3** and **4** give the Ru(IV) dihydride $RuH_2Cl[CH(C_2H_4PBu^t_2)_2]$ (**5**) in CD_2Cl_2 under H_2 and $RuD_2Cl[CD(CD_2CH_2PBu^t_2)_2]$ under D_2. NMR data for **5** are indicative of a structure similar to that of **1**.[14] Evidence for weak agostic bonding in **5** is furnished by the

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(5) The dihydride **1** (1.55 g) was treated in 10 mL of refluxing *tert*-butyl alcohol for 5 h under nitrogen. The carbene product **2** crystallized upon cooling. The mother liquor was removed with a pipet, and the solid was rinsed with 2 × 3 mL of methanol and dried in vacuo for 1 h. Yield: 1.39 g (90%). Anal. Calcd for $C_{21}H_{45}ClOsP_2$ (585.22): C, 43.10; H, 7.75. Found: C, 43.11; H, 7.85. IR (Nujol): ν(OsH) 2211 cm^{-1}. ^1H NMR (C_6D_6): δ −24.75 (t, $^2J_{HP} = 14.6$ Hz, 1H, Os*H*). $^1H\{^{31}P\}$ NMR (C_6D_6): δ 0.00 (ddd, $^2J_{HH} = 19.5$ Hz, $^3J_{HH} = 5.4, 9.0$ Hz, 2H, β-CH_2), 0.95 (ddd, $^2J_{HH} = 19.5$ Hz, $^3J_{HH} = 5.9, 8.4$ Hz, 2H, β-CH_2), 1.26 (s, 18H, Bu^t), 1.33 (s, 18H, Bu^t), 1.70 (ddd, $^2J_{HH} = 14.5$ Hz, $^3J_{HH} = 5.9, 9.0$ Hz, 2H, γ-CH_2), 1.88 (ddd, $^2J_{HH} = 14.5$ Hz, $^3J_{HH} = 8.4, 5.4$ Hz, 2H, γ-CH_2). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 24.2 (vt, $^vJ = 10.7$ Hz, γ-*C*H_2), 29.8, 30.2 (vt, $^vJ = 2.7$ Hz, *C*H_3), 36.6 (vt, $^vJ = 9.5$ Hz, P*C*), 40.0 (vt, $^vJ = 8.9$ Hz, P*C*), 67.3 (vt, $^vJ = 9.3$ Hz, β-*C*H_2), 280.5 (t, $^2J_{CP} = 1.2$ Hz, *C*=Os). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 83.8 (s, $^1J_{POs} = 213$ Hz).

(6) Crystal data for **1**: $C_{21}H_{47}ClOsP_2$, dark green, monoclinic, $P2_1/c$, 0.14 × 0.14 × 0.08 mm, $a = 12.3848(2)$ Å, $b = 14.3125(2)$ Å, $c = 14.6526(3)$ Å, $\alpha = 90°$, $\beta = 106.4130(10)°$, $\gamma = 90°$, $V = 2491.44(7)$ Å^3, $Z = 4$, 150 K, $\lambda = 0.710\ 73$ Å, $2.85 = \theta = 27.48°$, 15 682 total reflections, 5639 independent reflections (R(int) = 0.033), R1($I > 2\sigma(I)$) = 0.0255, wR2(all data) = 0.0516.

(7) Oki, M. In *Applications of Dynamic NMR Spectroscopy to Organic Chemistry*; VCH: Deerfield Beach, FL, 1985; Chapter 1.

(8) Deuterated **1** was prepared from **2** in CD_2Cl_2 under D_2. ^1H and ^2H NMR spectra showed deuterium incorporation in the β-CH_2 (14% **D**), α-CH (85% **D**), and H_a and H_b sites (64% **D**). A second treatment of this solution under D_2 afforded $OsD_2[CD(CD_2CH_2PBu^t_2)_2]$. Deuteration caused pronounced isotope shifts of H_a (−90 °C): from δ −24.202 [CD−OsH$_2$] to −23.926 [CH−OsH$_2$] ($\Delta\delta = 0.276$) and from δ −24.157 [CD−OsHD] to −23.883 [CH−OsHD] ($\Delta\delta = 0.274$). In the ^{13}C NMR spectrum (20 °C), α-CD was shifted to δ 82.10 vs δ 84.45 for α-CH ($\Delta\delta = 2.35$). Agostic bonding of C−D might be weaker than that of C−H.

(9) Desrosiers, P. J.; Cai, L.; Lin, Z.; Richards, R.; Halpern, J. *J. Am. Chem. Soc.* **1991**, *113*, 3027.

(10) Crystal data for **2**: $C_{21}H_{45}ClOsP_2$, dark brown, monoclinic, $P2_1/c$, 0.20 × 0.20 × 0.20 mm, $a = 12.0114(3)$ Å, $b = 16.2190(5)$ Å, $c = 13.0071(4)$ Å, $\alpha = 90°$, $\beta = 104.1340(10)°$, $\gamma = 90°$, $V = 2457.24(12)$ Å^3, $Z = 4$, 150 K, $\lambda = 0.710\ 73$ Å, $2.94 = \theta = 27.51°$; 20 523 total reflections, 5622 independent reflections (R(int) = 0.034), R1($I > 2\sigma(I)$) = 0.0258, wR2(all data) = 0.0584.

(11) A mixture of $[RuCl_2(cymene)]_2$ (1.47 g, 4.80 mmol), D^{t}BPP (1.85 g, 5.13 mmol), and lutidine (0.53 g, 4.93 mmol) in *tert*-butyl alcohol was stirred for 5 h at 90 °C. The product crystallized overnight and was filtered, washed with 4 × 3 mL of methanol, and dried in vacuo for 3 h. Yield: 2.05 g (86%). The product can be exposed to air for hours without decomposition. Anal. Calcd for $C_{21}H_{45}ClRuP_2$ (496.06): C, 50.85; H, 9.14. Found: C, 50.76; H, 9.24. IR (Nujol): ν(RuH) 2098 cm^{-1}. Selected NMR data in CD_2Cl_2 are as follows. ^1H NMR: δ −28.06 (ddd, $^2J_{HP} = 21.6, 16.8$ Hz, $^3J_{HH} = 2.3$ Hz, 1H, RuH_A), −23.98 (ddd, $^2J_{HP} = 20.1, 14.5$ Hz, $^3J_{HH} = 2.6$ Hz, 1H, RuH_B). $^1H\{^{31}P\}$ NMR: δ 2.68 (m, 1H, β-CH_A), 2.83 (m, $^3J_{HH} = 9.6, 6.9, 3.9, 2.6$ Hz, 1H, β-CH_B), 3.77 (m, $^3J_{HH} = 9.6, 6.3, 1.8$ Hz, 1H, α-CH_B), 4.05 (m, $^3J_{HH} = 9.0, 6.0, 5.7, 2.7$ Hz, 1H, α-CH_A). $^{31}P\{^1H\}$ NMR: δ −23.0, 87.1 (d, $^2J_{PP} = 282$ Hz, isomer A), −7.2, 84.7 (d, $^2J_{PP} = 298$ Hz, isomer B). $^{13}C\{^1H\}$ NMR: δ 39.4 (d, $J_{CP} = 19.0$ Hz, β-*C*H_A), 43.9 (d, $J_{CP} = 15.6$ Hz, β-*C*H_B), 66.8 (dd, $J_{CP} = 1.9, 2.1$ Hz, α-*C*H_B), 77.8 (dd, $J_{CP} = 2.1, 1.0$ Hz, α-*C*H_A). NOE was observed between RuH and β-CH_A in **4A** and between RuH and α-CH_B in **4B**; these hydrogens showed no ^3J coupling. In contrast, α-CH_A and β-CH_B were coupled to RuH ($^3J = 2.3, 2.6$ Hz) and did not show an NOE with the hydride.

(12) Crystal data for **4**: $C_{21}H_{45}ClRuP_2$, dark red, monoclinic, $P2_1/c$, 0.14 × 0.26 × 0.30 mm, $a = 12.0212(2)$ Å, $b = 16.2095(2)$ Å, $c = 12.8917(2)$ Å, $\alpha = 90°$, $\beta = 103.291(7)°$, $\gamma = 90°$; $V = 2444.76(9)$ Å^3, $Z = 4$, 150 K, $\lambda = 0.710\ 73$ Å, $2.9 = \theta = 25.1°$, 19 070 total reflections, 4312 independent reflections (R(int) = 0.026), R1($I > 2\sigma(I)$) = 0.0298, wR2(all data) = 0.0757.

(13) (*E*)-olefin complexes have also been obtained in dehydrogenation reactions of diphosphinoalkanes on rhodium:[2c] Bennett, M. A.; Neumann, H. *Aust. J. Chem.* **1980**, *33*, 1251.

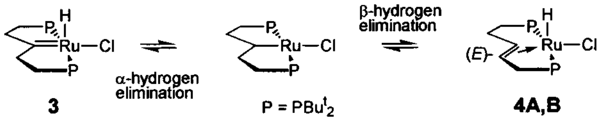
(14) NMR data for **5** are as follows. ^1H NMR (−20 °C, CD_2Cl_2): δ −16.80 (t, $^2J_{HP} = 13.5$ Hz, 2H, RuH_2), 1.17, 1.26 (vt, $^vJ = 6.5$ Hz, 36H, CH_3), 1.50 (m, 4H, γ, β-CH_2), 1.92 (m, 2H, γ-CH_2), 2.04 (m, 1H, α-CH), 2.43 (m, 2H, β-CH_2). $^{31}P\{^1H\}$ NMR (20 °C, CD_2Cl_2): δ 90.8. $^{13}C\{^1H\}$ NMR (−20 °C, CD_2Cl_2): δ 23.3 (vt, $^vJ = 8.6$ Hz, γ-*C*H_2), 28.7, 28.9 (*C*H_3), 34.3 (vt, $^vJ = 7.8$ Hz, P*C*), 35.9 (vt, $^vJ = 7.0$ Hz, P*C*), 44.0 (vt, $^vJ = 7.2$ Hz, β-*C*H_2), 86.9 (t, $^2J_{CP} = 1.3$ Hz, α-*C*H).

observation of $^{1}J_{CH} = 111$ Hz for CH−Ru. The exchange-averaged RuH_2 resonance undergoes decoalescence at −80 °C to give an AB system (δ −15.87, −18.10; $\Delta G^{\ddagger} = 8.1$ kcal/mol[7]) that shows a quantum exchange coupling[15] of 435 Hz between the hydrides at −110 °C. The T_1(min) value for the hydrides is 76.5 ms (−85 °C, 300 MHz), corresponding to an H···H distance of 1.55 Å,[9] if the phosphine contribution to the relaxation rate is 3.9 s^{-1} as in **1**.

Dihydride **5** is unstable under vacuum, unlike the analogous $RhHCl[CH(C_2H_4PBu^t{}_2)_2]$, and undergoes dehydrogenation to give **3** and **4** in the original 1.5:98.5 ratio. The loss of H_2 presumably results in formation of 14-electron $RuCl[CH(C_2H_4PBu^t{}_2)_2]$ that can give carbene and olefin complexes **3** and **4** by α- and β-hydrogen elimination, respectively (Scheme 3).

In summary, we have observed double C−H activation reactions of D^{t}BPP on osmium and ruthenium. The chemistry of these metals is qualitatively different, and the novel products show a thermodynamic preference for different hydrocarbon isomers: carbene for Os and olefin for Ru. New electronically unsaturated complexes are reactive species of interest for future synthetic, catalytic, and theoretical research.

Scheme 3



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Supporting Information Available: Tables of atomic coordinates, bond lengths and angles, and anisotropic thermal parameters for complexes **1**, **2**, and **4**. This material is available free of charge via Internet at http://pubs.acs.org.

OM020355M

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[15] (a) Heinekey, D. M.; Hinkle, A. S.; Close, J. D. *J. Am. Chem. Soc.* **1996**, *118*, 5353. (b) Sabo-Etienne, S.; Chaudret, B. *Chem. Rev.* **1998**, *98*, 2077.