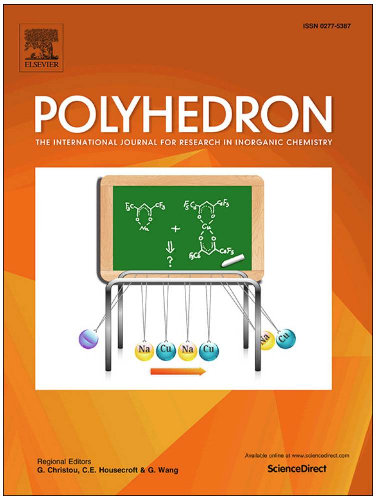


Synthesis, characterization and DFT studies of electron-rich iridium(I) carbonyl complexes of an unsymmetrical phosphine–phosphine monoselenide ligand and their reactivity towards alkyl halides

Bhaskar Jyoti Sarmah, Ankur Kanti Guha, Jayashree Nath, Lakshi Saikia

PII:	S0277-5387(20)30001-2
DOI:	https://doi.org/10.1016/j.poly.2020.114344
Reference:	POLY 114344
To appear in:	*Polyhedron*
Received Date:	28 November 2019
Revised Date:	20 December 2019
Accepted Date:	21 December 2019

Please cite this article as: B.J. Sarmah, A.K. Guha, J. Nath, L. Saikia, Synthesis, characterization and DFT studies of electron-rich iridium(I) carbonyl complexes of an unsymmetrical phosphine–phosphine monoselenide ligand and their reactivity towards alkyl halides, *Polyhedron* (2020), doi: https://doi.org/10.1016/j.poly.2020.114344

Synthesis, characterization and DFT studies of electron-rich iridium(I) carbonyl complexes of an unsymmetrical phosphine–phosphine monoselenide ligand and their reactivity towards alkyl halides

Bhaskar Jyoti Sarmah[a*], Ankur Kanti Guha[b*], Jayashree Nath[c] and Lakshi Saikia[d]
[a] Department of Chemistry, Jorhat Institute of Science and Technology, Jorhat, Assam
[b]Department of Chemistry, Cotton University, Guwahati, Assam
[c]Department of Chemistry, J. B. College (Autonomous), Jorhat, Assam
[d]Materials Sciences and Technology Division, CSIR-NEIST, Jorhat, Assam, India

Abstract

A series of halocarbonyliridium(I) complexes of the type $[Ir(CO)(P{\sim}Se)_2X]$ (**1**) {where P-Se = 1,2-bis(diphenylphosphinomethaneselenide); X = Cl (**1a**), Br (**1b**), I (**1c**)} have been synthesized by the reaction of $[Ir(CO)_2X_2]^-$ with the ligand $Ph_2PCH_2P(Se)Ph_2$. The complexes exhibit a single ν(CO) band in the region 1926 cm^{-1} which is significantly lower in frequency compared to Vaska's complex, *trans*-$[Ir(CO)Cl(PPh_3)_2]$ (1965 cm^{-1}), and substantiate the enhanced electron density at the metal centre. The complexes undergo oxidative addition (**OA**) reactions with electrophiles like CH_3I and C_2H_5I to form Ir(III) alkyl species like $[Ir(CO)R(P{\sim}Se)_2IX]$; [R = CH_3 (**2**), C_2H_5 (**3**)] which exhibit ν(CO) bands in the region of 2070 cm^{-1}. Kinetic measurements for the CH_3I oxidative addition with complex **1a** indicate a first order reaction. The complexes have been characterized by elemental analyses, IR and NMR spectroscopy. Density functional calculations reveal that the activation barrier for the **OA** is the lowest with **1a**, which is also in tune with the experimental observations.

Keywords: *Iridium carbonyl complexes, Bis(diphenylphosphino)methane selenide, Oxidative addition, DFT study, Oxidative addition*

Corresponding author email: bhaskar.rrl@gmail.com, ankurkantiguha@gmail.com

1. Introduction

Platinum metal complexes of functionalized poly phosphines, like $Ph_2P(CH_2)_nP(X)Ph_2$, $Ph_2As(CH_2)_nP(X)Ph_2$, $Ph_2PNHP(X)Ph_2$ and $Ph_2As(X)(CH_2)_nP(X)Ph_2$ (X = O, S, Se; n = 1-4) have attracted much attention in recent times because of their structural novelty, reactivity and widespread catalytic applications [1-16]. These types of ligands are of great importance due to their hemilabile nature, which facilitate oxidative addition (**OA**), a key step in many homogenous catalysis reactions. The activation of small molecules *via* **OA** at d^8 metal centers is of fundamental importance in homogenous hydrogenation, hydroformylation and carbonylation catalysis. Many of the fundamental studies of **OA** reactions have been carried out using Vaska's complex, *trans*-$[Ir(CO)(PPh_3)_2Cl]$, and its analogues [17-21]. Such square planar d^8 Ir(I) complexes react with a variety of substrates, including H_2, HX, X_2 and RX (X = Cl, Br, I; R = alkyl, aryl or acyl). The kinetics and thermodynamics of the oxidative addition depend on the steric and electronic properties of the coordinated ligands and on the substrate being added. The **OA** of methyl iodide and reductive elimination of acetyl iodide are key steps in the industrial processes for carbonylation of methanol to acetic acid, catalysed by $[M(CO)_2I_2]^-$ (M = Rh and Ir). Dutta *et. al.* [7] have demonstrated that Rh(I) complexes of hemilabile phosphine-chalcogen donor ligands are efficient catalysts for the carbonylation of methanol in which the metal chalcogen interactions are responsible for increasing the rate of the **OA** reaction.

In view of the above, we report here the synthesis, characterization and DFT studies of Ir(I) carbonyl complexes of the bis-phosphine monoselenide ligand $Ph_2PCH_2(Se)PPh_2$ and their oxidative reactivity towards different electrophiles, such as CH_3I and C_2H_5I.

2. EXPERIMENTAL

2.1. Materials and methods

All the solvents used were distilled under nitrogen prior to use. $IrCl_3{\cdot}3H_2O$ was purchased from M/S Arrora Matthey Ltd, Kolkata, India. Analytically pure $Ph_2P(CH_2)PPh_2$ and elemental selenium were purchased from M/S Aldrich, USA and used without further purification. The ligand $Ph_2PCH_2P(Se)Ph_2$ was prepared by refluxing a solution of $Ph_2P(CH_2)PPh_2$ in toluene with one molar equivalent of elemental selenium for 3 h under nitrogen (yield: 97%) and purified by chromatographic techniques [22-24]. FT-IR spectra in the range 400-4000 cm^{-1} were recorded using a Perkin-Elmer 2000 spectrophotometer with KBr disks. Carbon and hydrogen analyses were carried out on a Perkin-Elmer 2400 elemental analyzer. NMR data were recorded on a Bruker DPX 300 MHz spectrometer and the ^1H and ^{31}P NMR chemical shifts were quoted relative to $SiMe_4$ and 85% H_3PO_4 as internal and external standards respectively, using $CDCl_3$ and d_6-acetone as solvents.

2.2. Starting material

The starting metal complexes $[Ir(COE)_2Cl]_2$ and $Ph_4As[Ir(CO)_2X_2]$ (X = Cl, Br, I) were synthesized by following the published literature methods [25-26].

2.3. Synthesis

2.3.1. $[Ir(CO)X(P{\sim}Se)_2]$ X = Cl (1a), Br(1b), I(1c); P~Se = $PPh_2CH_2P(Se)Ph_2$:

0.25 mmol of $Ph_4As[Ir(CO)_2X_2]$ was dissolved in 10 cm^3 CH_2Cl_2 and to this 0.50 mmol of the ligand P~Se in 10 cm^3 CH_2Cl_2 was added. The reaction mixture was stirred at room temperature (r.t.) for about 30 min. and the solvent was evaporated under vacuum. The reddish-brown compound thus obtained was washed with diethyl ether and stored over silica gel in a desiccator.

2.3.2. $[Ir(CO)RIX(P{\sim}Se)_2]$ X = Cl(a), Br(b), I(c); R = CH_3(2); C_2H_5(3)

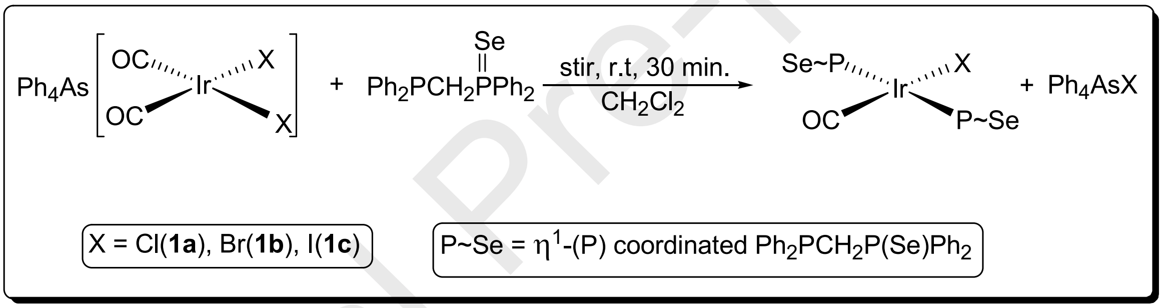
0.325 mmol of **1** was dissolved in 10 cm^3 CH_2Cl_2 and 3 cm^3 of each of the corresponding **RI** (R = CH_3 and C_2H_5) were added. The reaction mixture was stirred for 30 min. and 1 hr. for CH_3I and C_2H_5I respectively. Solvent and excess of alkyl halides were evaporated under reduced pressure to obtain a dark brown solid compound in each case.

2.4. Kinetic experiments

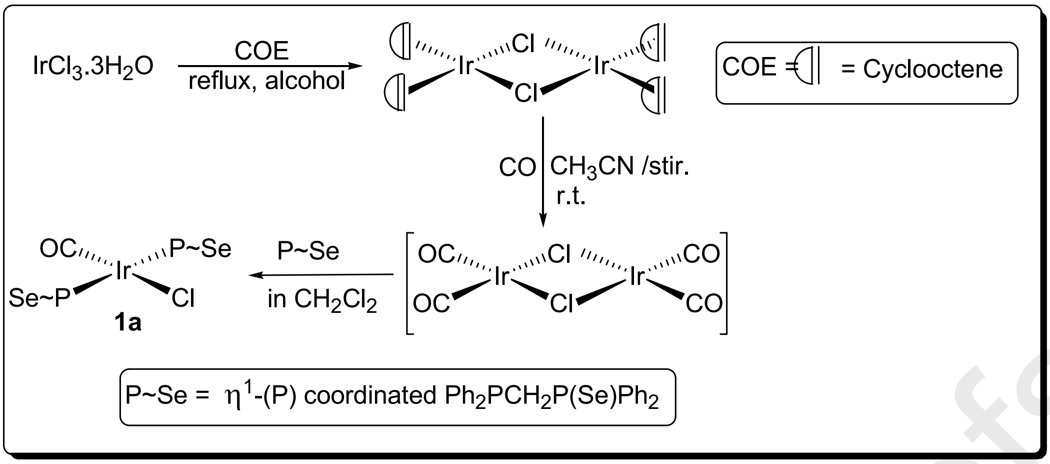
The kinetic experiments of the **OA** reaction of the complexes with CH_3I were monitored using FTIR spectroscopy in a solution cell (CaF_2 windows, 1.0 mm path length). In order to obtained pseudo first-order conditions, an excess of CH_3I relative to the metal complex was used. FTIR spectra (4.0 cm^{-1} resolution) were scanned in the ν(CO) region (2200-1600 cm^{-1}) and saved at regular time intervals using spectrum software. After completion of the experiment, absorbance versus time data for the appropriate ν(CO) frequencies were extracted by subtracting the solvent spectrum and analyzed off line using OriginPro 7.5 software. Kinetic measurements were made by following the decay of the lower frequency ν(CO) band of the complexes. The pseudo first-order rate constants were found from the gradient of the plot of $\ln(A_0/A_t)$ versus time, where A_0 is the initial absorbance and A_t is the absorbance at time t.

3. Results and discussion

The phosphine-phosphine monoselenide ligand $Ph_2PCH_2P(Se)Ph_2$ reacts with $Ph_4As[Ir(CO)_2X_2]$ (X = Cl, Br, I) in a 1:2 molar ratio to afford halocarbonyliridium(I) complexes of the type $[Ir(CO)(P{\sim}Se)_2X]$ where X = Cl (**1a**), Br (**1b**), I (**1c**) (Scheme 1). The chloro complex **1a** was directly obtained (Scheme 2) via treatment of the ligand P~Se with $[Ir(CO)_2Cl]_2$ generated *in situ* by carbonylation of the chlorobridged dimer $[Ir(COE)_2Cl]_2$ (COE = cyclooctene). The yields, elemental analyses and other characteristics of the synthesized complexes are shown in Table 1. The molecular compositions of the complexes are well supported by the elemental analysis data (Table 1). The IR spectra of the complexes (Table 2) exhibit a single terminal ν(CO) absorption at 1930-1920 cm^{-1}, indicating high electron density at the metal centre. The ν(P-Se) bands of the complexes, observed at 530-527 cm^{-1} are closer to the corresponding ν(P-Se) band of the free ligand P~Se (Table 2). This indicates that the ligand is coordinated to the metal center through only the P-donor site. It has been observed that the ν(CO) stretching frequencies of **1a-c** follow the order **1a** < **1b** < **1c**. It is well known that the π donor ability of halogen ligands increase in the order F < Cl < Br < I, therefore the observed trend of the ν(CO) stretching frequencies of **1a-c** is due to the variation in the π donation ability of the attached halo group to the metal centre. The ^1H NMR spectra of the complexes (Table 2) display two multiplet resonances in the range δ 7.16-7.43 and 7.57-7.82 ppm, attributed to non-equivalent phenylic protons and triplet resonances at around δ 3.89-4.25 ppm for the methylene protons of the P-Se ligand. The methylene protons of the complexes show a small downfield shift compared with the



Scheme 1: Synthesis of the Ir(I) carbonyl complexes of the P~Se donors ligand.



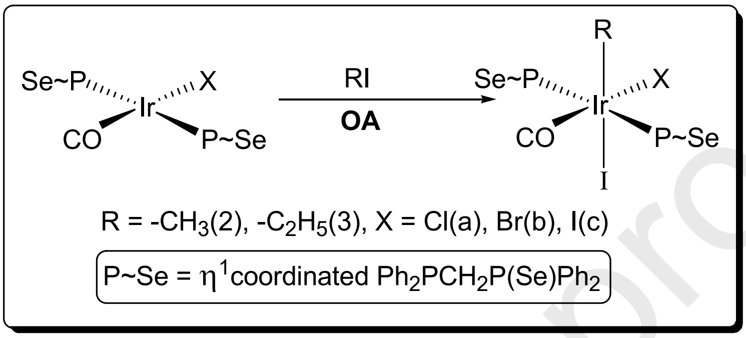
Scheme 2: Synthesis of the Ir(I) carbonyl complex **1a**.

corresponding free ligand, which further substantiates the non-chelating mode of the ligand. The ^{31}P NMR spectra of the complexes (Table 2) exhibit two doublet resonances at *δ* 32.36-44.30 ppm for the tertiary phosphorus atom (P1) and δ 24.79-28.20 ppm for pentavalent phosphorus atom (P2). The large downfield shifts of about 52-70 ppm for the P1 resonances compared to free ligand P~Se also substantiate the monodentate coordination to the metal centers through the tertiary phosphorus atom.

3.1. Reactivity of the complexes 1a-c towards various alkyl halides

The Ir(I) carbonyl complexes **1a**-c are coordinatively unsaturated and undergo **OA** with different electrophiles, like CH_3I and C_2H_5I, to yield the corresponding Ir(III) products. In contrast to the Rh(I) system, **OA** of alkyl halides to Ir(I) carbonyl complexes form stable Ir(III) alkyl products for which migratory insertion occurs only at elevated temperatures or in the presence of CO to form the Ir(III) acyl species. Compared to the rhodium complexes, the relative rates of **OA** and migratory insertion steps for the iridium complexes have been estimated as *ca.*150 and 10^{-5}-10^{-6}, respectively [27]. This can be explained in terms of the relative strength of the metal-carbon bonds for the 4d and 5d transition metals. The strength of a metal-carbon bond of a 5d metal is generally higher than that of a 4d transition metal [28]. As a consequence, if metal-carbon bond making plays a key role in a particular step, then the 5d metal is more likely to react faster (**OA**), whereas if a metal-ligand bond weakening or breaking step plays a key role in a process (as in migratory insertion), it is likely that the 4d metal will be the faster.

OA of CH_3I to the complexes **1a-c** yielded hexacoordinated Ir(III)-methyl species (Scheme 3) of the type $[Ir(CO)CH_3(P{\sim}Se)_2IX]$ (**2**), X = Cl (**a**), Br (**b**), I (**c**). The IR spectra of the complexes (Table 2) show a single terminal ν(CO) band in the region 2040-2050 cm^{-1}. The high value of the terminal ν(CO) band indicates the formation of the oxidized product. The ν(P-Se) bands of the complexes appear at 530-528 cm^{-1} confirming the monodentate coordination nature of the ligands. Apart from the characteristic resonances of the ligands, the ^1H NMR spectra of complexes **2a-c** (Table 2) show a singlet in the region δ 1.80-2.03 ppm, indicating the formation of the $COCH_3$ group. In a similar manner, **OA** reactions of C_2H_5I with the complexes **1a-c** also afforded six coordinated Ir(III)-alkyl complexes, viz. $[Ir(CO)C_2H_5(P{\sim}Se)_2IX]$, X = Cl (**3a**), Br (**3b**), I (**3c**) (Scheme 3). The IR spectral values (Table 2) of the ν(PSe) bands of these complexes clearly imply the tertiary P coordination of the ligands to the metal. The ν(CO) bands of the complexes occur in the range 2051-2064 cm^{-1}, attributable to the terminal carbonyl groups. The ^1H NMR spectra of complexes **3a-c** show one triplet in the range δ 2.15-2.26 ppm for the methyl protons and one quartet signal at around δ 3.28-3.54 ppm for the methylene protons of the ethyl group, in addition to the characteristic ligand peaks. The ^{31}P NMR data of all the oxidized complexes (Table 2) show a similar pattern of the spectral data to their corresponding parent complexes.



- **Scheme 3**: Oxidative reactivity of Ir(I) carbonyl complexes with a P~Se donor ligand towards alkyl halides

3.2. Kinetic study of the oxidative addition (OA) of CH_3I with Ir(I) carbonyl complexes containing a bis phosphine-phosphine monoselenide ligand

Ir(I) carbonyl complexes of the type $[Ir(CO)X(L)_2]$; where X = Cl (**1a**), Br (**1b**), I (**1c**) and L = $Ph_2PCH_2P(Se)Ph_2$, undergo **OA** with CH_3I to yield the stable methyliridium complexes **2a-c**, for which migratory insertion occurs at elevated temperature or in the presence of carbon monoxide. The kinetics of the reaction was monitored using IR

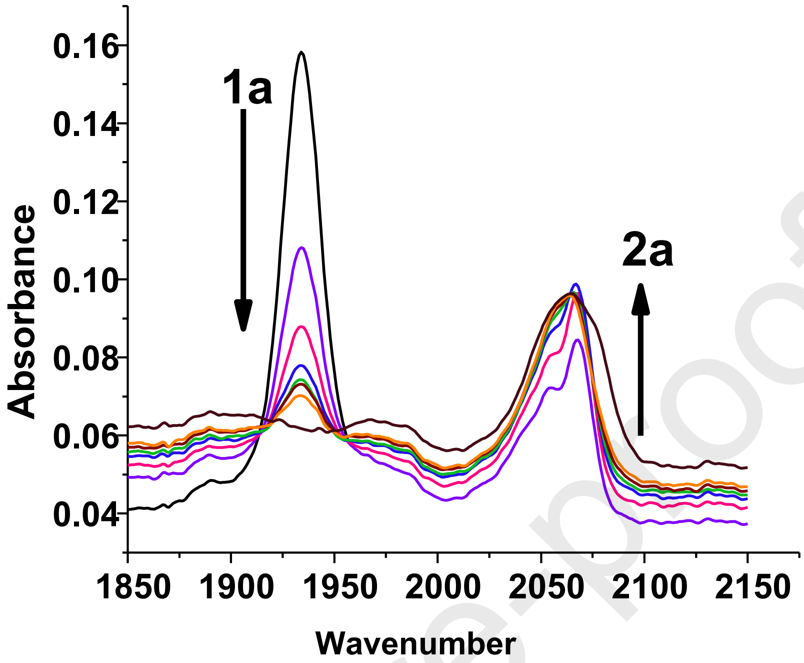
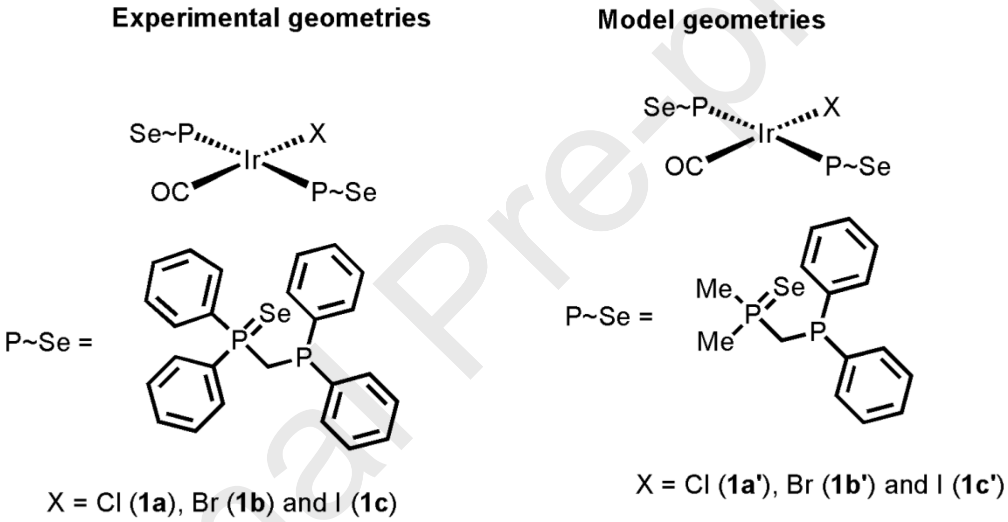


Fig. 1 Series of IR spectra {ν(CO) region} illustrating the reaction of **1a** with CH_3I at 25 °C. The arrows indicate the behavior of each band as the reaction progresses.

spectroscopy. During the reaction, the single intense ν(CO) band of the reactant **1a** at 1924 cm^{-1} decayed and a new absorption due to the product **2a** grew at 2042 cm^{-1}, as shown in Fig. 1. Absorbance versus time plots for the decay of the lower frequency band was well fitted by an exponential curve, revealing that the reaction is first order with respect to the Ir(I) complex. Values of the observed pseudo-first-order rate constant were calculated from the slope of the plot of $\ln(A_0/A_t)$ versus time, where A_0 and A_t are the absorbance at time t = 0 and t, and these were found to be $4.41\text{x}10^{-3}$, $3.35\text{x}10^{-3}$ and $1.59\text{x}10^{-3}$ s^{-1}, respectively, for the complexes **1a**, **1b** and **1c**. The values of these rate constants clearly indicate that the rate of **OA** follows the order **1a** > **1b** > **1c**. The observed trend of the rate constants may be due to the attachment of different X (X = Cl, Br and I) groups to the Ir(I) center.

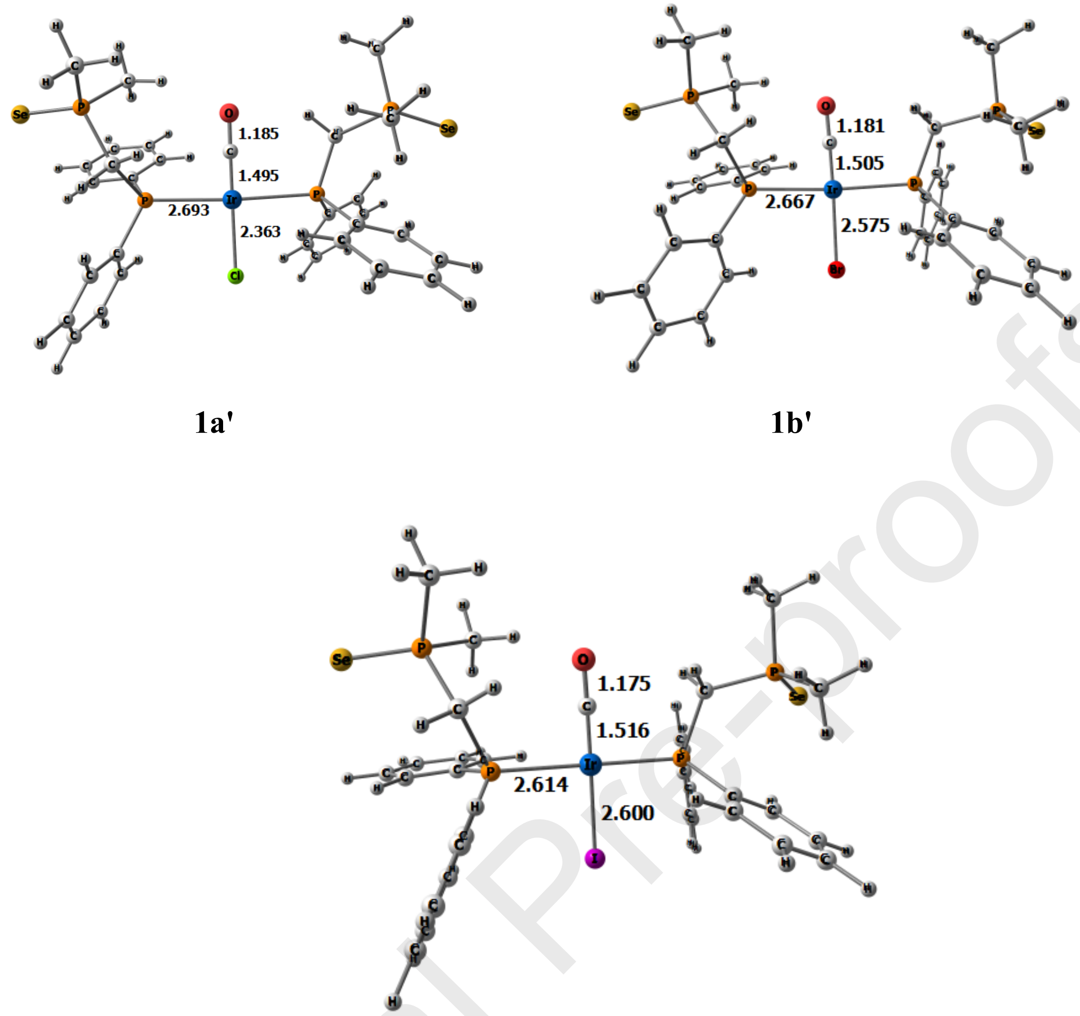
4. Computational details

For the sake of computational analysis, we have made a simple modification of the experimental geometry. The phenyl groups attached to the tetracoordinate P atoms were replaced by methyl groups (Scheme 4). All the structures were fully optimized without any symmetry constraints at the M06-2X level of theory [29]. We used 6-311++G** for the main group elements, while the relativistic small-core effective core potential of Stuttgart/Dresden (SDD) [30] was used for the iridium metal. Harmonic vibrational frequency calculations were carried out at the same level of theory to understand the nature of the stationary states. All these structures were found to be at their local minimum with all real values of the hessian matrix, while the transition states were characterized by one imaginary frequency. Natural bond orbital (NBO) [31] calculations were also performed to understand the electronic features of these complexes. All these calculations were performed using the Gaussian16 suite of programs [32].



Scheme 4. Experimental geometries and the model geometries for the computational analysis.

Figure 2 shows the optimized geometries of the square planar Ir complexes. In all the complexes, the P~Se ligand coordinates to the metal centre through only one P atom. This is also evident from the experimental IR analysis. The C-O distance follows the order **1a'** > **1b'** > **1c'**. This is also in tune with the experimental evidence that the CO stretching frequency follows the opposite order, i. e. **1a'** < **1b'** < **1c'**. Even the calculated un-scaled CO stretching frequencies of these complexes are 2231 cm^{-1} for **1a'**, 2254 cm^{-1} for **1b'** and 2287 cm^{-1} for **1c'**. This is due to fact that the π donating ability of the halides follows the order Cl < Br < I . The π donating ability of halides has been extensively proven by Frenking *et. al*. [33].



1a'

1b'

1c'

Figure 2. Optimized geometries of the square planar Ir(I) complexes. Bond lengths are in Å.

These square planar complexes are found to undergo oxidative addition with alkylhalides, with high rate constants. We, therefore, calculated the highest occupied molecular orbitals (HOMO) of these molecules. The higher the HOMO, the higher will be the tendency of these square planar complexes to undergo oxidative addition. Figure 3 shows the HOMO of **1a'**. It is evident from Figure 3 that the HOMO for **1a'** is the d_z^2 orbital. The eigen values of the HOMO for the complexes follow the order **1c'** < **1b'** < **1a'** (-0.45eV for **1c'**, -0.40 eV for **1b'** and -0.21 eV for **1a'**), which suggests that the oxidative addition will be fastest with **1a'**. The experimentally determined rate of this oxidative addition is also found to be the highest with **1a**. Thus, the theoretical calculations are in tune with the experimental observations.

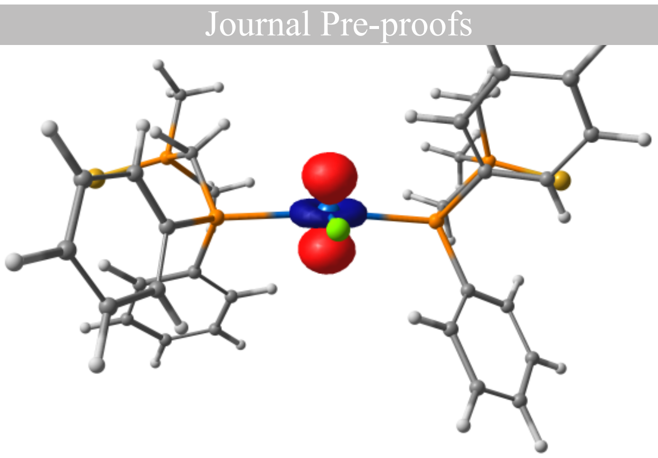


Figure 3. HOMO of complex **1a'**.

We have further carried out mechanistic investigations on the **OA** with the alkyl iodide CH_3I. Alkyl iodides are known to undergo oxidation addition via a S_N^2 type pathway [34-35]. The activation energies of the reactions follow the order **1a'** (13.4 kcal/mol) < **1b'** (21.3 kcal/mol) < **1c'** (32.2 kcal/mol). The optimized geometries of the transition states involved in the S_N^2 pathway are shown in Figure 4. The low activation barrier for **1a'** suggests that it is the most reactive towards **OA** among the synthesized complexes. This is in tune with our experimental observations.

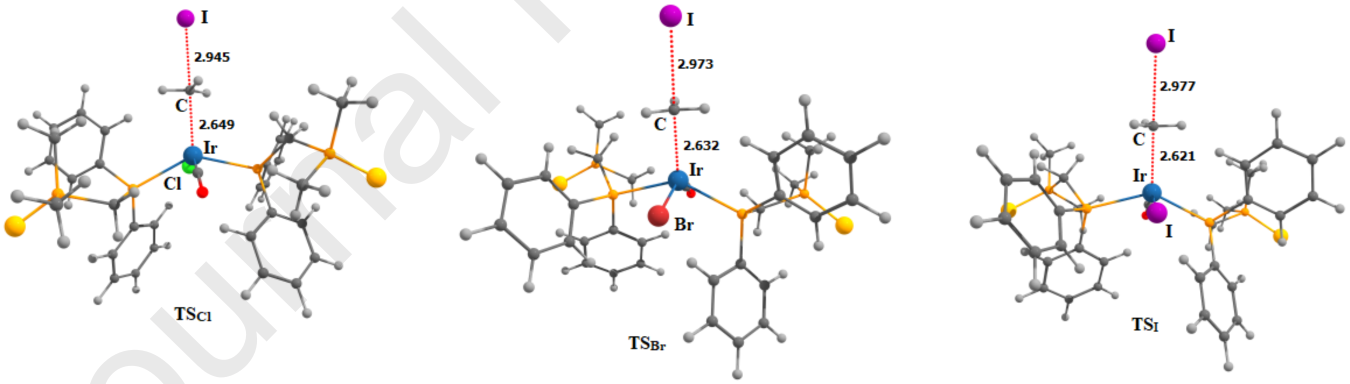


Figure 4. Optimized geometries of the transition states involved in the S_N^2 pathway for the oxidative addition. Bond lengths are in Å.

5. Conclusions

In conclusion, we have synthesized a series of new halocarbonyliridium(I) complexes of the type $[Ir(CO)(P{\sim}Se)_2X]$ {where P-Se = 1, 2-bis(diphenylphosphinomethaneselenide); X = Cl, Br, I}. The complexes exhibit a single ν(CO) band in the region 1926 cm^{-1}, which is significantly lower in frequency compared to Vaska's complex, *trans*-$[Ir(CO)Cl(PPh_3)_2]$

(1965 cm^{-1}), and substantiate the enhanced electron density at the metal centre. The complexes undergo an oxidative addition (**OA**) reaction with electrophiles like CH_3I and C_2H_5I to form Ir(III) alkyl species like [Ir(CO)R(P~Se)$_2$IX]; [R = CH_3(**2**), C2H$_5$(**3**)], which exhibit ν(CO) bands in the region 2070 cm^{-1}. Kinetic measurements for the CH_3I oxidative addition with complex **1a** indicate a first order reaction. Density functional calculations also reveal that the activation energy associated with the **OA** with **1a** is the lowest, which is in tune with the experimental observations.

6. Acknowledgement

BJS thanks Assam Science and Technology University [ASTU/TEQIP-III/Collaborative Research/2019/2569] and the University Grant Commission [Grant No: F.42-326/2013 (SR)] for providing partial financial grants.

Table 1. Elemental analysis and other characteristics of the iridium carbonyl complexes containing the P-Se donor ligand.

Complex	**Yield (%)**	**Colour**	**Elemental analysis (%) Found (Calc.)**	
			C	**H**
1a	92	Yellow	51.79 (51.76)	3.76 (3.72)
1b	94	Yellow	49.92 (49.88)	3.63 (3.58)
1c	96	Yellow	48.15 (48.04)	3.57 (3.45
2a	94	Reddish-brown	47.21 (47.11)	3.36 (3.55)
2b	92	Reddish-brown	44.16 (44.07)	3.41 (3.32)
2c	93	Reddish-brown	45.65 (45.59)	3.56 (3.43)
3a	89	Brown	47.63 (47.52)	3.82 (3.66)
3b	96	Brown	46.05 (45.99)	3.65 (3.54)
3c	94	Brown	44.54 (44.48)	3.46 (3.43)

Table 2. IR and NMR (^{1}H and ^{31}P) spectral data of the iridium carbonyl complexes containing the P-Se donor ligand.

Complex	**IR data (cm^{-1})**		**^{1}H NMR data (δ / ppm)**				**^{31}P NMR data (δ / ppm)**	
	ν(CO)	ν(P-Se)	C_6H_5	CH_2 (P~Se)	CH_2	CH_3	δ_P	$\delta_{P=Se}$
1a	1924	528	7.16-7.45 m 7.66-7.85 m	4.02 t	-	-	32.36 d	27.54 d
1b	1925	527	7.19-7.43 m 7.67-7.83 m	4.16 t	-	-	44.30 d	26.66 d
1c	1927	528	7.22-7.49 m 7.61-8.06 m	4.03 t	-	-	36.56 d	26.39 d
2a	2042	529	7.19-7.68 m 7.65-8.06 m	4.15 t	-	2.03 s	32.38 d	26.56 d
2b	2043	530	7.21-7.49 m 7.68-7.82 m	4.25 t	-	1.96 s	41.26 d	26.49 d
2c	2048	527	7.16-7.45 m 7.66-7.85 m	3.96 t	-	1.80 s	36.45 d	24.79 d
3a	2051	528	7.29-7.55 m 7.57-7.85 m	3.89 t	3.28 q	2.15 s	33.36 d	26.53 d
3b	2059	528	7.17-7.45 m 7.62-7.89 m	4.01 t	3.36 q	2.26 s	37.54 d	28.20 d
3c	2064	528	7.24-7.44 m 7.75-7.97 m	4.10 t	3.54 q	2.21 s	38.23 d	26.56 d

Free ligand (**P~Se**):

IR : ν(PSe): 527 ; ^{31}P NMR : δ_P and $\delta_{P=Se}$: -26.4, 31.3d; ^{1}H NMR: -(CH_2)- : 3.49d

s: singlet; d: doublet; t: triplet; q: quartet; m: multiplet

References:

[1]. *(a) New synthesis with carbon monoxide*, Ed. J. Falbe, Springer-Verlag, Heidelberg, NY, **1980**, 11, 286-89; (b) *Homogeneous Catalysis: Understanding the Art*, P. W. N. M. van Leeuwen, Springer Berlin Heidelberg, 2004. (c) I.D. Kostas, Recent Advances in P,N-Containing Ligands for Transition-Metal Homogeneous Catalysis, in: Atta-ur-Rahman (Ed.), Advances in Organic Synthesis, Vol. 6, Bentham Science, 2013, 3–58.

[2]. (a) C. Icsel , V.T. Yilmaz, M. Aygun , B Cevatemre, P. Alper , E. Ulukaya, *Dalton Trans*. **2018**, 47, 11397. (b) D. K. Dutta and B. Deb, *Coord. Chem. Rev.*, **2011**, 255, 1686. (c) Gemma M. Adams, Andrew S. Weller, *Coord. Chem. Rev.,* **2018**, 355, 150. (d) C. Fliedel, R. Poli, *Coord. Chem. Rev.,* **2018**, 355, 1.

[3]. (a) C.Pérez-Zúñiga, C.Negrete-Vergara, V.Guerchais, H.Le Bozec, S.A.Moya, P.Aguirre, *Mol. Catal.*, **2019**, 462, 126. (b) Vanessa R. Landaeta, Rafael E. Lugo, *J. Mol. Catal. A: Chem.*, **2017**, 426, 316. (c) K.A. Vallianatou, D.J. Frank, G. Antonopoulou, S. Georgakopoulos, E. Siapi, M. Zervou, I.D. Kostas, *Tetrahedron Lett.* **2013,** 54, 397. (d) I.D. Kostas, A.-C. Tenchiu, C. Arbez-Gindre, V. Psycharis, C.P. Raptopoulou, *Catal. Commun.*, **2014**, 51, 15. (e) W. L. Warton, S. Tanaka, C. M. S. Hauser, J. ChiehHsieh, K. Mereiter, K. Kirchner, *Polyhedron*, **2010**,29, 3097.

[4]. D. K. Dutta, B. Deb, B. J. Sarmah, J. D. Woollins, A.M. Z. Slawin, A. L. Fuller, R. A. M. Randall, *Eur. J. Inorg. Chem.*, **2011**, 835.

[5]. S. P. Pandey, M. K. Pandey, M. S. Balakrishna, *Polyhedron*, **2019**, 158, 173

[6]. (a) D. F. Steel, T. A. Stephenson, *J. Chem. Soc.*, **1972**, 19, 216; (b) P. Chutia, N. Kumari, M. Sharma, J. D.Woollins, A. M. Z. Slawin, D. K. Dutta, *Polyhedron*, **2004**, 23, 2725;

[7]. D. K. Dutta, J. D. Woollins, A. M. Z. Slawin, D. Konwar, P. Das, M. Sharma, P. Bhattacharya, S. M. Aucott, *Dalton Trans.*, **2003**, 2674;

[8]. P. Das, M. Sharma, N. Kumari, D. Konwar, D. K. Dutta, *Appl. Organometal. Chem.,* **2002**, 16, 302.

[9]. D. K. Dutta, P. Chutia, J. D. Woollins, A. M. Z. Slawin, *Inorg. Chim. Acta.*, **2006**, 359, 877.

[10]. D. K. Dutta, J. D. Woollins, A. M. Z. Slawin, D. Konwar, M. Sharma, P. Bhattacharyya, S. M. Aucott, *J. Organomet. Chem.*, **2006**, 69, 1229.

[11]. P. Chutia, B. J. Sarmah D. K. Dutta, *Appl. Organometal. Chem.*, **2006**, 20, 512.

[12]. P. H. Leung, A. C. Willis, S. B. Wild, *Inorg. Chem.,* **1992**, 31, 1406.

[13]. D. M. Morales, S. R. Morales, J. R. Dilworth, A. S. Pedrares, Y. Zheng, *Inorg. Chim. Acta,* **2002**, 332, 101.

[14]. D. A. Evans, K. R. Campos, J. S. Tedrow, F. E. Michael, M. R. Gagne, *J. Am. Chem. Soc.,* **2000**, 122**,** 7905.

[15]. M. Bressan, C. Bonuzzi, F. Morandini, A. Morvillo, *Inorg. Chim. Acta,* **1991**, 182, 153.

[16]. P. Bhattacharyya, A. M. Z. Slawin, D. J. Williams, J. D. Woollins, *J. Chem. Soc., Dalton Trans.,* **1995**, 3189.

[17]. R.H. Crabtree, *The Organometallic Chemistry of the Transition Metals*, New York: John Wiley & Sons, Inc. **1988**.

[18]. L. Vaska, *Acc. Chem. Res.*, **1968**, 1, 335–344.

[19]. a) G. J. Sunley, D. J. Watson, *Catal. Today*, **2000**, 58, 293–307; b) P. R. Ellis, J.M. Pearson, A. Haynes, H. Adams, N. A. Bailey, P.M. Maitlis, *Organometallics*, **1994**, 13, 3215–3226; c) T. R. Griffin, D. B. Cook, A. Haynes, J. M. Pearson, D. Monti, G. E. Morris, *J. Am. Chem. Soc.*, **1996**, 118, 3029–3030; d) M. Lei, W. Zhang, Y. Chen, Y. Tang, *Organometallics*, **2010**, 29, 543–548; e) R. D. Adams, B. Captain, L. Zhu, *J. Organomet. Chem.*, **2008**, 693, 819–833; f) W. B. Tolman, E. I. Solomon, *Inorg. Chem.*, **2010**, 49, 3555–3556; g) W. B. Tolman, *Activation of Small Molecules*, Wiley-VCH, Weinheim, Germany, **2006**; h) A. J. Muller, J. Conradie, W. Purcell, S. S. Basson, J. A. Venter, *S. Afr. J. Chem.*, **2010**, 63, 11–19.

[20]. a) D. Forster, *J. Am. Chem. Soc.*, **1976**, 98, 846–848; b) D. Forster, *Adv. Organomet. Chem.*, **1979**, 17, 255–267; c) D. Forster, T. C. Singleton, *J. Mol. Catal.*, **1982**, 17, 299–303.

[21]. a) G. J. Sunley, D. J. Watson, *Catal. Today*, **2000**, 58, 293–307; b) J. H. Jones, *Platinum Met. Rev.*, **2000**, 44, 94–105.

[22]. M. S. Balakrishna, R. Klein, S. Uhlenbrock, A. A. Pinkerton, R. G. Cavell, *Inorg. Chem.,* **1993**, 32, 5676.

[23]. T. S. Lobana, R. Singh, *Trans. Met. Chem.*, **1995**, 20, 501.

[24]. A. M. Bond, R. Colton, P. Panagiotidou, *Organometallics*, **1988**, 7, 1767.

[25]. J. L. Herde, J. C. Lambert, C. V. Senoff, *Inorg. Synth.*, **1974**, 15,18–20.

[26]. P. W. Vickers, J. M. Pearson, T. Ghaffar, H. Adams, A. Haynes, *J. Phys. Org. Chem.*, **2007**, 17, 1007.

[27]. R. Whyman, A. P. Wright, J. A. Iggo, B. T. Heaten, *J. Chem. Soc., Dalton Trans.*, **2002**, 771.

[28]. P. M. Maitlis, A. Haynes, G. J. Sunley, M. J. Howard, *J. Chem. Soc., Dalton Trans.*, **1996**, 2187.

[29]. Y. Zhao, D. G. Truhlar, *Theor. Chem. Acc.*, **2008**, 120, 215–241

[30]. M. Dolg, U. Wedig, H. Stoll, H. Preuss, *J. Chem. Phys.*, **1987**, 86, 866–872.

[31]. A. E. Reed, L. A. Curtiss, F. Weinhold, *Chem. Rev.*, 1988, 88, 899–926.

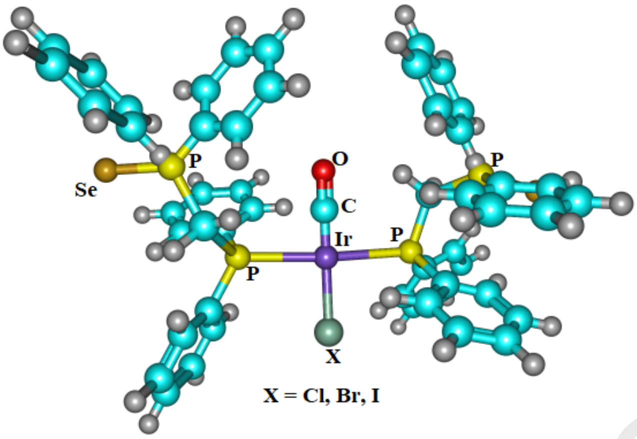
[32]. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, D. J. Fox, Gaussian 16, Revision A.03, Gaussian, Inc., Wallingford CT, 2016.

[33]. G. Frenking, S. Fau, C. M. Marchand, H. Grützmacher, *J. Am. Chem. Soc.*, **1997**, 119, 6648-6655.

[34]. R. Crabtree, *The Organometallic Chemistry of Transition Metals*. Wiley-Interscience. pp. 159-180.

[35]. L. M. Rendina, R. J. Puddaphatt, *Chem. Rev.*, **1997**, 97, 1735-1754.

TOC Graphic



TOC Text

Electron-rich iridium(I) carbonyl complexes of an unsymmetrical phosphine–phosphine monoselenide ligand have been synthesized. DFT studies have also been performed.

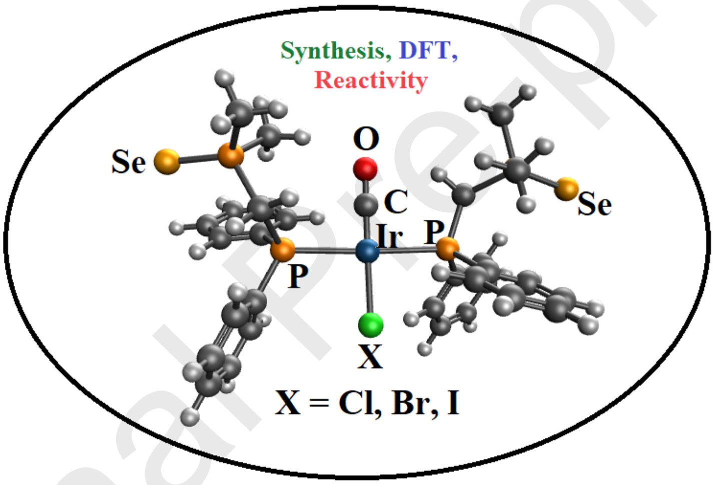
All authors contributed equally

Declaration of interests

☐ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Graphical abstract:

Electron-rich iridium(I) carbonyl complexes of an unsymmetrical phosphine-phosphine monoselenide ligand have been synthesized and characterized. The complexes exhibit a single ν(CO) band in the region 1926 cm^{-1} which is significantly lower in frequency compared to Vaska's complex, *trans*-[Ir(CO)Cl(PPh$_3$)$_2$] (1965 cm^{-1}). The complexes undergo oxidative addition (**OA**) reactions with electrophiles like CH_3I and C_2H_5I to form Ir(III) alkyl species like [Ir(CO)R(P~Se)$_2$IX]; [R = CH_3 (**2**), C_2H_5 (**3**)] which exhibit ν(CO) bands in the region of 2070 cm^{-1}. DFT study indicates that the theoretical calculations are in agreement with the experimental observations.



Electron-rich iridium(I) carbonyl complexes of an unsymmetrical phosphine–phosphine monoselenide ligand have been synthesized. DFT studies have also been performed.