DOI: 10.1002/slct.201802319

Inorganic Chemistry

Preparation of Diethylcyanamide and Cyanoguanidine Complexes of Iridium

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Diethylcyanamide $[IrCl(\eta^5\text{-}C_5Me_5)(N{\equiv}CNEt_2)\{P(OR)_3\}]BPh_4$ (**1**) and cyanoguanidine complexes $[IrCl(\eta^5\text{-}C_5Me_5)\{N{\equiv}CN(H)C(NH_2){=}NH\}\{P(OR)_3\}]BPh_4$ (**2**) were prepared by allowing chloro compounds $[IrCl_2(\eta^5\text{-}C_5Me_5)\{P(OR)_3\}]$ to react with an excess of cyanamide or cyanoguanidine, respectively. Alternatively, complexes **2** were prepared by reacting $[IrCl_2(\eta^5\text{-}C_5Me_5)\{P(OR)_3\}]$ with an excess of cyanamide $N{\equiv}CNH_2$. Bis(diethylcyanamide) $[Ir(\eta^5\text{-}C_5Me_5)(N{\equiv}CNEt_2)_2\{P(OR)_3\}](BPh_4)_2$ (**3**) and bis(cyanoguanidine) derivatives $[Ir(\eta^5\text{-}C_5Me_5)\{N{\equiv}CN{=}C(NH_2)_2\}_2\{P(OR)_3\}](BPh_4)_2$ (**4**) were also prepared by treating dichloro precursors $[IrCl_2(\eta^5\text{-}C_5Me_5)\{P(OR)_3\}]$ first with two equivalents of AgOTf and then with an excess of diethylcyanamide or cyanoguanidine, respectively. The compounds were characterised spectroscopically (IR and NMR) and by X-ray crystal structure determination of $[Ir(\eta^5\text{-}C_5Me_5)(N{\equiv}CNEt_2)_2\{P(OMe)_3\}](BPh_4)_2$.

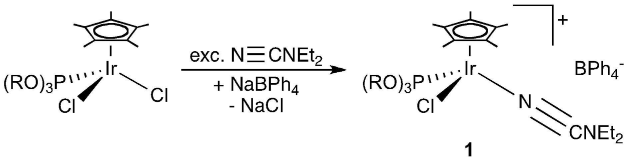
Introduction

The coordination chemistry and reactivity af amino-functionalised nitriles such as cyanamides $N{\equiv}CNH_2$ and $N{\equiv}CNR_2$ (R = alkyl or aryl) and its dimeric form cyanoguanidine $N{\equiv}CN(H)C(NH_2){=}NH$ have been well developed in the last years and a number of studies have been reported in the literature.[1-6] Interesting appear not only the preparation of new complexes, but also the nucleophilic attack on the cyanamide carbon atoms affording new derivatives.[1a,2a,b,4f,7] However, the papers reported on dialkylcyanamide and cyanoguanidine complexes of transition metals are still relatively few[1-6] as compared to nitrile RCN derivatives.[8] Molybdenum,[5] platinum,[4] copper[3] and the iron triad[9] are mainly involved as metal centres, whereas no example for iridium has ever been reported.[10]

We are interested in the chemistry not only of diazo complexes of transition metals[11] but also of nitrile,[12] cyanamide and cyanoguanidine derivatives[9,13] and have recently reported the synthesis of mono- and bis- derivatives of both the manganese and iron triads[9,13] of the type $[M(N{\equiv}CNEt_2)(CO)_nL_{5\text{-}n}]BPh_4$, $[M\{N{\equiv}CN(H)C(NH_2){=}NH\}(CO)_nL_{5\text{-}n}]BPh_4$ (M = Mn, Re; *n* = 2, 3), $[M(N{\equiv}CNEt_2)_2L_4](BPh_4)_2$, $[M\{N{\equiv}CN(H)C(NH_2){=}NH\}_2L_4](BPh_4)_2$ (M = Fe, Ru, Os), $[MCl(N{\equiv}CNEt_2)(\eta^6\text{-}p\text{-cymene})L]BPh_4$ and $[MCl\{N{\equiv}CN(H)C(NH_2){=}NH\}(\eta^6\text{-}p\text{-cymene})L]BPh_4$ (M = Ru, Os; L = phosphite). Now, as a part of these studies, we report the preparation of the first diethylcyanamide and cyanoguanidine complexes of iridium.

Results and Discussion

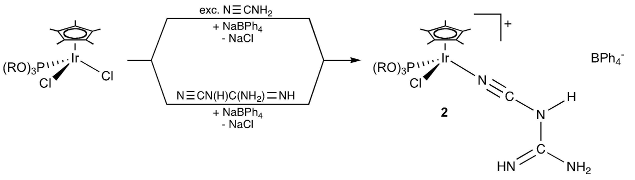
Diethylcyanamide complexes of iridium $[IrCl(\eta^5\text{-}C_5Me_5)(N{\equiv}CNEt_2)\{P(OR)_3\}]BPh_4$ (**1**) were prepared by reacting dichloro compounds $[IrCl_2(\eta^5\text{-}C_5Me_5)\{P(OR)_3\}]$ with an excess of $N{\equiv}CNEt_2$ in the presence of $NaBPh_4$, as shown in Scheme 1.



Scheme 1. Preparation of complexes **1**. R = Me (**a**), Et (**b**).

The reaction proceeds with the substitution of one chloro ligand with $N{\equiv}CNEt_2$ affording the cationic monodiethylcyanamide derivatives **1**. The presence of the cation Na^+ in the $NaBPh_4$ salt, which favours the substitution of Cl^-, allows the easy formation of complex **1** in high yield

Cyanamide $N{\equiv}CNH_2$ also reacts with dichloro compounds $[IrCl_2(\eta^5\text{-}C_5Me_5)\{P(OR)_3\}]$ in the presence of $NaBPh_4$, but affords cyanoguanidine derivatives $[IrCl(\eta^5\text{-}C_5Me_5)\{N{\equiv}CN(H)\ C(NH_2){=}NH\}\{P(OR)_3\}]BPh_4$ (**2**), which were isolated and characterised (Scheme 2).



Scheme 2. Preparation of complexes **2**. R = Me (**a**), Et (**b**).

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Supporting information for this article is available on the WWW under https://doi.org/10.1002/slct.201802319

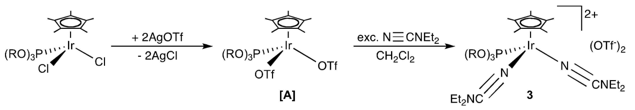
Cyanoguanidine complexes **2** were also prepared by treating the dichloro precursors $[IrCl_2(\eta^5\text{-}C_5Me_5)\{P(OR)_3\}]$ with an excess of free cyanoguanidine $N{\equiv}CN(H)C(NH_2){=}NH$ in ethanol (Scheme 2). In both cases, substitution of one Cl^- by a N-donor ligand afforded cyanoguanidine derivatives **2**.

The formation of cyanoguanidine complexes **2** from the reaction of cyanamide is not very surprising owing to the known ease of dimerisation of $N{\equiv}CNH_2$ yielding cyanoguanidine, which acts as a ligand in the complex. Dimerisation may be promoted by the coordination of one cyanamide, $[Ir]{-}N{\equiv}CNH_2$, followed by nucleophilic attack[8] on the $C{\equiv}N$ carbon atom of a second cyanamide affording, after H-shift, a N-bonded imine-cyanoguanidine derivative $[Ir]{-}NH{=}C(NH_2)N(H)C{\equiv}N$. Linkage isomerisation of this ligand gave the N-nitrile-bonded derivative.

We also attempted to prepare cyanamide complexes $[Ir]{-}N{\equiv}CNH_2$ by reacting $[IrCl_2(\eta^5\text{-}C_5Me_5)\{P(OR)_3\}]$ with $N{\equiv}CNH_2$ in 1:1 ratio but only cyanoguanidine derivatives **2** formed under all conditions. Nucleophilic attack of free $N{\equiv}CNH_2$ to give cyanoguanidine is probably faster than coordination of cyanamide, affording exclusively complexes **2** as final products.

The presence of two chloro ligands in the precursors prompted us to attempt the preparation of bis(diethylcyanamide) complexes by substituting both Cl^- groups. Unfortunately, only one chloro ligand can be substituted, affording in every condition mono-derivatives **1**, **2** or decomposition products.

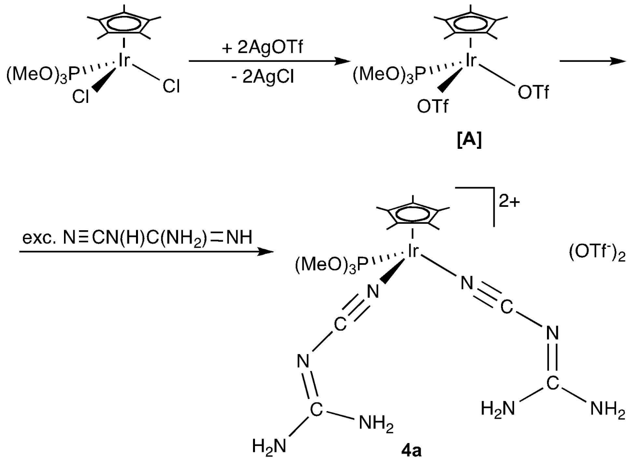
A different strategy was therefore adopted, involving the treatment of chloro precursors $[IrCl_2(\eta^5\text{-}C_5Me_5)\{P(OR)_3\}]$ first with two equivalents of AgOTf and then, after filtration to remove the AgCl formed, with an excess of diethylcyanamide, as shown in Scheme 3.



Scheme 3. Preparation of complexes **3**. R = Me (**a**), Et (**b**).

The reaction proceeds with the removal of the two chloro ligands and probable formation of the triflate intermediate **[A]**, which was not isolated. Substitution of the labile triflate ligands with diethylcyanamide affords the bis- derivatives $[Ir(\eta^5\text{-}C_5Me_5)(N{\equiv}CNEt_2)_2\{P(OR)_3\}]^{2+}$ (**3**), which were separated as BPh_4 salt and characterised. The success of this synthesis led us to try to prepare bis(cyanoguanidine) complexes $[Ir(\eta^5\text{-}C_5Me_5)\{N{\equiv}CN{=}C(NH_2)_2\}_2\{P(OR)_3\}](BPh_4)_2$ (**4**) following the method reported in Scheme 4.

The reaction proceeds like with $N{\equiv}CNEt_2$ affording bis-derivatives **4**, which were isolated as solid in the case of $P(OMe)_3$ or as an oily product in the case of $P(OEt)_3$. It is worth noting that while monocyanoguanidine complexes $[IrCl(\eta^5\text{-}C_5Me_5)\{N{\equiv}CN(H)C(NH_2){=}NH\}\{P(OR)_3\}]BPh_4$ (**2**) can be obtained reacting both cyanamide and cyanoguanidine with the chloro precursors $[IrCl_2(\eta^5\text{-}C_5Me_5)\{P(OR)_3\}]$, bis- derivatives $[Ir(\eta^5\text{-}C_5Me_5)\{N{\equiv}CN{=}C(NH_2)_2\}_2\{P(OR)_3\}](BPh_4)_2$ (**4**) were obtained only by reacting cyanoguanidine with the precursor **[A]**. The reaction of an excess of $N{\equiv}CNH_2$ with **[A]** does not give **4** but an intractable mixture of products. In addition, whereas mono-derivatives **2** contain the aminic form of the cyanoguanidine (Figure 1, **[B]**), the bis- derivative **4a** contains the iminic form (Figure 1, **[C]**).



Scheme 4. Preparation of complex **4a**.

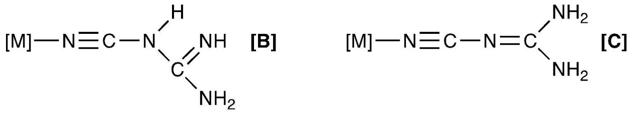


Figure 1. Aminic **[B]** and iminic **[C]** forms of cyanoguanidine.

Examples of dialkylcyanamide and cyanoguanidine complexes have been reported for several transition metals[1-7] but, to the best of our knowledge, no one involved iridium as the central metal. The use of the pentamethylcyclopentadienyl fragment $[Ir(\eta^5\text{-}C_5Me_5)\{P(OR)_3\}]$ with phosphite allows the synthesis of the first complexes of iridium containing both one and two diethylcyanamide and cyanoguanidine as ligands.

The new diethylcyanamide **1**, **3** and cyanoguanidine **2**, **4a** were isolated as yellow-orange solids stable in air and in solution of polar organic solvents, where they behave as either 1:1 (**1**, **2**) or 2:1 (**3**, **4**) electrolytes.[14] Analytical and spectroscopic (IR, NMR) data support the proposed formulation, which was further confirmed by X-ray crystal structure determination of the bis(diethylcyanamide) complex $[Ir(\eta^5\text{-}C_5Me_5)(N{\equiv}CNEt_2)_2\{P(OMe)_3\}](BPh_4)_2$ (**3a**), the ORTEP[15] of which is shown in Figure 2.

As stated in the Experimental section, the disorder of several atoms was not modelled, which are easy to identify in Figure 2 since they are sketched as spheres of arbitrary radius. The geometrical parameters of these atoms are consequently not accurate and even the position of the metal atom is

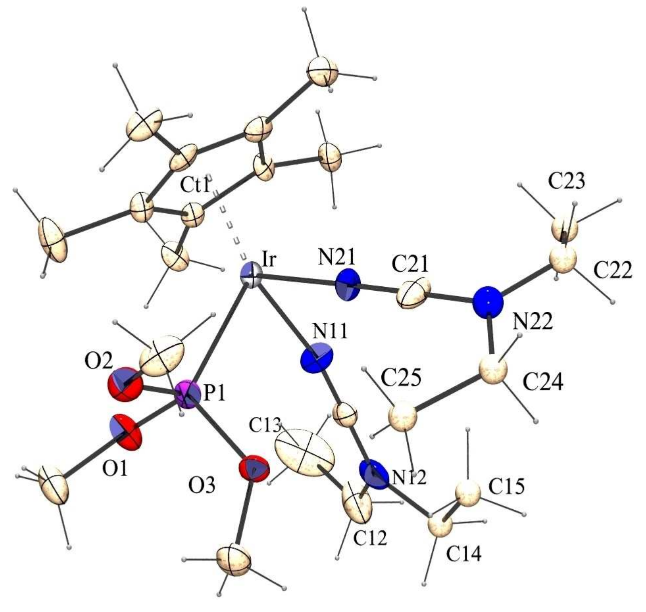


Figure 2. ORTEP view of complex **3 a**.

affected by this lack of fidelity and for this reason data discussed below should be used with caution. Nevertheless, the structure of the compound consists of two tetraphenylborate anion (not shown in the figure and also affected by disorder in several carbon atoms) and a cation formed of an iridium atom η^5-coordinated [ring-slippage 0.094 Å] to a pentamethylcyclopentadienyl (Cp) Note for typesetting: in pdf proofs the asterisk of Cp* does not appear superscript, this and the two succeeding in the paragraph and three monodentate ligands - one P(OMe)$_3$ phosphite and two monodentate diethylcyanamide ones - leading to the formation of a "three-legged piano stool" structure. The geometry of the complex is pseudo-octahedral and is marked by near-90° values for the angles among the legs (Table 1). Table 1 also contains the following parameters, that should be taken with caution: the centroid of the Cp ligand is located at about 1.812 Å from the metal atom, the average Ir–C bond distances for the Cp ligand are 2.179 Å and Ru–P bond length is 2.253(4) Å; these values are actually similar to those found in the literature.[16]

Table 1. Selected list of bond lengths [Å] and angles [°] for **3 a**.

Ir–CT1	1.8120(5)	Ir–P(1)	2.253(4)
Ir–N(21)	2.002(12)	Ir–N(11)	2.053(15)
Ir–C(1)	2.144(14)	Ir–C(2)	2.143(15)
Ir–C(3)	2.238(16)	Ir–C(4)	2.206(13)
Ir–C(5)	2.164(13)	Ir–C$_{av}$	2.179
N(11)–C(11)	1.15(2)	N(21)–C(21)	1.19(2)
C(11)–N(12)	1.27(2)	C(21)–N(22)	1.34(3)
N(12)–C(12)	1.36(3)	N(22)–C(22)	1.39(5)
N(12)–C(14)	1.50(3)	N(22)–C(24)	1.45(4)
CT1-Ir–N(11)	124.4(4)	CT1-Ir–P(1)	129.53(12)
CT1-Ir–N(21)	125.7(5)	N(21)-Ir–P(1)	91.4(5)
N(21)-Ir–N(11)	84.7(7)	N(11)-Ir–P(1)	87.8(5)
C(11)-N(11)-Ir	166.9(14)	C(21)-N(21)-Ir	172(2)
N(11)-C(11)-N(12)	179(2)	N(21)-C(21)-N(22)	177(3)
C(11)-N(12)-C(12)	131(2)	C(21)-N(22)-C(22)	119(3)
C(11)-N(12)-C(14)	118(2)	C(21)-N(22)-C(24)	120(3)
C(12)-N(12)-C(14)	111(2)	C(22)-N(22)-C(24)	120(3)
C(13)-C(12)-N(12)	106(3)	C(23)-C(22)-N(22)	121(5)
N(12)-C(14)-C(15)	113(2)	N(22)-C(24)-C(25)	116(3)

Although the NEt$_2$ fragments of the nitrile ligands are so disordered to prevent the discussion of the geometrical parameters, the N≡C bond lengths, 1.15(2) and 1.19(2) Å, are indicative of a triple bond and similar to those of the free related dimethylcyanamide, NCNMe$_2$ 1.1609(16) Å[17] and also of other metal complexes with diethylcyanamide ligand.[4c,h,5c,9,13] Coordination angles are close to linearity, 166.9(14) and 172(2)° like in the mentioned complexes. Also the nitrogen atoms of the amide group, N(12) and N(22), have a trigonal planar geometry rather than a pyramidal one; in fact, the root-mean-square deviations from the plane for the four atoms are 0.0004 and 0.0176 Å and the sum of angles around these atoms are close to 360°, although values from 111 to 131° are found in one of them, undoubtedly due to sterical effects but also to the disorder on these atoms. These data suggest a sp^2 hybridization of the nitrogen atom [and a double bond character for the C=N bond, as demonstrated by the distances 1.27(2) and 1.34(3) Å], and are indicative of some delocalisation.

The IR spectra of diethylcyanamide complexes **1 a** and **1 b** show a strong band at 2267 cm^{-1} attributed to the ν_{CN} of the N≡CNEt$_2$ ligand. Its presence is confirmed by the ^{1}H NMR spectra, which show the characteristic triplet at 1.26 or 1.27 ppm and quartet at 3.14 or 3.17 ppm (J_{HH}=7.0 Hz) of the ethyl groups of cyanamide. In the spectra, also appear the signals of the ancillary ligands η^5-C$_5$Me$_5$ and P(OR)$_3$ and of the anion BPh$_4$, whereas the ^{31}P NMR shows a singlet fitting the proposed formulation for the complexes.

Besides the medium-intensity bands at 3435–3228 cm^{-1} due to the ν_{NH} of the amine NH$_2$ and imine =NH of the cyanoguanidine ligand, the IR spectra of compounds [IrCl(η^5-C$_5$Me$_5$){N≡CN(H)-C(NH$_2$)=NH}{P(OR)$_3$}]BPh$_4$ (**2**) show one strong absorption at 2248 cm^{-1} attributed to the ν_{CN} of the nitrile group. The presence of only one ν_{CN} band also indicates that the cyanoguanidine ligand is present in the aminic form (Figure 1, **[B]**). In the spectra, also the δ_{NH2} band appears as a strong absorption at 1630–1628 cm^{-1}. The ^{1}H NMR spectra of cyanoguanidine complexes **2** show not only the signals of the ancillary ligands η^5-C$_5$Me$_5$ and P(OR)$_3$ but also, in CD$_2$Cl$_2$, a broad signal at 4.60 (**2 a**) and 4.58 (**2 b**) ppm attributed to the NH$_2$ or NH protons of cyanoguanidine. Instead, in acetone-d$_6$ two broad signals appear at 6.42 and 3.30 (**2 a**) and at 6.34 and 3.23 (**2 b**) ppm, which were attributed to one of the =NH iminic and to the NH$_2$ protons of N≡CN(H)C(NH$_2$)=NH (Figure 1, **[B]**).

However, lowering of the sample temperature caused a change in the spectra with the appearance (at -30 °C in CD$_2$Cl$_2$ for **2 a**) of three slightly-broad signals at 5.16, 4.79 and 4.20 ppm, with intensity ratio 1:1:2, which were attributed to the two =NH groups and to the NH$_2$ protons, respectively, of the cyanoguanidine ligand. The ^{13}C NMR spectra of complexes **1** and **2** fit the proposed formulation showing the characteristic signals of the η^5-C$_5$Me$_5$ and phosphite ligands and a broad singlet at 155.3 (**1 a**) and 156.5 (**2 a**) ppm attributed to the nitrile carbon atom N≡C–N of the cyanamide and cyanoguanidine ligands. Instead, the resonance of the CNH_2 carbon atom of $N{\equiv}CN(H)C(NH_2){=}NH$ appears as a singlet at 162.87 ppm for complex **2 a**.

The IR spectra of the bis(cyanamide) complexes $[Ir(\eta^5\text{-}C_5Me_5)(N{\equiv}CNEt_2)_2\{P(OR)_3\}](BPh_4)_2$ (**3**) show only one band at 2267–2265 cm^{-1} attributed to the ν_{CN} of cyanamide. The presence of only one band is rather surprising, as the two cyanamide ligands must be in a mutually *cis* postion and should thus show two ν_{CN} bands. The ν_{CN} values of the two cyanamides are probably so close that the instrument could only detect one slightly-broad signal. The ^1H NMR spectra of **3 a** and **3 b** confirm the presence of the $N{\equiv}CNEt_2$ ligand showing a quartet at 3.04 and a triplet at 1.17 ppm (J_{HH} = 7.0 Hz) of the ethyl substituents of cyanamide. The ^{31}P NMR spectra show a sharp singlet at 74.99 (**3 a**) and 69.25 (**3 b**) ppm, in agreement with a geometry of the complexes like that found in the solid state.

Unlike the related mono-derivatives **2 a** and **2 b**, the IR spectrum of the bis(cyanoguanidine) complex $[Ir(\eta^5\text{-}C_5Me_5)\{N{\equiv}CN{=}C(NH_2)_2\}_2\{P(OMe)_3\}](BPh_4)_2$ (**4 a**) shows two strong absorptions at 2208 and at 2164 cm^{-1} attributed to the ν_{CN} of cyanoguanidine, which appear at somewhat lower wavenumbers than in the related species **2 a** and **2 b**. In addition, only two medium-intensity bands at 3428 and 3333 cm^{-1} also appear in the spectrum, attributed to the ν_{NH} of the cyanoguanidine. On this basis we can hypothesise that cyanoguanidine is present in the iminic form (Figure 1, **[C]**) in our bis-deivative **4 a**, although the presence of two ν_{CN} bands may be in agreement with the *cis* position of the two cyanoguanidine groups (form **[B]**).

In order to clarify this problem, we recorded the ^1H NMR spectrum between +20 and -80 °C and, in contrast with the behaviour of the related **2 a**, no substantial profile variations were observed. Besides the signals of the ancillary ligands, only one broad signal near 3.9 ppm appeared, which was attributed to the aminic NH_2 protons of cyanoguanidine **[C]**. The absence of any iminic =NH proton signals even at -80 °C led us to propose the geometry of Scheme 4 for our bis(cyanoguanidine) derivative **4 a**.

Conclusions

This report describes the preparation of the first diethylcyanamide and cyanoguanidine complexes of iridium stabilised by the half-sandwich pentamethylcyclopentadienyl fragment $[IrCl(\eta^5\text{-}C_5Me_5)\{P(OR)_3\}]^+$. This fragment also allows the preparation of the first bis(diethylcyanamide) and bis(cyanoguanidine) derivatives for this metal. The structural parameters for $[Ir(\eta^5\text{-}C_5Me_5)(N{\equiv}CNEt_2)_2\{P(OMe)_3\}](BPh_4)_2$ were determined.

Supporting Information Summary

Complete Experimental section; details of crystal data and structure refinement (Table S1).

Acknowledgements

The financial support of MIUR - PRIN 2016 is gratefully acknowledged. We thank CACTI (Universidade de Vigo) for X-ray data collection. Thanks are also due to Daniela Baldan, of the Università Ca' Foscari Venezia (Italy), for technical assistance.

Conflict of Interest

The authors declare no conflict of interest.

Keywords: Cyanoguanidine complexes · Diethylcyanamide complexes · Iridium · Synthesis

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Submitted: July 24, 2018
Accepted: October 8, 2018