Pseudoelement Compounds, XIII[◇]

On the Ambident Behaviour of Dicyanmethanidonitrite; Syntheses and Characterization of Complexes of the Type $[M\{N(O)C(CN)_2\}(PPh_3)_n]$ ($M = Cu^I, Ag^I$; $n = 2, 3$)

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Complexes of the type $[M\{N(O)C(CN)_2\}(PPh_3)_n]$ ($M = Cu^I$, Ag^I, $n = 2, 3$) were synthesized by metathesis of $K[N(O)C(CN)_2]$ and $[M(NO_3)(PPh_3)_n]$. The complexes were characterized by ^{13}C-, ^{31}P-NMR and IR spectroscopy and elemental analyses. The crystal structures of $[M\{N(O)C(CN)_2\}(PPh_3)_2]_2$ ($M = Cu^I$, Ag^I) have been determined by X-ray diffraction. Depending on the metal atom in the complexes $[M\{N(O)C(CN)_2\}(PPh_3)_3]$ the ionic ligand is coordinated via the central nitrogen (copper) or the oxygen atom (silver). In addition the two copper and silver complexes $[M\{N(O)C(CN)_2\}(PPh_3)_2]_2$ are not isostructural but have quite different structures. For M = Cu the two copper atoms are doubly bridged by two NCCN sequences, forming an approximately planar $Cu(NCCN)_2Cu$ ring. On the other hand, in the homologous silver derivative the metal atoms are also doubly bridged, but by two NO groups, thus forming a planar six-membered ring.

Considering the fragment $C(CN)_2$ as an oxygen homologous functional group, the anions $[N(O)C(CN)_2]^-$ (dicyanmethanidonitrite) and $[N\{C(CN)_2\}_2]^-$ [bis(dicyanmethanido)nitrite] appear as pseudochalcogenonitrites[2]. The strength of this approach is emphasized by the fact that, like $[NO_2]^-$, $[N(O)C(CN)_2]^-$ also behaves ambidentately towards metal ions. In both species oxygen and the middle nitrogen atoms should be comparable from the electronic point of view[3]. According to the soft-soft and hard-hard orientation, exceptionally soft metal ions coordinate unidentately to these ligands via the central nitrogen (Re^I [4], Ir^I [5], Pt^{II} [6]) whilst more hard 3d-metal ions (Ni^{II} [7], Cu^{II} [8], Co^{III} [8], Fe^{III} [5]) coordinate via the oxygen atom. In contrast to this finding the ion $[N\{C(CN)_2\}_2]^-$ is preferentially linked through an end-on nitrile group (Pt^{II}). However, in solution a linkage isomerization can be assumed[6].

To our knowledge, no complexes with dicyanmethanidonitrite in bidentate function were crystallographically characterized up to now. Several bonding motifs can be expected because apart from oxygen and the central nitrogen, end-on nitrile groups can also be discussed as potential donor atoms. In the past compounds of the type $[M\{N(O)C(CN)_2\}_2L_2]$ have been synthesized; some of them have indeed proved to be addition products of the expected complex and a protic solvent such as $[Cu\{ONC(CN)C(NH)OEt\}_2(H_2O)_2]$[8]. In this context the silver salt $Ag[N(O)C(CN)_2]$[9] is also worth mentioning. Its crystal structure shows ligand-metal contacts via oxygen and both types of nitrogen atoms.

Results and Discussion

In order to study the ambidentate behaviour of dicyanmethanidonitrite, depending on the hard/soft nature of metal ions in complexes with this ligand (in a uni- and especially in a bidentate function) we prepared compounds of copper(I) and silver(I) of the types $[MX(PPh_3)_3]$ and $[MX(PPh_3)_2]_2$. The syntheses were carried out in boiling $CHCl_3$ or CH_2Cl_2.

$$\underset{\mathbf{1}}{K[N(O)C(CN)_2]} + \underset{\mathbf{2}}{[M(NO_3)(PPh_3)_3]} \longrightarrow \underset{\mathbf{3}}{[M\{N(O)C(CN)_2\}(PPh_3)_3]} + KNO_3 \quad (1)$$

$$2\,\mathbf{1} + 2\,\underset{\mathbf{4}}{[M(NO_3)(PPh_3)_2]} \longrightarrow \underset{\mathbf{5}}{[M\{N(O)C(CN)_2\}(PPh_3)_2]_2} + 2\,KNO_3 \quad (2)$$

2, 3, 4, 5	M
a	Cu^I
b	Ag^I

$$\mathbf{1} + \mathbf{4a} + MeOH \longrightarrow \underset{\mathbf{6}}{[Cu\{ONC(CN)C(NH)OMe\}(PPh_3)_2]} + KNO_3 \quad (3)$$

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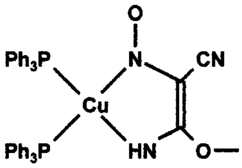
Dicyanmethanidonitrite tends to add protic agents[7] such as methanol or water. If K[N(O)C(CN)$_2$] is treated with [Cu(NO$_3$)(PPh$_3$)$_2$] in the presence of methanol the monomeric complex **6** is formed. In **6** [ONC(CN)C(NH)OMe]$^-$ acts as a chelating ligand which is coordinated through the nitrogen atoms of the NO and the NH groups, forming a five-membered ring (Figure 1)[10].

Figure 1. Schematic view of the molecular structure of **6**



The new compounds were characterized by ^{13}C-NMR, ^{31}P-NMR and IR spectroscopy. Surprisingly, in contrast to **1,** the vibrations ν_{as}(CNO) and ν(CC) of **3a** and **3b** are shifted in opposite directions (Table 1). The shift of ν_{as}(CNO) to higher wavenumbers characterizes [N(O)C(CN)$_2$]$^-$ as centrally *N*-bonded (3a)[6]. On the other hand, the decrease of the N−O bond order corresponds to coordination via the oxygen atom. The IR spectra of the species **5** are in agreement with the results of the crystal structure analyses. In contrast to **5b** the complex **5a** shows three ν(CN) bands indicating a stronger differentiation of the nitrile groups. In comparison to K[N(O)C(CN)$_2$] the shifts of the vibrations ν_{as}(CNO), ν_s(CNO), and ν(CC) of **5a** and **5b** are opposite in direction.

Table 1. Characteristic infrared absorptions (KBr [cm^{-1}]) of potassium dicyanmethanidonitrite and corresponding complexes **3a**, **3b**, **5a**, **5b**, and **6**

Compound	ν(CN)	ν_{as}(CNO)	ν_s(CNO)	ν(CC)	Mode
1	2236 vs, 2225 s	1325 vs	1275 vs	1236 vs	ionic
3a	2212 m, 2193 w	1345 m	1329 m	1208 s	unidentate
3b	2204 m	1306 s	1262 s	1275 vs	unidentate
5a	2216 m, 2207 m, 2188 w	1339 s	1253 w	1214 vs	bidentate
5b	2207 s	1326 vs	1288 vs	1245 vs	bidentate
6	2212 s, 2202 m	1359 vs	1330 vs	1313 vs	

Comparing the ^{13}C-NMR spectra of **1** with those of **3** and **5** very slight shifts, with no clear trend, can be observed. The ^{31}P-NMR chemical shifts of triphenylphosphane depend on the central metal atom. So the copper complexes show one resonance at about 0 ppm; the chemical shifts of **3b** or **5b** are δ 7.93 and 11.85 respectively.

According to the structure of the anionic ligand the infrared spectrum of **6** shows bands at 1606 (vs) and 1412 (vs) cm^{-1} which can be assigned to ν_{as}(C=N) and ν_s(C=N) vibrations. The (CN) vibration indicates an uncoordinated nitrile group. As expected for *N*O coordination the bands ν_{as}(CNO) and ν_s(CNO) are shifted to higher wavenumbers. In the ^{13}C-NMR spectrum resonances at δ 61.1 and 165.1 appear, confirming the assumed structure.

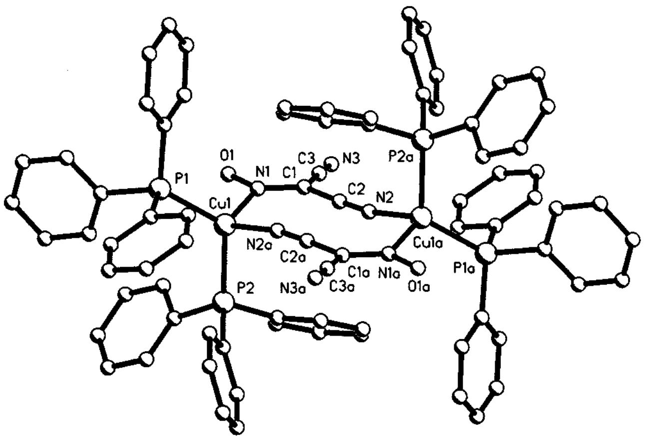
Crystal Structures of 5a and 5b

As a common feature, the homologous copper and silver complexes [M{N(O)C(CN)$_2$}(PPh$_3$)$_2$]$_2$ both exist in the crystal in form of discrete dimers in which the metal atoms are doubly bridged by two dicyanmethanidonitrite ligands [N(O)C(CN)$_2$]$^-$. But surprisingly, **5a** and **5b** are not isostructural and differ markedly with regard to the coordination mode of the ionic ligand. Depending on the central atom, the donor atoms are N(cyano) and N(central) in the copper complex **5a**, and O and N(central) in the silver complex **5b**.

The molecular structure of **5a** is shown in Figure 2. Two copper atoms are bridged by two ionic ligands [N(O)C(CN)$_2$]$^-$ coordinating the metal through the central and one cyano nitrogen atom. In this way a ten-membered ring, with a weakly pronounced chair conformation around a crystallographic inversion centre, is formed. The ligand itself is, to a good approximation, planar with significant deviations from planarity only for N1 [0.027(3) A] and O1 [0.016(3) A]. The copper atoms are at a distance of ±0.5188(4) A from the plane defined by the two NCCN fragments of the ring. The coordination geometry around Cu can be described as a distorted tetrahedron. The strongest deviation from the tetrahedral geometry is shown by the angle P1−Cu1−P2 with 122.62(3)°. The Cu−P bond lengths, being Cu1−P1 = 2.2853(8) A and Cu1−P2 = 2.2935(8) A, are in good agreement with the average value of 2.252(44) A established for Cu^I−PPh$_3$ complexes[11]. Surprisingly, the bond lengths between Cu and the two chemically non-equivalent N atoms are nearly the same [Cu1−N1 = 2.080(3) A, Cu1−N2a = 2.042(3) A]. In contrast to this finding, in the structurally analogous complex [Cu(NCNNO$_2$)(PPh$_3$)$_2$]$_2$[12], significantly different Cu−N bond lengths were found (Δ = 0.138 A). These relations are similar in the following complexes with trigonal-planar configured copper(I): [Cu{μ-NCNC(NH$_2$)$_2$}{NCNC(NH$_2$)$_2$}]$_2$A·2H$_2$O with A = SO$_4$ [Cu−N1 = 1.868(9) and 1.883(9) A, Cu−N2 = 2.25(1) and 2.250(9) A] and A = S$_2$O$_6$ [Cu−N1 = 1.874(4) A, Cu−N2 = 2.246(4) A][13]. On the other hand, for [Cu(NCNC$_6$H$_4$Me-4)(PPh$_3$)$_2$]$_2$ rather similar metal nitrogen bonds were found [Cu−N1 = 2.045(2) A and Cu−N2 = 2.095(2) A][14].

The molecular structure of **5b** is shown in Figure 3. The two silver atoms are doubly bridged by the NO groups of two dicyanmethanidonitrite ligands, and a centrosymmetric six-membered ring is formed in this way. A comparable bridging function is known for [NO$_2$]$^-$, and this is proved by X-ray analysis for [(H$_3$N)$_4$Co(NH$_2$)ON(O)Co(NH$_3$)$_4$]$^{4+}$[15]. The Ag(NO)$_2$Ag ring is planar to a good approximation, the maximum deviation from the best plane shown by the O atoms [±0.083(4) A]. The coordination geometry around Ag is that of a strongly distorted tetrahedron; the greatest deviations from the ideal value shown by the bond angles P1−Ag1−P2 with 132.83(4)° and N1−Ag1−O1a with 89.7(1)°. The two Ag−P bond lengths [Ag1−P1 = 2.444(1) A, Ag1−P2 = 2.447(1) A] are equal within experimental error and agree well with experience

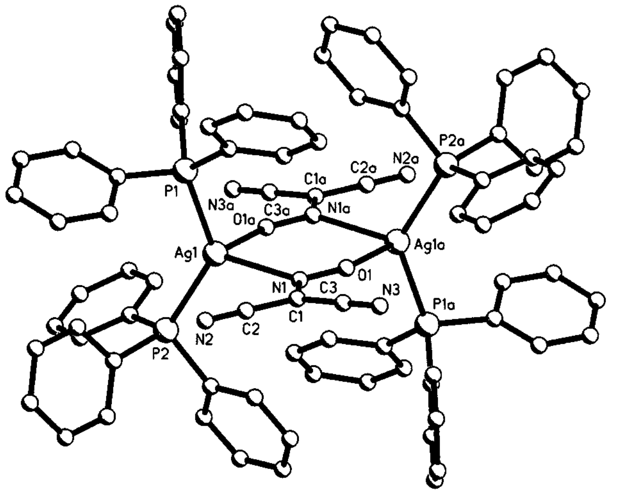
Figure 2. Molecular structure of **5a**[a]



[a] Selected bond lengths [Å] and angles [°]: Cu1−N1 2.080(3), Cu1−N2a 2.042(3), Cu1−P1 2.2853(8), Cu1−P2 2.2935(8), O1−N1−Cu1 113.4(2), C1−N1−Cu1 129.1(2), C2−N2−Cu1a 169.6(3), P1−Cu1−P2 122.62(3), N1−Cu1−N2a 104.98(10).

[2.419(46) Å as average of 27 Ag^I-PPh_3 complexes][11]. The Ag1−N1 distance of 2.413(3) Å is quite normal compared with the values of 2.400(4) and 2.416(4) Å in $[Ag(NCNNO_2)(PPh_3)_2]_2$[12] but longer than the range from 2.28(1) to 2.332(5) Å observed in a series of compounds $[Ag(NCS)L_n]$ (L = py-Me-2, py-Me-3, py-Me_2−2,6, quin)[16]. The Ag1−O1a distance of 2.504(3) Å is just in the middle of the wide range observed for Ag−O bond lengths, which depend on the coordination mode and are illustrated by the following examples: NO_2^- chelating in $AgNO_2$ [2.441(3) Å][17], NO_3^- terminal in $[AgONO_2(1\text{-Me-cytosine})]$ [2.469(3) Å][18] or chelating in $[AgNO_3(2\text{-pyridyleneaniline})]$ [2,259(3) Å][19] or bridging in $[AgNO_3(\text{cyclosarcosylsarcosine})_2]$ [2.612(8) and 2.679(7) Å][20].

Figure 3. Molecular structure of **5b**[a]



[a] Selected bond lengths [Å] and angles [°]: Ag1−N1 2.413(3), Ag1−O1a 2.504(3), Ag1−P1 2.444(1), Ag1−P2 2.447(1), O1−N1−Ag1 125.4(3), C1−N1−Ag1 117.1(3), P1−Ag1−P2 132.83(4), N1−Ag1−O1a 89.7(1).

A survey of the bond lengths and angles characterizing the geometry of the ambidentate dicyanmethanidonitrite X in its ionic (**1** = KX)[21], bidentate (**5a**, **5b**) and unidentately *N*-bonded (*trans*-$[Pt(H)X(PPh_3)_2]$)[6] or *O*-bonded function ($[Co(X)Cl(en)_2]X$)[22] is given in Table 2. A comparison of the listed values reveals no significant, or only slight to moderate, differences, depending on the coordination modes. Even **5a** and **5b** agree completely within experimental error. For both compounds, within their ONC fragments, the N−O bond is slightly shortened and the N−C bond is slightly lengthened with respect to the uncoordinated anion X^- in **1**. The N−O bond lengths in **5a** and **5b** are a little bit longer than the value of 1.240(3) or 1.248(3) Å found for the nitrite ion in the sodium[24] and the silver salt[17], respectively. All other bond lengths agree well with standard values[23]. The rigidity of the dicyanmethanidonitrite skeleton and its structural insensibility to variations in the coordination mode is also manifested by the small differences between the corresponding bond angles (Table 2). The maximum ranges of variation are shown by the angles C−C−C (Δ = 1.4°) and O−N−C (Δ = 3.9°).

Table 2. Geometric parameters [Å,°] of $[N(O)C(CN)_2]^-$ in **1**, **5a**, **5b**, *trans*-$[Pt(H)N(O)C(CN)_2(PPh_3)_2]$ (**7a**), and $[Co(Cl)ONC(CN)_2(en)_2][ONC(CN)_2]$ (**7b**)

Distance/angle	**1**	**5a**	**5b**	**7a**	**7b**[a]
O1−N1	1.287(1)	1.266(3)	1.260(4)	1.260(3)	1.310(2)
N1−C1	1.324(2)	1.338(4)	1.329(5)	1.333(4)	1.299(3)
C1−C2	1.431(2)	1.418(4)	1.400(7)	1.421(5)	1.432(4)
C1−C3	1.422(2)	1.423(5)	1.411(8)	1.417(5)	1.424(4)
N2−C2	1.135(2)	1.135(4)	1.127(7)	1.134(5)	1.130(4)
N3−C3	1.143(2)	1.128(4)	1.143(8)	1.148(4)	1.130(4)
N2−C2−C1	179.1(2)	177.3(3)	178.2(6)	178.0(4)	177.4(4)
N3−C3−C1	177.3(1)	178.3(5)	178.5(10)	178.1(4)	179.2(3)
C2−C1−C3	119.8(1)	118.8(3)	118.6(4)	119.8(3)	118.4(2)
O1−N1−C1	115.9(1)	115.7(3)	116.0(4)	118.1(3)	114.2(2)

[a] *O*-coordinated.

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Experimental Section

IR (KBr): Mattson 5000 FTIR. − ^{13}C NMR (TMS as reference): WP 200. − ^{31}P NMR (85% H_3PO_4 as reference, down-field shift positive): AC 80. The compounds **2a**[25], and **4a**[25] were prepared as described previously. For the synthesis of **2b** and **4b** known procedures were modified by using triphenylphosphane and silver nitrate[26][27].

General Method for the Syntheses of **3** *and* **5**: 2 mmol of **2a**, **4a** or **4b** were dissolved in 15 ml of $CHCl_3$, or 2 mmol of **2b** in 30 ml of CH_2Cl_2. While stirring the resulting mixture was treated with a solution of 2 mmol (0.25 g) of **1** in 20 ml of methanol or ethanol (synthesis of **3a**) and heated to reflux for 6 h in a water bath with exclusion of light. Afterwards the mixture was stirred at room temp. for 3 h. After filtration and evaporation of the solvent in vacuo the resulting solid was washed with methanol and dissolved in a small amount of $CHCl_3$ (**3a** in ethanol). A quantity of *n*-pentane was added until the onset of turbidity was observed and the solution kept at about 0°C. After some hours a microcrystalline solid was formed which was filtered off and dried in vacuo.

For the preparation of single crystals 0.010 g of **5a** or **5b** were dissolved in 2 ml of $CHCl_3$ and overlayed with 6 ml of petroleum ether.

Tris(triphenylphosphane)copper(I)dicyanmethanidonitrite (**3a**): slightly brown crystals, yield 80%, m.p. 143°C (dec). − IR (KBr): ν = 2212 s cm^{-1} [ν(CN)], 2193 w [ν(CN)], 1345 s [ν_{as}(CNO)], 1329 s [ν_{s}(CNO)], 1209 vs [ν(CC)], 694 vs (Ph), 742 vs (Ph), 1092 vs (Ph), 1434 vs (Ph), 1479 s (Ph), 3049 s (Ph). − ^{13}C NMR ($CDCl_3$): δ = 112.9 (s, CN), 119.0 (s, CN), 107.9 (s, methanide-C), 128.4, 128.5 [t, P−C-3,5, $^{1}J(^{31}P,^{13}C)$ = 8 Hz), 129.6 (s, P−C-4), 132.8, 133.0 [t, P−C1, $^{1}J(^{31}P,^{13}C)$ = 22.9 Hz], 133.6, 133.7 [t, P−C-2,6, $^{1}J(^{31}P,^{13}C)$ = 15.0 Hz]. − ^{31}P NMR ($CDCl_3$): δ = −0.27 (s, PPh_3).− $C_{57}H_{45}CuN_3OP_3$ (944.47): calcd. C 72.49, H 4.80, N 4.45; found C 70.70, H 4.67, N 4.04.

Tris(triphenylphosphane)silver(I)dicyanmethanidonitrite (**3b**): yellow crystals, yield 78%, m.p. 167.5°C. − IR (KBr): ν = 2204 s cm^{-1} [ν(CN)], 1306 s [ν_{as}(CNO)], 1262 s [ν_{s}(CNO)], 1226 vs [ν(CC)], 693 vs (Ph), 743 vs (Ph), 1093 vs (Ph), 1433 vs (Ph), 1479 vs (Ph), 3052 w (Ph). − ^{13}C NMR ($CDCl_3$): δ = 112.5 (s, CN), 118.6 (s, CN), 108.4 (s, methanide-C), 128.7, 128.8 [t, P−C-3,5, $^{1}J(^{31}P,^{13}C)$ = 10 Hz], 130.0 (s, P−C-4), 132.2, 132.4 [t, P−C1, $^{1}J(^{31}P,^{13}C)$ = 21.9 Hz], 133.7, 133.8 [t, P−C-2,6, $^{1}J(^{31}P,^{13}C)$ = 16.8 Hz]. − ^{31}P NMR ($CHCl_3$, capillary containing D_2O): δ = 6.98 (s, PPh_3), ^{31}P NMR ($CDCl_3$): δ = 7.93 (s, PPh_3). − $C_{57}H_{45}AgN_3OP_3$ (988.79): calcd. C 69.24 H 4.59 N 4.25; found C 68.74, H 4.50, N 4.28.

Bis(triphenylphosphane)copper(I)dicyanmethanidonitrite (**5a**): yellow crystals, yield 78%, m.p. 182−183°C. − IR (KBr): ν = 2216 s cm^{-1} [ν(CN)], 2207 m [ν(CN)], 2188 w [ν(CN)], 1339 s [ν_{as}(CNO)], 1253 m [ν_{s}(CNO)], 1214 vs [ν(CC)], 692 vs (Ph), 744 vs (Ph), 1091 vs (Ph), 1433 vs (Ph), 1479 vs (Ph), 3050 m (Ph). − ^{13}C NMR ($CDCl_3$): δ = 113.9 (s, CN), 108.3 (s, methanide-C), 128.4, 128.6 [t, P-C3,5, $^{1}J(^{31}P,^{13}C)$ = 8.4 Hz], 129.7 (s, P-C4), 132.7, 133.2 [t, P-C-1, $^{1}J(^{31}P,^{13}C)$ = 23.1 Hz], 133.6, 133.9 [t, P-C-2,6, $^{1}J(^{31}P,^{13}C)$ = 15.4 Hz]. − ^{31}P NMR ($CHCl_3$, capillary containing D_2O): δ = −0.95 (s, PPh_3). − ^{31}P NMR ($CDCl_3$): δ = 0.17 (s, PPh_3). − $C_{78}H_{60}Cu_2N_6O_2P_4$ (1364.36): calcd. C 68.67, H 4.43, N 6.16; found C 68.24, H 4.96, N 5.77.

Bis(triphenylphosphane)silver(I)dicyanmethanidonitrite (**5b**): slightly yellow crystals, yield 77%, m.p. 155°C. − IR (KBr): ν = 2208 vs cm^{-1} [ν(CN)], 1326 vs [ν_{as}(CNO)], 1287 vs [ν_{s}(CNO)], 1244 vs [ν(CC)], 693 vs (Ph), 744 vs (Ph), 1095 s (Ph), 1434 vs (Ph), 1479 vs (Ph), 3051 w (Ph). − ^{13}C NMR ($CDCl_3$): δ = 111.6 (s, CN), 116.9 (s, CN), 108.7 (s, methanide-C), 129.0, 129.1 [t, P-C-3,5, $^{1}J(^{31}P,^{13}C)$ = 10 Hz], 130.6 (s, P-C-4), 130.6, 130.8 [t, P-C-1, $^{1}J(^{31}P,^{13}C)$ = 30.9 Hz], 133.6, 133.7 [t, P-C-2,6, $^{1}J(^{31}P,^{13}C)$ = 17.0 Hz]. − ^{31}P NMR ($CHCl_3$, capillary containing D_2O): δ = 11.05 (s, PPh_3), ^{31}P NMR ($CDCl_3$): δ = 11.85 (s, PPh_3). − $C_{78}H_{60}Ag_2N_6O_2P_4$ (1453.02) calcd. C 64.48, H 4.16, N 5.78; found C 60.14, H 4.00, N 5.25.

Bis(triphenylphosphane)copper(I)-2-cyano-1-metoxy-2-nitrosovinylamide (**6**): After addition of 0.25 g (2 mmol) of **1** in 20 ml of methanol to a solution of 1.3 g (2 mmol) of **4a** in 20 ml of $CHCl_3$ the resulting mixture was heated to reflux in a water bath for 6 h. After filtration at room temp. the solvent was evaporated to dryness. The remaining solid was washed with methanol (2 × 10 ml) and dissolved in about 10 ml of $CHCl_3$. A quantity of *n*-pentane was added until the onset of turbidity was observed and the solu-

Table 3. Crystal data and experimental details of X-ray structure determination of **5a** and **5b**

	5a	**5b**·$CHCl_3$
Empirical formula	$C_{39}H_{30}CuN_3OP_2$	$C_{39}H_{30}AgN_3OP_2$· 0.5 $CHCl_3$
Molecular mass [g·mol^{-1}]	682.14	786.15
Crystal system	triclinic	monoclinic
Space group	*P*1	*C*2/c
Lattice parameters:		
a [Å]	12.216(1)	24.712(1)
b [Å]	12.958(1)	14.284(1)
c [Å]	13.475(1)	24.834(2)
α [°]	66.908(6)	90.0
β [°]	64.859(5)	121.401(4)
γ [°]	67.490(5)	90.0
V [Å^3]	1715.4(2)	7482.3(7)
Z	2	8
F(000)	704	3192
$D_{calc.}$ [g·cm^{-3}]	1.321	1.396
μ (MoK_α) [cm^{-1}]	7.65	7.66
Crystal dimensions [mm]	0.46 × 0.35 × 0.21	0.46 × 0.34 × 0.17
Check reflections	(555), (516), (431)	(800), (040), (067)
Intensity variations [%]	9.8	10.0
2Θ$_{max.}$ [°]	50.0	50.0
hkl range	±14, ±15, ±15	±29, ±16, ±29
Measured reflections	12046	13118
Unique reflections	6023	6559
$R_{int.}$	0.0380	0.0285
Obs. Reflections [$I > 2\sigma(I)$]	4443	4931
Refined parameters	415	438
Weighting coefficients a/b [a]	0.0310/0.4660	0.0431/11.5720
Absorption correction	empirical (Psi scans)	empirical (Psi scans)
$T_{min.}/T_{max.}$	0.6566/0.7898	0.6718/0.7709
*R*1/*wR*2/*S* (all data)	0.0706/0.0955/1.121	0.0661/0.1120/1.126
*R*1/*wR*2/*S* [$I > 2\sigma$(I)]	0.0392/0.0790/1.113	0.0408/0.0939/1.120
$(\Delta/\sigma)_{max.}$ in last l.s. cycle	0.000	−0.001
$\Delta\rho_{fin.}$ (min./max.) [e·Å^{-3}]	−0.231/0.263	−0.677/0.722

[a] $w = [\sigma^2(F_o^2) + (a\cdot P)^2 + b\cdot P]^{-1}$ where $P = 1/3\ (F_o^2) + 2_c^2)$

tion kept at about 0°C for 12 h. The resulting microcrystalline precipitate was filtered off and dried in vacuo. Orange crystals, yield 48%, m.p. 182−183°C. − IR (KBr): ν = 2212 s cm^{-1} [ν(CN)], 2202 s [ν(CN)], 1358 vs [ν_{as}(CNO)], 1330 vs [ν_{s}(CNO)], 1312 vs [ν(CC)], 695 vs (Ph), 744 vs (Ph), 1095 vs (Ph), 1434 vs (Ph), 1479 vs (Ph), 3052 w (Ph), 1606 vs [ν_{as}(OCN)], 1412 vs [ν_{s}(OCN)], 1385 vs [ν_{s}(OCN)]. − ^{13}C NMR (CDCl$_3$): δ = 113.4 (s, CN), 61.1 [s, *C*(NO)CN)], 126.4, 128.5, 129.6, 133.4 (s, Ph), 165.1 [s, C(NH)O], 13.8 (O−CH$_3$). − ^{31}P NMR (CDCl$_3$): δ = −0.02 (s, PPh$_3$). − $C_{40}H_{34}CuN_3O_2P_2$ (714.22) calcd. C 67.27, H 4.80, N 5.88; found C 66.98, H 4.69, N 5.72.

X-ray Crystal Structure Determination: A summary of crystal data along with details of the structure determination is given in Table 3[28]. All measurements were performed with a STOE-STADI4 diffractometer using graphite-monochromatized Mo-K_α radiation (λ = 0.71069 A) in the ω-2θ scanning mode at room temp.. For structure solution and refinement programs SHELXS-86[29] and SHELXL-93[30] were used. The molecular structures in Figures 2 and 3 were plotted by use of the program XP/PC[31].

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