Research Article

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Copper(I)-1,3,5-Triaza-7-phosphaadamantane (PTA)-Arylazoimidazole Complexes: Synthesis and Spectroscopic study.

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Abstract

Reaction of $[Cu(PTA)(tht)](OSO_2CF_3)$ with RaaiR$^/$ in CH_2Cl_2 medium following ligand addition leads to $[Cu(PTA)(RaaiR^/)](OTf)$ [PTA = 1,3,5-Triaza-7-phosphaadamantane, RaaiR$^/$ = p-R-C_6H_4-N=N-C_3H_2-NN-1-R$^/$, (1-3), abbreviated as N,N$^/$-chelator, where N(imidazole) and N(azo) represent N and N$^/$, respectively; R = H (*a*), Me (*b*), Cl (*c*) and R$^/$ = Me (*1*), CH_2CH_3 (*2*), CH_2Ph (*3*), OSO_2CF_3 is the triflate anion, tht is tetrahydrothiophen]. The ^{1}H NMR spectral measurements in D_2O suggest methylene, $-CH_2-$, in RaaiEt gives a complex AB type multiplet while in RaaiCH$_2$Ph it shows AB type quartets. ^{13}C NMR spectrum in D_2O suggest the molecular skeleton. In the ^{1}H-^{1}H COSY spectrum in D_2O as well as contour peaks in the ^{1}H-^{13}C HMQC spectrum in D_2O assign the solution structure.

Keywords: Cu(I), PTA, arylazoimidazole, NMR, IR, ESIMS.

Introduction

The transfer of an organic group to a Cu centre is traditionally carried out using organolithium compounds, Grignard reagents or organomercurials. There are however alternative transmetallation agents, which are particularly attractive because of their insensitivity to air and moisture, their mild reaction conditions and simple work-up. These include organotin compounds and boronic acids. Whilst the former have been used in the preparation of both gold compounds, the latter are so far limited to gold compounds represent interesting alternatives to other metal-based luminescent compounds with a d electron configuration [1-9]. For Pd and Pt complexes (in the absence of metal –metal interactions) the emissive excited state is either a metal-to-ligand charge transfer (MLCT) or an intraligand (IL) transition (or a mixture of both)

and of triplet-character (phosphorescence). Their metal centred transitions are usually at high energy and do not strongly influence the luminescence properties, which is important as these dd-states usually lead to a very efficient radiationless deactivation of the excited state [9-14]. Cu(I) complexes are much less investigated due to some preconditions which have to be fulfilled for an emissive behaviour: because of the high oxidation potential of gold in the oxidation state $^{+3}$ a MLCT is not favoured. For these complexes containing ligands with an extended -system an emissive IL excited state is feasible, but the energetically low lying dd-states quench potential emissive states of most Cu(I) complexes [15-20]. However, these dd-states can be destabilized by strong field ligands diminishing the radiationless deactivation. Consequently, several cyclometallated complexes of the general formula [Cu(C–N)L$_2$]n+(C–N = 2-phenylpyridine type ligand; L = acetylide, NHC;n= 0 or 2) and similar complexes bearing pincer type ligands including 2,6-diphenylpyridine or 6-phenyl-2,2 -bipyridine were reported to feature luminescence even in fluid solution at room temperatura [21-25]. The emissions are mostly assignable to an 3 IL-transition and sometimes these complexes also show a dual emission of both 1 IL and 3IL character [13] Luminescent cyclometallated Cu(III) complexes were reviewed in 2011 11 and since then, several new examples of this type were published. To the best of our knowledge, there is only one report on a luminescent Cu(III) complexbearing a biphenyl moiety: [Cu(Ppy)(Bip)] (Ppy = 2-phenyl-pyridine; Bip = biphenyl). However, the second chromophore (Ppy) complicates the precise assignment of the transition. Indeed, according to TD-DFT calculations, both a ligand-to-ligand charge transfer (^{3}LLCT) [(Bip) *(Ppy)] and 3 IL[(Bip) *(Bip)] contribute to the excited state. For this reason, the complexes presented below are particularly valuable, because they allow the investigation of the discrete chromophoric Au(III)-biphenyl moiety [26-30].

In 1973, Chatt and co-workers performed transition-metal-catalyzed reactions in water [31]. Since then, there has been a tremendous effort in the development of new water-soluble organotransition-metal complexes with the practical and environmental benefits in mind. This is principally accomplished through ligand design; thus, a variety of water-soluble ligand systems has been developed and explored. The most successful and noted of these systems have been phosphines with water-soluble substituents, such as sulfonated aryl groups, [32] ammonium groups, [33] and carboxylated aromatic groups. [34] Further, there has been much success with some nonaromatic groups such as tris(hydroxymethyl)phosphine (P(CH$_2$OH)$_3$). [35,36] Another nonionic aliphatic water-soluble phosphine is the tetrabasic 1,3,5-triaza-7-phosphaadamantane (PTA). Due to its utility as a water-soluble ligand and in efforts to explore the unique chemistry of this ligand, Darenberg´s group has been active in the investigation of the different facets of PTA. [37-43] Further, PTA has been investigated in many different areas such as photoluminecence of copper(II) phosphine complexes [34-38] and intermolecular hydrogen-metal interactions, [39] as well as its use as a precursor to other novel phosphine amine compounds and ligands. [50-53] Classical coordination chemistry began by using water both as solvent and as ligand for many compounds. As this discipline of chemistry advanced, new ligands, complexes, and reactions were discovered that required completely anhydrous reaction conditions as well as special apparatus and techniques so as to keep water *out* of reactions. [54] Today, the tide has turned and water is experiencing a renaissance as a solvent in inorganic and organometallic chemistry. This change, motivated largely by the ever-increasing awareness of environmental concerns in the design of industrially important chemical processes has been the main driving force in the exploration of water-based reactions and water-soluble catalysts. [55-57] However, the vast

majority of homogeneous catalysts available today are either insoluble or unstable in water; as a result, one key challenge for the inorganic/organometallic chemistry community today is the design and development of compounds that are both soluble and stable in aqueous medium. Our group has studied the addition of methanol to terminal alkynes catalyzed by various water-insoluble copper(I) and copper(II) complexes in aqueous medium, [58] and more recently, we reported the first examples of water-soluble and water-stable organometallic copper(I) and copper(II) compounds [59]. As a logical extension to this work, we were interested in trying to obtain water-soluble copper(II) derivatives and to study their catalytic activity in the addition of methanol to terminal alkynes. The chemistry of binuclear copper(I) complexes containing Cu-Cu bonds has been studied in some detail by various groups over the last 40 years with significant contributions originating from the laboratories of Schmidbaur, Fackler, Jr., and Bennett [60] and also from our group [61,62]. One commonly used strategy to impart water-solubility to a given metal complex involves the use of ligands possessing solubilizing groups or use of water-soluble ligands. Typical examples of such ligands are those selected for this study: 1,3,5-triaza-7-phosphaadamantane (PTA); 3,7-diacetyl-1,3,7-triaza-5-phosphabicyclo[3.3.1] nonane (DAPTA); monosulfonated triphenylphosphine (TPPMS); disulfonated triphenylphosphine (TPPDS); trisulfonated triphenylphosphin (TPPTS) [63]. All five phosphines are soluble in water and have previously been used as ligands in various metal complexes including some examples of copper(I) and Cu(II) [64-71]. In this paper, I examine the reaction of RaaiR$^{/}$ on Cu(I)PTA derivatives and the products are isolated, [Cu(PTA)(RaaiR$^{/}$)](OTf/Cl) [PTA = 1,3,5-triaza-7-phosphaadamantane, RaaiR$^{/}$ = p-R-C$_6$H$_4$-N=N-C$_3$H$_2$-NN-1-R$^{/}$, (*1-3*), abbreviated as N,N$^{/}$-chelator, where N(imidazole) and N(azo) represent N and N$^{/}$, respectively; R = H (*a*), Me (*b*), Cl (*c*) and R$^{/}$ = Me (*1*), CH$_2$CH$_3$ (*2*), CH$_2$Ph (*3*), OSO$_2$CF$_3$ is the triflate anion, that is tetrahydrothiophen]. The complexes are well characterised by i.r., ^{1}H n.m.r., ^{13}C nmr, ^{1}H-^{1}H COSY nmr, ^{1}H-^{13}C HMQC and ESI mass spectrometry.

Materials and Methods

Material and instrumentation

Published methods were used to prepare RaaiR$^{/}$ and Cu(PTA)(Cl) [1-11]. All other chemicals and organic solvents used for preparative work were of reagent grade (SRL, Sigma Alhrich). Microanalytical data (C, H, N) were collected using a Perkin Elmer 2400 CHN instrument. I.r. spectra were obtained using a JASCO 420 spectrophotometer (using KBr disks, 4000-200 cm^{-1}). The ^{1}H nmr spectra in CDCl$_3$ were obtained on a Bruker 500 MHz FT n.m.r spectrometer using SiMe$_4$ as internal reference, CFCl$_3$ (external ^{19}F). Solution electrical conductivities were measured using a Systronics 304 conductivity meter with solute concentration ~10^{-3} M in acetonitrile. Mass spectra were recorded on VG Autospec ESI-mass spectrometry. Electrochemical work was carried out using an EG & G PARC Versastat computer controlled 250 electrochemical system. All experiments were performed under a N$_2$ atmosphere at 298K using a Pt-disk milli working electrode at a scan rate of 50 mVs^{-1}. All results were referenced to a saturated calomel electrode (SCE).

Preparation of the complexes

[-(1,3,5-triaza-7-phosphaadamantane)\{1-ethyl-2-(p-tolylazo)imidazole\}aurate(III)]triflate, [Cu(PTA)(HaaiEt)](OTf), (2b)

To a CH$_2$Cl$_2$ solution (15 cm^3) of [Cu(PTA)Cl] (0.945 g, 0.20 mmol), [Ag(tht)(OTf)] was added (1:2) to produce de-bromo product, ie, [Cu(PTA)(tht)](OSO$_2$CF$_3$) (0.945 g, 0.20 mmol) into this, was added a yellow CH$_2$Cl$_2$ solution of 1-ethyl-2-(p-tolylazo)imidazole, slowly, dropwise, and the mixture was stirred at 343-353 K for 12 h. Where in path II direct chloride ligand substitution gives high yield than the Silver

assisted pathway. Where respectively added the other ligands, HeaaiMe (0.0186 g, 0.1 mmol, *1a*), MeaaiMe (0.020 g, 0.1 mmol, *1b*), ClaaiMe (0.0220 g, 0.1 mmol, *1c*), HaaiEt (0.020 g, 0.1 mmol, *2a*), MeaaiEt (0.0214 g, 0.1 mmol, *2b*), ClaaiEt (0.0235 g, 0.1 mmol, *2c*), HaaiBz (0.0262 g, 0.1 mmol, *3a*), MeaaiBz (0.0276 g, 0.1 mmol, *3b*), ClaaiBz (0.0297 g, 0.1 mmol, *3c*), The orange solution that resulted was concentrated (4 cm^3) and kept in a refrigerator overnight (1 h). The addition of hexane to the above red solution gives precipitate which was collected by filtration, washed thoroughly with hexane to remove excess ligand and then dried *in vacuo* over pump overnight. The yield was 0.088 g (80%). All other complexes were prepared similarly as stated above. Analysis for [Cu(PTA)(HaaiMe)](Cl), (*1a*), Found: C, 33.4, H, 3.9, N, 17.1, Calcd for [C$_{16}$H$_{22}$N$_7$PCu](Cl), C, 33.3, H, 3.9, N, 17.1; IR ν(N=N) 1370 ν(C=N) 1590 ν(PTA) 790, ^{31}P{H}NMR, ppm, -12.24; ESIMS, 575.5[M$^+$], 540[M-Cl]; ^{13}C{^{1}H}NMR, ppm, 52.2 (d, J=20Hz, NCH$_2$P), 72 (d, J=7Hz, NCH$_2$N), 134.5(C2), 124(C4), 125(C5), 125.3(C7,11), 129.2(C8,10), 134(C6), 22, (Me Gr.);

Analysis for [Cu(PTA)(MeaaiMe)](Cl), (*1b*), Found: C, 34.4, H, 4.1, N, 16.6, Calcd fof [C$_{17}$H$_{24}$N$_7$PCu](Cl), C, 34.3, H, 3.9, N, 16.1; IR ν(N=N) 1379, ν(C=N) 1599 ν(PTA) 799, ^{31}P{H}NMR, ppm, -12.29; ESIMS, 589.5[M$^+$], 554[M-Cl]; ^{13}C{^{1}H}NMR, ppm, 52.9 (d, J=28Hz, NCH$_2$P), 72.7 (d, J=17Hz, NCH$_2$N), 134(C2), 124(C4), 125(C5), 125(C7,11), 129.2(C8,10), 134(C6), 22 (Me Gr.); Analysis for [Cu(PTA)(ClaaiMe)](Cl), (*1c*), Found: C, 31.4, H, 3.4, N, 16.1, Calcd for [C$_{16}$H$_{21}$N$_7$PClCu](Cl), C, 31.3, H, 3.4, N, 16.1; IR ν(N=N) 1371, ν(C=N) 1590 ν(PTA) 790, ^{31}P{H}NMR, ppm, -12.24; ESIMS, 610[M$^+$], 574.5[M-Cl]; ^{13}C{^{1}H}NMR, ppm, 52(d, J=13Hz, NCH$_2$P), 72 (d, J=9Hz, NCH$_2$N), 134.5(C2), 124(C4), 125(C5), 125.3(C7,11), 129.2(C8,10), 134(C6), 22, (Me Gr.); Analysis for [Cu(PTA)(HaaiEt)](Cl), (*2a*), Found: C, 34.4, H, 3.9, N, 16.1, Calcd for [C$_{17}$H$_{24}$N$_7$PCu](Cl), C, 34.3, H, 3.9, N, 16.1; IR ν(N=N) 1379, ν(C=N) 1590 ν(PTA) 796,

^{31}P{H}NMR, ppm, -12.34; ESIMS, 589.5[M$^+$], 554[M-Cl]; ^{13}C{^{1}H}NMR, ppm, 52(d, J=16Hz, NCH$_2$P), 72 (d, J=7Hz, NCH$_2$N), 134(C2), 124(C4), 125(C5), 125.3(C7,11), 129(C8,10), 134(C6), 22,41.4 (Et Gr.); Analysis for [Cu(PTA)(MeaaiEt)](Cl), (*2b*), Found: C, 35.4, H, 4.3, N, 16.1, Calcd for [C$_{18}$H$_{26}$N$_7$PCu](Cl), C, 35.3, H, 4.3, N, 16.1; IR ν(N=N) 1370, ν(C=N) 1590 ν(PTA) 795, ^{31}P{H}NMR, ppm, -12.29; ESIMS, 603.5[M$^+$], 568[M-Cl]; ^{13}C{^{1}H}NMR, ppm, 52.2 (d, J=13Hz, NCH$_2$P), 72 (d, J=17Hz, NCH$_2$N), 134.5(C2), 124(C4), 125(C5), 125.3(C7,11), 129.2(C8,10), 134(C6), 22,40 (Et Gr.); Analysis for [Cu(PTA)(ClaaiEt)](Cl), (*2c*), Found: C, 32.4, H, 3.9, N, 15.1, Calcd for [C$_{17}$H$_{23}$N$_7$PClCu](Cl), C, 32.7, H, 3.7, N, 15.7; IR ν(N=N) 1370, ν(C=N) 1599, ν(PTA) 790, ^{31}P{H}NMR, ppm, -12.29; ESIMS, 624[M$^+$], 588.5[M-Cl]; ^{13}C{^{1}H}NMR, ppm, 52.2 (d, J=10Hz, NCH$_2$P), 72.5 (d, J=17Hz, NCH$_2$N), 134(C2), 124(C4), 125(C5), 125.3(C7,11), 129(C8,10), 134(C6), 22,40.9 (Et Gr.); Analysis for [Cu(PTA)(HaaiBz)](Cl), (*3a*), Found: C, 40.4, H, 3.9, N, 15.1, Calcd for [C$_{22}$H$_{26}$N$_7$PCu](Cl), C, 40.3, H, 3.9, N, 15.1; IR ν(N=N) 1370, ν(C=N) 1590, ν(PTA) 790, ^{31}P{H}NMR, ppm, -12.20; ESIMS, 651.5[M$^+$], 616[M-Cl]; ^{13}C{^{1}H}NMR, ppm, 52.2 (d, J=10Hz, NCH$_2$P), 72 (d, J=17Hz, NCH$_2$N), 134.5(C2), 124(C4), 125(C5), 125.3(C7,11), 129.2(C8,10), 134(C6), 22, 130-134 (Me Gr.); Analysis for [Cu(PTA)(MeaaiBz)](Cl), (*3b*), Found: C, 41.4, H, 4.2, N, 14.7, Calcd for [C$_{23}$H$_{28}$N$_7$PCu](Cl), C, 41.3, H, 4.2, N, 14.7; IR ν(N=N) 1375, ν(C=N) 1590, ν(PTA) 795, ^{31}P{H}NMR, ppm, -12.14; ESIMS, 665.5[M$^+$], 630[M-Cl]; ^{13}C{^{1}H}NMR, ppm, 52.2 (d, J=10Hz, NCH$_2$P), 72 (d, J=17Hz, NCH$_2$N), 134(C2), 124(C4), 125(C5), 125.3(C7,11), 129.2(C8,10), 134(C6), 22,130-133 (Bz Gr.); Analysis for [Cu(PTA)(ClaaiBz)](Cl), (*3c*), Found: C, 38.4, H, 3.6, N, 14.1, Calcd fof [C$_{22}$H$_{25}$N$_7$PClCu](Cl), C, 38.3, H, 3.6, N, 14.1; IR ν(N=N) 1370, ν(C=N) 1595, ν(PTA) 795, ^{31}P{H}NMR, ppm, -12.24; ESIMS, 686[M$^+$], 650.5[M-Cl]; ^{13}C{^{1}H}NMR, ppm, 52.2 (d, J=20Hz, NCH$_2$P), 72 (d, J=7Hz, NCH$_2$N), 134.5(C2), 124(C4), 125(C5), 125.3(C7,11), 129.2(C8,10), 134(C6), 22, 129.4-134.7(Bz. Gr).

Results and Discussion

Synthesis and formulation

The complexes, [Cu(PTA)(RaaiR$^/$)](OTf) [PTA = 1,3,5-triaza-7-phosphaadamantane, RaaiR$^/$ = *p*-R-C$_6$H$_4$-N=N-C$_3$H$_2$-NN-1-R$^/$, (*1-3*), abbreviated as N,N$^/$-chelator, where N(imidazole) and N(azo) represent N and N$^/$, respectively; R = H (*a*), Me (*b*), Cl (*c*) and R$^/$ = Me (*1*), CH$_2$CH$_3$ (*2*), CH$_2$Ph (*3*), OSO$_2$CF$_3$ is the triflate anion, tht is tetrahydrothiophen], were prepared by removing tht from [Cu(PTA)(tht)](OSO$_2$CF$_3$), with RaaiR$^/$ under stirring at 343-353 K in MeOH solution in poor yield (35-40%). Here the reaction goes through unknown gold-silver cluster formation. Whereas in path II, direct Cl substitution gives high yield (75-80%). The synthetic routes are shown in *Scheme 1*. The composition of the complexes is supported by microanalytical results. The red orange complexes are not soluble in common organic solvents viz. acetone, acetonitrile, chloroform, dichloromethane but soluble in H$_2$O, methanol, ethanol.

Spectral studies

I.r. spectra of the complexes, [Cu(PTA)(RaaiR$^/$)](OTf) show a 1:1 correspondence to the spectra of the bromo analogue, except the appearance of intense stretching at 1365-1370 and 1570-1580 cm^{-1} with concomitant loss of ν(Cu-Cl) at 320-340 cm^{-1}. They are assigned to ν(N=N) and ν(C=N) appear at 1365-1380 and 1570-1600 cm^{-1}, respectively. Other important frequencies are ν(PTA) at 1110-1120, 1200-1210, 1250-1260, 750-760, cm^{-1}.

The ESI mass spectrum of a 1:1, MeCN:H$_2$O solution in the positive ion mode is structurally enlightening, since it displays a series of characteristic singly. Population of gas phase ions generated by ESI often closely reflects that in solution.

Phosphorous n.m.r., ^{31}P{H}nmr, measured in D$_2$O, gives a concrete idea on the nature of complexes and is very much informative of the present series of complexes. Due to the presence of azo-imine function, which is pi acidic in nature, stabilises the gold (III) oxidation state giving the value of -12.23 (*Fig. 1*).

Fluorine n.m.r., ^{19}F{H}, measured in D$_2$O, of the present series of complexes show a sharp peak at -78 for the presence of triflate ion.

The ^{1}H n.m.r. spectra, measured in D$_2$O, of [Cu(PTA)(RaaiR$^/$)](OTf) (*1-3*) complexes were unambiguously assigned (*Table 1, Figure 1 and 2*) on comparing with [Cu(PTA)Cl] and the free ligand (RaaiR$^/$) [17,11]. Imidazole 4- and 5-H appear as doublet at the lower frequency side of the spectra (7.0-7.2 ppm for 4-H; 6.9-7.1 ppm for 5-H). The proton movement upon substitution (9-R) is corroborated with the electromeric effect of R. The aryl protons (7-H—11-H) of (*7-9*) are downfield shifted by 0.1-0.7 ppm as compared to those of the parent derivatives [11]. They are affected by substitution; 8- and 10-H are severely perturbed due to changes in the electronic properties of the substituents in the C(9)-position. The aryl protons 7-(7$^/$-) and 11-(11$^/$-)H resonate asymmetrically indicative of a magnetically anisotropic environment [18] even in the solution phase. The 1-R$^/$ [R$^/$ = Me, CH$_2$CH$_3$, CH$_2$(Ph)] exhibit usual spin-spin interaction. 1-Me appears as a singlet at 2.0 ppm for [Cu(PTA)(RaaiMe)]; the methylene protons, 1-CH$_2$-(CH$_3$) show AB type quartet (*ca*. 4.4, 4.6 ppm, J = 6-7 Hz) and (1-CH$_2$)CH$_3$ gives a triplet at 1.5 ppm (7.0-8.0 Hz) for [Cu(PTA)(RaaiCH$_2$CH$_3$)]. 1-CH$_2$(Ph) protons appear at AB type quartets (ca. 5.5, 5.7 ppm) with geminal coupling constant avg. 8.8 Hz in [Cu(PTA)(RaaiCH$_2$Ph)].

Table. 1. ^{1}H-n.m.r. spectral data, δ (J/Hz), ppm in D_2O of the complexes

Compd	4-H[c]	5-H[c]	11-H[c]	7-H[c]	8,10-H	N-CH$_3$	N-CH$_2$	PTA
(1a)[a]	7.15 (7.5)	7.06 (7.5)	8.03 (8.1)	7.99 (8.1)	7.45 (8.1)[d]	2.09[f]		4.2(CH$_2$P,6H),4.5(CH$_2$N,6H)
(1b)	6.98 (7.5)	6.86 (7.5)	8.17 (8.1)	8.04 (8.1)	7.34 (8.1)[c]	2.17[f]		4.2(CH$_2$P,6H),4.4(CH$_2$N,6H)
(1c)	7.13 (8.1)	7.02 (8.1)	8.15 (7.8)	7.95 (7.8)	7.55 (7.8)[c]	2.16[f]		4.2(CH$_2$P,6H),4.6(CH$_2$N,6H)
(2a)[a]	7.14 (7.5)	7.00 (7.5)	8.01 (7.8)	7.85 (7.8)	7.45 (8.1)[d]	1.52 (8.1)[d]	4.42,4.55 (10.0)[e]	4.2(CH$_2$P,6H),4.4(CH$_2$N,6H)
(2b)	7.33 (8.1)	7.24 (8.1)	8.11 (7.5)	8.04 (7.5)	7.52 (7.5)[c]	1.58 (8.1)[d]	4.54,4.56 (10.0)[e]	4.3(CH$_2$P,6H),4.4(CH$_2$N,6H)
(2c)	7.34 (8.1)	7.36 (8.1)	8.04 (7.5)	7.54 (7.5)	7.46 (7.5)[c]	1.55 (8.1)[d]	4.54,4.53 (11.0)[e]	4.2(CH$_2$P,6H),4.5(CH$_2$N,6H)
(3a)[a]	7.06 (7.8)	6.98 (7.8)	8.08 (8.1)	8.00 (8.1)	7.48 (8.1)[d]		5.48,5.73 (15.0)[g]	4.2(CH$_2$P,6H),4.4(CH$_2$N,6H)
(3b)	6.97 (8.1)	6.99 (8.1)	8.21 (8.1)	8.10 (8.1)	7.10 (8.1)[c]		5.46,5.73 (17.0)[g]	4.3(CH$_2$P,6H),4.4(CH$_2$N,6H)
(3c)	7.11 (7.8)	7.02 (7.8)	8.15 (8.1)	8.05 (8.1)	7.58 (8.1)[c]		5.44,5.70 (18.0)[g]	4.2(CH$_2$P,6H),4.4(CH$_2$N,6H)

[a] δ(9-H) 7.60 ppm(m); [b] δ (9-Me); [c] doublet; [d] triplet; [e] AB type sextet, geminal coupling constant; [f] 1-Me, singlet; [g] AB type quartet, geminal coupling constant; [h] Phenyl–H.
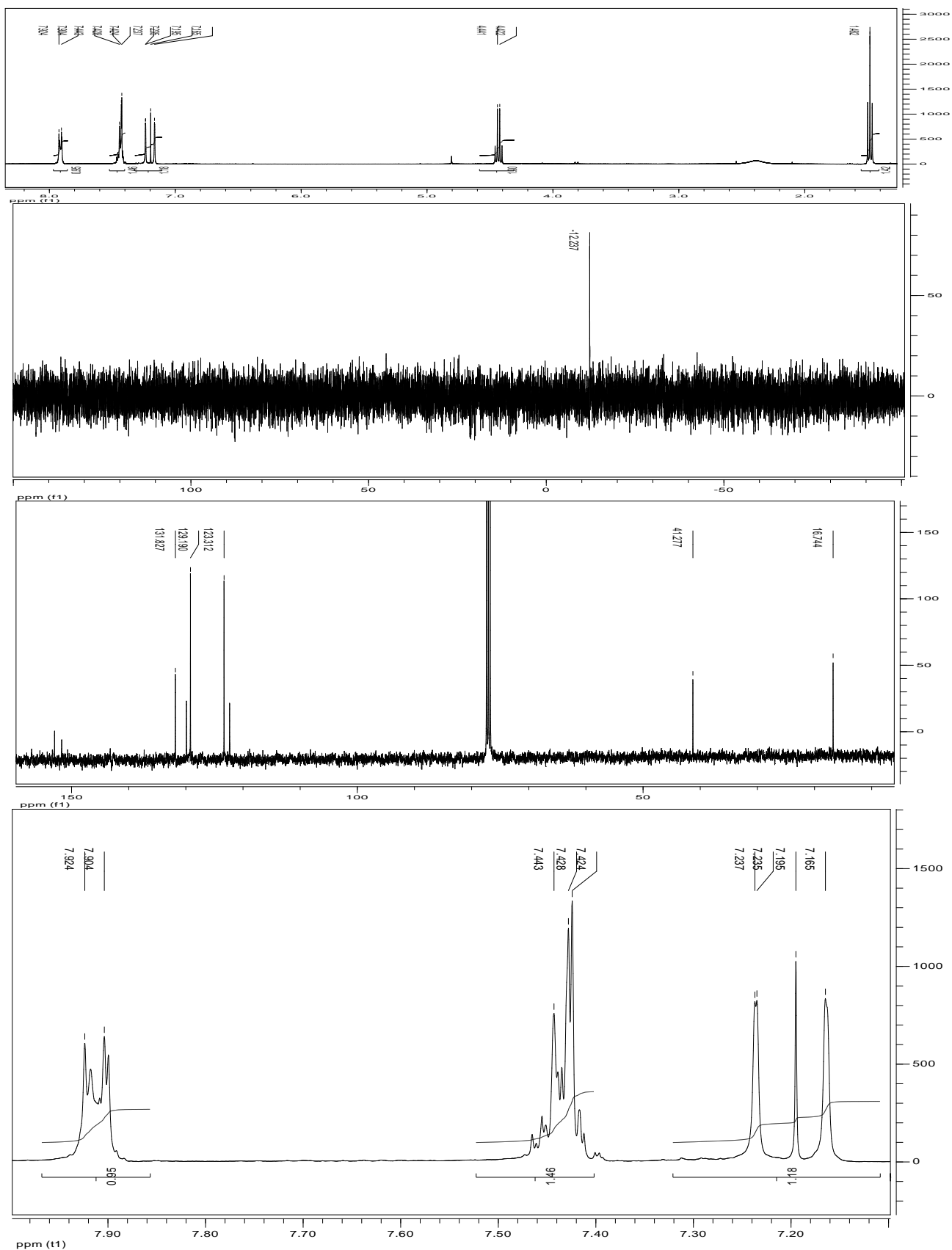
Fig. 1. ¹H NMR, ³¹P NMR , ¹³C NMR and ¹H NMR of complex **2a**

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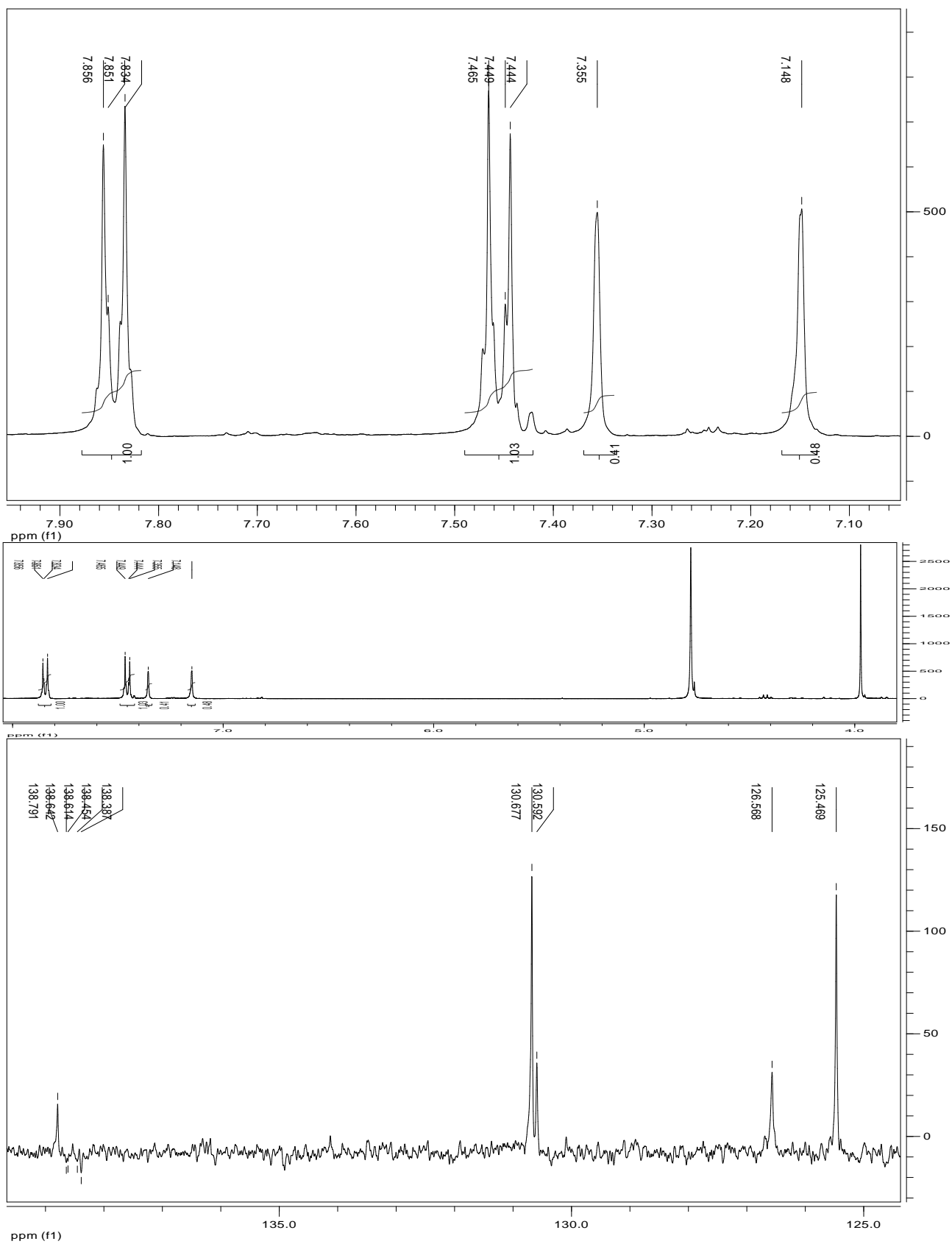
Fig. 2. ^{1}H NMR, ^{1}H NMR and ^{13}C NMR of complex **1c**

The ^{13}C NMR spectrum, measured in D_2O, provides direct information about the carbon skeleton of the molecule. Assignment of different resonant peaks to respective carbon atoms are done on nine complexes and the data are given on experimental section (*Fig 1,2*). Carbon atoms neighbouring the nitrogen atom shifted to downfield due to an increased electron density resulting from the presence of electronegative nitrigen atom and pi electron delocalisation in the magnetic environment. The non-protonated carbon atoms at C(2) and C(6) of the arylazoimidazole moiety is shifted farthest downfield in the spectrum effected by the magnetic interaction of two bulky phenyl rings environment and the methyl, ethyl, benzyl substituted imidazole rings and the pi electron delocalization on the =N-CC=N- and =N-CC=CC-. Similarly the carbon atom adjacent to the PPh_3 molecule in the complex resonance at a lower field resulting of the conjugative effect of the phenyl ring with more electronegative pi-conjugate system. The methyl carbon atom of the imidazole ring resonate at 30 ppm, resonably compare to the other carbon atoms resonance.

The COSY spectrum, measured in D_2O, reveals the [1]H-^{1}H coupling interactions in the molecule. The protons that are decoupled from the adjacent ones due to the lack of α-protons will show no coorelation in the spectrum. In the COSY spectrum, absence of any off-diagonal peaks extending from δ = 14.1 ppm and 9.5 ppm confirm their assignment of no proton on N(1) and N(3) respectively. However, extending horizontal and vertical lines from δ = 8.3 ppm [C(8)H] and 8.6 ppm [C(10)H] encounter cross peaks at δ = 7.12 ppm and 7.23 ppm, where the C(7)H and C(11)H resonances are merged into multiplets along with the phenyl ring proton resonances. The comperatively weaker coupling interections of C(8)H and C(10)H with the far apart positioned C(4)H and C(5)H protons of the imidazole moity are shown by the poorly resolved cross peaks at δ = 7.3 ppm and 7.31 ppm. The [1]H-^{13}C heteronuclear multiple-quantum coherence (HMQC) spectrum, measured in D_2O, provides information regarding the interaction between the protons and the carbon atoms to which they are directly attached. Here, the absence of any contours at higher frequency region assign them C2, C6, C-*ipso*, carbon atoms respectively. This is because, they belong to the non-protonated carbon atoms on the imidazole, phenyl and aryl rings. So they unable to show any direct [1]H-^{13}C heteronuclear multiple-quantum coherence. The peaks observed at δ = 134,131,135 ppm and 137 ppm assign them to the C(9),C(8), C(7), C(11), and C(10) carbon atoms respectively, due to their interaction with H resonance at δ = 7.4, 7.5, 7.8,7.80 ppm and 7.3 ppm.

Conclusion

Water soluble complexes are very less in literature. This work describes the isolation of a novel series of water soluble Cu(I) azo-imine complexes, [Cu[I](PTA)(RaaiR[/])](OTf)/Cl and their spectral and elemental characterisation. ^{1}H NMR study in D_2O suggests quartet splitting of ethyl substitution. ^{31}P {^{1}H}NMR, measured in D_2O, is very much informative and shows sharp signals at -12.23 ppm which is lower than the parent complex. ^{13}C (^{1}H)NMR study, measured in D_2O, suggests molecular skeleton. ^{1}H-^{1}H COSY spectrum as well as contour peaks in the [1]H-^{13}C HMQC spectrum, measured in D_2O, assign them to the carbon hydrogen interaction.

Acknowledgments

References

[1] Gold. Progress in Chemistry, Biochemistry and Technology, ed. Schmidbaur H., John Wiley & Sons, Chichester, 1999.

[2] Gold chemistry. Applications and future directions in the life Sciences, ed. Mohr F., Wiley-VCH, Weinheim, 2009.

[3]   Usón R., Vicente J. and Chicote M. T., Inorg. Chim. Acta,1979,35, L305–L306.

[4]   Usón A., Vicente J. and Chicote M. T.,J. Organomet. Chem.,1980,198, 105–112.

[5]   Usón R., Vicente J. and Chicote M. T.,J. Organomet. Chem.,1981,209, 271–279.

[6]   Usón R., Vicente J., Chicote M. T., Jones P. G. and Sheldrick G. M.,J. Chem. Soc., Dalton Trans., 1983, 1131–1136.

[7]   Meyer N., Sivanathan S. and Mohr F.,J. Organomet. Chem.,2011,696, 1244–1247.

[8]   Meyer N., Lehmann C. W., Lee T. K. M., Rust J., Yam V. W. W. and Mohr F.,Organometallics, 2009,28,2931–2934.

[9]   Partyka D. V., Zeller M., Hunter A. D. and Gray T. G.,Angew.Chem., Int. Ed., 2006, 25, 8188–8191.

[10]   Yam V. W. W. and Wong K. M. C.,Chem. Commun., 2011,47, 11579–11592.

[11]   Bronner C. and Wenger O. S.,Dalton Trans., 2011,40,12409–12420.

[12]   Yersin H., Rausch A. F., Czerwieniec R., Hofbeck T. and Fischer T.,Coord. Chem. Rev. , 2011,255, 2622–2652.

[13]   Kriechbaum M., List M., Berger R. J. F., Patzschke M. and Monkowius U.,Chem. – Eur. J., 2012,18, 5506–5509.

[14]   Au V. K. M., Zhu N. and Yam V. W. W.,Inorg. Chem., 2013,52, 558–567.

[15]   To W. P., Chan K. T., Tong G. S. M., Ma C., Kwok W. M., Guan X., Low K. H. and Che C. M.,Angew. Chem., Int. Ed.,2013,52, 6648–6652.

[16]   Szentkuti A., Bachman M., Garg J. A., Blacque O. and Venkatesan K.,Chem.– Eur. J., 2014,20, 2585–2596.

[17]   Tanaka Y., Wong K. M. C. and Yam V. W. W.,Chem. Sci.,2012,3, 1185–1191.

[18]   To W. P., Tong G. S. M., Lu W., Ma C., Liu J., Chow A. L. F. and Che C. M.,Angew. Chem., Int. Ed., 2012,51, 2654–2657.

[19]   Smith D. A., Ro ca D. A. and Bochmann M.,Organometal-lics, 2012,31, 5998–6000.

[20]   Muñoz-Rodríguez R., Buñuel E., Williams J. A. G. and Cárdenas D. J.,Chem. Commun. , 2012,48, 5980–5982.

[21]   Ro ca D. A., Smith D. A. and Bochmann M., Chem.Commun., 2012,48, 7247–7249.

[22]   Lu W., Chan K. T., Wu S. X., Chen Y. and Che C. M.,Chem.Sci., 2012,3, 752–755.

[23]   Garg J. A., Blacque O., Fox T. and Venkatesan K.,Inorg.Chem., 2010,49, 11463–11472.

[24]   Mohr F., Privér S. H., Bhargava S. K. and Bennett M. A.,Coord. Chem. Rev., 2006, 250, 1851–1888.

[25]   Schuh E., Valiahdi S. M., Jakupec M. A., Keppler B. K., Chiba P. and Mohr F.,Dalton Trans. , 2009, 10841–10845.

[26]   Schuh E., Pflüger C., Citta A., Folda A., Rigobello M. P., Bindoli A., Casini A. and Mohr F., J. Med. Chem., 2012,55,5518–5528.

[27]   Molter A., Rust J., Lehmann C. W. and Mohr F.,Tetra-hedron, 2012,68, 10586–10591.

[28]   Citta A., Schuh E., Mohr F., Folda A., Massimino M. L., Bindoli A., Casini A. and Rigobello M. P.,Metallomics,2013,5, 1006–1015.

[29]   Contel M., Edwards A. J., Garrido J., Hursthouse M. B., Laguna M. and Terroba R.,J. Organomet. Chem., 2000,607,129–136.

[30]   Gaillard S., Slawin A. M. Z., Bonura A. T., Stevens E. D. and Nolan S. P.,Organometallics , 2010,29, 394–402.

[31].   Chatt, J.; Leigh, G. J.; Slade, R. W. *J. Chem. Soc., Dalton Trans.* 1973, 2021.

[32].   (a) Herrmann, W. A.; Kellner, J.; Riepl, H. *J. Organomet. Chem.* 1990, *389*, 103. (b) Toth, Z.; Joo, F.; Beck, M. T. *Inorg. Chem. Acta* 1980, *42*, 153.

[33].   Mohr, B.; Lynn, D. M.; Grubbs, R. H. *Organometallics* 1996, *15*, 4317.

[34].   Hoots, J. E.; Rauchfuss, T. B.; Wrobleski, D. A. *Inorg. Synth.* 1982, *21*, 175.

[35].   Ellis, J. W.; Harrison, K. N.; Hoye, P. A. T.; Orpen, A. G.; Pringle, P. G.; Smith, M. B. *Inorg. Chem.* 1992, *31*, 3026.

[36].   Hoye, P. A. T.; Pringle, P. G.; Smith, M. B.; Worboys, K. *J. Chem. Soc., Dalton Trans.* 1993, 269.

10

[37]. Darensbourg, D. J.; Beckford, F. A.; Reibenspies, J. H. *J. Cluster Sci.* 2000, *11*, 95.

[38]. Darensbourg, D. J.; Robertson, J. B.; Larkins, D. L.; Reibenspies, J. H. *Inorg. Chem.* 1999, *38*, 2473.

[39]. Darensbourg, D. J.; Stafford, N. W.; Joo, F.; Reibenspies, J. H. *Organomet. Chem.* 1995, *488*, 99.

[40]. Joo, F., Nadasdi, L.; Benyei, A. C.; Darensbourg, D. J. *J. Organomet. Chem.* 1996, *512*, 45.

[41]. Darensbourg, D. J.; Decuir, T. J.; Stafford, N. W.; Robertson, J. B.; Draper, J. D.; Reibenspies, J. H. *Inorg. Chem.* 1997, *36*, 4218.

[42]. Darensbourg, D. J.; Joo, F.; Kannisto, M.; Katho, A.; Reibenspies, J. H. *Organometallics* 1992, *11*, 1990.

[43]. Darensbourg, D. J.; Joo, F.; Kannisto, M.; Katho, A.; Reibenspies, J. H.; Daigle, D. J. *Inorg. Chem.* 1994, *33*, 200.

[44]. Forward, J. M.; Assefa, Z.; Fackler, J. P. *J. Am. Chem. Soc.* 1995, *117*, 9103.

[45]. Forward, J. M.; Fackler, J. P.; Staples, R. J. *Organometallics* 1995, *14*, 4195.

[46]. Forward, J. M.; Assefa, Z.; Staples, R. J.; Fackler, J. P. *Inorg. Chem.* 1996, *35*, 16.

[47]. Assefa, Z.; McBurnett, B. G.; Staples, R. J.; Fackler, J. P. *Inorg. Chem.* 1995, *34*, 4965.

[48]. Assefa, Z.; McBurnett, B. G.; Staples, R. J.; Fackler, J. P. *Inorg. Chem.* 1995, *34*, 75.

[49]. Alyea, E. C.; Ferguson, G.; Kannan, S. *Chem. Commun.* 1998, 345.

[50]. Nadasdi, L. Joo, F. *Inorg. Chem. Acta* 1999, *293*, 218.

[51]. Assmann, B.; Angermaier, K.; Paul, M.; Reide, J.; Schmidbauer, H. *Chem. Ber.* 1995, *128*, 891.

[52]. Daigle, D. J.; Pepperman, A. B. *J. Heterocycl. Chem.* 1975, *12*, 579.

[53]. Daigle, D. J.; Boudreaux, G. J.; Vail, S. L. *J. Chem. Eng. Data* 1976, *21*, 240.

[54]. Shriver, D. F.; Drezdon, M. A. *The Manipulation of Air-Sensitive Compounds*; John Wiley & Sons: New York, 1986.

[55]. Cornils, B. *Org. Process Res. Dev.* 1998, *2*, 121-127.

[56]. Cornils, B.; Herrmann, W. A. *Aqueous-Phase Organometallic Catalysis Concepts and Applications*; Wiley-VCH: Weinheim, 1998.

[57]. Joó, F. *Aqueous Organometallic Catalysis*; Kluwer Academic Publishers: Dordrecht, 2001.

[58]. Casado, R.; Contel, M.; Laguna, M.; Romero, P.; Sanz, S. *J. Am. Chem. Soc.* 2003, *125*, 11925-11935

[59]. Mohr, F.; Cerrada, E.; Laguna, M. *Organometallics* 2006, *25*, 644-648.

[60]. See for example: (a) Schmidbaur, H.; Grohmann, A.; Olmos, M. E. Organogold chemistry. In *Gold Progress in Chemistry, Biochemistry and Technology*, Schmidbaur, H., Ed.; John Wiley & Sons: Chichester, 1999; pp 647-746. (b) Fackler, J. P., Jr. *Polyhedron* 1997, *16*, 1-17. (c) Mohr, F.; Privér, S. H.; Bhargava, S. K.; Bennett, M. A. *Coord. Chem. Rev.*, in press.

[61]. Laguna, A.; Laguna, M. *Coord. Chem. Rev.* 1999, *193-195*, 837-856.

[62]. Méndez, L. A.; Jiménez, J.; Cerrada, E.; Mohr, F.; Laguna, M. *J. Am. Chem. Soc.* 2005, *127*, 852-853.

[63]. Bhargava, S. K.; Mohr, F.; Bennett, M. A.; Welling, L. L.; Willis, A. C. *Organometallics*

[64]. See for example: (a) Phillips, A. D.; Gonsalvi, L.; Romerosa, A.; Vizza, F.; Peruzzini, M. *Coord. Chem. Rev.* 2004, *248*, 955-993. (b) Cornils, B.; Kuntz, E. G. *J. Organomet. Chem.* 1995, *502*, 177-186. (c) Pinault, N.; Bruce, D. W. *Coord. Chem. Rev.* 2003, *241*, 1-25. (d) Katti, K. V.; Hariprasad, G.; Smith, C. J.; Berning, D. E. *Acc. Chem. Res.* 1999, *32*, 9-17, and references therein. (e) Assefa, Z.; Forward, J. M.; Grant, T. A.; Staples, R. J.; Hanson, B. E.; Mohamed, A. A.; Fackler, J. P., Jr. *Inorg. Chim. Acta* 2003, *352*, 31.

[65]. Darensbourg, D. J.; Ortiz, C. G.; Kamplain, J. W. *Organometallics* 2004, *23*, 1747-1754.

[66]. Murray, H. H.; Fackler, J. P., Jr.; Porter, L. C.; Mazany, A. M. *J. Chem. Soc., Chem. Commun.* 1986, 321-322.

[67] Usón, R.; Laguna, A.; Laguna, M.; Jiménez, J.; Jones, P. G. *J. Chem. Soc., Dalton Trans.* 1991, 1361-1365.

[68]. Schmidbaur, H.; Grohmann, A.; Olmos, M. E. Gold, Progress in Chemistry, Biochemistry and Technology. In *Gold, Progress in Chemistry, Biochemistry and Technology*; Schmidbaur, H., Ed.; John Wiley & Sons: Chichester, 1999; p 747, and references therein.

[69]. Assefa, Z.; Omary, M. A.; McBurnett, B. G.; Mohamed, A. A.; Patterson, H. H.; Staples, R. J.; Fackler, J. P., Jr. *Inorg. Chem.* 2002, *41*, 6274-6280.

[70]. Fackler, J. P., Jr.; Trzcinska-Bancroft, B. *Organometallics* 1985, *4*, 1891-1893.

[71]. Bennett, M. A.; Bhargava, S. K.; Hockless, D. C. R.; Welling, L. L.; Willis, A. C. *J. Am. Chem. Soc.* 1996, *118*, 10469-10478.

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