

Synthesis, Characterization, Spectroscopic and Photophysical Properties of New $[\text{Cu}(\text{NCS})\{(\text{L}-\text{N})_2 \text{ or } (\text{L}'-\text{N}^{\wedge}\text{N})\}(\text{PPh}_3)]$ Complexes ($\text{L}-\text{N}$, $\text{L}'-\text{N}^{\wedge}\text{N}$ = Aromatic Nitrogen Base)

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The syntheses, spectroscopic characterization (IR, ^1H and ^{31}P NMR, ESI-MS) and conductivity studies of the mixed N,P-donor complexes of copper(I) thiocyanate: $[\text{Cu}(\text{NCS})(\text{py})_2(\text{PPh}_3)]$, (**2**), $[\text{Cu}(\text{NCS})(\text{Mepy})(\text{PPh}_3)]_2$, (**3**), $[\text{Cu}(\text{NCS})(\text{phen})(\text{PPh}_3)]$, (**4**), $[\text{Cu}(\text{NCS})(\text{bpy})(\text{PPh}_3)]$, (**5**), $[\text{Cu}(\text{NCS})(\text{bpy})(\text{PPh}_2\text{py})]$, (**6**), $[\text{Cu}(\text{NCS})(\text{py})(\text{PPh}_2\text{py})]$, (**7**), (py = pyridine; Mepy = 2-methylpyridine; phen = 1,10-phenanthroline, bpy = 2,2'-bipyridyl), together with single-crystal X-ray structural characterizations of **2**, **3**, **4** (new polymorph), **5** and **6** are reported, which provides an opportunity to study the effect of the introduction of a pair of nitrogen donors, both unidentate and chelate, on the bonding parameters of the Cu/NCS/P system. Cu–P and Cu–N₂(ar) are found to be similar [2.1974(5) and 2.091(2), 2.070(1) Å for py_2 adduct **2**, cf. 2.1748(9)–2.200(1) and 2.071(2)–2.106(4) Å for the counterpart values for bidentate adducts **4**–**6**]. However, Cu–N(CS) and Cu–N–C are 2.013(2) Å and 157.4(2)° for py_2 adduct **2** and 1.946(2)–1.981(8) Å and 166.7(2)–176.58(2)° for bidentate

counterparts **4**–**6**. The change is attributed primarily to the closure in the N–Cu–N angle [99.58(8)° for py_2 **2**; 77.7(6)–80.5(3)° for N[^]N-bidentate donors **4**–**6**]. In consequence of the increased steric profile of the Mepy ligand, we find the stoichiometry diminished to 1:1:1, which resulted in the formation of $[(\text{Ph}_3\text{P})\text{MepyCu}(\text{NCS})\text{Cu}(\text{Mepy})(\text{PPh}_3)]$ dimers. TDDFT/CPCM calculations were used to clarify the type of transitions involved in the UV/Vis absorption spectra, and the corresponding experimental photoemission data were acquired. The ^{31}P CPMAS spectra of the copper derivatives exhibit distorted quartets that afford values for $^1J_{\text{Cu,P}}$. Furthermore, the quadrupole-induced distortion factors were calculated, and in the cases of **2**, **4** and **5**, the quadrupole coupling constants were obtained, on the basis of the X-ray structures.

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Introduction

Some years ago, from solutions of appropriate stoichiometry of copper(I) halide, CuX ($\text{X} = \text{Cl}, \text{Br}, \text{I}$), triphenylphosphane and pyridine (py) in acetonitrile, adducts of stoichiometry $\text{CuX}/\text{PPh}_3/\text{py}$ (1:1:1 or 1:2:1) were crystallized and characterized by single-crystal X-ray studies;^[1–3] similar silver(I) counterparts were also defined.^[4,5] In ref.^[1] the authors commented that “no evidence has been

found for the existence of the $[\text{CuX}(\text{py})_2(\text{PPh}_3)]$ series”, seemingly still the case, although stabilization of the $[\text{CuXN}_2\text{P}]$ motif by the use of the bidentate bpy ($\text{bpy} = 2,2'$ -bipyridyl) ligand has been shown elsewhere.^[6] The latter systems are mononuclear $[\text{CuX}(\text{bpy}-\text{N},\text{N}')(\text{PPh}_3)]$, $\text{X} = \text{Cl}, \text{Br}, \text{I}$ (isomorphous); the structures of monohydrates of the chloride^[7] and of the bromide^[8] have also been recorded, as well as that of the *N*-thiocyanate/phenanthroline (phen) counterpart.^[9] The latter are consequent on an upsurge of interest in the use of such systems as catalysts,^[10] as well as species with more complex, derivative ligands. Very little work has been done on the counterpart silver(I) systems, and the structure of $[\text{AgBr}(\text{phen})(\text{PPh}_3)]$ is the only example so defined.^[11]

Further interest in such systems arises from the fact that $d^{10}(\text{I})$ complexes containing N-donor ligands exhibit a diverse variety of spectroscopic behaviours: luminescence thermochromism, luminescence, solvatochromism, luminescence rigidochromism and concentration luminochromism. For example, a variety of trinuclear Cu pyrazolates^[12] exhibiting fascinating optical phenomena and photolumines-

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cent mixed-ligand copper polymers have been recently reported.^[13,14] Copper phosphino and/or pyridine derivatives,^[15–19] emissive at room or at low temperature, have been described but attempts to describe the associated spectroscopic properties in terms of known structures of the complexes remain limited. Despite the considerable attention paid to cyclic trinuclear d^{10} complexes, a fundamental issue that remains outstanding concerns, for example, the role played by the transition metal in determining the molecular structure, photophysics and spectroscopic properties in mononuclear species. This paper reports the first systematic effort, by combining a number of different techniques, to unravel the role of the coinage metal and of the supporting ligands in determining the spectroscopic, structural and optical properties of a series of analogous mononuclear $\text{MX}(\text{N}_2)\text{P}$ -type complexes.

In extending existing studies^[1–3] to encompass the pseudohalogen $\text{X} = \text{SCN}$, it was found that crystallization of $[\text{Cu}(\text{SCN})(\text{PPh}_3)]$ from pyridine yielded a complex shown to be a 1:1:2 $\text{CuSCN}/\text{PPh}_3/\text{py}$ adduct (**2**), the first of that stoichiometry so defined. It was found to crystallize in a chiral space group and to be strongly luminescent, which prompted study of its photophysical properties, augmented by the synthesis and study of a number of $\text{N}^{\wedge}\text{N}$ -bidentate ligand counterparts: a new polymorph of $[\text{Cu}(\text{NCS})(\text{phen})(\text{PPh}_3)]$ (**4**) and $[\text{Cu}(\text{NCS})(\text{bpy})\text{L}]$ ($\text{L} = \text{PPh}_3, \text{PPh}_2\text{py}$) (**5**, **6**), all mononuclear. In contrast to **2**, the use of the more-hindered 2-methylpyridine base (Mepy) results in centrosymmetric, binuclear $[(\text{PPh}_3\text{P})(\text{Mepy})\text{Cu}(\text{NCS})\text{Cu}(\text{Mepy})(\text{PPh}_3)]$, (**3**). We report solid-state ^{31}P CP-MAS NMR and photoemission data of the above compounds, together with analyses of their quadrupolar splitting parameters due to the Cu–P interactions and correlation with the structural behaviour; the photoemission transitions were assigned with the assistance of TDDFT/CPCM calculations.

Results and Discussion

From the interaction of copper(I) thiocyanate and triphenylphosphane in a 1:1 metal to phosphane ratio, in pyridine at room temperature, we obtained derivative **1**, $\text{CuSCN}:\text{PPh}_3$ (1:1), which is a colourless and air- and moisture-stable compound that shows a sharp melting point; it is soluble in acetonitrile and chlorinated solvents. The most significant information from the infrared spectra in compounds such as **1** is related to the frequency of the absorption band at ca. $2050\text{--}2100\text{ cm}^{-1}$, which is due to the stretching vibration of $(\text{SC}\equiv\text{N})$; this band was reported to be sensitive to the bonding type of the NCS group in metal complexes.^[20,21] In the spectrum of **1**, this band is high-frequency shifted, at 2094 cm^{-1} , which is suggestive of a bridging Cu–NCS–Cu framework, perhaps in a dimer or a more complex polymeric system.

When the same reaction was carried out by warming at ca. $60\text{ }^\circ\text{C}$, the triboluminescent derivative **2** was afforded with a 1:2:1 $\text{Cu}:\text{py}:\text{PPh}_3$ ratio; that is, it contains two py molecules as ligands. A similar reaction carried out in 2-

methylpyridine (Mepy) afforded derivative **3**, but in this case, presumably in consequence of the steric hindrance of the methyl group in the 2-position of the pyridine, which prevents the coordination of a second Mepy molecule about the copper atom, a compound with a 1:1:1 $\text{Cu}/\text{Mepy}/\text{PPh}_3$ stoichiometry was obtained. In the IR spectra of **2** and **3**, the absorption bands of the NCS group fall at 2066 and 2095 cm^{-1} , respectively. Whereas the former is mononuclear with an N-bonded NCS group, as also demonstrated in the X-ray structure (see below), the possibility that the latter exists as a dinuclear structure with a bridging Cu–NCS–Cu system cannot be excluded, as confirmed by the X-ray work. In the ^1H NMR spectra of **2** and **3**, the expected integration of the resonances for the presence of two py to one PPh_3 (derivative **2**) ligand and a 1:1 Mepy/ PPh_3 ratio (derivative **3**) was observed. Variable temperature ^{31}P NMR spectra of **2** and **3** show no dissociation, either at room or low temperature.

The interaction of CuNCS with PPh_3 in acetonitrile, in the presence of chelating $\text{N}^{\wedge}\text{N}$ aromatic ligands, such as phen and bpy, afforded derivatives **4** and **5** of the form $\text{CuNCS}/\text{PPh}_3/\text{L}$ (1:1:1). They are stable solids with sharp melting points. The IR spectra show strong absorptions at 2082 and 2089 cm^{-1} , respectively, which are again indicative of Cu–NCS systems. The absorptions in the region $550\text{--}420\text{ cm}^{-1}$, as also found for all derivatives **1–7**, are clearly indicative of the presence of aromatic phosphanes and are attributable to Whiffen's "y" and "t" modes of vibration.^[22] In the ^1H NMR spectra, all the resonances of chelating phen (derivative **4**) or bpy (derivative **5**) beyond those of PPh_3 were detected. For **4** and **5**, the VT ^{31}P NMR spectra show no evidence for dissociation.

We also explored the use of a different ditopic chelating phosphane, diphenylpyridylphosphane (PPh_2py), which offers the possibility of py–N instead of, or as well as, P coordination within the one ligand. Its interaction with CuNCS in acetone, in the presence of bpy, afforded mononuclear derivative **6**, $\text{CuNCS}/\text{PPh}_2\text{py}/\text{bpy}$ (1:1:1). Finally, when the same reaction was performed in pyridine as solvent, derivative **7**, $\text{CuNCS}/\text{PPh}_2\text{py}/\text{py}$ (1:1:1), was obtained, with the possibility of a $\text{P}^{\wedge}\text{N}$ -bidentate PPh_2py ligand with a py molecule also bonded to the Cu centre. The IR $\nu(\text{S}-\text{C}\equiv\text{N})$ absorptions, which fall at 2087 and 2086 cm^{-1} for **6** and **7**, respectively, indicate that the NCS group is N-bonded to the Cu atom. In the ^1H NMR spectra of **6** and **7**, broad multiplets were observed owing to PPh_2py and to py (**7**). The VT ^{31}P NMR spectra of **6** seem to indicate a dissociative equilibrium involving a PPh_2py ligand, and three resonances at 2.07 , -0.78 and -3.65 ppm were detected; the latter presumably arose from a PPh_2py ligand not bound through the phosphorus atom. However we cannot, at present, discriminate between a fully dissociated and an N-coordinated PPh_2py ligand.

X-ray Diffraction Studies

The results of the single-crystal X-ray studies are consistent in terms of stoichiometry and connectivity with the

formulations of complexes **2** and **4–6** as $[\text{Cu}(\text{NCS})(\text{py})_2(\text{PPh}_3)]$ (**2**) and $[\text{Cu}(\text{NCS})(\text{N}^{\wedge}\text{N}\text{-chelate})(\text{R}_3\text{P})]$ (**4–6**). One molecule (Figure 1), devoid of crystallographic symmetry,

comprises the asymmetric unit of the structure in each case; the pyridine adduct crystallizes in a chiral space group so that each crystal is enantiomerically pure, although the

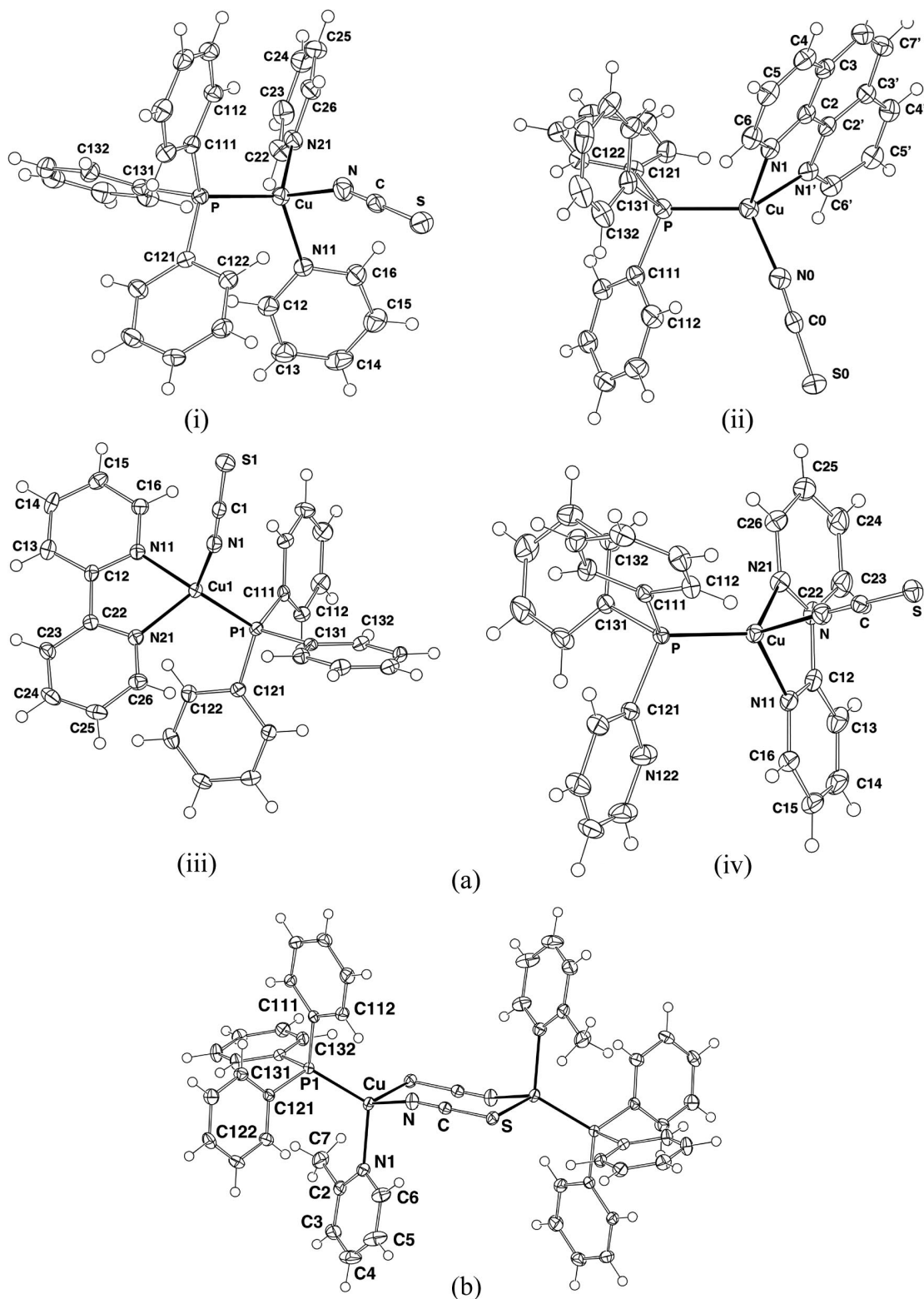


Figure 1. Projections of single molecules of (a) (i) $[\text{Cu}(\text{NCS})(\text{py})_2(\text{PPh}_3)]$ (**2**); (ii) $[\text{Cu}(\text{NCS})(\text{phen})(\text{PPh}_3)]$ (**4**); (iii) $[(\text{NCS})(\text{bpy})(\text{PPh}_3)]$ (**5**); (iv) $[\text{Cu}(\text{NCS})(\text{bpy})(\text{PPh}_2\text{py})]$ (**6**). (b) $[(\text{Ph}_3\text{P})(\text{Mepy})\text{Cu}^{\text{SCN}}\text{Cu}(\text{Mepy})(\text{PPh}_3)]$ (**3**).

molecule has a potential mirror plane. The metal centre in each molecule is four-coordinate, and the thiocyanate groups are N-coordinated with the coordination environments XMPN₂, N[^]N. The pyridine adduct is the first complex formulated as [CuX(unidentate-N-base)₂(R₃P)] to be isolated and structurally defined; the new polymorph of the Cu/phen/NCS adduct augments the arrays of the form [CuX(N,N'-bidentate ligand)(R₃P)] previously described for bpy/X = Cl, Br, I as above, also augmented by the addition of the thiocyanate analogue of the bpy arrays with PPh₃ and Ph₂pyP (**5**, **6**). In the report of the bpy adduct, for X = Cl,^[6] two independent molecules were found in that structure, and they were dependent on the conformation of the PPh₃ disposition vis-a-vis that of the (bpy)CuX array; one conformation (a) was only found for X = Br, I and two conformations (a,b) were found in the anhydrous chloride. The latter (b), which is a "rotamer" of (a), was also found in the hydrated form of the chloride, which is suggestive of an inversion in stability in the two forms depending on the bulk of the halide. Given that the donor of the pseudohalide NCS group in all of the present complexes is the smaller nitrogen atom, it is interesting to note the conformation belonging to type (b), as might be expected. Finally, we note that, in the array of **6**, the use of Ph₂pyP in place of PPh₃, which has an alternative N donor that may act as a unidentate or bridging donor or form a chelate with the phosphorus atom, does none of these things and simply forms mononuclear [Cu(NCS)(N[^]N-bpy)(Ph₂pyP)] (**6**), in which one molecule again comprises the asymmetric unit. There are no unusually close interactions with the pyridyl nitrogen atom of the Ph₂pyP ligand, which suggests an aggregate subtle interplay of intermolecular forces to be at work in determining that this complex is not isomorphous with its PPh₃ counterpart **6**. Geometries of the present complexes and those of the type (b) form of the chloride are presented comparatively in Table 1.

Steric control of the coordination number through the use of hindered unidentate nitrogen (in particular, pyridine) base donors in coinage metal(I) [in particular, copper(I)] complexes has long been exploited, as, for example, in the crystallisation of copper(I) perchlorate from (the conveniently liquid) pyridine, 2-methylpyridine and 2,6-dimethylpyridine, whereby ionic mononuclear adducts of the form [CuL_n](ClO₄), *n* = 4, 3, 2, respectively, were obtained.^[23] In the present situation, the use of Mepy in place of py results in the formation of a complex of diminished stoichiometry (1:1:1), as might have been anticipated. However, there is no associated diminution in the coordination number (CN) of the copper(I) metal centre, and a coordination number of four is maintained by substitution of the less-sterically demanding S-terminal of the ambidentate thiocyanate group so that the latter presents as terminally bridging SCN, within the context of the familiar binuclear eight-membered Cu^(SCN)₂Cu cyclic array. Thus, [(Ph₃P)(Mepy)-Cu^(SCN)₂Cu(Mepy)(PPh₃)] (**3**) is of the form that is similar to that of the pyridine/halide analogues.^[2] Introduction of the sulfur atom instead of the second pyridine or chelate N-donor has relatively little impact on the remaining geometries about the copper atom, and they are perhaps more closely allied to those of py₂ adduct **2**, rather than those of the N[^]N chelate complexes (Table 1, cf. Table 2).

In Table 1, it is of interest to note that, despite the change in the aromatic N₂-base donor array from a pair of unidentate ligands, (py)₂, to a bidentate ligand (phen or bpy), accompanied by a substantial diminution in the in N(ar)-Cu-N(ar) bite angle, Cu-P and Cu-N(ar) are similar in both types of complex. A notable change, however, is found in the Cu-NCS affiliation, as Cu-N(NCS) diminishes appreciably on passing from the (py)₂ to the N[^]N-chelate adducts, perhaps in consequence of a more spacious environment for the anion, consequent on incorporation of the bidentate ligand and a straighter Cu-N-C angle. Although it is ex-

Table 1. Selected geometries of [CuX(aromatic base-N,N')L] (L = PPh₃, PPh₂py).

L/N(^)N'/X Compound	PPh ₃ (py-N) ₂ /NCS ^[a] 2	PPh ₃ /phen/NCS ^[a,b] 4	PPh ₃ /bpy/NCS 5	PPh ₂ py/bpy/NCS 6	PPh ₃ /bpy/Cl,Cl·H ₂ O ^[c]
Distances [Å]					
Cu-X	2.013(2)	1.960(5), 1.981(8)	1.946(2)	1.9736(13)	2.307(6), 2.330(2)
Cu-N(ar)	2.091(2)	2.106(4), 2.099(8)	2.071(2)	2.0800(12)	2.10(1), 2.076(5)
	2.070(1)	2.072(3), 2.090(6)	2.063(2)	2.0874(12)	2.14(2), 2.087(6)
Cu-P	2.1974(5)	2.200(1), 2.189(3)	2.1748(9)	2.1813(4)	2.219(6), 2.180(2)
S-C	1.638(2)	1.638(6), 1.597(9)	1.632(2)	1.638(1)	–
C-N	1.168(3)	1.162(7), 1.15(1)	1.165(3)	1.163(2)	–
Angles [°]					
X-Cu-N(ar)	99.58(8)	114.3(2), 110.9(3)	102.47(9)	105.03(5)	111.2(4), 104.5(2)
	106.70(6)	102.8(2), 104.1(3)	115.56(9)	100.25(5)	109.3(5), 102.9(5)
X-Cu-P	115.34(6)	115.3(1), 115.8(3)	117.06(7)	120.61(4)	116.3(2), 117.1(1)
P-Cu-N(ar)	116.27(4)	111.2(1), 117.6(2)	124.25(6)	121.53(4)	118.7(5), 123.2(1)
	116.29(4)	128.4(1), 122.6(2)	112.55(6)	121.56(4)	117.5(4), 122.8(2)
N(ar)-Cu-N(ar)	100.37(7)	80.3(1), 80.5(3)	79.61(9)	79.28(5)	77.7(6), 79.2(2)
Cu-N-C	157.4(2)	170.8(3), 167.4(8)	166.7(2)	176.58(12)	–
N-C-S	179.5(2)	179.3(4), 179(1)	178.4(3)	178.98(13)	–

[a] Cu lies 0.006(3) and 0.155(3) Å out of the two pyridine C₅N planes in the (py)₂ complex and 0.216(3) Å out of the C₁₂N₂ plane of the present phen adduct. [b] The two entries are for the present polymorph, and for that of ref.^[9] [c] The two entries are for molecule 2 of the unsolvated chloride^[6] and the molecule of the hydrate,^[7] both of those being of the same conformation as the present.

Table 2. Selected geometries of $[(\text{Ph}_3\text{P})(\text{Mepy})\text{Cu}(\text{NCS})\text{Cu}(\text{Mepy})-(\text{PPh}_3)]$ (**3**).^[a]

Distances [Å]			
Cu–N	2.009(2)	Cu–P	2.2149(5)
Cu–N1	2.106(2)	Cu–S'	2.4170(5)
S–C	1.655(2)	C–N	1.159(2)
Angles [°]			
N–Cu–N1	100.75(7)	N1–Cu–P	116.61(5)
N–Cu–P	117.71(5)	N1–Cu–S'	103.34(5)
N–Cu–S'	101.21(5)	P–Cu–S'	114.83(2)
Cu–S'–C'	97.18(7)	Cu–N–C	154.0(2)
N–C–S	179.0(2)		

[a] Primed atoms are inversion related; N is the thiocyanate and N1 the pyridine donor.

pected that the Cu–NCS array should be quasilinear, the present situation may reflect greater rigidity in association with the shorter, stronger bonds.

Solid-State NMR Spectroscopy

The ^{31}P CPMAS spectra for all compounds under investigation are shown in Figure 2, and the NMR parameters are summarized in Table 3. All the spectra are characterized by a resonance that appears as a well-resolved quartet. The spectra of **3**, **6** and **7** are characterized by broad signals at -12.4 , 0.8 and -6.8 ppm, respectively. For compounds **6** and **7**, this is probably due to different quadrupole relaxation effects, as previously found by some of us for other three-coordinate copper halide complexes containing tricyclohexylphosphane.^[24] In the case of **3**, it also confirms the dimeric nature of the complex. Conversely, the spectra of samples **1**, **2**, **4** and **5**, where resonances fall at -9.8 , -7.2 , -2.8 and -3.8 ppm respectively, are characterized by one quartet with very sharp peaks.

There are two main reasons for the presence of the typical splitting pattern: the first is the presence of the ^{63}Cu and ^{65}Cu isotopes, which are both quadrupolar and NMR active (^{63}Cu : $I = 3/2$, natural abundance 69.09% and ^{65}Cu : $I = 3/2$, natural abundance 30.91%), that gives rise to two almost overlapped quartets mainly visible in the splitting of the outer resonances. This is particularly evident in the spectra of compounds **1**, **2**, **3**, **4** and **5** reported in Figure 2. The second reason for the presence of such a splitting pattern is the inefficient averaging by the magic angle spinning of the dipolar and indirect coupling anisotropy inter-

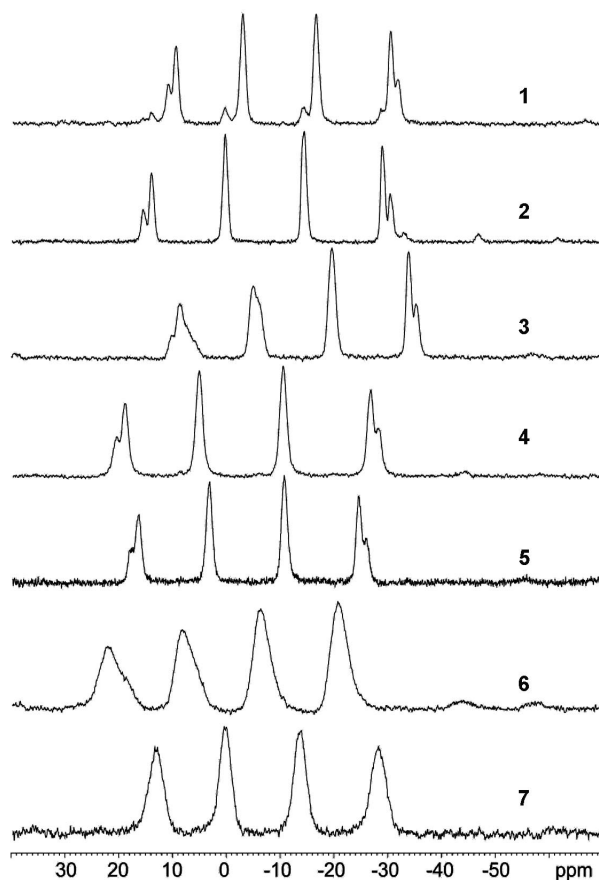


Figure 2. ^{31}P CPMAS NMR spectra of $[\text{Cu}(\text{NCS})(\text{PPh}_3)]_2$ (**1**), $[\text{Cu}(\text{NCS})(\text{py})_2(\text{PPh}_3)]$ (**2**), $[\text{Cu}(\text{NCS})(\text{Mepy})(\text{PPh}_3)]_2$ (**3**), $[\text{Cu}(\text{NCS})(\text{phen})(\text{PPh}_3)]$ (**4**), $[\text{Cu}(\text{NCS})(\text{bpy})(\text{PPh}_3)]$ (**5**), $[\text{Cu}(\text{NCS})(\text{bpy})(\text{PPh}_2\text{py})]$ (**6**) and $[\text{Cu}(\text{NCS})(\text{py})(\text{PPh}_2\text{py})]$ (**7**), recorded at 109.6 MHz with a spinning rate of 7 kHz.

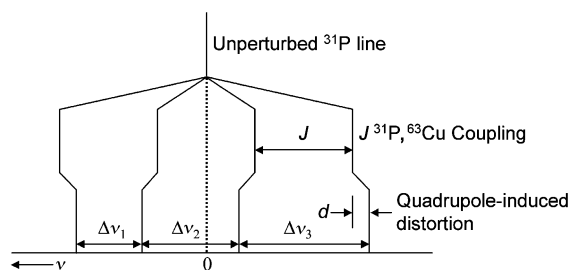
actions between Cu and P when the quadrupolar coupling is comparable to the Zeeman splitting energy. This produces different splittings between adjacent peaks in each quartet with respect to $^1J[^{31}\text{P}, ^{63}\text{Cu}]$.

The quartets are also somewhat distorted according to Scheme 1, because the axis of quantization for the quadrupolar copper isotopes is not exactly coincident with the direction of the applied magnetic field, B_0 . Spectral analysis allows us to extract structural information from these combined effects of dipolar, scalar and quadrupolar interactions,^[25] such as, for example, bond lengths and angles, ^{63}Cu quadrupole coupling constants and location of the

Table 3. ^{31}P CPMAS NMR spectroscopic data for **1–7**.

Compound	δ [ppm]	$\Delta\nu_1$ [Hz]	$\Delta\nu_2$ [Hz]	$\Delta\nu_3$ [Hz]	$\langle\Delta\nu\rangle$ [Hz]	d [Hz]	$d\nu_{\text{Cu}}/10^9$ [MHz]
$[\text{Cu}(\text{NCS})(\text{PPh}_3)]_2$ (1)	-9.8	1361	1489	1526	1459	-41.25	-2.95
$[\text{Cu}(\text{NCS})(\text{py})_2(\text{PPh}_3)]$ (2)	-7.2	1537	1568	1581	1562	-11.00	-0.79
$[\text{Cu}(\text{NCS})(\text{Mepy})(\text{PPh}_3)]_2$ (3)	-12.4	1489	1599	1556	1548	-16.75	-1.20
$[\text{Cu}(\text{NCS})(\text{phen})(\text{PPh}_3)]$ (4)	-2.8	1523	1712	1786	1674	-65.75	-4.71
$[\text{Cu}(\text{NCS})(\text{bpy})(\text{PPh}_3)]$ (5)	-3.8	1440	1520	1519	1493	-19.76	-1.41
$[\text{Cu}(\text{NCS})(\text{bpy})(\text{PPh}_2\text{py})]$ (6)	0.8	1550	1605	1575	1577	-6.25	-0.45
$[\text{Cu}(\text{NCS})(\text{py})(\text{PPh}_2\text{py})]$ (7)	-6.8	1409	1569	1562	1513	-38.25	-2.74

electric field gradients (EFG) at the copper atom with respect to the molecular frame. Many examples of copper–phosphane complexes have been discussed in the literature,^[26] and the analysis of such spectra has been described in detail.^[27,28]



Scheme 1.

For the interpretation of the present spectra a detailed theory with parameter definitions is available in the Supporting Information.^[26–31]

Accurate analysis of the quadrupole parameters is presented only for $[\text{Cu}(\text{NCS})(\text{py})_2(\text{PPh}_3)]$ (**2**), $[\text{Cu}(\text{NCS})(\text{Mepy})(\text{PPh}_3)]_2$ (**3**), $[\text{Cu}(\text{NCS})(\text{phen})(\text{PPh}_3)]$ (**4**), $[\text{Cu}(\text{NCS})(\text{bpy})(\text{PPh}_3)]$ (**5**) and $[\text{Cu}(\text{NCS})(\text{bpy})(\text{PPh}_2\text{py})]$ (**6**), for which X-ray structures are recorded. Indeed, when the P–Cu bond lengths are known from diffraction data, it is possible to establish the existence of anisotropic ΔJ effects, which are otherwise difficult to distinguish from dipolar effects.

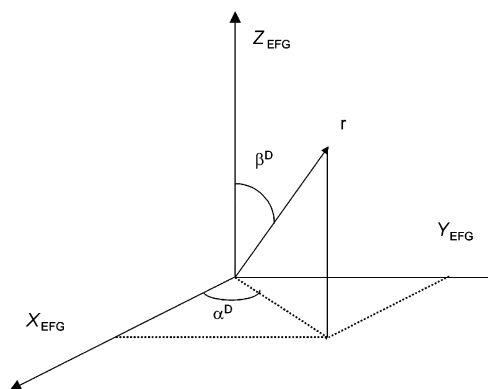
The ^{31}P CPMAS NMR spectrum of $[\text{Cu}(\text{NCS})(\text{py})_2(\text{PPh}_3)]$ (**2**) (Figure 2) consists of a single resonance split into a multiplet centred at $\delta = -7.2$ ppm. The values of $\Delta\nu_1$, $\Delta\nu_2$ and $\Delta\nu_3$ (defined as $\Delta\nu_1 = J - 2d$, $\Delta\nu_2 = J$ and $\Delta\nu_3 = J + 2d$, see Scheme 1) are measured as 1537, 1568 and 1581 Hz, respectively. The values of $\langle\Delta\nu\rangle = 1/3(\Delta\nu_1 + \Delta\nu_2 + \Delta\nu_3)$ and $\Delta\nu_2$ were used in approximating the J coupling constant $[^1J(^{31}\text{P}, ^{63}\text{Cu})]$ and are reported in Table 2.

Because in our case the centres of gravity of the quartets do not follow the relation $(\Delta\nu_1 - \Delta\nu_2) = (\Delta\nu_2 - \Delta\nu_3)$, the first-order perturbation theory results are inadequate to describe the observed ^{31}P splitting. Second-order effects were considered here for interpreting the ^{31}P NMR spectra, and so $d = (\Delta\nu_1 - \Delta\nu_3)/4$ defines the quadrupole-induced distortion.

For the location of the copper EFG axes in the molecular frame we followed the qualitative method described by Vega,^[30] which connects the relative electron populations and direction of EFG tensors in s–p hybrids of ^{14}N compounds when the molecules have a symmetry plane. The EFG is assumed to depend on the difference in electron density in the metal 4p orbital obtained by considering the first coordination sphere as defined by the X-ray diffraction study. A similar approach was used by Olivieri^[26j] to provide a qualitative picture of the ^{63}Cu EFG in different P_nCuX_m complexes.

Throughout this paper we will thus assume that the electron populations of the Cu–P bonds are higher than those

of the Cu–N bonds and that the EFG z axis is directed along the direction of higher electron density. We thus fix the azimuthal (α^D) and polar (β^D) angles of the $^{31}\text{P}, ^{63}\text{Cu}$ dipolar coupling constant (D) in the principal axis system of the electric field gradient at the copper nucleus (EFG principal axis system, PAS) (see Scheme 2) both equal to zero.



Scheme 2.

For evaluating the quadrupolar coupling constant (e^2qQ/h), D and the anisotropy of the J tensor (ΔJ) are still required; the former was obtained from the X-ray Cu–P distance. Indeed $D = 12900/r^3 \text{ Hz}$ and, considering $r = 2.197 \text{ \AA}$, we obtain $D = 1216 \text{ Hz}$. The anisotropy of the tensor $J(^{31}\text{P}, ^{63}\text{Cu})$, ΔJ , according to the literature,^[26j–26m] was fixed in reasonable approximation in the range 0.5–1.0 KHz.^[31] Thus, following the equation $d = -(3e^2qQ/20h\nu_{\text{Cu}})(D - \Delta J/3)(3\cos^2\beta^D - 1 + \eta\sin^2\beta^D\cos^2\alpha^D)$, we estimate a quadrupolar coupling constant value in the range 2.5–3.0 MHz for $[\text{Cu}(\text{NCS})(\text{py})_2(\text{PPh}_3)]$ (**2**). This value of the quadrupolar coupling constant is relatively small compared to other copper–phosphane complexes having tetrahedral coordination at the copper centre and indicates a relatively high symmetry for the copper coordination sphere. By following the same procedure, it was possible to obtain quadrupole coupling constant values of 3.9–4.7, 15.0–17.8, 4.3–5.1 and 1.4–1.6 MHz for compounds **3**, **4**, **5** and **6**, respectively.

The large variation in the quadrupolar coupling constants observed for the monomers $\text{Cu}(\text{NCS})(\text{L})(\text{PPh}_3)$ with $\text{L} = \text{py}$ (**2**), phen (**4**) and bpy (**5**) can be associated with the difference in the X-ray structure geometries (see above). Indeed, the reduced constraint of the pyridine ligands [$\text{N}_{\text{py}}\text{–Cu–N}_{\text{py}}$ angle of $100.37(7)^\circ$] with respect to the phen and bpy ligands results in a copper coordination sphere of **2** closer to tetrahedral geometry. Thus, the more symmetric copper environment is associated with a lower value of the quadrupolar coupling constant.

Conversely, the higher constraint of the phen and bpy ligands requiring smaller $\text{N}_{\text{ar}}\text{–Cu–N}_{\text{ar}}$ angles [ca. 80.4° for phen and $79.61(9)^\circ$ for bpy] results in a more unsymmetrical tetrahedral geometry around the metal centre, which leads to shorter Cu–NCS distances and higher quadrupolar coupling constants. The higher steric hindrance associated

with the phenanthroline ligand induces in **4** an increase in both the Cu–P and Cu–NCS distances and a larger difference in the Cu–N_{ar} bond lengths [2.106(4) Å and 2.072(3) Å for **4** and 2.063(2) Å and 2.071(2) Å for **5**]. Thus, the more distorted tetrahedral environment in **4** leads to a higher value of the quadrupolar coupling constant. In the case of compound **6**, the very low value of the induced distortion term *d* and of the calculated quadrupolar coupling constant are justified by the relative high symmetry around the copper atom. The dimeric structure and the different nature of the ligand in compound **3** do not allow further comparison with the monomeric systems.

The quadrupole-induced distortion parameters obtained for complexes **1** and **7** are in agreement with the *d* values previously reported in the literature.^[26]

Electrochemical and Photoluminescence Properties

The cyclic voltammetric (CV) response in CH₂Cl₂ at a glassy-carbon (GC) electrode of [Cu(NCS)(py)₂(PPh₃)] (**2**) shows a reversible oxidation at *E*_{1/2} = 0.454 V and a chemically irreversible reduction at about *E*_p = −1.08 V (Supporting Information, Figure S1). The oxidation process most likely corresponds to the redox couple Cu(+1/+2), whereas the ill-defined reduction is followed by the deposition of metallic copper on the electrode surface, which in turn undergoes anodic stripping at about −0.17 V. Copper deposition is observed also in CV experiments performed at higher scan rates (up to 50 V/s), which indicates fast decomposition of the corresponding radical anion. As the compound is fluorescent (see below), and there is a significant difference between the first oxidation and the first reduction potentials (i.e. the reaction could be “energy sufficient”^[32]), we tried to get electrochemiluminescence (ECL) emission by the annihilation method. No ECL emissions were detected, very probably due to the chemical irreversibility of the reduction.

The UV/Vis spectra of the d¹⁰ configuration of **2** shows broad absorption bands up to about 300–350 nm. This is not unexpected, as copper(I) prevents the stabilization of its excited states through ligand field. As a consequence, the charge transfer and intraligand transitions dominate its photophysics, and the emissions from Cu^I complexes are usually weak and with short lifetimes. Significant room-temperature phosphorescence is generally observed in multinuclear or cluster complexes of copper and rarely in mononuclear species.^[33] DFT and TDDFT calculations were carried out on complexes **2** and **4** in order to ascertain the type of UV/Vis transitions. Geometries were optimized in the gas phase, and the nature of all stationary points was confirmed by performing frequency calculations. Bond lengths and angles of the optimized geometries do not differ substantially from the corresponding X-ray values of compounds **2** and **4**. Cu–NCS bond lengths are slightly overestimated (about 0.01 Å), but this is a known typical feature of DFT calculations, possibly consequent upon lack of libration corrections in the X-ray work. Also, we optimized the structures of **2** and **4** in dichloromethane as solvent by means of the CPCM method. In the case of **2**, a very slow convergence was observed, which is probably due to the minimal rotational barrier of pyridine and phenyl rings around the Cu–N and P–C bonds, respectively. The structures in dichloromethane and in the gas phase only slightly differ from each other, which results in little difference in the calculated UV/Vis transitions when compared to the experimental broad spectra. The analysis of the shift of excited state energies passing from gas to solution is beyond the aim of the present study. The calculated UV/Vis spectrum of **2** is in agreement with the experimental broad absorption observed in the range between 300 and 350 nm. The assignments of the absorptions were made with the help of TDDFT/CPCM calculations in dichloromethane as solvent (16 singlet excited states were produced) by using the geometry optimized in solvent of **2** in the singlet ground

Table 4. TDDFT/CPCM calculated energies *E*_{cal} [nm] and oscillator strengths (*f*) of the first 16 singlet excited states of the solvent(CPCM)- and gas-phase-optimized geometries of [Cu(NCS)(py)₂(PPh₃)] (**2**) and [Cu(NCS)(phen)(PPh₃)] (**4**).

[Cu(NCS)(py) ₂ (PPh ₃)] (2)				[Cu(NCS)(phen)(PPh ₃)] (4)			
CPCM (CH ₂ Cl ₂)		Gas phase		CPCM (CH ₂ Cl ₂)		Gas phase	
<i>E</i> _{calcd.}	<i>f</i>	<i>E</i> _{calcd.}	<i>f</i>	<i>E</i> _{calcd.}	<i>f</i>	<i>E</i> _{calcd.}	<i>f</i>
345	0.0112	339	0.0274	421	0.0225	427	0.0303
336	0.0338	333	0.0080	415	0.0127	416	0.0021
330	0.024	324	0.0260	399	0.0052	406	0.0040
326	0.002	322	0.0110	388	0.0004	390	0.0005
313	0.0026	317	0.0008	365	0.0535	367	0.0641
311	0.0475	308	0.0013	354	0.0002	352	0.0019
307	0.0034	303	0.0057	348	0.01	351	0.0093
306	0.0514	298	0.0003	340	0.0042	338	0.0022
295	0.0086	297	0.0063	337	0.0031	335	0.0050
294	0.0045	293	0.0015	324	0.0004	323	0.0000
293	0.0042	290	0.1103	311	0.0041	313	0.0351
291	0.0222	289	0.0076	307	0.0168	308	0.0026
290	0.0148	286	0.0303	307	0.0251	302	0.0045
289	0.0159	285	0.0209	303	0.002	298	0.0062
288	0.0182	285	0.0076	297	0.0467	298	0.0388
287	0.0214	282	0.0283	293	0.0326	293	0.0278

state (see Table 4). Although TDDFT does not provide the electronic structures of the excited states, their electronic distribution and their localization may be visualized by using the electron density difference maps (EDDMs).^[34] The EDDMs of the most intense transitions of **2** were calculated and employed for the correct assignments of the transition types. The GAUSSSUM program^[35] was used for EDDMs and for the representation of the absorption spectra. This approach has precedent in the literature for determining the excited-state structures and electron distributions associated with metal complexes containing diimine and π -acceptor ligands.^[36] The four most intense absorptions of **2** (calculated at 336, 330, 311 and 306 nm) are of the MLLCT type. The corresponding EDDMs (Figure 3) show two transitions at 336 and 330 nm involving charge transfer from the metal (with the contribution of the SCN ligand) to the two pyridine rings, and two transitions at 311 and 306 nm involving charge transfer from the metal (with some contribution from the SCN ligand) to the triphenylphosphane. Similar results were obtained for **4** (Figure 4). In both cases, as expected, the transitions occurring at higher energies are characterized by charge transfer towards the triphenylphosphane ligand. Hence, it seems reasonable that the MLLCT is the photoemitting state for both complexes.

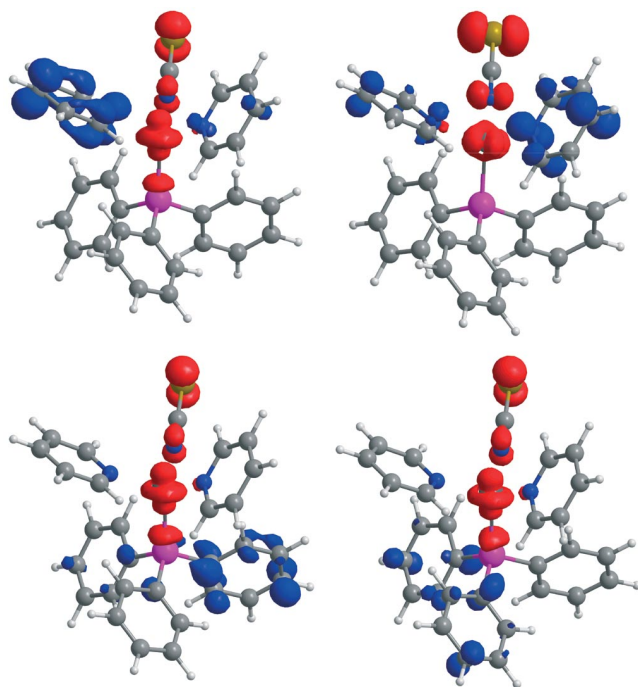


Figure 3. EDDMs of the four most intense transitions of $[\text{Cu}(\text{NCS})(\text{py})_2(\text{PPh}_3)]$ (**2**) calculated at 336, 330 (top) and 311, 306 nm (bottom). Red indicates a decrease in charge density, whereas blue indicates an increase in charge density.

The relevant photoluminescence data of the complexes under investigation collected at room temperature in CH_2Cl_2 (Supporting Information, Figure S2) are summarized in Table 5. The spectrum of each complex shows a broad emission at 370–490 nm.

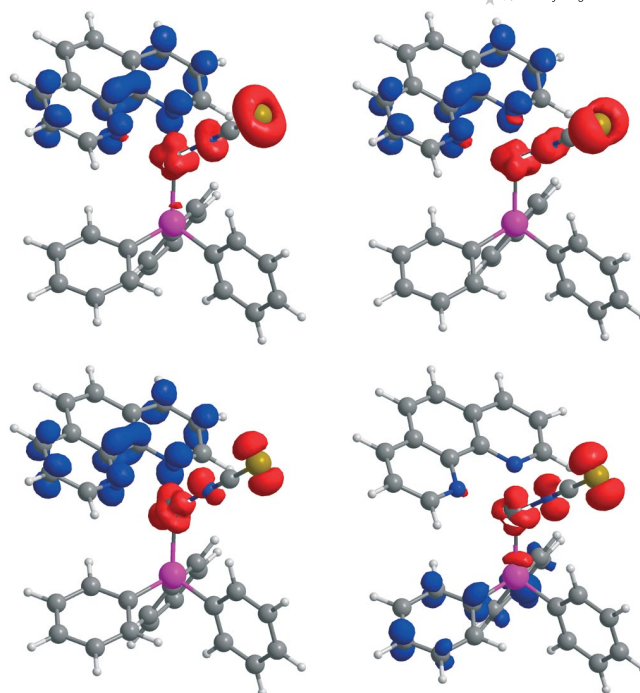


Figure 4. EDDMs of the four most intense transitions of $[\text{Cu}(\text{NCS})(\text{phen})(\text{PPh}_3)]$ (**4**) calculated at 421, 415 (top) and 365, 297 nm (bottom). Red indicates a decrease in charge density, whereas blue indicates an increase in charge density.

Table 5. Photoemission data of compounds **2** and **4**.

Compound	Emission [nm]	Lifetime [ns]
$[\text{Cu}(\text{NCS})(\text{py})_2(\text{PPh}_3)]$ (2)	426	5.8
$[\text{Cu}(\text{NCS})(\text{phen})(\text{PPh}_3)]$ (4)	490	15.3

Conclusions

This work has shown the accessibility of mixed N,P-donor complexes such as $[\text{Cu}(\text{NCS})(\text{Mepy})(\text{PPh}_3)]_2$, $[\text{Cu}(\text{NCS})(\text{phen})(\text{PPh}_3)]$, $[\text{Cu}(\text{NCS})(\text{bpy})(\text{PPh}_3)]$, $[\text{Cu}(\text{NCS})(\text{bpy})(\text{PPh}_2\text{py})]$ and $[\text{Cu}(\text{NCS})(\text{py})(\text{PPh}_2\text{py})]$, as well as $[\text{Cu}(\text{NCS})(\text{py})_2(\text{PPh}_3)]$. The formation and stoichiometry of the adducts are strongly dependent on the reaction conditions employed. The complexes were fully characterized by spectroscopic and X-ray diffraction studies. Their ^{31}P CPMAS NMR spectra were analyzed to obtain the values and signs of the quadrupole-induced distortion parameter, d , which characterizes the observed distortions in the ^{31}P quartets. The isotropic ^{31}P , $^{63,65}\text{Cu}$ indirect spin–spin coupling constants measured in this work were compared to the values describing the Cu local geometries previously obtained for the large family of copper–triphenylphosphane complexes; the coupling constants for the cases under investigation are quite sensitive to the copper environments.

The results of TDDFT/CPCM excited-state calculations in dichloromethane as solvent were fitted to the experimental UV/Vis absorption spectra of compounds **2** and **4**, and the four most intense transitions at lower energies were assigned to the MLLCT types.

Experimental Section

Material and methods: All reagents were purchased from Alfa (Karlsruhe) and Aldrich (Milwaukee) and used as received. The samples for microanalyses were dried in vacuo to a constant weight (20 °C, ca. 0.1 Torr). Elemental analyses (C, H, N, S) were performed in-house with a Fisons Instruments 1108 CHNS-O Elemental Analyzer. IR spectra were recorded from 4000 to 100 cm⁻¹ with a Perkin–Elmer System 2000 FTIR instrument. ¹H and ³¹P NMR solution spectra were recorded with a VXR-300 Varian spectrometer operating at room temperature (300 MHz for ¹H, 121.4 MHz for ³¹P). Melting points are uncorrected and were recorded with an SMP3 Stuart instrument and with a capillary apparatus.

Syntheses of Derivatives 1–7

[Cu(NCS)(PPh₃)₂] (1): A pyridine solution (5 mL) containing CuNCS (0.121 g, 1.0 mmol) and PPh₃ (0.262 g, 1.0 mmol) was stirred at room temperature until a colourless precipitate formed, which was immediately filtered and identified as compound **1**. It is soluble in chloroform and acetonitrile. Yield: 85%. M.p. 169–171 °C. IR (nujol): $\tilde{\nu}$ = 2094 (vs) ν (S–C≡N), 517 (vs), 503 (vs), 487 (m), 442 (m), 432 (m), 425 (w) ν (PPh₃) cm⁻¹. ¹H NMR (300 MHz, CDCl₃, 293 K): δ = 7.22, 7.34 (2 m, 15 H, PC₁₈H₁₅) ppm. ³¹P NMR (121.4 MHz, CDCl₃, 293 K): δ = -1.36 (s) ppm. C₁₈H₁₅CuNPS (371.90): calcd. C 59.44, H 3.94, N 3.65, S 8.35; found C 59.37, H 4.06, N 3.52, S 7.96.

[Cu(NCS)(py)₂(PPh₃)] (2): Compound **1** (0.192 g, 0.5 mmol) was dissolved in pyridine (5 mL) by gently warming (≈60 °C) until dissolution was complete. Slow cooling and evaporation to half the volume of the initial solution afforded a crystalline precipitate, which was identified as derivative **2**. It can be prepared also in the following manner: a pyridine solution (5 mL) containing CuNCS (0.121 g, 1 mmol) and PPh₃ (0.262 g, 1 mmol) was stirred by warming to about 70 °C for 3 h, after which slow cooling and evaporation to half the volume of the initial solution afforded a crystalline precipitate, which was identified as derivative **2**. It is soluble in chloroform and acetonitrile. Yield: 88%. M.p. At 114–120 °C, some decomposition was observed, with reduction in volume of the bulk mass of sample and it then melted in the range 172–174 °C. IR (nujol): $\tilde{\nu}$ = 2066 (vs) ν (S–C≡N), 1590 (m) ν (C=C + C=N), 520 (vs), 509 (vs), 494 (vs), 475 (m), 437 (m), 430 (m), 420 (m) ν (PPh₃) cm⁻¹. ¹H NMR (300 MHz, CDCl₃, 293 K): δ = 7.31 (m, 15 H, PC₁₈H₁₅), 7.35, 7.68, 8.62 (3 m, 10 H, C₅H₅N) ppm. ³¹P NMR (121.4 MHz, CDCl₃, 293 K): δ = 0.0 (br. s) ppm. ³¹P NMR (121.4 MHz, CDCl₃, 223 K): δ = -2.9 (br. s) ppm. C₂₈H₂₅CuN₃PS (530.11): calcd. C 64.25, H 4.65, N 7.75, S 5.91; found C 63.88, H 4.84, N 7.72, S 6.13.

[Cu(NCS)(Mepy)(PPh₃)₂] (3): Compound **3** was prepared by dissolving CuNCS (0.121 g, 1 mmol) and PPh₃ (0.262 g, 1 mmol) in 2-methylpyridine (15 mL) and allowing to stand. It is soluble in chloroform and acetonitrile. Yield: 83%. M.p. 211–213 °C. IR (nujol): $\tilde{\nu}$ = 2095 (vs) ν (S–C≡N), 1582 (w) ν (C=C + C=N), 523 (sh.), 516 (vs), 503 (vs), 487 (m), 442 (m), 433 (m), 425 (m), 416 (m) ν (PPh₃) cm⁻¹. ¹H NMR (300 MHz, CDCl₃, 293 K): δ = 2.55 (s, 3 H, CH₃C₅H₄N), 7.10 (m, 1 H, CH_{Mepy}), 7.17 (dd, *J* = 8 Hz, 1 H, CH_{Mepy}), 7.22–7.34 (m, 15 H, PC₁₈H₁₅), 7.58 (pt, *J* = 8 Hz, 1 H, CH_{Mepy}), 8.50 (br., 1 H, CH_{Mepy}) ppm. ³¹P NMR (121.4 MHz, CDCl₃, 293 K): δ = -0.65 (s) ppm. ³¹P NMR (121.4 MHz, CDCl₃, 223 K): δ = -2.08 (s) ppm. C₂₅H₂₂CuN₂PS (477.04): calcd. C 62.95, H 4.65, N 5.87, S 6.72; found C 62.68, H 4.72, N 5.70, S 6.25.

[Cu(NCS)(phen)(PPh₃)] (4): An acetonitrile suspension (20 mL) containing CuNCS (0.121 g, 1 mmol), PPh₃ (0.262 g, 1 mmol) and

phen (0.180 g, 1 mmol) was stirred at room temperature for 1 h, during which time a pale-yellow precipitate formed that was filtered off, washed with acetonitrile (5 mL) and identified as compound **4**. It is soluble in chloroform and only poorly soluble in acetonitrile. Yield: 92%. M.p. 216–218 °C (dec.). IR (nujol): $\tilde{\nu}$ = 2082 (vs) ν (S–C≡N), 1619 (br. m) ν (C=C + C=N), 526 (vs), 505 (vs), 485 (vs), 448 (m), 427 (m), 420 (m), 420 (m) ν (PPh₃) cm⁻¹. ¹H NMR (300 MHz, CDCl₃, 293 K): δ = 7.24–7.38 (m, 15 H, PC₁₈H₁₅), 7.66, 7.83, 8.32, 8.85 (2 m and 2 s, 8 H, CH_{phen}) ppm. ³¹P NMR (121.4 MHz, CDCl₃, 293 K): δ = 0.65 (br. s) ppm. ³¹P NMR (121.4 MHz, CDCl₃, 223 K): δ = 0.06 (br. s) ppm. C₃₁H₂₃CuN₃PS (564.12): calcd. C 66.00, H 4.11, N 7.45, S 5.68; found C 65.70, H 4.16, N 7.61, S 6.01.

[Cu(NCS)(bpy)(PPh₃)] (5): Compound **5** was prepared following a procedure similar to that reported for **4** by using CuNCS (0.121 g, 1 mmol), PPh₃ (0.262 g, 1 mmol) and bpy (0.156 g, 1 mmol) in acetonitrile. The product is soluble in chloroform and only poorly soluble in acetonitrile. Yield: 87%. M.p. 189–192 °C. IR (nujol): $\tilde{\nu}$ = 2089 (vs) ν (S–C≡N), 1592 (br. m), 1566 (m), 1560 (m) ν (C=C + C=N), 519 (vs), 500 (vs), 473 (vs), 431 (m), 409 (m) ν (PPh₃) cm⁻¹. ¹H NMR (300 MHz, CDCl₃, 293 K): δ = 7.25–7.35 (m, 17 H, PC₁₈H₁₅ + CH_{bpy}), 7.85 (pt, *J* = 8 Hz, 2 H, CH_{bpy}), 8.11 (br., 2 H, CH_{bpy}), 8.54, (br., 2 H, CH_{bpy}) ppm. ³¹P NMR (121.4 MHz, CDCl₃, 293 K): δ = 0.45 (br. s) ppm. ³¹P NMR (121.4 MHz, CDCl₃, 223 K): δ = -0.04 (br. s) ppm. C₂₉H₂₃CuN₃PS (540.10): calcd. C 64.49, H 4.29, N 7.78, S 5.94; found C 64.50, H 4.26, N 7.77, S 6.02.

[Cu(NCS)(bpy)(PPh₂py)] (6): Compound **6** was prepared following a procedure similar to that reported for **4** by using CuNCS (0.121 g, 1 mmol), PPh₂py (0.263 g, 1 mmol) and bpy (0.156 g, 1 mmol) in acetone. The product is soluble in chloroform and slightly soluble in acetone and acetonitrile. Yield: 91%. M.p. 162–164 °C. IR (nujol): $\tilde{\nu}$ = 2089 (vs) ν (S–C≡N), 1593 (s), 1567 (s), 1560 (sh.) ν (C=C + C=N), 522 (vs), 503 (vs), 473 (w), 430 (m), 410 (m), 395 (w) ν (PPh₃) cm⁻¹. ¹H NMR (300 MHz, CDCl₃, 293 K): δ = 7.18, 7.59, 7.87, 8.16, 8.63 [5 m, 12 H, P(C₅H₄N)(C₆H₅)₂ and CH_{bpy}], 7.30, 7.45 [2 m, 10 H, P(C₅H₄N)(C₆H₅)₂] ppm. ³¹P NMR (121.4 MHz, CDCl₃, 293 K): δ = 0.97 (br.) ppm. ³¹P NMR (121.4 MHz, CDCl₃, 223 K): δ = 0.76 (br.) ppm. C₂₈H₃₂CuN₄PS (551.17): calcd. C 62.15, H 4.10, N 10.35, S 5.93; found C 61.82, H 4.03, N 10.35, S 6.17.

[Cu(NCS)(py)(PPh₂py)] (7): A pyridine solution (5 mL) containing CuNCS (0.121 g, 1 mmol) and PPh₂py (0.263 g, 1 mmol) was stirred by gently warming (≈60 °C) for 2 h. The clear solution was reduced to half volume and acetone (30 mL) was added. A colourless precipitate slowly formed that was filtered off, washed with acetone (5 mL) and identified as compound **7**. It is soluble in chloroform. Yield: 78%. M.p. 152–153 °C. IR (nujol): $\tilde{\nu}$ = 2086 (s) ν (S–C≡N), 1594 (m), 1558 (m), 1540 (m) ν (C=C + C=N), 517 (s), 500 (vs), 452 (s), 427 (m), 417 (m) ν (PPh₃) cm⁻¹. ¹H NMR (300 MHz, CDCl₃, 293 K): δ = 7.30, 7.55, 7.67, 8.64 (4 m, 14 H, PC₁₇H₁₄N) ppm. ³¹P NMR (121.4 MHz, CDCl₃, 293 K): δ = -0.63 (s) ppm. ³¹P NMR (121.4 MHz, CDCl₃, 223 K): δ = -2.48 (br. s) ppm. C₂₃H₁₉CuN₃PS (464.00): calcd. C 59.54, H 4.13, N 9.06, S 6.91; found C 59.18, H 4.22, N 9.15, S 7.23.

Structure Determinations: CCD area detector diffractometer data were measured (ω -scans, monochromatic Mo-*K*_α radiation, λ = 0.71073 Å) yielding *N*_{total} reflections, and these merged to *N* unique (*R*_{int} cited) after “empirical”/multiscan absorption correction (proprietary software); *N*_o with *F* > 4σ(*F*) were considered “observed” and used in the full-matrix least-squares refinements by refining anisotropic displacement parameter forms for the non-hydrogen

atoms. Hydrogen atom treatment followed a “riding” model. Neutral atom complex scattering factors were employed within the Xtal 3.7 and SHELXL 97 programs.^[37] Pertinent results are given below and in the Tables and Figures, the latter showing non-hydrogen atoms with 50% probability amplitude displacement envelopes and hydrogen atoms having arbitrary radii of 0.1 Å. Individual variations in procedure are noted as “Variata”. CCDC-617187, -617188, -642533, -653453, -642534 and -653454 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Crystal/Refinement Data

[Cu(NCS)(py)₂(PPh₃)] (2) ≡ C₂₉H₂₅CuN₃PS, *M_r* = 542.1. Monoclinic, space group *P*2₁ (*C*₂, No. 4), *a* = 9.4371(8) Å, *b* = 15.186(1) Å, *c* = 10.2446(9) Å, β = 116.948(2)°, *V* = 1309 Å³. *D*_{calcd.} (*Z* = 2) = 1.376 g cm⁻³. μ_{Mo} = 1.00 cm⁻¹; specimen: 0.45 × 0.35 × 0.30 mm; *T*_{min/max} = 0.93. 2θ_{max} = 65°; *N*_{total} = 26542, *N* = 4700 (*R*_{int} = 0.015), *N*_o = 4414; *R* = 0.022; *R*_w = 0.027; *S* = 1.02. |Δρ_{max}| = 0.34 e Å⁻³. *T* = ca. 153 K. Variata: “Friedel” data were retained distinct, and *x*_{abs} was refined to -0.015(9). (*x*, *y*, *z*, *U*_{iso})_H were also refined.

[(PPh₃P(Mepy)Cu(NCS)(Mepy)(PPh₃)] (3) ≡ C₅₀H₄₄Cu₂N₄P₂S₂, *M_r* = 954.0. Triclinic, space group *P*1̄ (*C*₁, No. 2) *a* = 8.3766(3) Å, *b* = 9.2419(3) Å, *c* = 15.8188(5) Å, α = 87.279(1)°, β = 78.615(1)°, γ = 66.758(1)°, *V* = 1102 Å³. *D*_{calcd.} (*Z* = 1) = 1.437 g cm⁻³. μ_{Mo} = 1.17 cm⁻¹; specimen: 0.30 × 0.15 × 0.06 mm; *T*_{min/max} = 0.87. 2θ_{max} = 60°; *N*_{total} = 9482, *N* = 6126 (*R*_{int} = 0.019), *N*_o = 5004; *R*₁ = 0.032; *wR*₂ = 0.093; *S* = 1.09. |Δρ_{max}| = 0.53 e Å⁻³. *T* = ca. 170 K.

[Cu(NCS)(phen)(PPh₃)] (4) ≡ C₃₁H₂₃CuN₃PS, *M_r* = 564.1. Triclinic, space group *P*1̄, *a* = 10.403(2) Å, *b* = 10.920(2) Å, *c* = 12.913(2) Å, α = 72.710(2)°, β = 77.642(3)°, γ = 69.234(2)°, *V* = 1300 Å³. *D*_{calcd.} (*Z* = 2) = 1.441 g cm⁻³. μ_{Mo} = 1.01 cm⁻¹; specimen: 0.22 × 0.12 × 0.10 mm; *T*_{min/max} = 0.77. 2θ_{max} = 58°; *N*_{total} = 15420, *N* = 6430 (*R*_{int} = 0.042), *N*_o = 4553; *R* = 0.050; *R*_w = 0.054; *S* = 1.55. |Δρ_{max}| = 1.09 e Å⁻³. *T* = ca. 153 K.

[Cu(NCS)(bpy)(PPh₃)] (5) ≡ C₂₉H₂₃CuN₃PS, *M_r* = 540.1. Triclinic, space group *P*1̄, *a* = 9.115(2) Å, *b* = 9.150(2) Å, *c* = 16.950(4) Å, α = 91.56(2)°, β = 91.64(2)°, γ = 116.95(2)°, *V* = 1258 Å³. *D*_{calcd.} (*Z* = 2) = 1.425 g cm⁻³. μ_{Mo} = 1.04 cm⁻¹; specimen: 0.14 × 0.13 × 0.05 mm; *T*_{min/max} = 0.97. 2θ_{max} = 64°; *N*_{total} = 20064, *N* = 8150 (*R*_{int} = 0.052), *N*_o = 4592; *R*₁ = 0.041; *wR*₂ = 0.11; *S* = 0.91. |Δρ_{max}| = 0.47 e Å⁻³. *T* = ca. 100 K.

[Cu(NCS)(bpy)(PPh₂py)] (6) ≡ C₂₈H₂₂CuN₄PS, *M_r* = 541.1. Monoclinic, space group *P*2₁/c, *a* = 15.9005(7) Å, *b* = 8.8266(4) Å, *c* = 18.2233(7) Å, β = 98.769(2)°, *V* = 2528 Å³. *D*_{calcd.} (*Z* = 4) = 1.419 g cm⁻³. μ_{Mo} = 1.42 cm⁻¹; specimen: 0.60 × 0.60 × 0.42 mm; *T*_{min/max} = 0.86. 2θ_{max} = 64°; *N*_{total} = 39363, *N* = 7976 (*R*_{int} = 0.027), *N*_o = 7039; *R*₁ = 0.030; *wR*₂ = 0.080; *S* = 1.11. |Δρ_{max}| = 0.60 e Å⁻³. *T* = ca. 170 K. Variata: Assignment of the PPh₂py pyridyl nitrogen atom was made on the basis of refinement behaviour.

Physical Measurements: Electrochemistry was performed either with an EG&G PAR 273 electrochemical analyzer or with an AMEL potentiostat model 7050 connected to a PC. All experiments employed a standard three-electrode cell; the reference electrode was a 3-M KCl calomel electrode, the auxiliary electrode a platinum wire and the working electrode a glassy carbon (GC) with a diameter of 1 mm (CV) or 2 mm (ECL measurements). Positive feedback IR compensation was applied routinely. Measurements were carried out in CH₂Cl₂ distilled from calcium hydride just before use. The supporting electrolyte was 0.1-M tetrabutylammonium

hexafluorophosphate (TBAPF₆). The locally constructed instrumentation for ECL measurements was described elsewhere.^[38]

Fluorescence lifetime measurements employed a Fluorolog-3 – TCSPC Picosecond Life-time measurement system (Horiba Jobin Yvon) in time-correlated single-photon counting (TCSPC) mode. The excitation source was a 295-nm wavelength NanoLED pulsed laser with a repetition rate of 1 MHz by employing a IBH TBX-04 picosecond photon detector under TCSPC conditions. The instrument response function (prompt) was obtained at 295 nm by using Ludox suspension. The emission decay data were analyzed by using the software DAS6 provided with the instrument. The analysis used the statistical method, with iterative least-squares deconvolution by assuming an exponential decay function. The best-fit assessment was based on the parameter χ², which was close to 1.0 for all samples and the distribution of weighted residual along the zero line.

Density functional calculations were carried out with the GAUSSIAN 03 program.^[39] The singlet ground-state geometries of the complexes were optimized in the gas phase by the B3LYP^[40] functional. The basis sets employed were the Los Alamos double-ζ (LanL2Dz) for Cu by using the relativistic core potential (ECP), which replaces the inner core electrons, and the 6-31G* for all other atoms. Time-dependent density functional theory^[41] (TDDFT) combined with the conductor-like polarizable continuum model (CPCM)^[42] method with dichloromethane as solvent was used to calculate the excited-state energies by means of G03.

The ³¹P CP MAS NMR spectra were measured with a JEOL GSE 270 (6.34 T) spectrometer operating at 109.6 MHz for ³¹P. Cylindrical 5 mm o.d. zirconium rotors with a sample volume of 120 μL and a spin rate in the range 6.0–7.0 KHz were employed. In a typical experiment the CP contact time was 3.5 ms and the recycle time 10 s. Phosphorus chemical shifts are quoted relative to the signal from 85% phosphoric acid. For all samples the magic angle was carefully adjusted from ⁷⁹Br MAS spectra of KBr by minimizing the line-width of the spinning side-bands of the satellite transitions.

Supporting Information (see footnote on the first page of this article): Detailed NMR theory with parameter definitions for the ³¹P spectrum interpretation; TDDFT/CPCM calculated UV absorption spectra of **2** and **4**; cyclic voltammogram of **2**.

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