Au(III) Cyclometallated Compounds with 2-Arylpyridines

Subjects: Chemistry, Inorganic & Nuclear

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A large numbers of reports (>100) described molecules (>500) and single crystal X-ray structures (>200) indicated that the Au(III) compounds with 2-arylpyridines* and their derivatives or analogues are interesting from the chemical, spectroscopic, and structural viewpoints. The most popular Au(III)-2PPY* species are those with 2-phenylpyridine* and 2-(4-methylphenyl)pyridine*, while among Au(III)-2ArPY* molecules-those containing 2-benzylpyridine* ring system.

Keywords: Au(III) compounds ; 2-phenylpyridine ; cyclometallation ; 15N NMR

1. Au(III)-2PPY* Compounds

1.1. Au(III)-2PPY* Dihalides

The simplest representative of this class of chemicals is [Au(2-phenylpyridine*)Cl_2] (i.e., [Au(2ppy*)Cl_2]), described for the first time in 1989 by Constable et al. [1]. It is widely used as a precursor for the synthesis of some other Au(III)-2ppy* compounds; thus, the number of articles where it appears is really large, and the most noteworthy papers are those in which its NMR characterization was given [1][2][3][4][5][6][7][8][9][10], together with the single crystal X-ray structure (IJAQEP) [3]. Surprisingly, despite numerous reports about this dichloride [Au(2ppy*)Cl_2] species, there are no literature data on its analogues with some other halogens (F, Br, I)—although they are available for similar Au(III)-2PPY* (2PPY* ≠ 2ppy*) dihalides.

Among the dihalides having the general formula [Au(2PPY*)XY] (X, Y = F, Cl, Br, I), including [Au(2PPY*)X_2], and particularly, the most popular [Au(2PPY*)Cl_2] one, 43 (not counting [Au(2ppy*)Cl_2]) were reported and characterised by NMR spectroscopy and/or by single crystal X-ray diffraction [2][5][8][9][10][11][12][13][14][15][16][17][18][19][20][21][22][23][24].

A total of 3 of them contained 2ppy* derivatives, substituted only in the pyridine ring (R^1 = 3-methyl-, 4-*n*-propyl-, 5-*n*-butyl-) [2][10][11], while 25 had 2ppy* derivatives with substituent(s) exclusively in the phenyl ring (R^2 = 2-, 3- and 4-methyl-; 3-*n*-butyl; 4-*tert*-butyl-; 2- and 4-fluoro-; 2,4-difluoro-; 4-chloro-; 3- and 4- trifluoromethyl-; 3- and 4-methoxy-; 4-*n*-butoxy-; 3,5-dimethoxy-; 2- and 4-trifluoromethoxy-; 4-formyl-; 2-, 3- and 4-phenyl; 4-(9-bromo)-*n*-nonoxy)-; 4-(9-trimethylammonium-*n*-nonoxy)-; 4-(9-(4-methylphenylsulfonoxy)-*n*-nonoxy-) [5][8][9][10][11][12][13][14][15][16][17][18][19][20]. Then, 15 possessed 2ppy* derivatives substituted in both the pyridine and the phenyl ring (3-methyl-2-(2-fluorophenyl)pyridine*, 3-methyl-2-(3,4,5-trimethoxyphenyl)pyridine*, 5-carboxy-2-(4-carboxyphenyl)pyridine*, 5-ethoxycarbonyl-2-(4-ethoxycarbonylphenyl)pyridine*, 4-dimethylamino-2-(2,3,4-trifluorophenyl)pyridine*, 4-dimethylamino-2-(3-trifluoromethylphenyl)pyridine*, 4-dimethylamino-2-(4-trifluoromethoxyphenyl)pyridine*) [21][22][23][24].

All these [Au(2PPY*)XY] dihalides (Scheme 1 left, for L^1 = X and L^2 = Y) are listed (the 2PPY* ligands are presented as 2ppy* derivatives, variously substituted in the pyridine ring (by R^1) and/or in the phenyl ring (by R^2), so having the general formula/name of a-R^1-2-(b-R^2-phenyl)pyridine* (a = 3–6, b = 2–5)), together with the main solvents used upon the NMR studies and the CCDC reference codes for the respective single crystal X-ray structures; moreover, the biological (BIO) and catalytic (CAT) activity, as well as luminescence properties (LUM), are indicated. The same notations will be used in all other tables.

Among these [Au(2PPY*)XY] compounds, [Au(2-(4-*tert*-butylphenyl)pyridine*)Cl_2] is biologically active, revealing anti-tumour properties (against breast or lung cancer and leukemia) [25][26]. Some other [Au(2PPY*)Cl_2] dichloride species have catalytic properties (in reactions between alkynes, carbonyl compounds, and amines or imines—yielding amines, allenes, or oxazoles [16][17]—as well as between propargyl esters and styrene—yielding cyclopropane derivatives [22]).

1.2. Au(III)-2ppy* Compounds with Auxiliary Ligands Other Than Halides

In addition to [Au(2ppy*)Cl_2], 92 Au(III)-2ppy* compounds with various auxiliary ligands (both organic and inorganic, but not halides), having the general formula [Au(2ppy*)L^1L^2] (in case of L^1 = L^2, i.e., identical L ligands: [Au(2ppy*)L_2]) or [Au(2ppy*)(L^1L^2)] (in case of symmetrical LL ligands: [Au(2ppy*)(LL)])(left or right, respectively; for R^1 = R^2 = H), were reported and characterised by NMR spectroscopy and/or by single crystal X-ray diffraction [2][3][5][6][7][8][11][15][19][27][28][29][30][31][32][33][34][35][36][37][38][39][40][41][42][43][44][45][46][47][48][49][50]. In case when the sum of electric charges at auxiliary ligand(s) was different from −2 (0 or −1), the concerned Au(III)-2ppy* compound was cationic (+2 or +1 charge), and the relevant anion presented in a separate column *Counterion*; otherwise (the sum of electric charges at auxiliary ligand(s) being −2), the Au(III)-2ppy* molecule was electrically neutral.

Many these Au(III)-2ppy* compounds are biologically active, revealing anti-tumour properties (against various breast, cervix, colon, liver, lung, and ovarian cancers, as well as glioblastoma, leukemia, and melanoma) [3][8][9][11][28][31][33][43][51]. Some others have catalytic properties (in the hydration of alkynes to enoles [7] and photo-oxidation of benzylic amines to imines [42]). Then, a large number reveals luminescence, with lifetimes of either >10 µs [15][19][37][39][42] or <10 µs [15][27][38][41].

1.3. Au(III)-2PPY* Compounds with Auxiliary Ligands Other Than Halides

In addition to [Au(2PPY*)XY] (including [Au(2PPY*)X_2]) and [Au(2ppy*)L^1L^2], including [Au(2ppy*)L_2]) or [Au(2ppy*)(L^1L^2)], including [Au(2ppy*)(LL)]) compounds, 209 Au(III)-2PPY* species with various auxiliary ligands (other than halides)), having the general formulae [Au(2PPY*)L^1L^2] (in particular, [Au(2PPY*)L_2]; L^1, L^2, L ≠ F, Cl, Br, I) or [Au(2PPY*)(L^1L^2)] (in particular, [Au(2PPY*)(LL)]) were reported and characterised by NMR spectroscopy and/or by single crystal X-ray diffraction [2][5][8][11][12][14][15][18][19][21][22][23][24][25][26][27][31][37][47][52][53][54][55][56][57][58][59][60][61][62][63][64][65][66][67][68][69][70][71][72][73][74][75][76] (for 2PPY* ≠ 2ppy* and L^1, L^2 ≠ F, Cl, Br, I).

A total of 5 of them contained 2ppy* derivatives, substituted only in the pyridine ring (R^1 = 3-methyl-, 5-*n*-butyl-, 4-*tert*-butyl-, 3,5-dimethyl-) [2][11], while 137—only in the phenyl ring (2- and 4-methyl-; 3-ethyl-; 3- and 4-*n*-butyl; 4-*tert*-butyl-; 3,5-dimethyl-; 4-fluoro-; 2,4- and 3,5-difluoro-; 3-, 4- and 5-trifluoromethyl; 4-methoxy-; 4-*n*-butoxy-; 2- and 4-trifluoromethoxy-; 4-formyl; 4-nitro-; 4-phenyl-; 3,5-bis(pentafluorophenyl)-), with a predominance of the 2-(4-methylphenyl)pyridine* ligand (95 species) [5][8][11][12][14][15][18][19][25][26][27][31][37][47][51][52][53][54][55][56][57][58][59][60][61][62][63][64][65][66].

Then, 67 had 2ppy* derivatives with substituents in both the pyridine and the phenyl ring (2,6-bis(4-*tert*-butylphenyl)pyridine*; 3-methyl-2-(2-fluorophenyl)pyridine*; 4- and 5-methyl-2-(4-methoxyphenyl)pyridine*; 6-methyl-2-(4-methylphenyl)pyridine*; 5-*tert*-butyl-2-(4-*tert*-butylphenyl)pyridine*; 4-trifluoromethyl-2-(4-methylphenyl)pyridine*; 5-trifluoromethyl-2-(4-methoxyphenyl)pyridine*; 5-trifluoromethyl-2-(2-diphenylaminophenyl)pyridine*; 3-, 4-, and 6-methoxy-2-(4-methylphenyl)pyridine*; 5-carboxy-2-(4-carboxyphenyl)pyridine*; 5-ethoxycarbonyl-(2-(4-ethoxycarbonylphenyl)pyridine*; 4-dimethylamino-2-(2,3,4-trifluorophenyl)pyridine*; 4-dimethylamino-2-(3-trifluoromethylphenyl)pyridine*; 4-dimethylamino-2-(4-trifluoromethoxyphenyl)pyridine*; 3-nitro-2-(4-methylphenyl)pyridine*) [21][22][23][24][37][53][67][68][69][70][71][72][73][74][75][76]. Among these ligands, 2,6-bis(4-*tert*-butylphenyl)pyridine* is especially interesting because 2,6-bis(4-*tert*-butylphenyl)pyridine can chelate transition metal ions, not only in the bidentate way (κ^2-N(1),C(6′)*), but also in the tridentate mode (κ^3-N(1),C(6′)*,C(6″)*)—forming Au(III)-(2,6-bis(4-*tert*-butylphenyl)pyridine**) pincer compounds (2,6-bis(4-*tert*-butylphenyl)pyridine** = dianionic form of 2,6-bis(4-*tert*-butylphenyl)pyridine, deprotonated in both phenyl groups at the *ortho*- carbons C(6′)* and C(6″)*).

Many these Au(III)-2PPY* compounds are biologically active, revealing anti-tumour (against various breast, cervix, colon, liver, lung, mammary, and ovarian cancers, as well as glioblastoma, leukemia, and melanoma) [8][9][11][25][26][31][51][63][64], as well as anti-bacterial (against *Escherichia coli*, *Bacillus subtilis*, and *Pseudomonas aeruginosa*) and anti-fungal (against *Candida albicans*, *Trichophyton mentagrophytes*, and *Cladosporium resinae*) [63] properties. Some others have catalytic activity (in reactions between propargyl esters and styrene—yielding cyclopropane derivatives [22] and upon CO oxidation by air to CO_2 [65]). Then, a number of these species exhibits luminescence, with lifetimes of either >10 µs [19][37] or <10 µs [15][18][24][27][75].

2. Au(III)-2ArPY* Compounds

2.1. Au(III)-2ArPY* Dihalides

A total of 68 Au(III) dihalides with 2-arylpyridines*, other than 2PPY* (denoted as 2ArPY*), having the general formula [Au(2ArPY*)X_2] (X = F, Cl, Br, I), were reported and characterised by NMR spectroscopy and/or by single crystal X-ray diffraction [6][9][13][16][17][18][19][30][33][40][62][77][78][79][80][81][82][83][84][85][86][87][88][89][90].

The contained 2ArPY* ligands are of two principal types: (A) containing a bridge (denoted as Z) between the pyridine and the phenyl ring (–CH_2– in 2-benzylpyridine*, –CO– in 2-benzoylpyridine*, –O– in 2-phenoxypyridine*, –S– in 2-phenylsulfanylpyridine*, –NH– in 2-anilinopyridine*; Scheme 2) and (B) having the pyridine ring linked to any aryl (but not phenyl) ring system (naphth-2-yl, 9,9-dialkylfluoren-2-yl, dibenzofuran-4-yl; Scheme 3).

There are 61 [Au(2ArPY*)X_2] molecules with 2ArPY* ligands of type A [9][13][16][17][18][30][33][40][62][77][78][79][80][81][82][83][84][85][86][87][88][89] (including 8 compounds having one or two substituents at the Z bridge, with this position being numbered as 1 of the aryl moiety: –CH_2– (6 species with 2ArPY* = 2-(1-methylbenzyl)pyridine*, 2-(1,1-dimethylbenzyl)pyridine*, 2-(1-methoxybenzyl)pyridine*, 2-(1-phenylbenzyl)pyridine*, 2-(1-carboxymethoxyiminobenzyl)pyridine* and 2-(1-benzoxyiminobenzyl)pyridine*) [17][77][83][84], or –NH– (2 species with 2ArPY* = 2-(1-methylanilino)pyridine* and 2-(1-propionylanilino)pyridine*) [40][83][89]), as well as 7 [Au(2ArPY*)X_2] molecules with 2ArPY* ligands of the type B [6][19][90].

Then, the [Au(2ArPY*)X_2] compounds with 2ArPY* of type A can be divided for those containing unsubstituted pyridine and phenyl rings (16 species) [9][13][16][17][18][30][33][40][62][77][78][79][80][81][82][83][84][85][86][87][89], substituted pyridine rings and unsubstituted phenyl rings (32 species) [83][88], as well as unsubstituted pyridine rings and substituted phenyl rings (13 species) [17][83][89], whereas those with simultaneously substituted pyridine and phenyl rings are absent. Similarly, the [Au(2ArPY*)X_2] compounds with 2ArPY* of the type B can be divided for these having no substituents in the pyridine and aryl ring (four species) [6][19][90], having substituents in the pyridine ring only (two species) [6][90] or in the aryl ring only (one species) [90], but not in both rings. Furthermore, if treating [Au(2ArPY*)X_2] molecules with 2ArPY* of the types A and B together, 20 has no substituents in both ring systems [6][9][13][16][17][18][19][30][33][40][62][77][78][79][80][81][82][83][84][85][86][87][89][90], while 48 is substituted either in the pyridine ring (34 examples) [6][83][88][90] or in the aryl ring (14 examples) [17][83][89][90].

A few [Au(2ArPY*)Cl_2] compounds are biologically active, revealing anti-tumour properties (against various breast, colon, kidney, lung, mammary, ovarian, pancreas, and prostate and uterus cancers, as well as leukemia) [25][30][79][83]. Some others exhibit catalytic activity (in reactions between alkynes, carbonyl compounds, and amines or imines—yielding amines, allenes, or oxazoles) [16][17].

2.2. Au(III)-2ArPY* Compounds with Auxiliary Ligands Other Than Halides

In addition to [Au(2ArPY*)X_2] dihalides, 108 Au(III)-2ArPY* compounds (2ArPY* ≠ 2PPY*) with various auxiliary ligands (other than halides), having the general formula [Au(2ArPY*)L^1L^2] (particularly [Au(2ArPY*)L_2]) or [Au(2ArPY*)(L^1L^2)]) (particularly [Au(2ArPY*)(LL)]) were reported and characterised by NMR spectroscopy and/or by single crystal X-ray diffraction [6][9][14][18][19][25][30][31][33][39][40][45][51][62][63][64][75][77][79][82][85][87][89][90][91][92][93][94][95][96][97][98][99][100][101][102].

As many as 97 Au(III)-2ArPY* compounds contain unsubstituted (or substituted only at the Z bridge) 2ArPY* ligands [6][9][14][18][19][25][30][31][33][39][40][45][51][62][63][64][77][79][82][85][87][89][90][91][92][93][94][95][96][97][98][99][100][101][102] (all 88 molecules with 2ArPY* of the type A [9][14][18][25][30][31][33][40][45][51][62][63][64][77][79][82][85][87][89][91][92][93][94][95][96][97][98][99][100][101], including the predominant 2-benzylpyridine*—52 species and 9 molecules of the type B [6][19][39][90][102]).

In contrast, there are only 11 Au(III)-2ArPY* compounds with substituent(s) in the 2ArPY* ring system (except for those at the Z bridge). All these molecules are with 2ArPY* ligands of the type B [6][75][90], and eight are substituted in the pyridine ring only [6][75][90]; 1—in the aryl ring only [90], and 2—in both rings [75].

Many above Au(III)-2ArPY* compounds are biologically active, revealing anti-tumour (against various bowel, breast, colon, lung, and mammary and ovarian cancers, as well as leukemia) [9][25][31][33][51][63][64][79][82][92][93][96][97][99], as well as anti-bacterial (against *Escherichia coli*, *Bacillus subtilis*, and *Pseudomonas aeruginosa*) and anti-fungal (against *Candida albicans*, *Trichophyton mentagrophytes*, and *Cladosporium resinae*) [63][96][97] properties.

3. Au(III)-ArPY$^{\#}$* Compounds

A total of 33 Au(III) compounds with analogues of 2-arylpyridines* (e.g., 2-phenylquinoline*, 1- or 3-phenylisoquinoline* and 7,8-benzoquinoline*) and their derivatives (generally denoted as ArPY$^{\#}$*), with various auxiliary ligands (including

halides), having the general formula [Au(ArPY$^{\#}$*)L^{1}L^2] (particularly [Au(ArPY$^{\#}$*)L$_2$], including [Au(ArPY$^{\#}$*)X$_2$]) or [Au(ArPY$^{\#}$*)(L^{1}L^2)]) (particularly [Au(ArPY$^{\#}$*)(LL)]) were reported and characterised by NMR spectroscopy and/or by single crystal X-ray diffraction [2][5][9][10][15][19][27][37][39][41][45][75][102][103][104][105][106][107][108].

A total of 5 compounds are [Au(ArPY$^{\#}$*)X$_2$] dihalides [2][5][9][10][15][19][104][105][106], while 28 molecules contain some other monodentate or bidentate ligands, revealing the general formula [Au(ArPY$^{\#}$*)L^{1}L^2] (including [Au(ArPY$^{\#}$*)L$_2$]) or [Au(ArPY$^{\#}$*)(L^{1}L^2)]) (including [Au(ArPY$^{\#}$*)(LL)]) [2][9][15][19][27][37][39][41][45][75][102][103][105][106][107][108].

Taking into account the type of ArPy$^{\#}$* molecule, these are Au(III) species (their respective numbers in parentheses) with heterocycles based on 2-phenylquinoline* (4) [2][103], 1-phenyl-, 1-(naphth-2-yl)- or 1-(9,9-di(*n*-hexyl)fluoren-2-yl)isoquinoline* (9) [10][19][27][37][39][75], 3-phenyl- or 3-(9,9-bis(2-hydroxyethyl)fluoren-2-yl)isoquinoline* (6) [45][102][103], and 7,8-benzoquinoline* (14) [5][9][10][15][41][45][103][105][106][107][108] ring systems.

Two of the above Au(III)-ArPY$^{\#}$* compounds are biologically active, revealing anti-tumour properties (against various breast, colon, liver, and lung and ovarian cancers, as well as melanoma) [9][102]. Some of the others have catalytic properties (in reactions between benzaldehyde, piperidine, and phenylacetylenes—yielding propargylamines—and between alkynyl alcohols and 1-methylindol—yielding substituted indols [103]—as well as upon hydroarylation reactions between diphenylacetylene and 1,3,5-trimethoxybenzene—yielding styrene derivatives [107]). Then, a number of these species exhibits luminescence, with lifetimes of either >10 μs [15][19][37][39][75] or <10 μs [27][41].

4. Single Crystal X-ray Structures

Nearly all Au(III)-2PPY* (including Au(III)-2ppy*), Au(III)-2ArPY*, and Au(III)-ArPY$^{\#}$* compounds have coordination number 4 and square-planar geometry (the only exclusions are [Au(2-phenylpyridine*)(1,4,7-trithiacyclononane-κ^3-S,S,S)]$^{2+}$ and [Au(2-(4-methylphenyl)pyridine*)(1,4,7-trithiacyclononane-κ^3-S,S,S)]$^{2+}$ in their hexafluorophosphate salts—MOCFOB, MOCFIV [5]—which exhibit coordination number 5). Thus, in cases of L^1 ≠ L^2 or unsymmetrical L^{1}L^2 ligands, two geometric isomers are possible—differing in the position of both donor atoms versus the nitrogen of the pyridine (or pyridine-like) ring and the metallated carbon of the phenyl (or, more generally, aryl) ring.

The comparison of these X-ray structures exhibits that the molecules having various elements, as donor atoms of the auxiliary ligand(s) usually adopt the following geometries:

***trans*(N,N)**, instead of *trans*(O,N) (MAXQEH [2], KIGPEY [25], BAZSEB [96]) or *trans*(Cl,N) (XEWBUX [63]);

***trans*(S,N)**, instead of *trans*(O,N) (ILETIC [28], ICUMEY [51]), *trans*(Cl,N) (AZOKUY [30]) or *trans*(N,N) (ILETOI, ILETEY [28], LORCOM, LORCEC, LORCIG [34], FUJHUQ [99], MIRLIK, MIRLOQ [101]);

***trans*(I,N)**, instead of *trans*(Cl,N) (VUVKOP [23]), *trans*(N,N) (EWIXAL [105]) or *trans*(Br,N) (VUVLEG [23]);

***trans*(C,N)**, instead of *trans*(F,N) (DAJRUE, DAJROY [21]), *trans*(O,N) (BIGREP [29], XOLCEI [42], FONDIX, FONCIW [43], IDAJII, IDAJOO [54], FUWXIG, FUWXOM [57], YIDHIF, YIDGIE, YIDHEB, YIDHAX, YIDGOK, YIDGAW, YIDGUQ, YIDGEA, YIDFUP [58], QEFVUV, QEFWAC [59], PEZQUI [67], KEKGEP [73], QEZYAX [74], FIBROA [106]), *trans*(Cl,N) (MAXQUX [2], FONSAE, FONRUX [14], BIGRAL [29], IVAZAI [36], GIVRIO, GIVROU [41], ECEGOM, ECEGOM 01 [95], FIBRUG [106]), *trans*(N,N) (XOLCUY, XOLCIM, XOLCOS [42], IPISEH, IPISAD [60], ZINHUB [103]), *trans*(Br,N) (DAJRIS [21], JOTROB [12], ROVYAF [55], LUWKAS [56]), *trans*(I,N) (GIVSOV [41]), and *trans*(P,N) (XOLDAF, XOLDEJ [42], IDAJUU [54]);

***trans*(P,N)**, instead of *trans*(F,N) (IVAZEM [36]), *trans*(Cl,N) (QUNSIE [35], IVAYUB, IVAYOV [36], QUMZIJ [79], PUKYEZ [85], FIKQAR [87]), or *trans*(S,N) (MAXQIL [2]).

Hence, generally, less electronegative (less electron-acceptor) elements are preferred to be positioned *trans* to the pyridine (or pyridine-like) nitrogen. The exception is the pair of *trans*(C,N) and *trans*(P,N), as in the X-ray structures XOLDAF, XOLDEJ, and IDAJUU, and the former geometry is preferred [42][54], although carbon is more electronegative than phosphorus.

Even more important exclusions are the X-ray structures MIZHEL, MIYXOK, and MIYXUQ, where the *trans*(Cl,N) geometry was observed, instead of the seemingly more expected *trans*(C,N) one, upon the presence of the $C_6F_5^-$ and Cl^- ligands [18]. However, it can be explained by the fact that, despite a large difference in the electronegativity of carbon and chlorine, in these molecules, there is a competition (in occupying *trans* to nitrogen position) of the pentafluorophenyl anion

with the chloride one—while the former has extremely strong electron-acceptor properties, due to the presence of five fluorine atoms in the phenyl ring.

In the majority of cases, the Au–N bonds are longer than those of Au–C, which is well-reflected by comparison of their mean bond lengths, averaged for 206 X-ray structures (among all 207; in case of FONREH the interatomic distances could not be deduced, due to the bad quality of data), after preliminary averaging of these parameters for each Au(III) species (when two or more slightly differing, crystallographically inequivalent molecules are present in the crystal lattice): 2.072 Å versus 2.028 Å. Similarly, the range of Au–N bond lengths (1.975–2.283 Å) also corresponds to higher values than that for Au–C (1.845–2.100 Å), despite their partial overlapping.

The N–Au–C bond angles vary within a 79.2–91.0° range, with a mean value of 82.5°.

It is interesting to compare the X-ray structures of the cyclometallated [Au(2PPY*)Cl_2] and [Au(2ArPY*)Cl_2] dichlorides with the respective [Au(2PPY)Cl_3] and [Au(2ArPY)Cl_3] trichloride complexes. Such pairs of X-ray structural data are available for Au(III) compounds with 2-phenylpyridine [3][109], 2-(2,4-difluorophenyl)pyridine [16], 2-(2-trifluoromethoxyphenyl)pyridine [18], 2-benzylpyridine [16], 2-benzoylpyridine [18][85], and 2-phenylsulfanylpyridine [87][110].

This comparison, however, does not reveal any clear relationship between the Au–N bond lengths in the respective dichloride and trichloride species. Their differences for the corresponding Au(III) compounds are of variable sign and small absolute magnitude, being statistically not significant. This is also exhibited by the overlapping of both ranges of this parameter: 2.01–2.06 Å for [Au(2PPY*)Cl_2] and [Au(2ArPY*)Cl_2] versus 2.03–2.06 Å for [Au(2PPY)Cl_3] and [Au(2ArPY)Cl_3], as well as by nearly the same mean values: 2.039 Å for [Au(2PPY*)Cl_2] and [Au(2ArPY*)Cl_2] versus 2.047 Å for [Au(2PPY)Cl_3] and [Au(2ArPY)Cl_3].

5. ^{15}N NMR Spectra

In addition to the routine ^{1}H and/or ^{13}C (and, optionally, ^{19}F or ^{31}P) NMR spectra, some Au(III)-2PPY* (including Au(III)-2ppy*), Au(III)-2ArPY*, and Au(III)-ArPY$^{\#*}$ compounds were studied by ^{15}N NMR [4][7][53][60][78][80][86][104].

In all cases, the Au(III) coordination of 2PPY* (including 2ppy*), 2ArPY*, or ArPY$^{\#*}$ leads to a large decrease of the ^{15}N NMR chemical shift of the metallated nitrogen (comparing to the parent heterocycle, measured preferably in the same solvent), reflecting a strong ^{15}N shielding phenomenon and resulting in a significant low-frequency (i.e., upfield) shift of the ^{15}N signal (thus, the Δ^{15N}_{coord} values are negative). The absolute magnitude of this effect is ca. 45–105 ppm.

In two reviews by Pazderski [111][112], the dependency was identified in that of square-planar Au(III) complexes or organometallics with aza aromatic ligands (such as azines, e.g., pyridine derivatives, etc.), and the absolute magnitude of the ^{15}N NMR coordination shift ($|\Delta^{15N}_{coord}|$) mainly reflected the type of a donor atom in the *trans* position, with respect to the Au(III)-bonded nitrogen. For example, in the two pairs of [$Au^{III}LCl_3$] and *trans*-[$Au^{III}L_2Cl_2]^+$ species, the $|\Delta^{15N}_{coord}|$ parameter for the former compound (nitrogen *trans* to Cl) was smaller than for the latter one (nitrogen *trans* to N): 84.8 ppm versus 87.2 ppm for L = pyridine, and 78.1 ppm versus 91.0 ppm for L = 4-methylpyridine [111][112].

Such observations can also be performed for some of the presently reviewed Au(III) species, when compared to the compounds containing the same cycloaurated ligand. Such a comparison is possible for the series of [Au(2-(4-methylphenyl)pyridine*)L^1L^2] molecules with various L^1 and L^2 ligands (methyl, allyl, phenyl, acetate, trifluoroacetate, and bromide anions). Thus, for [Au(2-(4-methylphenyl)pyridine*)(acetate)$_2$] and [Au(2-(4-methylphenyl)pyridine*)(trifluoroacetate)$_2$] (nitrogen *trans* to O), the $|\Delta^{15N}_{coord}|$ parameter is much larger than for [Au(2-(4-methylphenyl)pyridine*)(methyl)$_2$] (nitrogen *trans* to C): 89.5–90.7 ppm versus 56.1 ppm [53]. In this way, based on the ^{15}N NMR spectra only, one could assume that, in all other “unsymmetrical” [Au(2-(4-methylphenyl)pyridine*)LBr] (L = methyl, allyl, phenyl) compounds, the nitrogen atoms are positioned *trans* to C, rather than *trans* to Br, because their $|\Delta^{15N}_{coord}|$ values (46.7–53.0 ppm) are rather small and close to that of [Au(2-(4-methylphenyl)pyridine*)(methyl)$_2$] (56.1 ppm). In fact, the proposed *trans*(C,N) geometry for these three molecules was actually confirmed by the X-ray structure of [Au(2-(4-methylphenyl)pyridine*)(allyl)Br] (ROVYAF [55]), in accordance with the already mentioned preference to form *trans*(C,N), instead of *trans*(C,Br) isomers.

A more detailed discussion of this issue is difficult, due to the small number of X-ray structures, for which, the ^{15}N NMR data were also reported. They are available only for the pair of [Au(2-(4-methylphenyl)pyridine*)L_2] molecules (QICNUN for L = methyl and QICPAV for L = trifluoroacetate) [52], where the increase of $|\Delta^{15N}_{coord}|$ upon the CH_3 → CF_3COO ligand transition can be related to the shortening of the Au–N bond (2.130(3) Å → 1.991(6) Å). However, this is only one example, not allowing for general conclusions.

The analysis of the other ^{15}N NMR data exhibits that relatively large $|\Delta^{15N}_{coord}|$ parameters are observed for all [Au(2PPY*)$(CF_3COO)_2$] (ca. 66–105 ppm; nitrogens *trans* to O) and [Au(ArPY$^{\#}$*)Cl_2] (ca. 69–105 ppm; nitrogens *trans* to Cl) species, with no significant differences between both classes of molecules.

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