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Reactivity with aryldiazonium cations of hydrazine complexes of ruthenium and osmium

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ABSTRACT

The bis(amine) derivative $[Os(NH_3)_2L_4](BPh_4)_2$ (**1**) formed when bis(hydrazine) complex $[Os(NH_2NH_2)_2L_4](BPh_4)_2$ was reacted with aryldiazonium salt $[ArN_2](BF_4)$ in CH_2Cl_2 [L = P(OEt)$_3$; Ar = 4-$CH_3C_6H_4$]. Instead, reaction in $(CH_3)_2CO$ afforded the bis(hydrazone) derivative $[Os\{NH_2N{=}C(CH_3)_2\}_2L_4](BPh_4)_2$ (**2**). The chloro-amine derivative $[RuCl(NH_3)L_4](BPh_4)$ (**3**) formed by reaction with $[ArN_2](BF_4)$ in CH_2Cl_2 of complex $[Ru(NH_2NH_2)_2L_4](BPh_4)_2$, whereas amine-carbonyl derivative $[Ru(NH_3)(CO)L_4](BPh_4)_2$ (**4**) was obtained from $[Ru(CO)(NH_2NH_2)L_4](BPh_4)_2$. Treatment of $[Ru(NH_2NH_2)_2L_4](BPh_4)_2$ with $[ArN_2](BF_4)$ in $(CH_3)_2CO$ afforded the bis(hydrazone) derivative $[Ru\{NH_2N{=}C(CH_3)_2\}_2L_4](BPh_4)_2$ (**5**). The complexes were characterised by IR and NMR spectroscopy and by X-ray crystal structure determination of complex **2**.

1. Introduction

The chemistry of hydrazine complexes of transition metals has developed extensively in recent years [1,2], mainly due to their close relationship with the dinitrogen fixation process [3,4]. Many hydrazine complexes have thus been synthesised and several reactivity studies have been reported [1,2]. Among the former, oxidation of coordinated NH_2NH_2 to give stable 1,2-diazene derivatives [M]–NH=NH [3] and reduction to ammonia are the most interesting [4,5]. Deprotonation reactions with strong bases, affording both 1,2-diazene and dinitrogen derivatives [2], as well as the reaction with ketones yielding hydrazone derivatives, have also received attention [6]. However, although several reactivity studies have been reported, none of them concerns the reaction of coordinated hydrazine with aryldiazonium cations $[ArN_2]^+$.

We are interested in the chemistry of diazo complexes of transition metals and have reported the synthesis and reactivity of mono- and bis(hydrazine) complexes of the iron triad [7] of the type $[M(CO)(NH_2NH_2)L_4](BPh_4)_2$ and $[M(NH_2NH_2)_2L_4](BPh_4)_2$ (L = phosphites). Oxidation with $Pb(OAc)_4$ at low temperature of these complexes was extensively studied, affording new examples of mono- and bis(1,2-diazene) derivatives. We have now extended these studies to include reactivity with aryldiazonium salts of mono- and bis(hydrazine) complexes. This paper reports the results of these investigations.

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. $RuCl_3{\cdot}3H_2O$ and OsO_4 were Pressure Chemical Co. (USA) products, used as received. Triethylphosphite P(OEt)$_3$ was an Aldrich product, purified by distillation. Hydrazine NH_2NH_2 was prepared by decomposition of hydrazine cyanurate (Fluka) following the reported method [8]. Diazonium salt $[4\text{-}CH_3C_6H_4N_2](BF_4)$ was obtained in the usual way [9]. 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 (^1H, ^{31}P) were obtained on AC200 or AVANCE 300 Bruker spectrometers at temperatures between −80 and +30 °C, unless otherwise noted. ^1H spectra are referenced to internal tetramethylsilane; $^{31}P\{^1H\}$ 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 [10] was used to treat NMR data. The conductivity of 10^{-3} mol dm^{-3} solutions of the complexes in CH$_3$-

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NO_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 $[M(NH_2NH_2)_2\{P(OEt)_3\}_4](BPh_4)_2$ and $[M(CO)(NH_2NH_2)\{P(OEt)_3\}_4](BPh_4)_2$ (M = Ru, Os) were prepared following the methods previously reported [7a,7e].

2.3. $[Os(NH_3)_2\{P(OEt)_3\}_4](BPh_4)_2$ (**1**)

In a 25-mL three-necked round-bottomed flask were placed 100 mg (0.064 mmol) of $[Os(NH_2NH_2)_2\{P(OEt)_3\}_4](BPh_4)_2$, an excess of $[4\text{-}CH_3C_6H_4N_2](BF_4)$ (29 mg, 0.14 mmol) and 10 mL of dichloromethane. The reaction mixture was stirred at room temperature for 1 h and then the solvent was removed under reduced pressure leaving an oil, which was triturated with ethanol (2 mL) containing $NaBPh_4$ (68 mg, 0.2 mmol). A white solid slowly separated out, which was filtered and crystallised from CH_2Cl_2 and EtOH. Yield: 80 mg (82%). IR (KBr pellet): ν_{NH} = 3302, 3285 (w) cm^{-1}. ^1H NMR (CD_2Cl_2, 25 °C): δ = 7.33–6.89 (m, 40 H, Ph), 5.46 (s br, 6 H, NH_3), 4.14, 4.01 (m, 24 H, CH_2), 1.34, 1.29 (t, 36 H, CH_3) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C): δ = A_2B_2 spin syst, δ_A 84.91, δ_B 76.99 ppm, J_{AB} = 43.7 Hz. Λ_M = 128.6 Ω^{-1} mol^{-1} cm^2. *Anal.* Calc. for $C_{72}H_{106}B_2N_2O_{12}OsP_4$ (1527.37): C, 56.62, H, 7.00; N, 1.83. Found: C, 56.84; H, 6.89; N, 1.75%.

2.4. $[Os\{NH_2N{=}C(CH_3)_2\}_2\{P(OEt)_3\}_4](BPh_4)_2$ (**2**)

In a 25-mL three-necked round-bottomed flask were placed 100 mg (0.064 mmol) of $[Os(NH_2NH_2)_2\{P(OEt)_3\}_4](BPh_4)_2$, a small amount of $[4\text{-}CH_3C_6H_4N_2](BF_4)$ (4 mg, 0.02 mmol) and 10 mL of acetone. The reaction mixture was stirred at room temperature for 1 h and then the solvent was removed under reduced pressure leaving an oil, which was triturated with ethanol (2 mL) containing $NaBPh_4$ (68 mg, 0.2 mmol). The white solid, which slowly separated out, was filtered and crystallised from CH_2Cl_2 and EtOH. Yield: 90 mg (86%). IR (KBr pellet): ν_{NH} = 3306, 3233 (w) cm^{-1}. ^1H NMR (CD_2Cl_2, 25 °C): δ = 7.33–6.89 (m, 40 H, Ph), 6.34 (s br, 4 H, NH_2), 4.11, 4.03 (m, 24 H, CH_2), 2.00, 1.90 (s, 12 H, CH_3 propyl), 1.32, 1.30 (t, 36 H, CH_3 phos) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C): δ = A_2B_2, δ_A 84.95, δ_B 77.75 ppm, J_{AB} = 42.6 Hz. Λ_M = 124.4 Ω^{-1} mol^{-1} cm^2. *Anal.* Calc. for $C_{78}H_{116}B_2N_4O_{12}OsP_4$ (1637.52): C, 57.21; H, 7.14; N, 3.42. Found: C, 57.04; H, 7.20; N, 3.30%.

2.5. $[RuCl(NH_3)\{P(OEt)_3\}_4](BPh_4)$ (**3**)

In a 25-mL three-necked round-bottomed flask were placed 100 mg (0.068 mmol) of $[Ru(NH_2NH_2)_2\{P(OEt)_3\}_4](BPh_4)_2$, an excess of the aryldiazonium salt $[4\text{-}CH_3C_6H_4N_2](BF_4)$ (31 mg, 0.15 mmol) and 10 mL of dichloromethane. The reaction mixture was stirred at room temperature for 2 h and then the solvent was removed under reduced pressure to give an oil, which was triturated with ethanol (2 mL) containing an excess of $NaBPh_4$ (34 mg, 0.1 mmol). A white solid slowly separated out, which was filtered and crystallised from CH_2Cl_2 and EtOH. Yield: 58 mg (75%). IR (KBr pellet): ν_{NH} = 3288 (w), 3216 (m) cm^{-1}. ^1H NMR (CD_2Cl_2, 25 °C): δ = 7.32–6.88 (m, 20 H, Ph), 5.04 (s br, 3 H, NH_3), 4.13, 3.83 (qnt, 24 H, CH_2), 1.31, 1.17, 1.15 (t, 36 H, CH_3) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C): δ = AB_2C spin syst, δ_A 133.15, δ_B 127.5, δ_C 120.6 ppm, J_{AB} = 70.5, J_{AC} = 62.7, J_{BC} = 59.6 Hz. Λ_M = 53.6 Ω^{-1} mol^{-1} cm^2. *Anal.* Calc. for $C_{48}H_{83}BClNO_{12}P_4Ru$ (1137.40): C, 50.69; H, 7.36; Cl, 3.12; N, 1.23. Found: C, 50.51; H, 7.44; Cl, 3.25; N, 1.16%.

2.6. $[Ru(NH_3)(CO)\{P(OEt)_3\}_4](BPh_4)_2$ (**4**)

In a 25-mL three-necked round-bottomed flask were placed 100 mg (0.068 mmol) of $[Ru(CO)(NH_2NH_2)\{P(OEt)_3\}_4](BPh_4)_2$, an excess of the aryldiazonium salt $[4\text{-}CH_3C_6H_4N_2](BF_4)$ (17 mg, 0.082 mmol) and 10 mL of dichloromethane. The reaction mixture was stirred at room temperature for 4 h and then the solvent was removed under reduced pressure to give an oil, which was triturated with ethanol (2 mL) containing an excess of $NaBPh_4$ (34 mg, 0.1 mmol). A white solid slowly separated out, which was filtered and crystallised from CH_2Cl_2 and EtOH. Yield: 64 mg (65%). IR (KBr pellet): ν_{NH} = 3313, 3241 (w); ν_{CO} = 2086 (s) cm^{-1}. ^1H NMR (CD_2Cl_2, 25 °C): δ = 7.50–6.85 (m, 40 H, Ph), 5.64 (s br, 3 H, NH_3), 4.28, 4.00 (m, 24 H, CH_2), 1.39, 1.35, 1.27 (t, 36 H, CH_3) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C): δ = AB_2C spin syst, δ_A 124.4, δ_B 114.6, ν_C 110.8, J_{AB} = 52.7, J_{AC} = 55.8, J_{BC} = 66.7 Hz. Λ_M = 122.1 Ω^{-1} mol^{-1} cm^2. Anal. Calc. for $C_{73}H_{103}B_2NO_{13}P_4Ru$ (1449.18): C, 60.50; H, 7.16; N, 0.97. Found: C, 60.69; H, 7.22; N, 0.89%.

2.7. $[Ru\{NH_2N{=}C(CH_3)_2\}_2\{P(OEt)_3\}_4](BPh_4)_2$ (**5**)

In a 25-mL three-necked round-bottomed flask were placed 100 mg (0.068 mmol) of $[Ru(NH_2NH_2)_2\{P(OEt)_3\}_4](BPh_4)_2$, a small amount of $[4\text{-}CH_3C_6H_4N_2](BF_4)$ (4 mg, 0.02 mmol) and 10 mL of acetone. The reaction mixture was stirred at 0 °C for 4 h and then the solvent was removed under reduced pressure leaving an oil, which was triturated with ethanol (2 mL) containing $NaBPh_4$ (68 mg, 0.2 mmol). A white solid slowly separated out, which was filtered and crystallised from CH_2Cl_2 and EtOH. Yield: 57 mg (54%). IR (KBr pellet): ν_{NH} = 3315, 3253 (w) cm^{-1}. ^1H NMR (CD_2Cl_2, 25 °C): δ = 7.34–6.89 (m, 40 H, Ph), 5.59 (s br, 4 H, NH_2), 4.08 (m, 24 H, CH_2), 2.03, 1.94 (s, 12 H, CH_3 propyl), 1.35, 1.33 (t, 36 H, CH_3 phos) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C): δ = A_2B_2 spin syst, δ_A 131.4, δ_B 1.18 ppm, J_{AB} = 31.6 Hz. Λ_M = 129.5 Ω^{-1} mol^{-1} cm^2. *Anal.* Calc. for $C_{78}H_{116}B_2N_4O_{12}P_4Ru$ (1548.36): C, 60.50; H, 7.55; N, 3.62. Found: C, 60.31; H, 7.67, N, 3.50%.

2.8. X-ray data collection and refinement of $[Os\{NH_2N{=}C(CH_3)_2\}_2\{P(OEt)_3\}_4](BPh_4)_2$ (**2**)

Crystallographic data were collected on a Bruker Smart 1000 CCD diffractometer at CACTI (Universidade de Vigo) using graphite monochromated Mo K(α) radiation (λ = 0.71073 Å) and were corrected for Lorentz and polarisation effects. The software SMART [11] was used for collecting frames of data, indexing reflections, and the determination of lattice parameters, SAINT [12] for integration of intensity of reflections and scaling, and SADABS [13] for empirical absorption correction.

The crystallographic treatment was performed with the Oscail program [14]. The structure was solved by direct methods and refined by a full-matrix least-squares based on F^2 [15]. Most non-hydrogen atoms were refined with anisotropic displacement parameters, but the low quality of the data [*R*(int) = 0.1443 *R*(sigma) = 0.2069] did not allow anisotropic refinement for all of them, so atoms labelled as N(21) and C(15) [the latter belonging to a methoxy group of one phosphite] were refined isotropically. It is worth noting that highest difference peak is found at 1.05 Å from Os atom on the P(1)–Os bond [*trans* to N(21)–Os bond]. We thought that any disorder could justify this electronic density, and *trans* ligands are probably implied in an occupancy disorder, but the low quality of data did not allow to check this. Hydrogen atoms were included in idealised positions and refined with isotropic displacement parameters. Details of crystal data and structural refinement are given in Table 1.