Journal of Organometallic Chemistry 883 (2019) 17–24

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

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

# Amine involvement in the self-association of planar complexes of the type, *cis*-Ir$(CO)_2$Cl(primary amine)

Emily M. Gussenhoven, Marilyn M. Olmstead**, Alan L. Balch*

*Department of Chemistry, University of California, Davis, CA, 95616, USA*

ARTICLE INFO

*Article history:*
Received 15 October 2018
Received in revised form
30 December 2018
Accepted 3 January 2019
Available online 11 January 2019

ABSTRACT

Examination of crystals of *cis*-Ir$(CO)_2$X(*p*-toluidine) (X = Cl, Br, I), by single crystal X-ray diffraction shows that the individual monomers self-associate to form extended columns with Ir•••Ir separations ranging from 3.33 Å for the chloro complex to 3.68 Å in the iodo complex. The columnar structure is reinforced by hydrogen bonding between the halide ligand in one molecule with an N-H group in an adjacent molecule. This hydrogen bonding causes adjacent molecules to adopt nearly eclipsed orientations. In contrast, the positions of the methyl groups in *cis*-Ir$(CO)_2$Cl(*o*-toluidine) and *cis*-Ir$(CO)_2$Cl(2,6-dimethylaniline) limit intermolecular interactions to the formation of dimers connected by Ir•••Ir interactions, and hydrogen bonding again occurs between the halide ligand in one molecule and the N-H group in an adjacent molecule. The UV/vis spectrum of *cis*-Ir$(CO)_2$Cl(*p*-toluidine) provides evidence that the self-association also occurs in solution. The positive ion mass spectrum of laser ablated crystals of *cis*-Ir$(CO)_2$Br(*p*-toluidine) reveals the presence of monomeric, dimeric, and trimeric cations.

## 1. Introduction

Coordination complexes of metal ions with $d^8$ or $d^{10}$ electronic configuration frequently undergo self-assocation in the solid phase to form dimers, trimers and extended linear chains [1–4]. Such self-assocation is particularly common for four-coordinate Pt(II) [5–9] and Rh(I) [10–15] as well as for two-coordinate Au(I) [16,17] complexes. This self-association occurs because of interactions between the filled $d_z^2$ orbital and the empty $p_z$ orbitals that are directed colinearly and perpendicular to the molecular plane [18,19]. These orbitals can overlap with similarly directed orbitals on the adjacent molecules to form metallophillic interactions. These metallophillic interactions direct the supramolecular assembly of these compounds, particularly in the solid state. However, because such *pseudo*-closed shell interactions tend to be rather weak, the structures that result can be altered and/or augmented by other weak interactions such as hydrogen-bonding and ligand size.

The self-association of Ir(I) complexes has received less attention than their isoelectronic Pt(II) and Rh(I) counterparts. Crystals of *cis*-Ir$(CO)_2$Cl(pyridine) [20] and *cis*-Ir$(CO)_2$Cl(pyrazine) [21] contain extended columns of the metal complexes with Ir•••Ir separations of 3.602(12) Å and 3.579(3) Å, respectively. Light yellow needles of Ir$(CO)_2$(acetylacetonate) crystallize in columns with alternating Ir•••Ir distances of 3.242 Å and 3.260 Å [22,23]. Four polymorphs of the planar chelate $Ir^I(CO)_2(OC(CH_3)CHC(CH_3)N($*p*-tol) have been identified (amber, pale yellow, orange, and low temperature orange) [24]. The amber and pale yellow forms contain dimers connected by Ir•••Ir interactions (3.5540(2) Å for the amber polymorph, 3.5934(8) and 4.0397(8) Å for the pale yellow polymorph at 90 K). The orange and low temperature orange forms contain extended columns of molecules with Ir•••Ir separations of 3.4126(5) and 3.6237(5) Å at 90 K. Finally, the dimer $(F_3P)_2Ir(\mu\text{-}Cl)_2Ir(PF_3)_2$ (with an intramolecular Ir•••Ir separation of 2.941(1) Å) self-associates into chains with an intermolecular Ir•••Ir separation of 3.271(1) Å [25].

Unlike the previous examples, copper-colored needles of $Ir(CO)_3Cl$ contain stacks of the planar complex with a remarkably short Ir···Ir distance of 2.844 Å [26,27]. Within the stacks, the planar complexes are staggered. Crystals of this compound are electrically conductive. Consequently, $Ir(CO)_3Cl$ has been considered to be a partially oxidized material such as $Ir(CO)_{2.93}Cl_{1.07}$ [28]. Computations can explain the short Ir···Ir separation without invoking partial oxidation, but they cannot account for the conductivity of this material [29]. Several other partially oxidized and electrically conductive iridium complexes such as $A_{0.60}[Ir(CO)_2X_2]$ (with A = K, Cs, TTF (TTF = tetrathiafulvalene) and X = Cl, Br) and K

---

* Corresponding author.
** Corresponding author.
*E-mail addresses:* mmolmstead@ucdavis.edu (M.M. Olmstead), albalch@ucdavis.edu (A.L. Balch).

https://doi.org/10.1016/j.jorganchem.2019.01.002

$[Ir(CO)_2X_2]_2$ have been made through chemical or electrochemical oxidation of the planar anion *cis*-$[Ir(CO)_2X_2]^-$ or reduction of iridium(III) salts [30–33].

The metallic red color of solid *cis*-$Ir(CO)_2Cl$(*p*-toluidine) [34] contrasts with the usual yellow color seen for monomeric iridium(I) complexes such as $Ir(CO)Cl(PPh_3)_2$ [35] and $(Ph_4As)[Ir(CO)_2Cl_2]$ [36] and suggests that this compound undergoes some sort of self-association in the solid state. *Cis*-$Ir(CO)_2Cl$(*p*-toluidine), has been used on several occasions as a starting material for the synthesis of more complex molecules and ions [37–39]. Here, we examine the structures of some compounds of the type *cis*-$Ir(CO)_2X$(primary amine) (X = Cl, Br, I) with attention to the role of the amine group in the assisting interactions between individual molecules.

## 2. Results and discussion

The complexes, *cis*-$Ir(CO)_2X$(*p*-toluidine) (X = Cl, Br, I), *cis*-$Ir(CO)_2Cl$(*o*-toluidine), and *cis*-$Ir(CO)_2Cl$(2,6-dimethylaniline) have been prepared by minor variations of the route previously reported for the synthesis of *cis*-$Ir(CO)_2Cl$(*p*-toluidine) [34].

### *2.1. The structures of cis-$Ir(CO)_2Cl$(p-toluidine), cis-$Ir(CO)_2Br$(p-toluidine), cis-$Ir(CO)_2I$(p-toluidine) with exended columnar aggregates*

The solid-state structures of the solvate-free iridium(I) complexes *cis*-$Ir(CO)_2Cl$(*p*-toluidine), *cis*-$Ir(CO)_2Br$(*p*-toluidine), *cis*-$Ir(CO)_2I$(*p*-toluidine) have been determined by X-ray crystallography at 90(2) K. The complexes differ only by the nature of the halide ligand, which results in subtle, yet interesting differences in their solid-state properties. The three crystal structures are isostructural, and each contains two molecules in the asymmetric unit in the monoclinic space group $P2_1/n$. Crystallographic data are presented in Table 1, while Table 2 contains selected bond lengths

**Table 1**

Crystallographic data for iridium complexes.

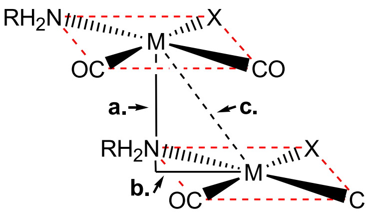
| Compound | *cis*-$Ir(CO)_2Cl$(*p*-toluidine) | *cis*-$Ir(CO)_2Br$(*p*-toluidine) | *cis*-$Ir(CO)_2I$(*p*-toluidine) |
|---|---|---|---|
| Emp. Formula | $C_9H_9ClIrNO_2$ | $C_9H_9BrIrNO_2$ | $C_9H_9IIrNO_2$ |
| Formula weight | 390.82 | 435.28 | 428.27 |
| Color | metallic red | red-green | metallic green |
| Habit | block | needle | needle |
| Crystal system | Monoclinic | Monoclinic | Monoclinic |
| Space group | $P2_1/n$ | $P2_1/n$ | $P2_1/n$ |
| *a* (Å) | 6.6695(2) | 6.7639(7) | 7.1440(13) |
| *b* (Å) | 15.4857(6) | 15.5272(15) | 15.545(3) |
| *c* (Å) | 20.4408(8) | 20.466(2) | 20.651(4) |
| $\alpha$ (°) | 90 | 90 | 90 |
| $\beta$ (°) | 99.7980(10) | 99.326(2) | 99.781(4) |
| $\gamma$ (°) | 90 | 90 | 90 |
| *V* ($Å^3$) | 2080.37(13) | 2121.0(4) | 2260.1(7) |
| *Z* (units/cell) | 8 | 8 | 8 |
| *T* (K) | 90(2) | 90(2) | 90(2) |
| $\rho_{calc}$ (g $cm^{-3}$) | 2.496 | 2.725 | 2.835 |
| MoK$\alpha$, $\lambda$ (Å) | 0.71073 | 0.71073 | 0.71073 |
| $\mu$ ($mm^{-1}$) | 13.064 | 16.320 | 14.521 |
| Unique data | 6083 | 6279 | 4204 |
| Obs. data ($I > 2\sigma(I)$) | 4730 | 5140 | 3836 |
| Restraints | 4 | 6 | 0 |
| Params. refined | 271 | 256 | 241 |
| R1 [a] (obs. data) | 0.0192 | 0.0451 | 0.0246 |
| *w*R2 [b] (all data, $F^2$ refinement) | 0.034 | 0.1277 | 0.0653 |

| Compound | *cis*-$Ir(CO)_2Cl$ (*o*-toluidine) | *cis*-$Ir(CO)_2Cl$ (2,6-dimethylaniline) |
|---|---|---|
| Emp. Formula | $C_9H_9ClIrNO_2$ | $C_{10}H_{11}ClIrNO_2$ |
| Formula weight | 390.82 | 424.30 |
| Color | Orange-red | Red |
| Habit | Plate | Prism |
| Crystal system | Monoclinic | Monoclinic |
| Space group | $P2_1/n$ | $P2_1/n$ |
| *a* (Å) | 14.8018(13) | 17.012(15) |
| *b* (Å) | 7.9031(7) | 13.415(12) |
| *c* (Å) | 19.4446(17) | 21.747(19) |
| $\alpha$ (°) | 90 | 90 |
| $\beta$ (°) | 104.2845(12) | 102.05(2) |
| $\gamma$ (°) | 90 | 90 |
| *V* ($Å^3$) | 2204.3(3) | 4854(7) |
| *Z* (units/cell) | 8 | 16 |
| *T* (K) | 90(2) | 90(2) |
| $\rho_{calc}$ (g $cm^{-3}$) | 2.355 | 2.322 |
| MoK$\alpha$, $\lambda$ (Å) | 0.71073 | 0.71073 |
| $\mu$ ($mm^{-1}$) | 12.329 | 11.415 |
| Unique data | 5064 | 11120 |
| Obs. data ($I > 2\sigma(I)$) | 4461 | 8536 |
| Restraints | 0 | 0 |
| Params. refined | 255 | 581 |
| R1 [a] (obs. data) | 0.0265 | 0.0361 |
| *w*R2 [b] (all data, $F^2$ refinement) | 0.0650 | 0.0754 |

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum[\omega(F_o^2 - F_c^2)^2]/\sum[\omega(F_o^2)]]^{1/2}$

**Table 2**
Dimensions within linear chain complexes (see Scheme 1).

| Compound | cis-Ir(CO)$_2$Cl(p-toluidine) | | cis-Ir(CO)$_2$Br(p-toluidine) | | cis-Ir(CO)$_2$I(p-toluidine) | |
|---|---|---|---|---|---|---|
| | Molecule 1 | Molecule 2 | Molecule 1 | Molecule 2 | Molecule 1 | Molecule 2 |
| Distances (Å) | | | | | | |
| M1···M2, 2A **c** | 3.3341(2) | 3.3576(2) | 3.3801(6) | 3.4201(6) | 3.5409(7) | 3.6767(8) |
| M1–X1 | 2.3752(9) | 2.3699(9) | 2.4750(13) | 2.4670(13) | 2.6623(6) | 2.6573(6) |
| N1–H1A···Cl2A | 3.488(3) | | 3.552(9) | | 3.782(7) | |
| N1–H1B···Cl2 | 3.453(3) | | 3.530(9) | | 3.753(7) | |
| N2–H2A···Cl1A | | 3.464(3) | | 3.542(9) | | 3.771(7) |
| N2–H2B···Cl1 | | 3.472(2) | | 3.532(9) | | 3.760(7) |
| *Inter*planar Sepn. **a** | 3.33 | 3.33 | 3.37 | 3.39 | 3.51 | 3.63 |
| Lateral Shift **b** | 0.19 | 0.40 | 0.24 | 0.45 | 0.43 | 0.61 |
| M Displacement | 0.0072(16) | 0.0063(16) | 0.003(4) | 0.002(5) | 0.002(4) | 0.006(4) |
| M/Ring Plane | 89.2 | 87.6 | 89.6 | 87.3 | 89.8 | 86.5 |
| Angles (°) | | | | | | |
| M2···M1···M2A | 170.675(6) | | 168.39(2) | | 163.62(1) | |



**Scheme 1.** A diagram of (a) interplanar separations (IS), (b) lateral shifts (LS), and (c) the metal-metal distances between adjacent planar Ir(I) molecules.

and angles, together with metallophilic geometry and hydrogen bonding. Scheme 1 defines the interplanar separations (IS) and lateral shifts (LS) used to characterize the self-association of these planar molecules.

In *cis*-Ir(CO)$_2$Cl(*p*-toluidine), and also in the analogous bromo and iodo complexes, the four-coordinate molecular units pack to form crystals with the planar moieties aligned in columnar arrays with non-covalent, face-to-face interactions through $d^8$-$d^8$ contacts as seen in Fig. 1. This column is composed of alternating Ir···Ir interactions with distances of 3.3341(2) and 3.3575(2) Å. There is a minimal kinking of the columnar chains, with an Ir2···Ir1···Ir2A angle of 170.682(6) °. Individual columns are separated by 6.669(4) Å.

In crystals of *cis*-Ir(CO)$_2$Cl(*p*-toluidine) the carbonyl ligands are oriented *cis* to each other in the columns and adopt nearly eclipsed conformations. In addition, the *cis*-Ir(CO)$_2$Cl(*p*-toluidine) molecules are oriented with alternating locations of the *p*-toluidine and chloride groups. This arrangement not only prevents potential repulsive interactions between aryl carbon atoms, but also maximizes potential hydrogen bonding contacts between the primary amine protons and adjacent chloro ligands. The extensive hydrogen bonds are integral to the columnar structure within the crystalline structure; they help to direct the self-association of these units and to supplement the weak metallophilic networks between iridium(I) centers. A similar hydrogen bonding pattern along a columnar structure is also present in crystalline *cis*-Rh(CO)$_2$Cl(methylamine), although this hydrogen bonding interaction was over looked by the original authors [40].

Although the molecular structures for the chloro, bromo and iodo iridium(I) complexes of *cis*-Ir(CO)$_2$X(*p*-toluidine) are similar, the isostructural complexes are differentiated mainly in the dimensions of the solid-state structural packing. In the case of the bromo and iodo complexess, again the two unique molecules in each asymmetric unit pack to form metal-metal contacts that increase as the size of the halogen increases: 3.3801(6) and 3.4201(6) Å for *cis*-Ir(CO)$_2$Br(*p*-toluidine); 3.5409(7) and 3.6767(8) Å for *cis*-Ir(CO)$_2$I(*p*-toluidine). Additionally, the hydrogen bonding interactions for both the bromo and iodo forms are slightly longer than for the chloro analog: *ca.* 3.54 Å for *cis*-Ir(CO)$_2$Br(*p*-toluidine) and 3.76 Å for *cis*-Ir(CO)$_2$I(*p*-toluidine). The chain linearity decreases with increasing size of the halide ligand, and the chains become more kinked: the angle Ir2A···Ir1···Ir2 is 168.39(2) ° for *cis*-Ir(CO)$_2$Br(*p*-toluidine), 163.62(1) ° for *cis*-Ir(CO)$_2$I(*p*-toluidine).

### *2.2. Infrared spectra of cis-Ir(CO)$_2$Cl(p-toluidine), cis-Ir(CO)$_2$Br(p-toluidine), and cis-Ir(CO)$_2$I(p-toluidine)*

Information regarding the infrared spectra of *cis*-Ir(CO)$_2$Cl(*p*-toluidine), *cis*-Ir(CO)$_2$Br(*p*-toluidine), and *cis*-Ir(CO)$_2$I(*p*-toluidine) is collected in Table 3. In solution, *cis*-Ir(CO)$_2$Cl(*p*-toluidine) displays two carbonyl stretching bands due to the carbon monoxide

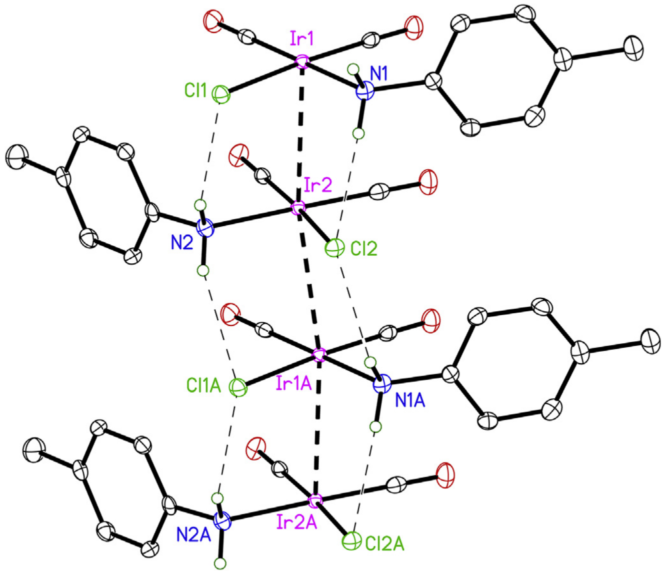


**Fig. 1.** Linear chains of four square planar *cis*-Ir(CO)$_2$Cl(*p*-toluidine) molecules. Metallophilic interactions between the Ir(I) centers alternate with short and long contacts, which are supported by parallel hydrogen bonding interactions between N–H···Cl. The structures of *cis*-IrX(CO)$_2$X(*p*-toluidine) (X = Br, I) are similar.

**Table 3**
Selected Infrared Spectroscopic Properties of *cis*-$IrCl(CO)_2$(amine) Complexes.

| Complex | $\nu$(C≡O) (cm$^{-1}$) | $\nu$(C≡O) (cm$^{-1}$) | $\nu$(N–H) (cm$^{-1}$) |
|---|---|---|---|
| *cis*-[$IrCl(CO)_2$(*p*-tol)]<br>solid state | 2080*vs*<br>2049*w* | 2020*vs*<br>1975*w* | 3240<br>3204 |
| *cis*-[$IrCl(CO)_2$(*p*-tol)]<br>dichloromethane solution[a] | 2075 | 1997 | |
| *cis*-[$IrBr(CO)_2$(*p*-tol)]<br>solid state | 2077*vs*<br>2051*w* | 2019*vs*<br>1975*w* | 3240<br>3200 |
| *cis*-[$IrI(CO)_2$(*p*-tol)]<br>solid state | 2072*vs*<br>2051*w* | 2014*vs*<br>1979*w* | 3233 |

[a] A. L. Balch, R. D. Cooper, J. Organomet. Chem. 169 (1979) 97-105.

ligands *trans* to the chloride and amine ligands [41]. However, four bands are seen in the solid state as revealed in Table 3. These bands arise from the presence of two different iridium sites that are coupled through metallophillic interactions in the crystals. Similarly, both *cis*-$Ir(CO)_2Br$(*p*-toluidine) and *cis*-$Ir(CO)_2I$(*p*-toluidine) display four carbonyl stretching frequencies in the solid state. Notice that changing the halide anion in these complexes has a rather small effect on the energies of the carbonyl stretching bands. A similar situatuion is seen for the anions *cis*-$[Ir(CO)_2X_2]^-$ with X = Cl, Br, I [36].

### 2.3. The formation of discrete dimers in the structures of cis-Ir(CO)₂Cl(o-toluidine) and cis-Ir(CO)₂Cl(2,6-dimethyl aniline)

The effect of the changing the bulk of the amine substituent on the molecular packing, orientation, and degree of ordering in crystalline structures of *cis*-$Ir(CO)_2Cl$(primary amine) was studied. Utilizing the ligands *o*-toluidine and 2,6-dimethylaniline, crystals were obtained for complexes *cis*-$Ir(CO)_2Cl$(*o*-toluidine) and *cis*-$Ir(CO)_2Cl$(2,6-dimethylaniline) and their structures determined by X-ray crystallography. Crystallographic data and structure refinement parameters for each complex are listed in Table 1, while selected geometrical parameters are listed in Table 4.

Orange-red plates of *cis*-$Ir(CO)_2Cl$(*o*-toluidine) crystallize with two molecules in the asymmetric unit in monoclinic space group $P2_1/n$. Despite the similarity in space group and number of molecules in the asymmetric unit, the structures of *cis*-$Ir(CO)_2Cl$(*o*-toluidine) and *cis*-$Ir(CO)_2Cl$(*p*-toluidine) are quite different. The molecular structure of *cis*-$Ir(CO)_2Cl$(*o*-toluidine) and some aspects of its packing are shown in Fig. 2. The two molecules in the asymmetric unit form a dimer, with an Ir1···Ir2 distance of 3.4012(7) Å. Within the dimer the ligands are nearly eclipsed and the amine group positioned so that a hydrogen bond is formed between N2 on one molecule and Cl1 on the adjoining molecule. The *o*-toluidine ring is nearly perpendicular to the metal coordination plane. The angles between the two planes are 86.7° for the molecule involving Ir1 and 85.7° for the molecule containing Ir2. This orientation of the aromatic rings blocks the outer faces of the dimer and precludes the formation of the extended chains seen for $Ir(CO)_2Cl$(*p*-toluidine). The dimers also interact with one another through additional hydrogen bonding that connects Cl2 of one dimer with N2A of another and also N2 with Cl1A as shown in Fig. 2.

Red prisms of *cis*-$Ir(CO)_2Cl$(2,6-dimethylaniline) crystallize with four molecules in the asymmetric unit in the monoclinic space group $P2_1/n$. These four unique molecules form two dimeric units with similar Ir···Ir distances: 3.394(3) Å for Ir1···Ir2 and 3.402(3) Å for Ir3···Ir4 as seen in Fig. 3. Again as the data in Table 4 indicate, the two coordination planes in each dimer are nearly parallel to each other. As in *cis*-$Ir(CO)_2Cl$(*o*-toluidine), there are hydrogen bonds between amine and chloro groups in each dimer. These hydrogen bonding interactions insure that the dimers have nearly eclipsed arrangements and augment the Ir···Ir interactions in holding the dimers together. The angle of the plane of the aniline group with the metal coordination plane varies from an 80.7° in the dimer formed by Ir3 and Ir4 to 85.7° in the dimer involving Ir1 and Ir2. Again these groups protrude outward and protect opposite faces of the dimer so that extended chains do not form. For this complex, there are no hydrogen bonds that connect the two dimers.

### 2.4. Self-association in solution

The dicarbonylhalide(amine) complexes of iridium(I) are readily soluble in halogenated solvents such as dichloromethane and chloroform. For the electronic spectra of these complexes dichloromethane was used to obtain absorption data in solution. When dissolved in dichloromethane, *cis*-$Ir(CO)_2Cl$(*p*-toluidine) forms dark amber solutions at 298 K. UV/vis spectra in the solid-state were obtained in Nujol mulls.

Fig. 4 shows some representative data for *cis*-$Ir(CO)_2Cl$(*p*-toluidine). The absorbance features vary with concentration. In dilute solutions, the maxima occur at 310 nm and 356 nm; in addition, a low-energy shoulder occurs at *ca.* 395 nm. However, at the higher concentration new absorption bands are observed at 430, 525 and 694 nm. These additional features are associated with the

**Table 4**
Dimensions within dimeric complexes (see Scheme 1).

| Compound | *cis*-$IrCl(CO)_2$(*o*-toluidine) | | *cis*-$Ir(CO)_2Cl$(2,6-dimethylaniline) | | | |
|---|---|---|---|---|---|---|
| | Molecule 1 | Molecule 2 | Molecule 1 | Molecule 2 | Molecule 3 | Molecule 4 |
| Distances (Å) | | | | | | |
| M1···M2, **c** | 3.4036(3) | | 3.443(3) | | 3.453(3) | |
| M1–Cl1 | 2.3552(12) | 2.3477(12) | 2.376(2) | 2.377(2) | 2.380(2) | 2.390(2) |
| N1–H1A···Cl2 | 3.323(4) | | 3.365(6) | | | |
| N2–H2A···Cl1 | 3.383(4) | 3.383(4) | | 3.319(6) | | |
| N2–H2A···Cl2A | | 3.437(4) | | | | |
| N3–H3A···Cl4 | | | | | 3.412(6) | |
| N4–H4A···Cl3 | | | | | | 3.391(6) |
| *Inter*planar Sepn. **a** | 3.37 | | 3.36 | | 3.39 | |
| Lat. Shift **b** | 0.47 | | 0.76 | | 0.65 | |
| M Displacement | 0.014(2) | 0.004(2) | 0.014(3) | 0.037(3) | 0.009(3) | 0.041(3) |
| M/Ring Plane | 86.7 | 85.7 | 85.7 | 82.7 | 83.4 | 80.7 |

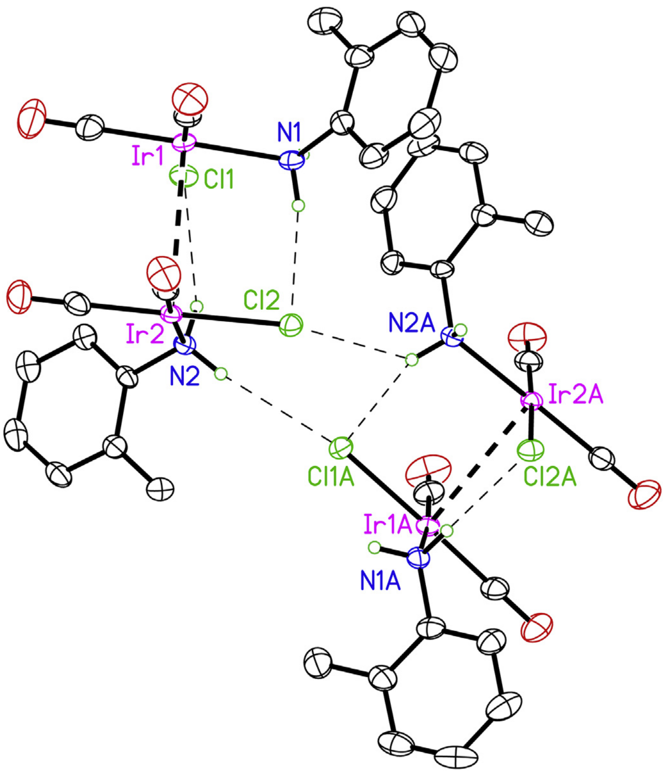


**Fig. 2.** Interactions between four molecules of *cis*-Ir(CO)$_2$Cl(*o*-toluidine) molecules.

formation of aggregates similar to the self-association seen in the solid state. Notice that the spectrum obtained from the solid itself shows features similar to those seen in the more concentrated solution.

### 2.5. Self Assocaitaion in the Gas Phase, Mass Spectrometry

We have seen aggregation of iridium(I) dicarbonylhalide(amine) complexes in both the solid and solution phases and wanted to determine if the supramolecular organization of the square planar moieties could be detected in the gas phase. Thus, the matrix-assisted laser desorption/ionization (MALDI) mass spectrum of *cis*-Ir(CO)$_2$Br(*p*-toluidine) was collected. Crystals of the iridium(I) complex were affixed (without the presence of a matrix) to a stainless steel plate using a minimum amount of Super Glue and were subsequently ionized. This represents a novel dry method for obtaining mass spectral time of flight (TOF) data, without the assistance of ionizing matrices that are typically acidic in nature and can interfere with the metal coordination site. Mass spectra, which show peaks for the monomeric, dimeric and trimeric forms of [*cis*-Ir(CO)$_2$Br(*p*-toluidine)]$^+$, are shown in Fig. 5 along with the computed spectra. Both positive and negative ionization conditions were attempted; however, intelligible results were only obtained in the positive ion mode. Under positive ionization conditions, peaks due to monomers, dimers, and trimers were observed. The corresponding isotope distributions correlate well with the theoretical absolute mass assignments and splitting patterns. Interestingly, the dimer peaks were nearly four times more intense than either the monomer or trimer signals. The results show that the self-association of these metal complexes can be detected even in the gas phase. Detection of self-association of $d^8$ metal complexes by mass spectrometry is rare [33].

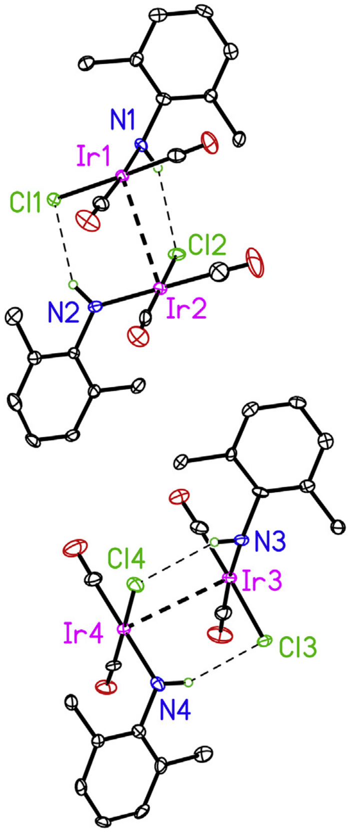


**Fig. 3.** Interactions between the four independent molecules of *cis*-Ir(CO)$_2$Cl(2,6-dimethylaniline).

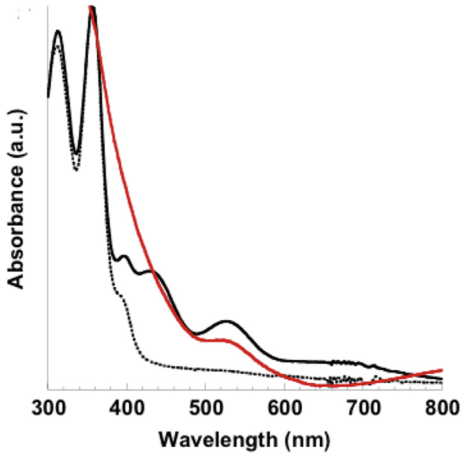


**Fig. 4.** UV/vis spectra of *cis*-Ir(CO)$_2$Cl(*p*-toluidine) in Nujol mulls (red trace) and in dichloromethane solutions (4.5 mM —; 45 mM ▪). Solution spectra were normalized to the peak at 356 nm. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

## 3. Conclusions

The solid state structures of $d^8$ planar complexes of the type *cis*-Ir(CO)$_2$X(primary amine) (X = Cl, Br, I) are influenced by the presence of Ir⋯Ir interactions, hydrogen bonding between an N-H

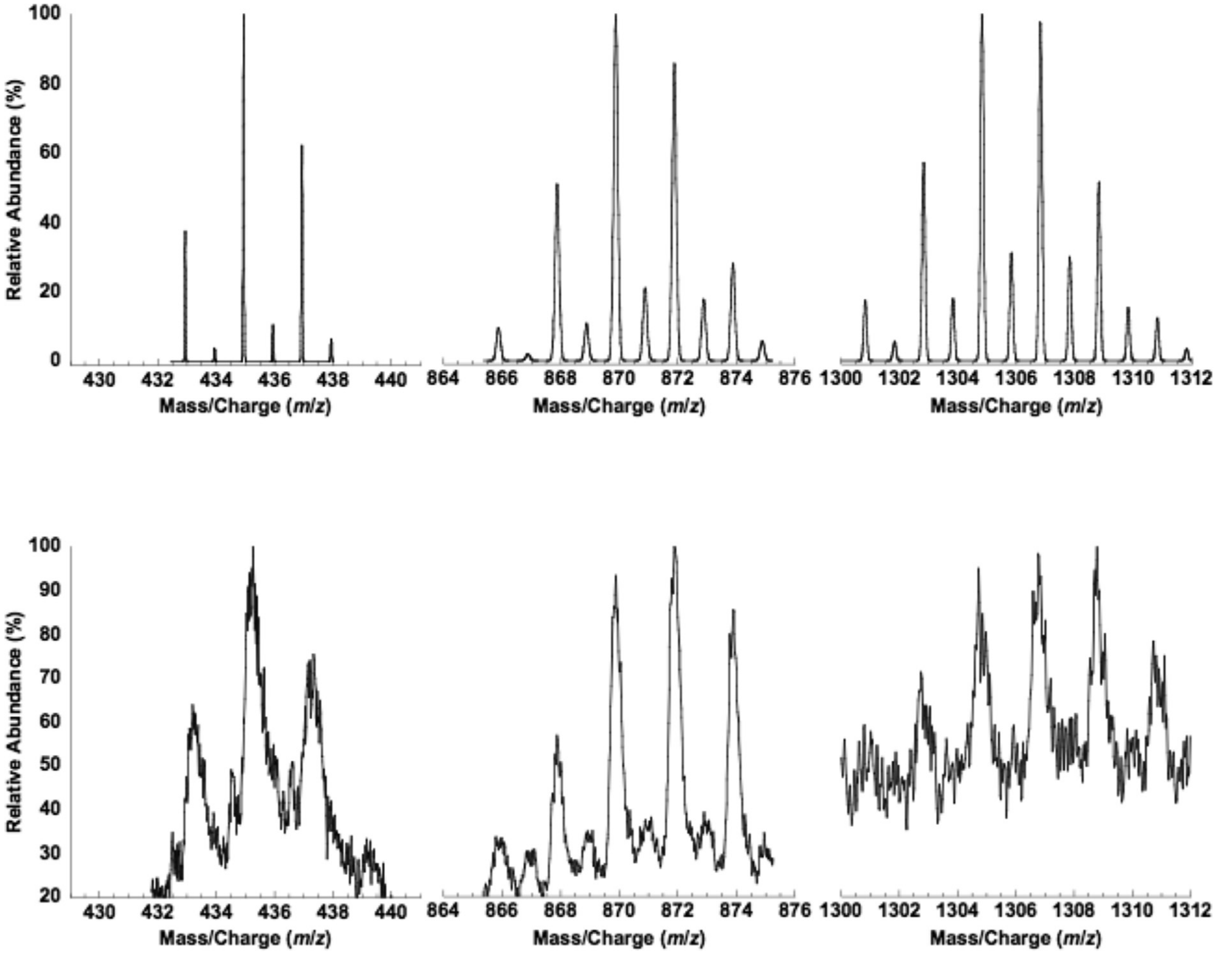


**Fig. 5.** MALDI TOF/TOF mass spectra (positive ion mode) isotope distributions for the peaks of the monomeric, dimeric and trimeric units of *cis*-Ir(CO)$_2$Br(*p*-toluidine). The upper plots show the theoretical isotope distributions. The lower plots show the experimental data from a cluster of crystals of *cis*-Ir(CO)$_2$Br(*p*-toluidine), glued to the target plate.

group on one molecule and a halide ligand on an adjacent molecule, and the steric bulk of the amine ligand. In *cis*-Ir(CO)$_2$X(*p*-toluidine) (X = Cl, Br, I) the four-coordinate, planar molecules pack so that the molecules form columnar arrays with unsupported, face-to-face interactions through $d^8$-$d^8$ contacts with additional hydrogen bonding between N-H groups and chloride ligands that runs along the columns. In *cis*-Ir(CO)$_2$Cl(*o*-toluidine) and *cis*-Ir(CO)$_2$Cl(2,6-dimethylaniline) the methyl groups of the amine protrude from one face of the monomer in such a fashion that the formation of extended chains is precluded. In these two cases, dimers are formed. These dimers are again connected by Ir⋯Ir interactions and by N-H⋯Cl hydrogen bonding. The Ir⋯Ir distances in the dimers (3.4036(3) Å for *cis*-IrCl(CO)$_2$(*o*-toluidine), 3.443(3), 3.453(3) Å for *cis*-Ir(CO)$_2$Cl(2,6-dimethylaniline)) are similar but slightly longer than the Ir⋯Ir distances 3.3341(2) and 3.3576(2) Å for in the extended chain complex *cis*-Ir(CO)$_2$Cl(*p*-toluidine). In all cases, the adjacent planar molecules have nearly eclipsed structures.

The extended chains in *cis*-Ir(CO)$_2$Cl(*p*-toluidine) with Ir⋯Ir separations of 3.3341(2) and 3.3576(2) Å and a nearly eclipsed arrangement of adjacent molecules are quite different from those in Ir(CO)$_3$Cl, where the Ir⋯Ir separation is shorter (2.844 Å) and adjacent complexes are arranged in a eclipsed fashion. However, the stacking of molecules of the type in *cis*-Ir(CO)$_2$Cl(primary amine) resembles that seen in *cis*-Ir(CO)$_2$Cl(pyridine) [20], *cis*-Ir(CO)$_2$Cl(pyrazine) [21], and Ir(CO)$_2$(acetylacetonate) [22,23] where with Ir⋯Ir separations fall in the range 3.242–3.602(12) Å. Thus, Ir(CO)$_3$Cl remains as an outlier in the nature of self-association of Ir(I) complexes. As expected, the Ir⋯Ir separations seen in the crystals considered here are significantly longer than the range of Ir-Ir distances (2.6622(3) Å to 2.8393(12) Å) found in Ir(II) dimers that contain single Ir(II)-Ir(II) bonds [42].

## 4. Experimental

### 4.1. Materials

Samples of IrCl$_3\cdot$3H$_2$O were purchased from Pressure Chemical Company. Sodium bromide, sodium iodide, 2-methoxyethanol, *p*-toluidine, *o*-toluidine, and 2,6-dimethylaniline were purchased from Aldrich Chemicals and used as received. Carbon monoxide gas (C.P. grade) was obtained from Airgas Inc. Carbon monoxide is a toxic gas that needs to be handled in a well ventilated fume hood.

### 4.2. Synthesis of cis-Ir(CO)$_2$Cl(amine) where amine = p-toluidine, o-toluidine, or 2,6-dimethylaniline

These complexes were prepared with minor modifications to the literature procedure developed for *cis*-Ir(CO)$_2$Cl(*p*-toluidine) [34]. A sample of IrCl$_3\cdot$3H$_2$O (0.729 g, 2.07 mmol) was treated with lithium chloride (0.421 g, 9.94 mmol) and excess carbon monoxide in a solution of 2-methoxyethanol (27 mL), and water (3 mL). After refluxing overnight under a stream of carbon monoxide, the pale yellow solution containing the non-isolated $Li[IrCl_2(CO)_2]$ was charged with *p*-toluidine (0.224 g, 2.09 mmol) and concentrated to ca. 5 mL under dinitrogen. The concentrated solution was poured into 100 mL of deionized water. A navy/purple fluffy precipitate formed immediately. The solid was collected by filtration on a Büchner funnel, washed with water, and dried over anhydrous sodium sulfate (yield, 0.540 g, 67%).

For *cis*-$Ir(CO)_2Cl$(*p*-toluidine), deep red blocks with a metallic sheen suitable for X-ray diffraction experiments were grown by the slow evaporation of a concentrated hexane solution of the complex under dinitrogen.

For *cis*-$Ir(CO)_2Cl$(*o*-toluidine) orange-red, metallic plate-like crystals were grown from the slow evaporation of a concentrated benzene solution of the complex under dinitrogen. Mp 143–144 °C.

For *cis*-$Ir(CO)_2Cl$(2,6-dimethylaniline), red prisms, suitable for X-ray diffraction experiments, were grown by the slow evaporation of a pentane solution of the complex. Mp 155–156 °C.

### 4.3. Synthesis of *cis*-$Ir(CO)_2X$ (*p*-toluidine) where X = Br or I

To prepare *cis*-$Ir(CO)_2I$(*p*-toluidine), a three-neck, 100 mL round bottom flask was charged with $IrCl_3 \cdot 3H_2O$ (0.701 g, 1.99 mmol), sodium iodide (1.529 g, 10.20 mmol), 2- methoxyethanol (27 mL), and water (3 mL). A reflux condenser topped with an oil bubbler was affixed to the center neck, while a carbon monoxide inlet tube was placed in a side port; the third neck was stoppered. The reaction solution was initially degassed with flowing carbon monoxide for 15 min at room temperature, then refluxed at 393 K overnight, with continuous passage of carbon monoxide. Overnight, the reaction solution turned from dark red to yellow. After cooling to room temperature, *p*-toluidine (0.262 g, 2.44 mmol) was added, and the solution was concentrated to ca. 5 mL under a stream of dinitrogen. This concentrated solution was poured into 100 mL of deionized water; a purple fluffy precipitate formed immediately. The solid was collected on a Büchner funnel by filtration, washed with water, and dried over anhydrous sodium sulfate (yield: 0.724 g, 76%). Green, dichroic needles of *cis*-$Ir(CO)_2I$(*p*-toluidine), suitable for X-ray diffraction experiments, were grown from the slow diffusion of hexane into a dichloromethane solution of the complex.

For *cis*-$Ir(CO)_2Br$(*p*-toluidine), an analogous procedure was used with sodium bromide replacing sodium iodide. Red/green dichroic needles of *cis*-$Ir(CO)_2Br$(*p*-toluidine), suitable for X-ray diffraction, were grown by the vapor diffusion of hexane into a dichloromethane solution of the complex.

### 4.4. Mass Spectrometry

Mass spectra for the metal complexes were acquired in the positive ion mode, after calibration, on an Applied Biosystems 4700 MALDI TOF/TOF (Foster City, CA) instrument using direct laser desorption. A crystalline sample was manually fixed to the stainless steel target plate using Super Glue, before insertion into the instrument. The sample was subjected to irradiation from a Nd:YAG laser (354 nm), and the accelerating voltage applied was 20 kV. The instrument was operated in a standard reflectron operating mode and spectra were the average of 2000 shots, and the laser fluence used was the minimum necessary to achieve a signal from the analyte.

### 4.5. Spectroscopic Methods

Electronic absorption spectra were recorded on a PharmaSpec UV-1700 spectrophotometer (Shimadzu). Spectra of solids were acquired from samples dispersed in Nujol mulls. Infra red spectra of neat powders of these complexes were recorded on a Mattson Genesis II FT-IR spectrometer, fitted with a Specac Attenuated Total Reflectance (ATR) accessory.

### 4.6. Single crystal X-ray diffraction

The crystals were removed from the vials or tubes in which they were grown and immediately coated with hydrocarbon oil on microscope slides. Suitable crystals were mounted on glass fibers with silicone grease and placed in a cold stream of either a Bruker SMART 1000 or a Bruker SMART ApexII diffractometer. Dinitrogen cooling (90(2) K) was accomplished by use of CRYO Industries devices. A multiscan method utilizing equivalents was employed to correct for the absorption of heavy atoms [43]. The crystal structures were solved by direct methods, and all data were refined (based on $F$ [2]) using SHELXTL 5.1 [44] or SHELXL-2018 [45] software. Hydrogen atoms were located in a difference map, added geometrically, and refined with a riding model with the exception that the N-H protons were restrained to have N-H distances of 0.91(2) Å and were otherwise freely refined in all chloro complexes. Crystallographic data are found in Table 1.

## Dedication

Dedicated to Professor Richard J. Puddephatt for his many significant contributions to organometallic chemistry on the occasion of his 75th birthday.

## Acknowledgements

We thank the Petroleum Research Fund (Grant 37056-AC) for support, and the Tyco Foundation for a fellowship for E. M. G., and Dr. Jay R. Stork for collecting the diffraction data for *cis*-$Ir(CO)_2Cl$(*p*-toluidine). The Bruker SMART 1000 diffractometer was funded in part by NSF Instrumentation grant CHE-9808259.

## Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jorganchem.2019.01.002.

## References

[1] A.L. Balch, Struct. Bond 123 (2007) 1–40.
[2] G. Aullón, S. Alvarez, Chem. Eur J. 3 (1997) 655–664.
[3] V.W.-W. Yam, V.K.-M. Au, S.Y.-L. Leung, Chem. Rev. 115 (2015) 7589–7728.
[4] P. Pyykkö, Chem. Rev. 97 (1997) 597–636.
[5] J.M. Williams, A.J. Schultz, A.E. Underhill, K. Carneiro, in: J.S. Miller (Ed.), In Extended Linear Chain Compounds vol. 1, Plenum Press, New York, 1982, p. 73.
[6] A.E. Underhill, D.M. Watkins, J.M. Williams, K. Carneiro, in: J.S. Miller (Ed.), In Extended Linear Chain Compounds vol. 1, Plenum Press, New York, 1982, p. 119.
[7] K.M.-C. Wong, V.W.-W. Yam, Accounts Chem. Res. 44 (2011) 424–434.
[8] J. Kang, X. Zhang, H. Zhou, X. Gai, T. Jia, L. Xu, J. Zhang, Y. Li, J. Ni, Inorg. Chem. 55 (2016) 10208–10217.
[9] C. Po, A.Y.-Y. Tam, K.M.-C. Wong, V.W.-W. Yam, J. Am. Chem. Soc. 133 (2011) 12136–12143.
[10] K.R. Mann, J.G. Gordon, , II, H.B. Gray, J. Am. Chem. Soc. 97 (1975) 3553–3555.
[11] K.R. Mann, N.J. Lewis, R.M. Williams, H.B. Gray, J.G. Gordon, II, Inorg. Chem. 17 (1978) 828–834.
[12] N. Tran, J.R. Stork, D. Pham, M.M. Olmstead, J.C. Fettinger, A.L. Balch, Chem.

Commun. (2006) 1130–1132.
[13] N.T. Tran, J.R. Stork, D. Pham, C.J. Chancellor, M.M. Olmstead, J.C. Fettinger, A.L. Balch, Inorg. Chem. 46 (2007) 7998–8007.
[14] Y. Chen, K. Li, H.O. Lloyd, W. Lu, S.S.-Y. Chui, C.-M. Che, Angew. Chem. Int. Ed. 49 (2010) 9968–9971.
[15] A.K.-W. Chan, K.M.-C. Wong, V.W.-W. Yam, J. Am. Chem. Soc. 137 (2015) 6920–6931.
[16] R.L. White-Morris, M.M. Olmstead, A.L. Balch, J. Am. Chem. Soc. 125 (2003) 1033–1040.
[17] M.A. Malwitz, S.H. Lim, R.L. White-Morris, D.M. Pham, M.M. Olmstead, A.L. Balch, J. Am. Chem. Soc. 134 (2012) 10885–11089.
[18] M.-H. Whangbo, R. Hoffmann, J. Am. Chem. Soc. 100 (1978) 6093–6098.
[19] J.J. Novoa, G. Aullon, P. Alemany, S. Alvarez, J. Am. Chem. Soc. 117 (1995) 7169–7171.
[20] D.Y. Jeter, E.B. Fleischer, J. Coord. Chem. 4 (1974) 107–111.
[21] C. Dragonetti, M. Pizzotti, D. Roberto, S. Galli, Inorg. Chim. Acta. 330 (2002) 128–135.
[22] C.G. Pitt, L.K. Monteith, L.F. Ballard, J.P. Collman, J.C. Morrow, W.R. Roper, D. Ulku, J. Am. Chem. Soc. 88 (1966) 4286–4287.
[23] K.V. Zherikova, N.V. Kuratieva, N.B. Morozova, J. Struct. Chem. 50 (2009) 574–576.
[24] E.M. Gussenhoven, M.M. Olmstead, J.C. Fettinger, A.L. Balch, Inorg. Chem. 47 (2008) 4570–4578.
[25] P.B. Hitchcock, S. Morton, J.F. Nixon, J. Chem. Soc., Chem. Commun. (1984) 603–604.
[26] A.H. Reis Jr., V.S. Hagley, S.W. Peterson, J. Am. Chem. Soc. 99 (1977) 4184–4186.
[27] A.H. Reis, S.W. Peterson, Ann. N. Y. Acad. Sci. 313 (1978) 560–572.
[28] K.W. Krogman, W. Binder, H.D. Hausen, Angew. Chem., Int. Ed. Engl. 7 (1968) 812.
[29] Y. Tsuji, R. Hoffmann, J.S. Miller, Polyhedron 103 (2016) 141–149.
[30] A.P. Ginsberg, J.W. Koepke, J.J. Hauser, K.W. West, F.J. Di Salvo, C.R. Sprinkle, R.L. Cohen, Inorg. Chem. 15 (1976) 514–519.
[31] M. Wysocka, K. Winkler, J.R. Stork, A.L. Balch, Chem. Mater. 16 (2004) 771–780.
[32] K. Winkler, M. Wysocka-Zołopa, M.M. Oleksicka, K. Recko, L. Dobrzynski, J.R. Stork, E.M. Gussenhoven, M.M. Olmstead, A.L. Balch, Electrochim. Acta 53 (2008) 7288–7297.
[33] D.E. Bikiel, J.M. Ramallo-López, F.G. Requejo, O.B. Oña, M.B. Ferraro, J.C. Facelli, F. Doctorovich, Polyhedron 30 (2011) 221–227.
[34] U. Klabunde, Inorg. Synth. 15 (1974) 82–84.
[35] L. Vaska, J.W. DiLuzio, J. Am. Chem. Soc. 83 (1961) 2784–2785.
[36] D. Forster, Inorg. Nucl. Chem. Lett. 5 (1969) 433–436.
[37] M. Rahim, K.J. Ahmed, Inorg. Chem. 33 (1994) 3003–3004.
[38] A.L. Balch, L.A. Fossett, M.M. Olmstead, P.E. Reedy Jr., Organometallics 5 (1986) 1929–1937.
[39] S.W. Carr, B.L. Shaw, Polyhedron 6 (1987) 111–117.
[40] K. Jang, I.G. Jung, H.J. Nam, D.-Y. Jung, S.U. Son, J. Am. Chem. Soc. 131 (2009) 12046–12047.
[41] A.L. Balch, R.D. Cooper, J. Organomet. Chem. 169 (1979) 97–105.
[42] H. Huang, A.L. Rheingold, R.P. Hughes, Organometallics 28 (2009) 1575–1578.
[43] G. M Sheldrick, SADABS 2007/2, University of Göttingen: Göttingen, Germany, 2007.
[44] G.M. Sheldrick, SHELXS and SHELXL-97, Acta Crystallogr. A64 (2008) 112–122.
[45] G.M. Sheldrick, SHELXL, Acta Crystallogr. Sect. C71 (2015) 3–8.