Polyhedron 138 (2017) 133–139

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

Preparation of half-sandwich azine complexes of osmium

Gabriele Albertin [a,*], Stefano Antoniutti [a], Jesús Castro [b], Francesca Sibilla [a]

[a] Dipartimento di Scienze Molecolari e Nanosistemi, Università Ca' Foscari Venezia, Via Torino 155, 30172 Mestre Venezia, Italy
[b] Departamento de Química Inorgánica, Universidade de Vigo, Facultade de Química, Edificio de Ciencias Experimentais, 36310 Vigo (Galicia), Spain

ARTICLE INFO

Article history:
Received 10 July 2017
Accepted 14 September 2017
Available online 22 September 2017

Keywords:
Osmium
Half-sandwich
Azine
Synthesis
Metalated species

ABSTRACT

Half-sandwich azine complexes [OsCl(η^6-*p*-cymene){κ^1-[N=C(H)C_6H_4R1]–N=C(H)C_6H_4R1}{P(OR)$_3$}]BPh_4 (**1**, **2**) and [OsCl(η^6-*p*-cymene){κ^1-[N=C$(CH_3)_2$]N=C$(CH_3)_2$}{P(OR)$_3$}]BPh_4 (**3**, **4**) [R = Me (**1**, **3**), Et (**2**, **4**); R1 = H (**a**), 4-CH_3 (**b**), 2,6-$(CH_3)_2$ (**c**)] were prepared by allowing chloro compounds [$OsCl_2$(η^6-*p*-cymene){P(OR)$_3$}] to react first with one equivalent of AgOTf and then with azine. Instead, treatment of chloro compounds with acetone azine afforded hydrazone derivatives [OsCl(η^6-*p*-cymene){NH_2N=C$(CH_3)_2$}{P(OR)$_3$}]BPh_4 (**5**, **6**) [R = Me (**5**), Et (**6**)]. In solution, κ^1-azine complexes undergo metalation reaction, giving chelate derivatives [Os{κ^2-R1C_6H_3C(H)=N–N=C(H)C_6H_4R1}(η^6-*p*-cymene){P(OR)$_3$}]BPh_4 (**7**, **8**) [R = Me (**7**), Et (**8**); R1 = H (**a**), 4-CH_3 (**b**)]. The complexes were characterised by spectroscopy (IR, NMR) and X-ray crystal structure determination of [OsCl(η^6-*p*-cymene){κ^1-[N=C(H)Ph]–N=C(H)Ph}{P(OEt)$_3$}]BPh_4 (**2a**).

1. Introduction

The interaction of azine (Chart 1) with transition metal complexes has been studied in recent years [1–3] for the interesting reactions shown, involving C–H activation, C–C coupling and N–C cleavage, affording ketimido and five-membered metallacycle derivatives.

Cyclometalation of azine [4] involving C–Cl and C–F bond activation has been observed with cobalt, and N–N bond cleavage and N–N bond coupling were reported in Rh [2d] and Fe [2e] complexes. In addition, simple σ-coordination of azine on a metal centre through the N atoms was often observed [1,3,5,6] and a number of transition metal complexes have been reported. However, their coordination chemistry is still relatively unexplored when compared with the rich and various coordination chemistry of azo and diazo molecules such as imines, hydrazines and hydrazones [7].

We are interested in the chemistry of transition metals with azo ligands [8] such as hydrazine, diazene and diazoalkane and have recently reported the synthesis of monodentate aldazine and ketazine complexes of ruthenium [9] stabilised by half-sandwich fragments of the types [RuCl(η^6-*p*-cymene){κ^1-[N=C(H)R1]N=C(H)R1}L]BPh_4, [RuCl(η^6-*p*-cymene){κ^1-[N=C$(CH_3)_2$]-N=C$(CH_3)_2$}L]BPh_4 and [Ru(η^5-C_5Me_5){κ^1-[N=C(H)R1]N=C(H)R1}(PPh_3)L]BPh_4 (L = phosphine and phosphite; R1 = aryl). Now we have extended study to include osmium as central metal and found a new metalation reaction, affording five-membered metallacycle derivatives. The results on the synthesis of κ^1- and κ^2-azine complexes of osmium are reported here.

2. Experimental

2.1. General comments

All synthetic work was carried out in an appropriate atmosphere (Ar, N_2) using standard Schlenk techniques or a vacuum atmosphere dry-box. All solvents were dried over appropriate drying agents, degassed on a vacuum line, and distilled into vacuum–tight storage flasks. OsO_4 was a Pressure Chemical Co. (USA) product, used as received. Phosphites P(OMe)$_3$ and P(OEt)$_3$ were Aldrich products, purified by distillation. Azines were prepared following the known methods [10]. Other reagents were purchased from commercial sources in the highest available purity and used as received. Infrared spectra were recorded on Perkin-Elmer Spectrum One FT-IR spectrophotometer. NMR spectra (^{1}H, ^{13}C, ^{31}P) were obtained on Bruker AVANCE 300 or AVANCE III 400 spectrometers at temperatures between −80 and +30 °C, unless otherwise noted. ^{1}H and ^{13}C spectra are referenced to internal tetramethylsilane; ^{31}P{^{1}H} chemical shifts are reported with respect to 85% H_3PO_4, with downfield shifts considered positive. The COSY, HMQC and HMBC NMR experiments were performed using their standard programs. The iNMR software package [11] was used to treat NMR data. The conductivity of 10^{-3} mol dm^{-3}

* Corresponding author. Fax: +39 0412348594.
E-mail address: albertin@unive.it (G. Albertin).

https://doi.org/10.1016/j.poly.2017.09.023
0277-5387/

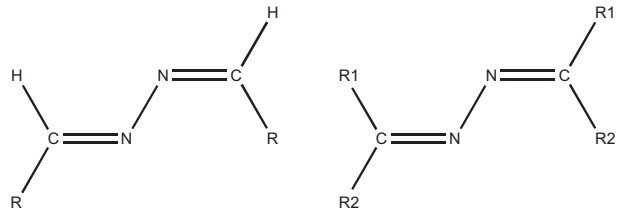

Chart 1. R, R1, R2 = alkyl or aryl.

solutions of the complexes in CH_3NO_2 at 25 °C were measured with a Radiometer CDM 83. Elemental analyses were determined in the Microanalytical Laboratory of the Dipartimento di Scienze del Farmaco of the University of Padua, Italy.

2.2. Synthesis of complexes

Compounds $[OsCl_2(\eta^6\text{-}p\text{-cymene})]_2$ and $[OsCl_2(\eta^6\text{-}p\text{-cymene})\{P(OR)_3\}]$ were prepared following the reported methods [8d,e,12].

2.3. $[OsCl(\eta^6\text{-}p\text{-cymene})\{\kappa^1\text{-}[N{=}C(H)C_6H_4R1]\text{–}N{=}C(H)C_6H_4R1\}\{P(OR)_3\}]BPh_4$ (**1, 2**) [R = Me (**1**), Et (**2**); R1 = H (**a**), 4-CH_3 (**b**), 2,6-$(CH_3)_2$ (**c**)]

In a 25-mL three-necked round-bottomed flask were placed 0.18 mmol of the appropriate complex $[OsCl_2(\eta^6\text{-}p\text{-cymene})\{P(OR)_3\}]$, an equimolar amount of AgOTf (0.18 mmol, 46.3 mg) and 5 mL of CH_2Cl_2. The reaction mixture was stirred in the dark for 24 h and then filtered to remove the AgCl formed. A slight excess of the appropriate azine $R1C_6H_4C(H){=}N\text{–}N{=}C(H)C_6H_4R1$ (0.20 mmol) in 3 mL of CH_2Cl_2 was added and the reaction mixture stirred for 4 h. The solvent was removed under reduced pressure to give an oil, which was triturated with ethanol (1 mL) containing an excess of $NaBPh_4$ (0.36 mmol, 123 mg). A yellow solid slowly separated out, which was filtered and crystallised from CH_2Cl_2 and EtOH. Yield: 145 mg (80%) for **1a**, 155 mg (82%) for **2a**, 150 mg (77%) for **2b**, 158 mg (79%) for **2c**.

1a: IR (KBr pellet): $\nu_{C=N}$ 1603 (m) cm^{-1}. ^1H NMR (CD_2Cl_2, 25 °C) δ: 8.63 (s, 1H, NN=CH), 7.83 (s, 1H, OsN=CH), 7.76–6.87 (m, 30H, Ph), 5.80, 5.76, 5.58, 5.56 (d, 4H, Ph *p*-cym), 3.72 (d, J_{PH} = 11.2 Hz, 9H, CH_3 phos), 2.76 (m, 1H, CH Pr^i), 2.17 (s, 3H, *p*-CH_3 *p*-cym), 1.27, 1.25 (d, J_{HH} = 6.9 Hz, 6H, CH_3 Pr^i). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ: 71.53 (s). Λ_M = 52.6 Ω^{-1} mol^{-1} cm^2. $C_{51}H_{55}BClN_2O_3OsP$ (1011.46): calcd. C 60.56, H 5.48, Cl 3.51, N 2.77; found C 60.38, H 5.55, Cl 3.38, N 2.84%.

2a: IR (KBr pellet): $\nu_{C=N}$ 1618 (m) cm^{-1}. ^1H NMR (CD_2Cl_2, 25 °C) δ: 8.65 (s, 1H, NN=CH), 7.88 (s, 1H, OsN=CH), 7.76–6.86 (m, 30H, Ph), 5.82, 5.79, 5.60, 5.53 (d, 4H, Ph *p*-cym), 4.08 (qnt, 6H, CH_2), 2.77 (m, 1H, CH Pr^i), 2.18 (s, 3H, *p*-CH_3 *p*-cym), 1.28 (d, J_{HH} = 7.0 Hz, 6H, CH_3 Pr^i), 1.25 (t, J_{HH} = 7.0 Hz, 9H, CH_3 phos). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ: 67.40 (s). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ: 164.21 (s, NN=CH), 161.22 (s, OsN=CH), 165–122 (m, Ph), 114.83 (d, C1 *p*-cym), 97.40 (d, C4 *p*-cym), 83.11, 82.51 (d, C3/C5 *p*-cym), 82.03, 76.15 (d, C2/C6 *p*-cym), 64.40 (d, CH_2), 31.08 (s, CH Pr^i), 22.56, 21.56 (s, CH_3 Pr^i), 18.48 (s, *p*-CH_3 *p*-cym), 16.32 (d, CH_3 phos) ppm. Λ_M = 51.4 Ω^{-1} mol^{-1} cm^2. $C_{54}H_{61}BClN_2O_3OsP$ (1053.54): calcd. C 61.56, H 5.84, Cl 3.37, N 2.66; found C 61.34, H 5.92, Cl 3.26, N 2.73%.

2b: IR (KBr pellet): $\nu_{C=N}$ 1619 (m) cm^{-1}. ^1H NMR (CD_2Cl_2, 25 °C) δ: 8.58 (s, 1H, NN=CH), 7.87 (s, 1H, OsN=CH), 7.71–6.87 (m, 28H, Ph), 5.80, 5.78, 5.57, 5.52 (d, 4H, Ph *p*-cym), 4.08 (qnt, 6H, CH_2), 2.75 (m, 1H, CH Pr^i), 2.47, 2.40 (s, 6H, CH_3 *p*-tol), 2.19 (s, 3H, *p*-CH_3 *p*-cym), 1.27 (d, J_{HH} = 6.8 Hz, 6H, CH_3 Pr^i), 1.25 (t, J_{HH} = 7.0 Hz, 9H, CH_3 phos). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ: 67.21 (s). Λ_M = 53.0 Ω^{-1} mol^{-1} cm^2. $C_{56}H_{65}BClN_2O_3OsP$ (1081.59): calcd. C 62.19, H 6.06, Cl 3.28, N 2.59; found C 62.01, H 6.13, Cl 3.17, N 2.68%.

2c: IR (KBr pellet): $\nu_{C=N}$ 1615 (m) cm^{-1}. ^1H NMR (CD_2Cl_2, 25 °C) δ: 8.96 (s, 1H, NN=CH), 7.83 (s, 1H, OsN=CH), 7.32–6.87 (m, 26H, Ph), 5.90, 5.76, 5.63, 5.54 (d, 4H, Ph *p*-cym), 4.16 (m, 6H, CH_2), 2.83 (m, 1H, CH Pr^i), 2.54, 2.30, 2.24 (s, 12H, CH_3 *o*-Me_2), 2.21 (s, 3H, *p*-CH_3 *p*-cym), 1.30 (t, J_{HH} = 7.0 Hz, 9H, CH_3 phos), 1.29, 1.24 (d, J_{HH} = 6.9 Hz, 6H, CH_3 Pr^i). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ: 65.20 (s). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ: 166.90 (s, NN=CH), 158.41 (s, OsN=CH), 165–122 (m, Ph), 115.01 (d, C1 *p*-cym), 98.33 (d, C4 *p*-cym), 82.89, 82.64 (d, C3/C5 *p*-cym), 81.36, 76.42 (d, C2/C6 *p*-cym), 65.04 (d, CH_2), 31.08 (s, CH Pr^i), 22.60, 20.44 (s, CH_3 Pr^i), 21.60, 21.48, 20.44 (s, CH_3 *o*-Me_2), 18.61 (s, *p*-CH_3 *p*-cym), 16.37 (d, CH_3 phos) ppm. Λ_M = 51.4 Ω^{-1} mol^{-1} cm^2. $C_{54}H_{61}BClN_2O_3OsP$ (1053.54): calcd. C 62.78, H 6.27, Cl 3.19, N 2.52; found C 62.54, H 6.36, Cl 3.10, N 2.61%.

2.4. $[OsCl(\eta^6\text{-}p\text{-cymene})\{\kappa^1\text{-}[N{=}C(CH_3)_2]\text{–}N{=}C(CH_3)_2\}\{P(OR)_3\}]BPh_4$ (**3, 4**) [R = Me (**3**), Et (**4**)]

These complexes were prepared exactly like the related aldazine complexes **1**, **2**, using acetone azine $(CH_3)_2C{=}N\text{–}N{=}C(CH_3)_2$ as a reagent. Yield: 127 mg (77%) for **3**, 129 mg (75%) for **4**.

3: IR (KBr pellet): $\nu_{C=N}$ 1635 (m) cm^{-1}. ^1H NMR (CD_2Cl_2, 25 °C) δ: 7.75–6.87 (m, 20H, Ph), 5.65, 5.63, 5.52, 5.50 (d, 4H, Ph *p*-cym), 3.73 (d, J_{PH} = 11.2 Hz, 9H, CH_3 phos), 2.78 (m, 1H, CH Pr^i), 2.37, 2.30 (s, 6H, N=CCH_3), 2.21 (s, 3H, *p*-CH_3 *p*-cym), 2.06 (s, 6H, free N=CCH_3), 1.23 (d, J_{HH} = 6.9 Hz, 6H, CH_3 Pr^i). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ: 73.84 (s). Λ_M = 52.4 Ω^{-1} mol^{-1} cm^2. $C_{43}H_{55}BClN_2O_3OsP$ (915.38): calcd. C 56.42, H 6.06, Cl 3.87, N 3.06; found C 56.27, H 6.13, Cl 3.99, N 3.01%.

4: IR (KBr pellet): $\nu_{C=N}$ 1639 (m) cm^{-1}. ^1H NMR (CD_2Cl_2, 25 °C) δ: 7.31–6.86 (m, 20H, Ph), 5.83, 5.62, 5.27, 5.25 (d, 4H, Ph *p*-cym), 4.08 (m, 6H, CH_2), 2.73 (m, 1H, CH Pr^i), 2.30, 2.23 (s, 6H, N=CCH_3), 2.10 (s, 3H, *p*-CH_3 *p*-cym), 2.07 (s, 6H, free N=CCH_3), 1.32, 1.23 (d, 6H, CH_3 Pr^i), 1.30 (t, J_{HH} = 7.0 Hz, 9H, CH_3 phos). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ: 63.35 (s). Λ_M = 52.5 Ω^{-1} mol^{-1} cm^2. $C_{46}H_{61}BClN_2O_3OsP$ (957.46): calcd. C 57.70, H 6.42, Cl 3.70, N 2.93; found C 57.53, H 6.29, Cl 3.58, N 3.00%.

2.5. $[OsCl(\eta^6\text{-}p\text{-cymene})\{NH_2N{=}C(CH_3)_2\}\{P(OR)_3\}]BPh_4$ (**5, 6**) [R = Me (**5**), Et (**6**)]

In a 25-mL three-necked round-bottomed flask were placed 0.1 mmol of the appropriate complex $[OsCl_2(\eta^6\text{-}p\text{-cymene})\{P(OR)_3\}]$, an excess of $NaBPh_4$ (0.36 mmol, 123 mg), 10 mL of EtOH and 5 mL of CH_2Cl_2. An excess of acetone azine $(CH_3)_2C{=}N\text{–}N{=}C(CH_3)_2$ (0.54 mmol, 72 μL) was added to the resulting solution, which was stirred for 24 h. The solvent was removed under reduced pressure to give an oil, which was triturated with ethanol (2 mL). A yellow solid slowly separated out, which was filtered and crystallised from CH_2Cl_2 and EtOH. Yield: 58 mg (66%) for **5**, 56 mg (61%) for **6**.

5: IR (KBr pellet): ν_{NH} 3263, 3206 (m); δ_{NH2} 1647 (m) cm^{-1}. ^1H NMR (CD_2Cl_2, 25 °C) δ: 6.66, 6.23 (d br, 2H, NH_2), 7.35–6.87 (m, 20H, Ph), 5.82, 5.54, 5.30, 4.99 (d, 4H, Ph *p*-cym), 3.53 (d, J_{PH} = 11.2 Hz, 9H, CH_3 phos), 2.46 (m, 1H, CH Pr^i), 2.23, 1.98 (s, 6H, $=C(CH_3)_2$), 2.20 (s, 3H, *p*-CH_3 *p*-cym), 1.14, 1.08 (d, J_{HH} = 6.9 Hz, 6H, CH_3 Pr^i). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ: 79.40 (s). Λ_M = 54.7 Ω^{-1} mol^{-1} cm^2. $C_{40}H_{51}BClN_2O_3OsP$ (875.31): calcd. C 54.89, H 5.87, Cl 4.05, N 3.20; found C 54.66, H 5.82, Cl 4.14, N 3.07%.

6: IR (KBr pellet): ν_{NH} 3255, 3201 (m); $\nu_{C=N}$ 1643 (m) cm^{-1}. ^1H NMR (CD_2Cl_2, 25 °C) δ: 6.69, 6.37 (d br, 2H, NH_2), 7.33–6.87 (m, 20H, Ph), 5.62, 5.59, 5.53, 5.35 (d, 4H, Ph *p*-cym), 4.11 (m, 6H, CH_2), 2.73 (m, 1H, CH Pr^i), 2.15 (s, 3H, *p*-CH_3 *p*-cym), 2.10, 1.92