

## Iridium and rhodium complexes containing dichalcogenoimidodiphosphinato ligands

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Dedicated to Professor Brain R. James on the occasion of his 70th birthday.

### Abstract

Treatment of  $[MCl(CO)(PPh_3)_2]$  with  $K[N(R_2PQ)_2]$  afforded  $[M\{N(Ph_2PQ)_2\}(CO)(PPh_3)]$  ( $M = Ir, Rh$ ;  $Q = S, Se$ ). The IR C=O stretching frequencies for  $[M(CO)(PPh_3)\{N(Ph_2PQ)_2\}]$  were found to decrease in the order  $S > Se$ . Treatment of  $[M(COD)Cl]_2$  with  $K[N(Ph_2PQ)_2]$  afforded  $[M(COD)\{N(Ph_2PQ)_2\}]$  ( $COD = 1,5\text{-cyclooctadiene}$ ;  $M = Ir, Rh$ ;  $Q = S, Se$ ). Treatment of  $[Ir(ol)_2Cl]$  with  $K[N(Pr^i_2PQ)_2]$  afforded  $[Ir(ol)_2\{N(Pr^i_2PQ)_2\}]_2$  ( $ol = \text{cyclooctene COE, } C_2H_4$ ;  $Q = S, Se$ ). Oxidative addition of  $[Ir(CO)(PPh_3)\{N(Ph_2PS)_2\}]$  and  $[Ir(COD)\{N(Ph_2PS)_2\}]$  with HCl afforded  $[Ir(H)(Cl)(CO)(PPh_3)\{N(Ph_2PS)_2\}]$  and *trans*- $[Ir(H)(Cl)(COD)\{N(Ph_2PS)_2\}]$ , respectively. Oxidative addition of  $[Ir(CO)(PPh_3)\{N(Ph_2PS)_2\}]$  with MeI afforded  $[Ir(Me)(I)(CO)(PPh_3)\{N(Ph_2PS)_2\}]$ . Treatment of  $[Ir(COE)_2Cl]_2$  with  $K[N(R_2PO)_2]$  afforded  $[Ir(COE)_2\{N(Ph_2PO)_2\}]$  that reacted with MeOTf (OTf = triflate) to give  $[Ir\{N(Ph_2PO)_2\}(COE)_2(Me)(OTf)]$ . The crystal structures of  $[Ir(CO)(PPh_3)\{N(Ph_2PS)_2\}]$ ,  $[M(COD)\{N(Ph_2PS)_2\}]$  ( $M = Ir, Rh$ ),  $[Ir(ol)_2\{N(Pr^i_2PS)_2\}]$  ( $ol = COE, C_2H_4$ ), *trans*- $[Ir(H)(Cl)(COD)\{N(Ph_2PS)_2\}]$ , and  $[Ir(COE)_2\{N(Ph_2PO)_2\}]$  have been determined.  
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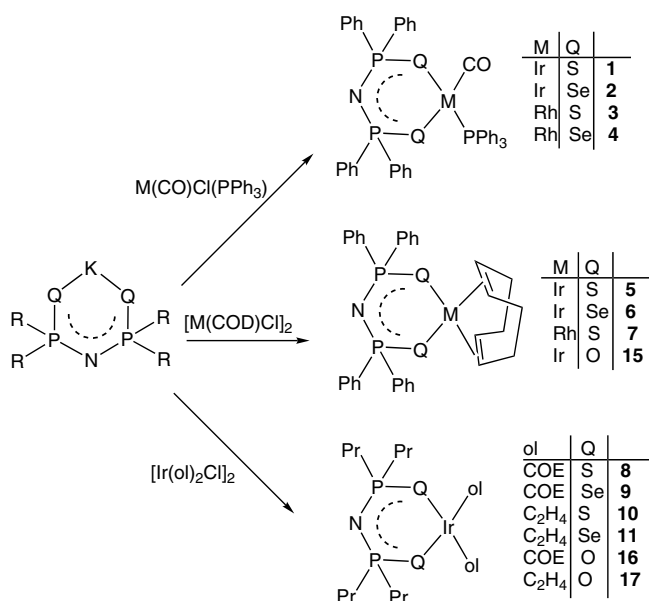
**Keywords:** Iridium; Rhodium; Chalcogen ligands; Crystal structures; Oxidative addition

### 1. Introduction

The coordination chemistry of dichalcogenoimidodiphosphinates  $[N(R_2PQ)_2]^-$  ( $Q = S, Se$ , Scheme 1) has received increasing attention due to recent reports on convenient syntheses of these ligands [1–6]. Bidentate  $[N(R_2PQ)_2]^-$  can be considered as the chalcogen analogues of acetylacetonate (acac). A range of main group and transition metal ions with  $[N(R_2PQ)_2]^-$  have been synthesized. Metal complexes with  $[N(R_2PQ)_2]^-$  have been used as catalysts for organic reactions [7] and NMR shift reagents [8]. Despite the high affinity of  $[N(R_2PQ)_2]^-$  for late transition metal ions, their complexes with Ir and Rh have not been

well explored. The only structurally characterized Ir and Rh dichalcogenoimidodiphosphinates are the half-sandwich complexes  $[Cp^*M\{N(R_2PQ)_2\}X]$  [9–11]. Previously, we have demonstrated that the unsaturated  $[Ru^{II}\{N(R_2PS)_2\}_2]$  core can stabilize a variety of reactive species including sulfur monoxide [12], diazene [13], carbene, and vinylidene [14]. To further explore the organometallic chemistry of dichalcogenoimidodiphosphinates, we sought to synthesize Ir and Rh compounds with  $[N(R_2PQ)_2]^-$  ligands. Also of interest are organoiridium compounds containing  $[N(R_2PO)_2]^-$  due to a recent report that Ir compounds with O-donor ligands, notably acetylacetonate, can catalyze anti-Markovnikov hydroarylation of olefins [15]. We here describe the syntheses and crystal structures of Ir and Rh dichalcogenoimidodiphosphinate compounds containing carbonyl, 1,5-cyclooctadiene, and

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olefin co-ligands, and their oxidative addition reactions with MeI and HCl.

## 2. Experimental

### 2.1. General

All manipulations were carried out under nitrogen by standard Schlenk techniques. Solvents were purified, distilled and degassed prior to use. NMR spectra were recorded on a Varian Mercury 300 spectrometer operating at 300 and 121.5 MHz for  $^1\text{H}$  and  $^{31}\text{P}$ , respectively. Chemical shifts ( $\delta$ , ppm) were reported with reference to  $\text{SiMe}_4$  ( $^1\text{H}$ ) and  $\text{H}_3\text{PO}_4$  ( $^{31}\text{P}$ ). 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  $\text{K}[\text{N}(\text{R}_2\text{PQ})_2]$  ( $\text{R} = \text{Ph}$ ,  $\text{Q} = \text{O}$ ,  $\text{S}$  [16],  $\text{Se}$  [17], and  $\text{R} = \text{Pr}^i$ ,  $\text{Q} = \text{O}$ ,  $\text{S}$ ,  $\text{Se}$  [18,19]) and the compounds  $[\text{M}(\text{CO})\text{Cl}(\text{PPh}_3)_2]$  ( $\text{M} = \text{Ir}$ ,  $\text{Rh}$  [20]),  $[\text{Ir}(\text{COD})\text{Cl}]_2$  ( $\text{M} = \text{Ir}$ ,  $\text{Rh}$  [21]), and  $[\text{Ir}(\text{ol})_2\text{Cl}]_2$  ( $\text{ol} = \text{cyclooctene COE}$  [22],  $\text{C}_2\text{H}_4$  [23]) were prepared according to the literature methods.

### 2.2. Syntheses of $[\text{M}(\text{CO})(\text{PPh}_3)_2\{\text{N}(\text{Ph}_2\text{PQ})_2\}]$

To a solution of  $[\text{M}(\text{CO})\text{Cl}(\text{PPh}_3)_2]$  ( $\text{M} = \text{Rh}$  (97 mg),  $\text{Ir}$  (109 mg); 0.14 mmol) in THF (15 ml) was added with 1 equivalent of  $\text{K}[\text{N}(\text{Ph}_2\text{PQ})_2]$  ( $\text{Q} = \text{S}$  (68 mg),  $\text{Se}$  (84 mg); 0.14 mmol), and the reaction mixture was stirred at room temperature overnight. The solvent was pumped off and the residue was washed with hexane and ether. Recrystallization from  $\text{CH}_2\text{Cl}_2$ – $\text{Et}_2\text{O}$  afforded yellow crystals.

$\text{M} = \text{Ir}$ ,  $\text{Q} = \text{S}$  (1): Yield: 109 mg, 84%. *Anal.* Calc. for  $\text{C}_{43}\text{H}_{35}\text{IrNOP}_3\text{S}_2 \cdot \text{CH}_2\text{Cl}_2$ : C, 52.0; H, 3.7; N, 1.4. Found: C, 51.9; H, 3.6; N, 1.2%.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):

$\delta = 7.27$ – $8.06$  (m, 35H, Ph) ppm.  $^{31}\text{P}\{^1\text{H}\}$  NMR (121.5 MHz,  $\text{CDCl}_3$ ):  $\delta = 18.26$  (dd,  $J = 10.3$ , 23.5 Hz,  $\text{PPh}_3$ ), 33.26 (d,  $J = 23.0$ , 2.4 Hz), 33.95 (t,  $J = 10.3$ , 2.4 Hz) ppm. IR (KBr,  $\text{cm}^{-1}$ ): 1952 [ $\nu(\text{CO})$ ].

$\text{M} = \text{Ir}$ ,  $\text{Q} = \text{Se}$  (2): Yield: 76 mg, 53%. *Anal.* Calc. for  $\text{C}_{43}\text{H}_{35}\text{IrNOP}_3\text{Se}_2 \cdot \text{CH}_2\text{Cl}_2$ : C, 47.6; H, 3.4; N, 1.3. Found: C, 47.9; H, 3.5; N, 1.0%.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.28$ – $8.07$  (m, 35H, Ph) ppm.  $^{31}\text{P}\{^1\text{H}\}$  NMR (121.5 MHz,  $\text{CDCl}_3$ ):  $\delta = 18.19$  (dd,  $J = 29.4$ , 10.2 Hz,  $\text{PPh}_3$ ), 21.85 (d,  $J = 29.4$  Hz), 23.45 (d,  $J = 10.2$  Hz) ppm. IR (KBr,  $\text{cm}^{-1}$ ): 1946 [ $\nu(\text{CO})$ ].

$\text{M} = \text{Rh}$ ,  $\text{Q} = \text{S}$  (3): Yield: 84 mg, 71%. *Anal.* Calc. for  $\text{C}_{43}\text{H}_{35}\text{IrNOP}_3\text{RhS}_2 \cdot \text{CH}_2\text{Cl}_2$ : C, 57.0; H, 4.0; N, 1.7. Found: C, 57.2; H, 4.0; N, 1.5%.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.27$ – $8.05$  (m, Ph) ppm.  $^{31}\text{P}\{^1\text{H}\}$  NMR (121.5 MHz,  $\text{CDCl}_3$ ):  $\delta = 36.19$  (m,  $\text{PPh}_3$ ), 37.84 (d,  $J = 7.3$ , 20.1 Hz), 39.15 (dd,  $J = 7.3$ , 19.7 Hz) ppm. IR (KBr,  $\text{cm}^{-1}$ ): 1965 [ $\nu(\text{CO})$ ].

$\text{M} = \text{Rh}$ ,  $\text{Q} = \text{Se}$  (4): Yield: 89 mg, 68%. *Anal.* Calc. for  $\text{C}_{43}\text{H}_{35}\text{IrNOP}_3\text{RhSe}_2 \cdot \text{CH}_2\text{Cl}_2$ : 51.8; H, 3.8; N, 1.4. Found: C, 51.6; H, 3.7; N, 1.3%.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.31$ – $8.04$  (m, Ph) ppm.  $^{31}\text{P}\{^1\text{H}\}$  NMR (121.5 MHz,  $\text{CDCl}_3$ ):  $\delta = 24.50$  (m,  $\text{PPh}_3$ ), 37.52 (m), 38.91 (m) ppm. IR (KBr,  $\text{cm}^{-1}$ ): 1958 [ $\nu(\text{CO})$ ].

### 2.3. Syntheses of $[\text{M}(\text{COD})\{\text{N}(\text{PPh}_2\text{Q})_2\}]$

To a solution of  $[\text{M}(\text{COD})\text{Cl}]_2$  ( $\text{M} = \text{Rh}$ , 148 mg;  $\text{Ir}$ , 200 mg; 0.30 mmol) in THF (15 ml) was added 2 equivalents of  $\text{K}[\text{N}(\text{Ph}_2\text{PQ})_2]$  (0.60 mmol), during which the color turned from yellowish-orange to yellow immediately. The reaction mixture was stirred at room temperature for 0.5 h. The solvent was then pumped off. Recrystallization from hexane– $\text{Et}_2\text{O}$ – $\text{CH}_2\text{Cl}_2$  afforded yellow crystals.

$\text{M} = \text{Ir}$ ,  $\text{Q} = \text{S}$  (5): Yield: 422 mg, 94%. *Anal.* Calc. for  $\text{C}_{32}\text{H}_{32}\text{IrNP}_2\text{S}_2 \cdot \text{CH}_2\text{Cl}_2$ : C, 47.5; H, 4.1; N, 1.7. Found: C, 47.6; H, 4.1; N, 1.7%.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta = 1.48$ – $1.55$  (m, 2H, COD), 2.01–2.04 (m, 6H, COD), 3.76 (m, 4H, COD), 7.35–7.92 (m, 20H, Ph) ppm.  $^{31}\text{P}\{^1\text{H}\}$  (121.5 MHz,  $\text{CDCl}_3$ ):  $\delta = 33.30$  (s) ppm.

$\text{M} = \text{Ir}$ ,  $\text{Q} = \text{Se}$  (6): Yield: 246 mg, 89%. *Anal.* Calc. for  $\text{C}_{32}\text{H}_{32}\text{IrNP}_2\text{Se}_2 \cdot 1/2\text{CH}_2\text{Cl}_2$ : C, 44.1; H, 3.8; N, 1.6. Found: C, 44.1; H, 3.9; N, 1.5%.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta = 1.36$ – $1.52$  (m, 5H, COD), 1.97 (m, 3H, COD), 3.76 (m, 4H, COD), 7.36–7.93 (m, 20H, Ph) ppm.  $^{31}\text{P}\{^1\text{H}\}$  (121.5 MHz,  $\text{CDCl}_3$ ):  $\delta = 23.20$  (s) ppm.

$\text{M} = \text{Rh}$ ,  $\text{Q} = \text{S}$  (7): Yield: 276 mg, 70%. *Anal.* Calc. for  $\text{C}_{32}\text{H}_{32}\text{NP}_2\text{RhS}_2 \cdot \text{H}_2\text{O}$ : C, 56.7; H, 5.1; N, 2.1. Found: C, 56.8; H, 4.9; N, 2.1%.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta = 1.72$ – $1.80$  (m, 4H, COD), 2.16–2.19 (m, 4H, COD), 4.19 (m, 4H, COD), 7.34–7.95 (m, 20H, Ph) ppm.  $^{31}\text{P}\{^1\text{H}\}$  NMR (121.5 MHz,  $\text{CDCl}_3$ ):  $\delta = 37.37$  (d,  $J_{\text{RhP}} = 3.0$  Hz) ppm.

### 2.4. Syntheses of $[\text{Ir}(\text{ol})_2\{\text{N}(\text{PPr}^i_2\text{Q})_2\}]$

To a suspension of  $[\text{Ir}(\text{ol})_2\text{Cl}]_2$  (0.1 mol, L = COE (90 mg)),  $\text{C}_2\text{H}_4$  (57 mg) in  $\text{Et}_2\text{O}$  (10 ml) was added 2 equiv-

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