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Copper carbene complexes. Synthesis and structural analysis of a chloro-bridged dicopper cation and the triosmium-copper carbene cluster complex $HOs_3(CO)_{11}[\mu\text{-}Cu(IPr)]$†

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ABSTRACT

The chloro-bridged carbene-substituted dicopper salt $[\{(IPr)Cu\}_2(\mu\text{-}Cl)][PF_6]$, **1**, IPr = [N,N′-bis(2,6-diisopropylphenyl)imidazolin-2- ylidene], was synthesized by the reaction of (IPr)CuCl with $Tl[PF_6]$. Reaction of **1** with the anion, $[HOs_3(CO)_{11}]^-$ of the salt $[PPN][HOs_3(CO)_{11}]$, **2** yielded the Cu - Os heterometallic cluster complex, $HOs_3(CO)_{11}[\mu\text{-}Cu(IPr)]$, **3**, the first example of Cu - Os bimetallic cluster complex containing a N-heterocyclic carbene ligand. Compounds **1** and **3** were characterized by IR, ^1H NMR and structurally by single-crystal X-ray diffraction analysis. Compound **3** contains a triosmium carbonyl cluster with a bridging Cu(IPr) group on one edge of the cluster and a terminally-coordinated hydrido ligand on one of the Cu-bridged osmium atoms.

1. Introduction

The Group 11 elements, Cu, Ag and Au, widely referred to as the "coinage metals", are well-known for their stability in their elemental forms and because of their monetary value, they have been used as forms of currency throughout the world [1]. In recent years, a variety of ligated forms of ions of these metals have been synthesized and shown to exhibit useful chemistry including catalytic transformations of organic compounds [2–6]. Copper has been one of the more chemically investigated members of this family of metals [3,4], and N-heterocyclic carbenes have been shown to be particularly effective ligands for ions of copper [7]. In the present study, we have prepared the new chloro-bridged dicopper complex $[\{(IPr)Cu\}_2(\mu\text{-}Cl)][PF_6]$, **1**, IPr = N,N′-bis(2,6-diisopropylphenyl)imidazolin-2- ylidene from the reaction of (IPr)CuCl with $Tl[PF_6]$ and investigated its structure and reactivity.

Recently, there has been great interest in the potential of heterometallic materials to perform heterogeneous catalysis [8]. These materials frequently exhibit improved activity, selectivity and longevity compared to their homometallic components. Copper has been shown to be an effective modifier and cocatalyst for bimetallic catalysts [9]. It has been shown that bi- and polymetallic cluster complexes can serve as excellent precursors to heterometallic catalysts and this has stimulated interest in the synthesis of heterometallic cluster complexes for this purpose [10].

Efforts have been made successfully to introduce carbene ligated-copper groupings into metal carbonyl cluster complexes [11], but to date there are no examples of copper carbene complexes containing osmium. In the present work, we have investigated the reaction of the new dicopper cation of **1** with the triosmium carbonyl anion $[HOs_3(CO)_{11}]^-$ obtained via the salt $[PPN][HOs_3(CO)_{11}]$, **2**. This reaction has yielded the new bimetallic complex $Os_3(CO)_{11}(H)[\mu\text{-}Cu(IPr)]$, **3**, the first example of Cu - Os carbonyl cluster complex containing a N-heterocyclic carbene ligand. Compounds **1** and **3** were both characterized by IR and ^1H NMR spectroscopy and structurally by single-crystal X-ray diffraction analyses.

2. Experimental data

2.1. General data

All reactions were performed under an atmosphere of nitrogen by using standard Schlenk techniques. Reagent grade solvents were dried by the standard procedure and were freshly distilled under nitrogen prior to use. Infrared spectra were recorded on a Nicolet IS10 Midinfrared FT-IR spectrophotometer. ^1H NMR spectra were obtained by using a Varian Mercury 300 spectrometer operating at 300 MHz. Mass spectrometric (MS) measurements performed by a direct-exposure probe by using

† Dedicated to Professor Shariff Kabir on the occasion of his retirement.

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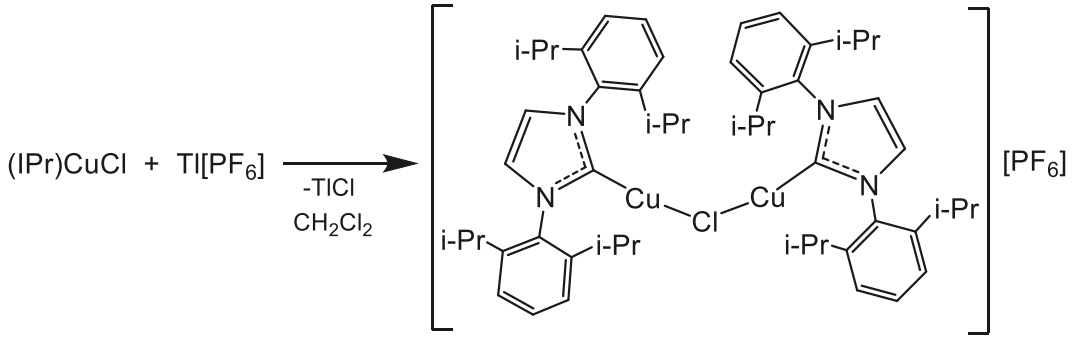


Scheme 1. A schematic for the synthesis of cation **1**.

electron impact ionization (EI) or electrospray ionization (ESI) on a VG 70S instrument. $Os_3(CO)_{12}$ and $TlPF_6$ were obtained from STREM and used without further purification. (IPr)CuCl, IPr = [N,N′-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene] was purchased from Sigma Aldrich and was used without further purification. [PPN][$Os_3(CO)_{11}(\mu$-H)], **2**, PPN = $[Ph_3PNPPh_3]^+$ was prepared according to a previously reported procedure [12].

2.2. Preparation of the dicopper carbene complex, $[\{(IPr)Cu\}_2(\mu$-Cl)][PF_6], 1

100.0 mg (0.205 mmol) of (IPr)CuCl was added to 5 mL of methylene chloride in a 100 mL three-neck flask under nitrogen. In an another 100 ml three-neck flask, 143 mg (0.41 mmol) of $TlPF_6$ was added to 5 mL of methanol and stirred until it was completely dissolved. The methanol solution of Tl[PF_6] was then added dropwise into the methylene chloride solution of the (IPr)CuCl. After stirring for 30 min at room temperature, this mixture was passed through a frit containing a celite bed into a 100 ml three-neck flask. Then the solvent was removed in vacuo and compound [{(IPr)Cu}$_2$(μ-Cl)][PF_6], **1** was isolated by solvent extraction and filtration by using methylene chloride solvent. After reducing the extract and adding few drops of hexane, small white crystals of **1** (71% yield) were obtained. Spectral data for **1**: ^{1}H NMR (CD_2Cl_2, δ): 7.53 (t, 4H, J = 7.8 Hz, para C**H**-$(CH)_2$), 7.30 (d, 8H, J = 7.8 Hz, meta CH-(C**H**)$_2$), 7.20 (s, 4H, N(C**H**)$_2$), 2.46 (sept, 8H, J = 6.9 Hz, C**H**-$(CH_3)_2$), 1.21 (d, 24H, J = 6.9 Hz, CH-(C**H**$_3$)$_2$), 1.12 (d, 24H, J = 6.9 Hz, CH-(C**H**$_3$)$_2$). Mass Spec. ESI+/MS m/z: 939, M^+

2.3. Preparation of Cu-Os_3 heterometallic cluster complex, $HOs_3(CO)_{11}[\mu$-Cu(IPr)], 3

In a 100 mL flask, 54.7 mg (0.039 mmol) of [PPN][$HOs_3(CO)_{11}$], **2** was added to 10 mL of methylene chloride under a slow purge of nitrogen. To this mixture was added 72.4 mg (0.067 mmol) of **1**. After stirring for 15 min at room temperature, the solvent was removed in vacuo. The product, $HOs_3(CO)_{11}$[μ-Cu(IPr)], **3** (10% yield) was then obtained in a pure form by a combination of extraction using hexane, filtration and crystallization from pure hexane at -78 °C. Spectral data for **3**: IR spectra, ν_{CO} (cm^{-1} in hexane): 2106.1(w), 2069.1(w), 2052.6(m), 2037.6(s), 2020.0(vs), 2002.6(w), 1979.3(w), 1960.4(vw), 1955.3(vw). ^{1}H NMR (CD_2Cl_2, δ in ppm): 7.45 (t, 2H, J = 7.5 Hz, para C**H**-$(CH)_2$), 7.33 (d, 4H, J = 7.5 Hz, meta CH-(C**H**)$_2$), 7.18 (s, 2H, N(C**H**)$_2$), 2.82 (sept, 4H, J = 6.3 Hz, C**H**-$(CH_3)_2$), 1.38 (d, 12H, J = 6.3 Hz, CH(C**H**$_3$)$_2$), 1.16 (d, 12H, J = 6.3 Hz, CH(C**H**$_3$)$_2$), -10.04 (s, 1H). Mass Spec. ESI/MS m/z: 1333, M^+.

2.4. Crystallographic analyses

Single crystals of compounds **1** and **3** suitable for X-ray diffraction analyses were obtained by slow evaporation of solvent from solutions at room temperature. Each data crystal was glued onto a glass fiber. X-ray diffraction intensity data for compound **1** was obtained by using a Bruker SMART APEX CCD-based diffractometer by using Mo Kα radiation (λ = 0.71073 Å). The raw data frames were integrated with the SAINT + program by using a narrow frame integration algorithm [13]. Correction for Lorentz and polarization effects were also applied with SAINT+. An empirical absorption correction based on the multiple measurements of equivalent reflections was applied by using the program SADABS were applied in each analysis [13]. X-ray intensity data for compound **3** was obtained by using a Bruker D8 QUEST diffractometer equipped with a PHOTON-100 CMOS area detector and an Incoatec microfocus source (Mo Kα radiation, λ = 0.71073 Å). The data collection strategy consisted of three 180° ω-scans at different φ settings and one 360° φ-scan, with a scan width per image of 0.5°. The crystal-to-detector distance was 4.0 cm and each image was measured for 5 s in shutterless mode. The average reflection redundancy was 9.6. The raw area detector data frames were reduced, scaled and corrected for absorption effects using the SAINT [14] and SADABS [15] programs. All structures were solved by a combination of direct methods and difference Fourier syntheses, and refined by full-matrix least squares refinement on F^2 by using the SHELXTL software package [16]. All non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were placed in geometrically idealized positions and were included as standard riding atoms during the final least-squares refinements with C-H distances fixed at 0.96 Å. Compound **1** crystallized in the monoclinic crystal system whereas compound **3** crystallized in the orthorhombic crystal system. The space group $P2_1/c$ was uniquely identified for compound **1** based on systematic absences observed in the intensity data. The space group Cmcm was identified for compound **3** on the basis of the systematic absences observed in the intensity data. Crystal data, data collection parameters, and results for the analyses for both compounds are listed in Table S1.

3. Results and discussion

The dicopper cation [{(IPR)Cu}$_2$(μ-Cl)]$^+$ of the salt [{(IPr)Cu}$_2$(μ-Cl)][PF_6], **1**, was obtained in 71% yield from the reaction of (IPr)CuCl with Tl[PF_6] in CH_2Cl_2 solvent at room temperature in 30 min, see Scheme 1. A number of ligand-bridged bis(copper carbene) complexes have been reported in recent years [17], but very few of them contain bridging chloro ligands. Compound **1** was characterized by ^{1}H NMR spectroscopy and electrospray ionization (ESI+) mass spectrometry and single-crystal X-ray diffraction analysis.

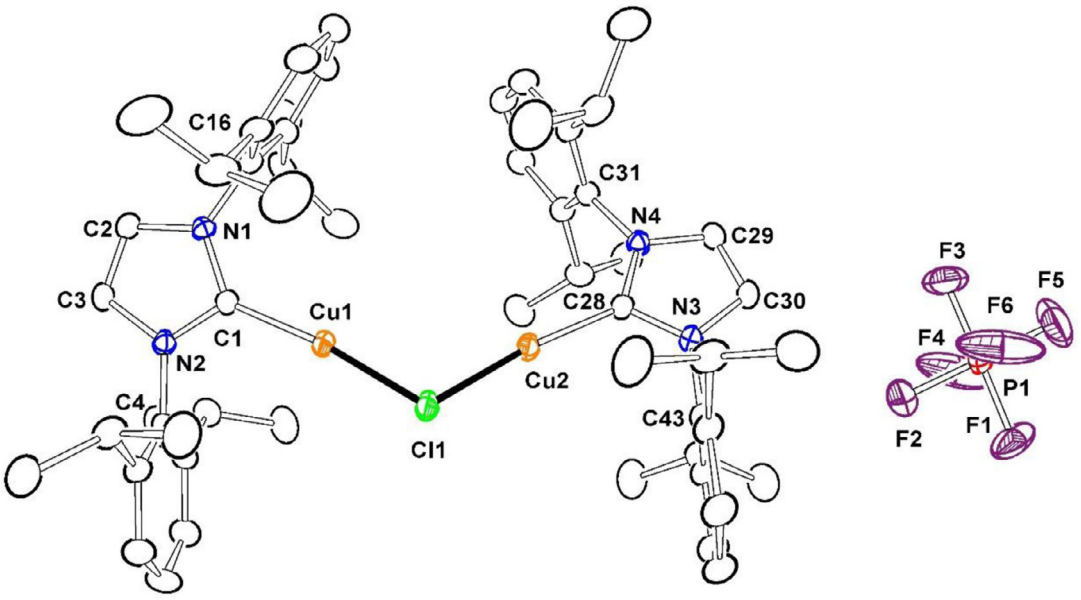
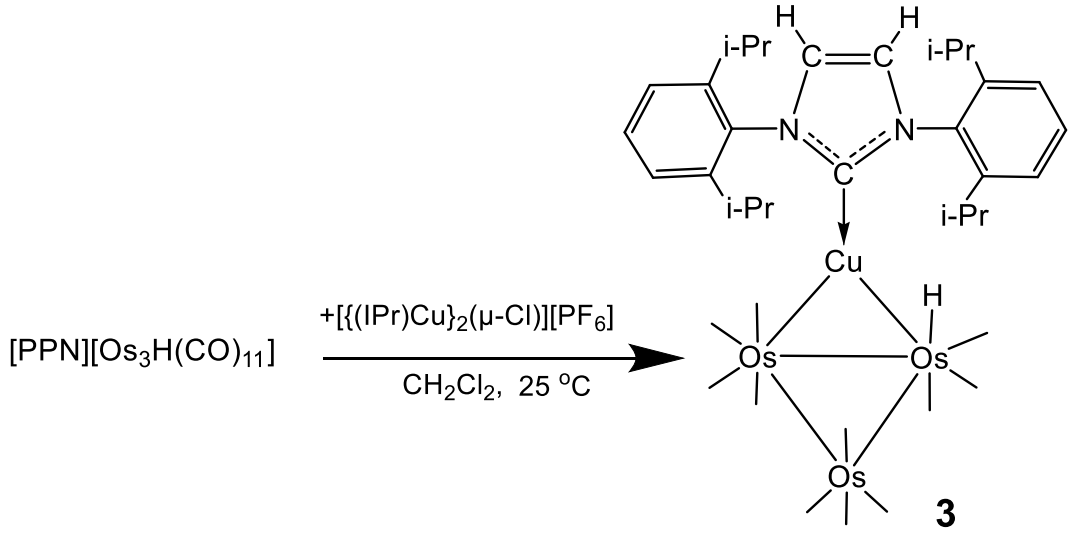


Fig. 1. ORTEP diagram of the molecular structure of $[\{(IPr)Cu\}_2(\mu\text{-}Cl)][PF_6]$, **1** showing 15% thermal ellipsoidal probabilities. Selected interatomic distances (Å) and angles (°) are as follows: Cu1-Cl1 = 2.1207 (15), Cu2-Cl1 = 2.1247 (15), Cu1-C1 = 1.874(4), Cu2-C28 = 1.876(5). C1-Cu1-Cl1 = 172.53(16), C28-Cu2-Cl1 = 171.52(15), Cu1-Cl1-Cu2 = 115.24(7).



Scheme 2. A schematic of the synthesis and structure of the Cu - Os_3 cluster complex **3**. The CO ligands in **3** are represented only as lines from the Os atoms.

An ORTEP diagram of the molecular structure of compound **1** is shown in Fig. 1.

This cation of **1** contains two Cu(IPr) groupings linked to each other via a nonlinear, bridging chloro ligand. The Cu - Cl bond distances are equal in length within experimental error, Cu1 - Cl1 = 2.120(15) Å, Cu2 - Cl1 = 2.124(15) Å, but are slightly longer than the Cu–Cl bond distance, 2.089 Å, in the precursor complex (IPr)CuCl in which the Cl ligand is bonded to only one Cu atom [18]. Each copper atom in **1** exhibits an almost linear coordination geometry, C1-Cu1-Cl1 = 172.53(16) and C28-Cu2-Cl1 = 171.52(15)°. The Cu1-Cl1-Cu2 angle is nonlinear, 115.2(7)°. The nonlinearity could be interpreted as bonding to a sp^3-hybridized octet of electrons in Cl which is expanded due to steric repulsions between the bulky carbene ligands on the copper atoms. Floriani also found a nonlinear, bridging chloro ligand in the cationic dicopper complex $[\{Cu(Me_2NCH_2CH_2NMe_2)(CO)\}_2(\mu\text{-}Cl)]^+$, Cu - Cl - Cu = 103.0(1)° [19]. On the other hand, Kunz found a linear bridging chloro ligand in the cationic dicopper(carbene) complex, $[\{Cu(bimcaMe)\}_2(\mu\text{-}Cl)]^+$, bimca = bis(imidazolin-2-ylidene)carbazolide, which contains a very bulky chelating bis(NHC) carbazolide pincer ligand on each copper atom [20]. Interestingly, for comparison, the Cu - S - Cu angle in the neutral molecule $\{(IPr^*)Cu\}_2(\mu\text{-}S)$ is 120.15(9)° [21].

The reaction of the dinuclear copper cation **1** with the triosmium cluster anion $[Os_3(CO)_{11}(\mu\text{-}H)]^-$, **2** at room temperature yielded the heterometallic Cu - Os cluster complex $HOs_3(CO)_{11}[\mu\text{-}Cu(IPr)]$, **3** containing the IPr ligand in 10% yield, see Scheme 2. Compound **3** was characterized structurally by using single-crystal X-ray diffraction analysis.

An ORTEP diagram of the molecular structure of compound **3** is shown in Fig. 2.

Compound **3** consists of a triangular cluster of three osmium atoms with a bridging copper carbene ligand lying in the plane of the Os_3 triangle on one edge of the cluster. The compound crystallizes in the space group Cmcm with only ¼ of the molecule in the asymmetric crystal unit. Thus, the molecule is disordered about a

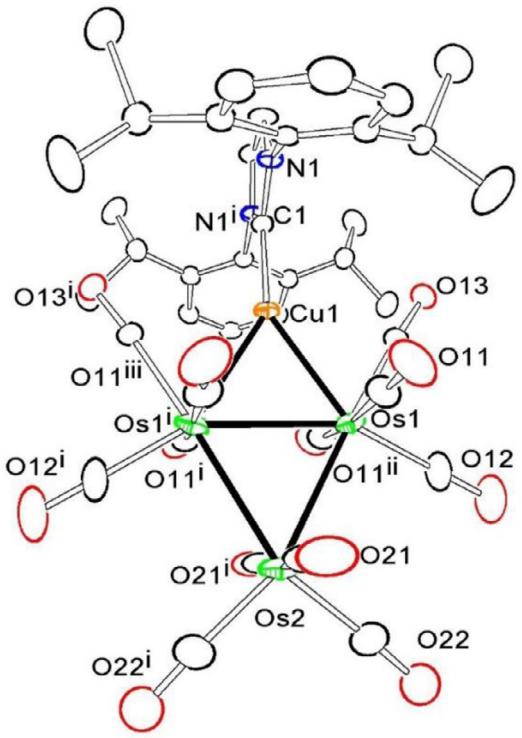


Fig. 2. ORTEP diagram of the molecular structure of the disordered molecule in the crystal of $HOs_3(CO)_{11}[\mu\text{-}Cu(IPr)]$, **3** at 10% ellipsoidal probability. C(13) - O(13) and C(13^i) - O(13^i) have only 50% occupancy at each site and are equally disordered with the one hydrido ligand in the complex. Selected interatomic distances (Å) and angles (°) are as follows: Os1-Cu1 = Cu1-$Os1^i$ = 2.6654(19), Os1-$Os1^i$ = 2.9319(17), Os1-Os2 = 2.8858(10), Cu1-C1 = 1.915(17), C1-N1 = 1.361(14).

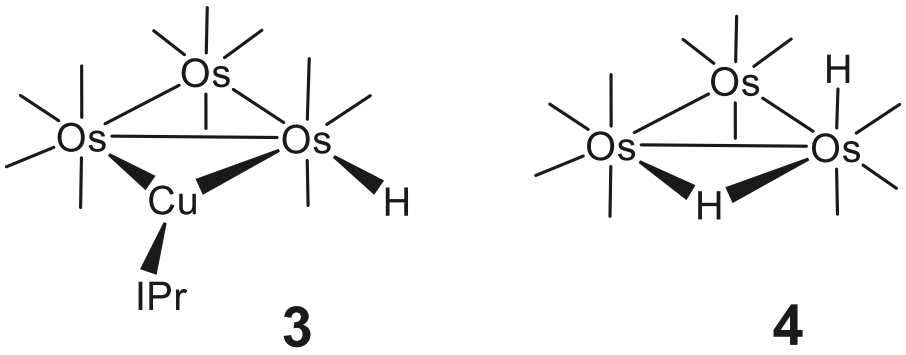
crystallographic C_2 axis. Atoms Os(2), Cu(1) and C(1) lie on this axis. In addition, the three osmium atoms and the copper atom also lie on a crystallographic symmetry plane. In addition, there is a second crystallographic symmetry plane that lies perpendicular to the first symmetry plane. The CN_2C_2 plane of the carbene ligand lies in the second symmetry plane. The two symmetry planes intersect on the C_2 axis. Overall, the molecule contains C_{2v} crystallographic symmetry. One of the CO ligands, C(13) - O(13), that lies in the first symmetry plane is equally disordered between the two sites, C(13), O(13) and $C(13)^i$, $O(13)^i$, by virtue of the C_2 axis and the second symmetry plane, see Fig. 2. This ligand has 50% occupancy in each of these two sites. This hydrido ligand was not observed directly in the crystallographic analysis. It is believed to be located proximate to the two carbon atoms sites, C(13) and $C(13)^i$, of the disordered carbonyl ligand in the remaining 50% occupancy of these two positions. The bridging copper atom Cu(1) in **3** is bonded equally to the two osmium atoms Os(1) and $Os(1)^i$, Os1-Cu1 = $Os1^i$-Cu1 = 2.6654(19) Å. The Os - Cu bond distances to the bridging Cu atom in the related triosmium - copper phosphine complex, $H_3Os_3(CO)_{10}[\mu\text{-}Cu(PPh_3)]$, were 2.695(5) Å and 2.726(5) Å [22]. The Cu-bridged Os1-Os1' bond in this structure is elongated, Os1-$Os1^i$ = 2.9319(17) Å, as compared to the unbridged Os - Os bonds Os1 - Os2 = Os2 - Os1' = 2.8858(10) Å. For comparison, the Os - Os bond lengths in the parent compound $Os_3(CO)_{12}$ are 2.8771(27) Å [23]. The Cu - C distance to the carbene ligand in **3**, Cu1-C1= 1.915(17) Å, is slightly longer than Cu - C bonds to the carbene ligands in the cation of **1**, 1.874(4) Å and 1.876(5) Å. This may be due to steric interactions between the carbene ligand and the carbonyl ligands on the osmium cluster.

The hydrido ligand in **3** exhibits a resonance in the ^1H NMR spectrum at δ = -10.03. The resonance shift is consistent with its assignment as a terminally-coordinated ligand. For reference, the resonances of the terminally-coordinated and bridging hydrido ligands in $Os_3(CO)_{11}H(\mu\text{-}H)$, **4** occur at δ = -10.25 and δ = -19.96, respectively, see Scheme 3 [23]. It is interesting to compare the structure of **3** with the structure of **4** which contains a bridging hydrido ligand in the location corresponding to the bridging Cu(IPr) grouping in **3** [24]. In **4** the terminally-coordinated hydrido ligand is positioned perpendicular to the plane of the Os_3 triangle. By comparison, our structural studies, see above, have indicated that the terminally-coordinated hydrido ligand in **3** lies in the plane of the Os_3 triangle proximate to the bridging Cu atom, Scheme 3.

The hydrido ligand and the bridging Cu(IPr) grouping in **3** each serve only as a 1-electron donor to the Os_3 cluster. Thus, the three osmium atoms in **3** contain a total of 48 valence electrons which is consistent with the observed triangular cluster having three Os - Os single bonds, as also found in **4** [24].

4. Conclusions

In this work, we have reported the synthesis of the salt $[\{(IPr)Cu\}_2(\mu\text{-}Cl][PF_6]$, **1** containing the dicopper cation $[\{(IPr)Cu\}_2(\mu\text{-}Cl]^+$, obtained by using $Tl[PF_6]$ to assist in the removal of one of the chloro ligands from one of two copper complexes, (IPr)CuCl, involved in the synthesis. The second equivalent of (IPr)CuCl then combines with the chloro-deficient one to form the dicopper cation having a bridging chloro ligand. The dicopper cation of **1** was found to react with the anion $[Os_3H(CO)_{11}]^-$ of **2** at room temperature to yield the heterometallic Cu - Os cluster complex, $HOs_3(CO)_{11}[\mu\text{-}Cu(IPr)]$, **3** which contains a IPr ligand on the copper atom that bridges a pair of osmium atoms in the triangular Os_3 cluster. The hydride ligand was not directly observed in the study, but it is believed to lie in the plane of the Os_3 triangular cluster in a terminal coordination site proximate to the Cu atom.



Scheme 3. Line structures of **3** and **4** comparing the relative positions of the hydrido ligands.

Declaration of Competing Interest

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.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2021.121799.

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