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Ruthenium and rhodium nitrosyl complexes containing dichalcogenoimidodiphosphinate ligands

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Abstract

Interaction of $[Ru(NO)Cl_3(PPh_3)_2]$ with $K[N(R_2PS)_2]$ in refluxing *N*,*N*-dimethylformamide afforded *trans*-$[Ru(NO)Cl\{N(R_2PS)_2\}_2]$ (R = Ph (**1**), Pr^i (**2**)). Reaction of $[Ru(NO)Cl_3(PPh_3)_2]$ with $K[N(Ph_2PSe)_2]$ led to formation of a mixture of *trans*-$[Ru(NO)Cl\{N(Ph_2PSe)_2\}_2]$ (**3**) and *trans*-$[Ru(NO)Cl\{N(Ph_2PSe)_2\}\{Ph_2P(Se)NPPh_2\}]$ (**4**). Reaction of $Ru(NO)Cl_3 \cdot xH_2O$ with $K[N(Ph_2PO)_2]$ afforded *cis*-$[Ru(NO)(Cl)\{N(Ph_2PO)_2\}_2]$ (**5**). Treatment of $[Rh(NO)Cl_2(PPh_3)_2]$ with $K[N(R_2PQ)_2]$ gave $Rh(NO)\{N(R_2PQ)_2\}_2]$ (R = Ph, Q = S (**6**) or Se (**7**); R = Pr^i, Q = S (**8**) or Se (**9**)). Protonation of **8** with HBF_4 led to formation of *trans*-$[Rh(NO)Cl\{HN(Pr^i_2PS)_2\}_2][BF_4]_2$ (**10**). X-ray diffraction studies revealed that the nitrosyl ligands in **2** and **4** are linear, whereas that in **9** is bent with the Rh–N–O bond angle of 125.7(3)°.

Keywords: Ruthenium; Rhodium; Nitrosyl; Chalcogen ligands; Crystal structures

1. Introduction

Nitrosyl is a versatile ligand for coordination and organometallic compounds [1–5]. The chemistry of metal nitrosyl complexes has become a focus of intensive research recently [6] due in part to the important roles of nitric oxide in biological systems [7]. In this connection, the study of metal nitrosyls that can release NO under photochemical conditions has attracted much attention [8,9]. Ru nitrosyls appear as promising candidates for NO generation because they are photolabile but thermally stable under physiological conditions. Of note, Prakash and coworkers synthesized a Ru nitrosyl compound with a polydentate amino-thiolate ligand that can release NO upon irradiation with visible light [10]. This prompts us to explore the chemistry of Ru nitrosyl complexes in sulfur-rich ligand environments.

Dichalcogenoimidodiphosphinates, $[N(R_2PQ)_2]^-$ (R = aryl, alkyl; Q = S, Se) (Scheme 1), which have been recognized as chalcogen analogues of acetylacetonate, can form stable complexes with a range of main group and transition metal ions [11–15]. Owing to their electron-donating ability and steric bulk, $[N(R_2PQ)_2]^-$ can stabilize electron-rich, unsaturated metal compounds. For example, we have synthesized the 16-electron Ru(II) complexes $[Ru\{N(R_2PQ)_2\}_2(PPh_3)]$ that can bind to reactive species such as sulfur monoxide [16] and diazene [17]. Although $Ru\{N(Ph_2PQ)_2\}$ complexes with π acid ligands such as CO [16] are known, analogous compounds containing nitrosyl have not been synthesized. In this paper, we describe the synthesis and crystal structures of Ru nitrosyl complexes supported by $[N(R_2PQ)_2]^-$. Analogous Rh compounds containing bent nitrosyl ligands have also been prepared.

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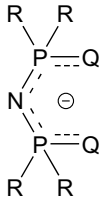

R = aryl, alkyl
Q = O, S, Se

Scheme 1.

2. Experimental

All manipulations were carried out under nitrogen by standard Schlenk techniques unless otherwise stated. Solvents were purified, distilled and degassed prior to use. NMR spectra were recorded on a Varian Mercury 300 spectrometer operating at 300, 121.5, and 282.5 MHz for ^{1}H, ^{31}P, and ^{19}F, respectively. Chemical shifts (δ, ppm) were reported with reference to $SiMe_4$ (^{1}H), H_3PO_4 (^{31}P), and $CF_3C_6H_5$ (^{19}F). Infrared spectra (KBr) were recorded on a Perkin–Elmer 16 PC FT-IR spectrophotometer. Elemental analyses were performed by Medac Ltd, Surrey, UK. The ligands $K[N(R_2PQ)_2]$ (R = Ph, Q = O, S, or Se; R = Pr^i, Q = S or Se) [18–21] and $[Ru(NO)Cl_3(PPh_3)_2]$ [22] and $[Rh(NO)Cl_2(PPh_3)_2]$ [23] were prepared according to literature methods. $Ru(NO)Cl_3 \cdot xH_2O$ was purchased from Strem Ltd and used as received.

2.1. Preparation of trans-[Ru(NO)(Cl){N(R$_2$PS)$_2$}$_2$] (R = Ph (1), Pr^i (2))

A suspension of $[Ru(NO)Cl_3(PPh_3)_2]$ (200 mg, 0.26 mmol) and 2 equiv. of $K[N(Ph_2PS)_2]$ (256 mg, 0.53 mmol) in dmf (20 ml) was heated at reflux for 2–3 h, during which the color changed from dark green to orange. The solvent was pumped off, and the residue was washed with Et_2O and then extracted with CH_2Cl_2. Recrystallization from CH_2Cl_2–Et_2O–hexane afforded orange crystals.

Compound **1**: Yield: 83 mg (30%). *Anal.* Calc. for $C_{48}H_{40}ClN_3OP_4RuS_4 \cdot CH_2Cl_2$: C, 51.2; H, 3.7; N, 3.7. Found: C, 51.1; H, 3.9; N, 3.5%. ^{1}H NMR ($CDCl_3$): δ 6.94–7.96 (m, C_6H_5). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ 38.20 (s). IR (KBr, cm^{-1}): 1834 [ν(N≡O)].

Compound **2**: Yield: 28 mg (42%). ^{1}H NMR ($CDCl_3$): δ 2.46–2.60 (m, 4H, C*H*(CH_3)$_2$), 2.10–2.23 (m, 4H, C*H*(CH_3)$_2$), 1.21–1.34 (m, 48H, CH(C*H*$_3$)$_2$). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ 60.84 (s). IR (KBr, cm^{-1}): 1841, 1826 [ν(N≡O)].

2.2. Preparations of trans-[Ru(NO)(Cl){N(Ph$_2$PSe)$_2$}$_2$] (3) and trans-[Ru(NO)(Cl){N(Ph$_2$PSe)$_2$}{Ph$_2$P(Se)NPPh$_2$}] (4)

A mixture of $[Ru(NO)Cl_3(PPh_3)_2]$ (200 mg, 0.26 mmol) and 2 equiv. of $K[N(Ph_2PSe)_2]$ (305 mg, 0.53 mmol) was heated in dmf (20 ml) at reflux for 3 h, during which the color changed from dark green to orange. The solvent was pumped off, and the residue was purified by column chromatography (silica gel) using CH_2Cl_2–hexane (1:1) as eluant. Complexes **3** and **4** were isolated as orange and reddish orange crystals, respectively.

Compound **3**: $R_f = 0.11$. Yield: 125 mg (38%). *Anal.* Calc. for $C_{48}H_{40}ClN_3OP_4RuSe_4 \cdot CH_2Cl_2$: C, 44.1, H, 3.2; N, 3.2. Found: 44.5; H, 3.1; N, 3.1%. ^{1}H NMR ($CDCl_3$): δ 7.20–7.94 (m, 40H, C_6H_5). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ 28.98 (s). IR (KBr, cm^{-1}): 1834 [ν(N≡O)].

Compound **4**: $R_f = 0.23$. Yield: 40 mg (13%). *Anal.* Calc. for $C_{48}H_{40}ClN_3OP_4RuSe_3 \cdot 1.5CH_2Cl_2$: 45.8; H, 3.3; N, 3.2. Found: C, 45.9; H, 3.3; N, 3.4%. ^{1}H NMR ($CDCl_3$): δ 6.89–8.10 (m, 40H, C_6H_5). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ 71.49 (ddd, $J_{PP} = 40.0$ Hz, $J_{PP} = 9.8$ Hz, $J_{PP} = 6.2$ Hz, PPh_2), 55.66 (d, $J_{PP} = 40.0$ Hz, P(Se)Ph_2 *trans* to PPh_2), 31.88 (dd, $J_{PP} = 3.5$ Hz, $J_{PP} = 9.8$ Hz), 26.91 (dd, $J_{PP} = 3.5$ Hz, $J_{PP} = 6.2$ Hz). IR (KBr, cm^{-1}): 1837 [ν(N≡O)].

2.3. Preparation of cis-[Ru(NO)Cl{N(Ph$_2$PO)$_2$}$_2$] (5)

A suspension of $Ru(NO)Cl_3 \cdot xH_2O$ (25 mg, 0.098 mmol) and 2 equiv. of $K[N(Ph_2PO)_2]$ (89 mg, 0.20 mmol) in acetone (15 ml) was heated at reflux for overnight. The solvent was removed, and the residue was extracted with CH_2Cl_2. Recrystallization from CH_2Cl_2–Et_2O–hexane afforded pale reddish brown crystals. Yield: 47 mg (48%). *Anal.* Calc. for $C_{48}H_{40}ClN_3O_5P_4Ru \cdot CH_2Cl_2$: C, 54.3; H, 3.9; N, 3.9. Found: C, 54.1; 3.9; N, 3.8%. ^{1}H NMR ($CDCl_3$): δ 6.85–7.93 (m, 40H, C_6H_5). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ 38.94 (d, $J_{PP} = 4.0$ Hz), 34.74 (d, $J_{PP} = 3.3$ Hz), 34.64 (d, $J_{PP} = 3.7$ Hz), 31.52 (d, $J_{PP} = 3.7$ Hz). IR (KBr, cm^{-1}): 1863 [ν(N≡O)].

2.4. Preparation of [Rh(NO){N(Ph$_2$PQ)$_2$}$_2$] (R = Ph, Q = S (6) or Se (7); R = Pr^i, Q = S (8))

A mixture of $[Rh(NO)Cl_2(PPh_3)_2]$ (50 mg, 0.069 mmol) and $K[N(Ph_2PQ)_2]$ (0.14 mmol) in THF (10 ml) was heated at reflux for 1 h. The solvent was pumped off and the residue was washed with hexane. Recrystallization from CH_2Cl_2–hexane (**6** and **7**) or Et_2O–hexane (**8**) afforded red crystals.

Compound **6**: Yield: 45 mg (63%). *Anal.* Calc. for $C_{48}H_{40}N_3OP_4RhS_4$: C, 56.0; H, 3.9; N, 4.1. Found: C, 55.7; H, 3.9; N, 3.0%. ^{1}H NMR ($CDCl_3$): δ 7.77–7.84 (m, 16H, C_6H_5), δ 7.26–7.37 (m, 24H, C_6H_5). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ 37.85 (d, $J_{RhP} = 3.5$ Hz). IR (KBr, cm^{-1}): 1655 [ν(N≡O)].

Compound **7**: Yield: 46 mg (65%). *Anal.* Calc. for $C_{48}H_{40}N_3OP_4RhSe_4$: C, 47.4; H, 3.3; N, 3.5. Found: C, 47.4; H, 3.3; N, 3.4%. ^{1}H NMR ($CDCl_3$): δ 7.77–7.83 (m, 16H, C_6H_5), 7.26–7.39 (m, 24H, C_6H_5). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ 27.97 (d, $J_{RhP} = 4.1$ Hz). IR (KBr, cm^{-1}): 1629 [ν(N≡O)].