Pseudoelement Compounds, X[◇]

Synthesis and Crystal Structure of New Complexes of the Type *trans*-[Pt(H)X(PPh_3)$_2$] with Cyanamide and Cyanomethanide Ligands☆

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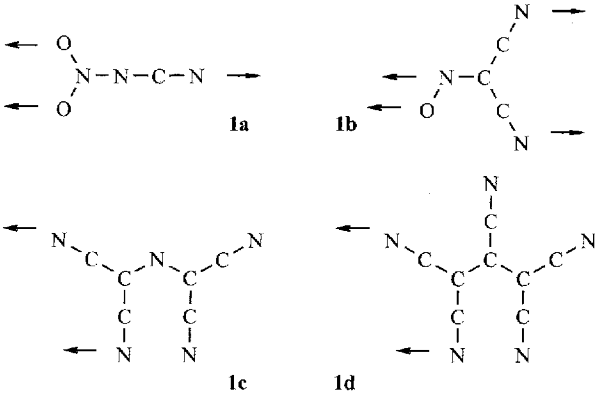
The new coordination compounds *trans*-[Pt(H)X(PPh_3)$_2$] with NCN- and $C(CN)_2$-functionalized anions (X^- = $[N(O)C(CN)_2]^-$, $[NO_2NCN]^-$, $[N\{C(CN)_2\}_2]^-$, $[NCC\{C(CN)_2\}_2]^-$) have been characterized by ^1H-, ^{31}P-, ^{13}C-NMR, and IR spectroscopy and elemental analyses. The crystal structures of *trans*-[Pt(H)N(O)C(CN)$_2$(PPh_3)$_2$], *trans*-[Pt(H)N{C(CN)$_2$}$_2$(PPh_3)$_2$], and *trans*-[Pt(H)NCC{C(CN)$_2$}$_2$(PPh_3)$_2$] have been determined by X-ray diffraction. Remarkably, $[N(O)C(CN)_2]^-$ is coordinated through the central nitrogen atom, while $[N\{C(CN)_2\}_2]^-$ and $[NCC\{C(CN)_2\}_2]^-$ are bonded through terminal nitrogen atoms of a $C(CN)_2$ unit.

Introduction

In transition metal complexes the dicyanamide and tricyanomethanide anions are exclusively coordinated through their terminal nitrogen atoms[2,3]. When coordinated in a monodentate fashion, the same is true for the modified species $[N(CN)X]^-$ (X = $R_2P(O)$, $R_2P(S)$[4], RSO_2[5]) and $[C(CN)_2X]^-$ (X = RSO_2[6]). Amongst these classes of ligands, the ions $[NO_2NCN]^-$ and $[N(O)C(CN)_2]^-$ can be considered as being somewhat different. They can be classified as cyanamide or dicyanomethanide derivatives of the types $[N(CN)X]^-$ (X = NO_2) and $[C(CN)_2X]^-$ (X = NO), respectively. They are also related to nitrate $[NO_3]^-$ and nitrite $[NO_2]^-$ in the sense that one chalcogen atom is substituted by the pseudochalcogens NCN or $C(CN)_2$[7].

For the series of ions $[NO_2NCN]^-$ (**1a**), $[N(O)C(CN)_2]^-$ (**1b**), $[N\{C(CN)_2\}_2]^-$ (**1c**), and $[NCC\{C(CN)_2\}_2]^-$ (**1d**), information on the coordination behaviour has hitherto only been available for **1b**. The principal donor atoms of these species are highlighted in Figure 1. Recently, by the crystallographic characterization of Me_3SnX[1], $[CuX(PPh_3)_2]_2$[8], $[AgX(PPh_3)_2]_2$[8], and $[CuX_2(iz)_2]$[9] we showed that $[NO_2NCN]^-$ behaves as an ambidentate bridging ligand. Depending on the hard/soft character of the central metal atom, the ligand coordinates either via both the nitrogen atoms of the NCN group[1,8] or via the terminal oxygen and nitrogen atoms[9]. The ion **1b** does not constitute a typical representative of the family of cyanomethanides, which tend to form coordination polymers via end-on nitrile groups. It behaves like a homologue of nitrite. Characteristically, it coordinates in a monodentate fashion through the oxygen atom (Ni^{II}, Cu^{II}[10], Nd^{III}[11], Yb^{III}[12]). It seems that only very soft metal ions are coordinated by this ligand through its central nitrogen atom. To date, $[ReN(O)C(CN)_2(CO)_5]$ is the only example where the existence of such a bond has been proven by crystal structure analysis[13].

Figure 1. Potential donor atoms in coordination compounds of the ionic ligands $[NO_2NCN]^-$ (**1a**), $[N(O)C(CN)_2]^-$ (**1b**), $[N\{C(CN)_2\}_2]^-$ (**1c**), and $[NCC\{C(CN)_2\}_2]^-$ (**1d**)



For the ions **1c** and **1d**, quantum chemical investigations indicate that the nitrogen atoms of the $C(CN)_2$ groups should be the preferential donor sites[14]. The crystal structure of $[CuNCC\{C(CN)_2\}_2(PPh_3)_2]_2$ confirms such theoretical predictions. In the dimeric complex, the metal atoms are bridged by one of the two $C(CN)_2$ fragments of each ionic ligand[15]. The complex $[CuCl(bipy)_2][NCC\{C(CN)_2\}_2]$ is also worthy of a mention in this context. In this case, the crystal structure analysis indicates a purely ionic interaction of the ligand **1d**[16].

[◇] Part IX: Ref.[1].

Results and Discussion

With the aim of proving the ambidentate nature of the anions **1a**–**1d** depending on the hard/soft character of the bonding partner and to study the gradual change of the properties of the donor atoms in this series of ligands, we report herein on complexes of the type *trans*-$[Pt(H)X(PPh_3)_2]$ with a rather soft central atom. Additionally, study of these complexes by ^1H-NMR spectroscopy should allow some insight into the *trans* influence of the anions to be gained. The complexes were isolated from reactions of *trans*-$[Pt(H)Cl(PPh_3)_2]$ with the silver salts **3a**–**3d** in boiling dichloromethane.

$$\underset{\mathbf{2}}{trans\text{-}[Pt(H)Cl(PPh_3)_2]} + \underset{\mathbf{3}}{AgX} \rightarrow \underset{\mathbf{4}}{trans\text{-}[Pt(H)X(PPh_3)_2]} + AgCl \quad (1)$$

3, 4	$[X]^-$
a	$[NO_2NCN]^-$
b	$[N(O)C(CN)_2]^-$
c	$[N\{C(CN)_2\}_2]^-$
d	$[NCC\{C(CN)_2\}_2]^-$

First and foremost, ^{13}C-NMR and IR spectroscopic studies of these complexes should provide information on the coordination modes of the ligands. Pertinent IR data are listed in Tables 1 and 2. Compared to the spectra of the corresponding potassium salts, the spectra of **4a**, **4c**, and **4d** show a shift of the bands $\nu_{as}(NCN)$ and $\nu(CN)$, respectively, to higher wavenumbers. This tendency indicates that the NCN- or $C(CN)_2$-modified anions are end-on coordinated via their nitrile groups. In the case of **4c** and **4d**, coordination causes a differentiation of the nitrile groups, which thus give rise to two distinct, strong $\nu(CN)$ absorptions. In accordance with these observations, in the ^{13}C-NMR spectra of the complexes **4** the anionic ligands **1** are characterized by two (**4b**: δ = 111.3 and 115.3), four (**4c**: δ = 110.6, 110.7, 116.4, and 116.7) and five (**4d**: δ = 111.7, 113.6, 114.4, 114.6, and 118.9) resonances, respectively, whereas the uncoordinated species $[N\{C(CN)_2\}_2]^-$ and $[NCC\{C(CN)_2\}_2]^-$ show only two and three signals, respectively, in this region[14].

Table 1. Characteristic $\nu(CN)$ and $\nu_{as}(NCN)$ infrared absorptions (KBr; [cm^{-1}]) of the potassium salts of the ionic ligands X and the corresponding complexes **4a**–**4d**

X	KX	*trans*-$[Pt(H)X(PPh_3)_2]$
$[NO_2NCN]^-$	2195 vs	2199 vs
$[N(O)C(CN)_2]^-$	2232 vs 2225 s	2206 s 2182 sh
$[N\{C(CN)_2\}_2]^-$	2209 vs	2223 vs 2197 vs
$[NCC\{C(CN)_2\}_2]^-$	2208 vs	2228 s 2205 vs

Table 2. Characteristic infrared absorptions (KBr; [cm^{-1}]) of $K[N(O)C(CN)_2]$ and **4a**

	ν_{as} (C–N=O)	ν_s (C–N=O)	ν (C–C)
$K[N(O)C(CN)_2]$	1325 vs	1275 vs	1236 vs
4b	1363 vs	1322 s	1250 w

In comparison to **1b**, in the IR spectrum of **4b** we observe a shift of the CN absorptions to lower wavenumbers. From this observation it can be concluded that the nitrile groups are not coordinated. Indeed, the bands representing the vibrations $\nu_s(CNO)$, $\nu_{as}(CNO)$, and $\nu(CC)$ are found at higher frequencies. Shifts in this direction are consistent with **1b** being coordinated through the central nitrogen atom[17].

The complex **2** shows an absorption of medium intensity at $\tilde{\nu}$ = 2228 cm^{-1}, which represents a $\nu(Pt-H)$ vibration. In the spectra of **4a**–**4d** we do not find corresponding bands since these are probably overlapped by the generally very strong $\nu(CN)$ bands.

The ^1H- and ^{31}P-NMR data are summarized in Table 3. Surprisingly, in the ^1H-NMR spectra of **4c** and **4d** we found two signals for the hydride ligand with rather similar chemical shifts. Analogously, the ^{31}P-NMR spectrum of **4c** exhibits two signals for the equivalent phosphane P atoms. It is worth mentioning that the relative intensities of these signals show a solvent-dependence. For instance, the ^1H-NMR spectrum of a solution of **4c** in $CDCl_3$ features two triplets attributable to hydridic H atoms in a ratio of 2:3 (^1H: δ = −16.02 and −16.23; ^{31}P: δ = 27.3 and 27.9). However, in benzene this ratio is found to be 2.4:1. The ^1H-NMR spectrum of **1d** in $CDCl_3$ shows two resonances at δ = −16.13 and −16.34 in the ratio 2.1:1, whereas in benzene solution only one signal can be detected.

Table 3. Selected ^1H and ^{31}P NMR chemical shifts (δ values) and coupling constants J [Hz] of **2** and **4a**–**4d**

	$\delta(^1H)$[a]	$^1J(^{195}Pt-^1H)$	$^2J(^{31}P-^1H)$	$\delta(^{31}P)$[b]	$^1J(^{195}Pt-^{31}P)$
2	−16.27	1198	27.0	28.42	3023
4a	−16.62	1080	25.4	26.98	2951
4b	−17.66	991	26.7	27.92	3115
4c	−16.02	1133	23.8	27.30	2912
	−16.23	1116	24.6	27.93	2912
4d	−16.13	1136	23.1	28.08	2905
	−16.37	1148	24.3		

[a] In $CDCl_3$. – [b] In $CHCl_3$/capillary containing D_2O.

We ascribe these findings to linkage isomers of **4c** and **4d**. Ligand **1c** can be coordinated either through a terminal or the central N atom. Similarly, **1d** can be bonded through a nitrogen atom of one of the $C(CN)_2$ moieties or through the central nitrile group.

The chemical shifts of the hydridic H atoms lie in the expected range, the values varying between δ = −16.0 and −17.7. The signals are split to give a triplet with peak intensities in the ratio 1:2:1 by coupling with two equivalent ^{31}P nuclei. This triplet is further split giving two triplets by coupling with the ^{195}Pt nucleus of spin 1/2. The compounds **4a**, **4c**, and **4d** exhibit very similar chemical shifts. The comparability of these with data from the pseudohalide complexes *trans*-$[Pt(H)X(PPh_3)_2]$ with X = NCO (δ = −16.7), NCS (δ = −16.8), NCN–CN (δ = −16.7), $NCC(CN)_2$ (δ = −16.5), and $NCNSO_2C_6H_4Cl$-4 (δ = −16.8) shows that all these complexes can be grouped together as having the common structural motif [Pt]–N=C=Y [Y = O, S, NCN, $C(CN)_2$][5,6].

Because of the different character of the donor N atoms, the hydridic H atom of **4b** shows a slightly different chemical shift, which is comparable to that of the corresponding NO_2[18] complex. However, considering the expected *trans* influence of both species, a further downfield shifted signal might have been anticipated.

Generally speaking, there is a relationship between the chemical shift δ ^1H in the complexes *trans*-$[Pt(H)X(PPh_3)_2]$ (solvent: $CHCl_3$ or CH_2Cl_2)[23] and the *trans* influence[24] of the ligand, although there are minor irregularities. Nevertheless, from the chemical shift of the proton at platinum one can reliably distinguish between the different modes of bonding.

$$CO \approx CF_2 > PPh_3 \approx C_6H_5^- > CN^- > CF_3^- > SC(O)CH_3^- > NCY^- \approx N(O)C(CN)_2^- > OC(O)CF_3^- \; [Y = O, S, NCN, C(CN)_2]$$

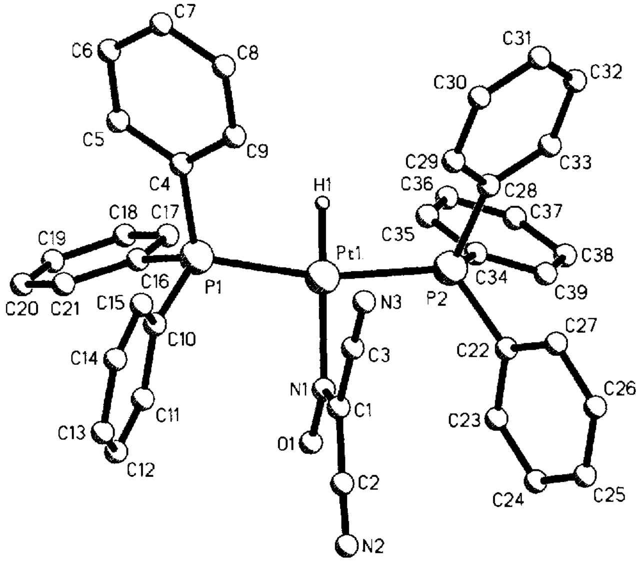
The coupling constants $^1J(^{195}Pt\text{-}^1H)$ and $^2J(^{31}P\text{-}^1H)$ are found in the ranges 991-1148 Hz and 23−27 Hz, respectively. Similar data have been reported for other complexes of the type *trans*-$[Pt(H)X(PEt_3)_2]$[18]. The $^1J(^{195}Pt\text{-}^{31}P)$ values, which are derived from ^{31}P-NMR spectra, vary between 2905 and 3135 Hz. Such values are typical of a *trans* arrangement of the phosphane ligands[18−22].

Crystal Structure Analyses of 4b, 4c, and 4d

The structures of **4b**, **4c**, and **4d** can be described as discrete *trans*-$[Pt(H)X(PPh_3)_2]$ units with an almost planar $PtHNP_2$ coordination geometry. For **4b**, the Pt−H bond length was experimentally determined to be 1.42(3) Å, which is similar to the values found in other complexes of the type *trans*-$PtHNP_2$, e.g. 1.448(9) Å in *trans*-$[Pt(H)\{NC(=CHPh)C(O)OC(O)\}(PPh_3)_2]$[22]. In the case of **4c** and **4d**, an unequivocal localization of the H atom was not possible. For their structures the Pt−H distance was assumed to be the same as that in **4b**.

The molecular structure of **4b** is shown in Figure 2. Unlike 3d-metal complexes[8], the nearly planar ionic ligand is coordinated not through the oxygen but through the central nitrogen atom. The best plane of ligand **1b** is almost perpendicular to that defined by atoms $PtHNP_2$. The distance N1−O1 [1.260(3) Å] is slightly shortened compared to that in $[N(O)C(CN)_2]^-$ [potassium salt: N−O 1.287(1) Å[25]]. In the nitrite ion, a bond length of 1.244(4) Å[25] has been found. The bond N1−C1, at 1.333(4) Å, is 0.04 Å longer than the standard value of a double bond (1.29 Å[26]). With values of about 1.42 Å the lengths of bonds C1−C2 and C1−C3 agree well with the standard given for the single bond type $C(sp^2)-C(sp)$ (1.432 Å). Both C−N triple bonds are only marginally shorter than the standard value (C≡N 1.156 Å). The angle O1−N1−C1 amounts to 118.2(3)°. It is surprising that no correlation between the value of this angle in different compounds and the corresponding coordination mode of **1b** can be observed: KX 115.9(1)°[25], $[CuNCS(1,10\text{-}phen)_2]X$ 111.3(3)°[27], $[ReX(CO)_5]$ 117.0(8)°[11], $[CuX_2(meiz)_4]$ 113.0(7)° and 118.4(7)°[8].

Figure 2. Molecular structure of **4b** in the crystal[a]

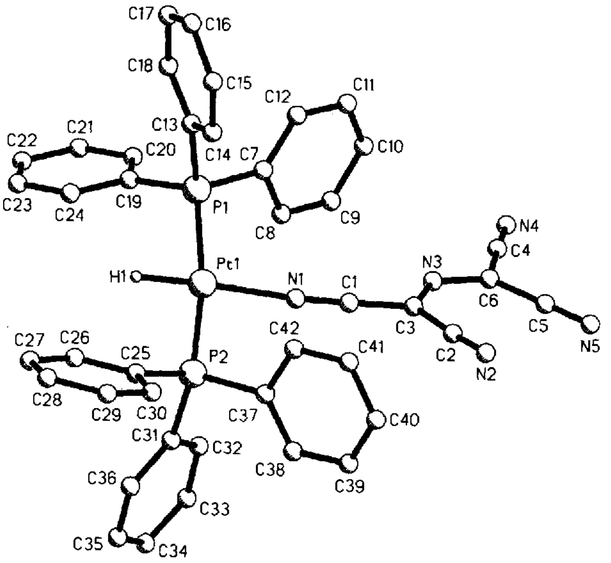


[a] Selected bond lengths [Å] and angles [°]: Pt1−H1 1.43(3), Pt1−N1 2.096(3), Pt1−P1 2.288(1), Pt1−P2 2.289(1), N1−O1 1.260(3), C1−N1 1.333(4), C1−C2 1.417(5), C1−C3 1.421(5), C2−N2 1.148(4), C3−N3 1.134(5); N1−Pt1−P1 95.80(7), N1−Pt1−P2 95.97(7), P1−Pt1−P2 167.21(3), N1−Pt1−H1 175(1), P1−Pt1−H1 86(1), P2−Pt1−H1 83(1), O1−N1−C1 118.1(3), O1−N1−Pt1 119.1(2), C1−N1−Pt1 122.8(2), N3−C3−C1 178.0(5), N1−C1−C3 118.8(3), N1−C1−C2 121.4(3), C3−C1−C2 119.8(3), N2−C2−C1 178.1(4).

Figure 3 shows the molecular structure of **4c**. In contrast to **1b**, the nearly planar **1c** [the maximum deviation from planarity is shown by N2 with 0.109(4) Å] is coordinated through a nitrile N atom. The interplanar angle $PtHNP_2$/**1c** amounts to 30.1°. Comparison of **1c** in the potassium salt $K[N\{C(CN)_2\}_2] \cdot 1/2\ H_2O$[28] and in the complex **4c** does not reveal any significant changes in the bond parameters caused by the coordination to the platinum atom. Compared with the mean C−N distance for the three uncoordinated nitrile groups of 1.134(5) Å, the bond length C1−N1 [1.161(3) Å] is very slightly lengthened. Between C3−N3 [1.329(3) Å] and C6−N3 [1.312(3) Å] a very small difference is observed. Both lengths are, as expected, somewhat greater than the standard value of 1.29 Å for a C=N bond.

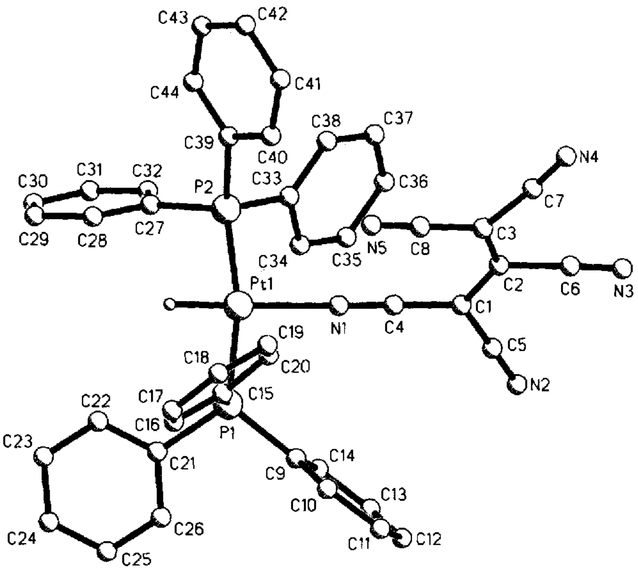
The molecular structure of **4d** is illustrated in Figure 4. Like **1c**, the ligand **1d** is also coordinated to platinum through a nitrile group of a $C(CN)_2$ unit in an end-on manner. The ligand **1d** is almost planar; the maximum deviations from the best plane defined by its 13 atoms are shown by N1 [0.380(3) Å] and N5 [0.347(5) Å]. The plane of **1d** and the $PtHNP_2$ plane intersect at an angle of 78.8°. On inspection of the five C−N bond lengths in **4d** it is apparent that coordination of **1d** to the platinum has no observable effect on the bond parameters of the nitrile groups. Thus, the distance C4−N1 (coordinated) at 1.140(5) Å falls in the middle of the range of all C−N distances [1.112(5)−1.160(7) Å]. The central C1−C2−C3 subunit ex-

Figure 3. Molecular structure of **4c** in the crystal[a]



[a] Selected bond lengths [Å] and angles [°]: Pt1−N1 2.066(2), Pt1−P1 2.297(1), Pt1−P2 2.292(1), C1−N1 1.161(3), C1−C3 1.411(4), C3−N3 1.329(3), C2−C3 1.427(4), C2−N2 1.132(4), C6−N3 1.312(3), C4−C6 1.436(4), C4−N4 1.140(4), C5−C6 1.440(4), C5−N5 1.130(4); P1−Pt1−P2 170.94(2), N1−Pt1−P2 93.05(6), N1−Pt1−P1 95.85(6), Pt1−N1−C1 174.9(2), N1−C1−C3 178.3(3), C6−N3−C3 127.8(3), N2−C2−C3 176.6(4), N5−C5−C6 175.7(4), N4−C4−C6 177.1(3).

Figure 4. Molecular structure of **4d** in the crystal[a]



[a] Selected bond lengths [Å] and angles [°]: Pt1−N1 2.080(3), Pt1−P1 2.286(1), Pt1−P2 2.288(1), N1−C4 1.140(5), C1−C4 1.405(6), C1−C5 1.418(7), C5−N2 1.160(7), C1−C2 1.408(6), C2−C6 1.521(7), C6−N3 1.139(7), C2−C3 1.339(7), C3−C7 1.469(7), C7−N4 1.112(5), C3−C8 1.402(7), C8−N5 1.117(6); P1−Pt1−P2 168.04(3), N1−Pt1−P1 95.33(9), N1−Pt1−P2 96.39(9), C4−N1−Pt1 175.4(3), N1−C4−C1 176.8(4), C3−C2−C1 131.6(4).

hibits a striking asymmetry with regard to the C−C bond lengths: the distance C1−C2 = 1.408(6) Å on the side turned to the platinum is significantly longer than that on the other side [C2−C3 = 1.339(7) Å].

In the three investigated complexes, the observed Pt−N bond lengths fall in the narrow range from 2.066(2) to 2.096(3) Å. Compared with *trans*-[Pt(H){*N*C(=CHPh)-C(O)O*C*(O)}$(PPh_3)_2$] [Pt−N = 2.151(14) Å[22]] or other complexes containing ionic nitrogen ligands [e.g. *N*CS: Pt−N = 2.024(9) Å[28], 4-MeC_6H_4*N*NNC_6H_4Me-4: Pt−N = 2.09(2) Å[29]] the observed distances can be classified as being in the middle of the range.

In **4b**−**4d**, the Pt−P distances vary between 2.286(1) and 2.297(1) Å and thus agree well with the value of 2.298(32) Å established as the average of a large number of Pt−PPh_3 complexes[30]. For steric reasons, the angles P−Pt−P are somewhat smaller than 180°, falling in the range 167.21(3)−170.94(2)°.

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Experimental Section

IR (KBr): Mattson 5000 FT-IR. − ^{1}H and ^{13}C NMR (TMS as reference): WP 200. − ^{31}P NMR (85% H_3PO_4 as reference, downfield shift positive): AC 80. The compounds **2**[31], **3a**[32], **3b**[33], **3c**[34], and **3d**[35] were prepared as described previously.

General Method for the Syntheses of trans-[Pt(H)X(PPh₃)₂] **4a**−**4d**: 0.92 mmol (0.7 g) of *trans*-[Pt(H)Cl$(PPh_3)_2$] (**2**), 0.93 mmol of the silver salt **3** and 30 ml of CH_2Cl_2 are heated for 8 h under exclusion of light. After filtration the product is precipitated by the addition of about 50 ml of petroleum ether. The solid is filtered off and dried in vacuo.

trans-(Hydrido)(nitrocyanamido)bis(triphenylphosphane)platinum(II) (**4a**): Crystallization with one equivalent of CH_2Cl_2, colorless crystals, yield 95%, m.p. 184−185°C (dec.). − IR: $\tilde{\nu}$ = 2201 cm^{-1} [ν(CN)], 1256 [ν(NO_2)], 693, 744 (Ph). − ^{1}H NMR ($CDCl_3$): δ = −16.62 [t, $^1J(^{195}Pt-^1H)$ = 1080 Hz, $^2J(^{31}P-^1H)$ = 25.4 Hz, 1H], 7.24−7.63 (m, 30H, Ph). − ^{31}P NMR ($CHCl_3$, capillary containing D_2O): δ = 26.98 [s, $^1J(^{195}Pt-^{31}P)$ = 2951 Hz]. − ^{13}C NMR ($CDCl_3$): δ = 116.1 (s, CN), 130.7 [dd, P-C-1, $^1J(^{31}P-^{13}C)$ = 28.7 Hz], 128.8 [dd, C-2,6, $^2J(^{31}P-^{13}C)$ = 6.8 Hz], 134.1 [dd, C-3,5, $^3J(^{31}P-^{13}C)$ = 5.5 Hz], 131.2 (s, C-4). − $C_{38}H_{33}Cl_2N_3O_2P_2Pt$ (891.63): calcd. C 51.19, H 3.73, N 4.71; found C 51.37, H 4.01, N 4.54.

trans-(Hydrido)(nitrosodicyanomethanido)bis(triphenylphosphane)platinum(II) (**4b**): Light-yellow crystals, yield 94%, m.p. 184°C (dec.). − IR: $\tilde{\nu}$ = 2206, 2182 cm^{-1} [ν(CN)], 1363 [ν_{as}(CNO)], 1322 [ν_s(CNO)], 1250 [ν(CC)], 3051, 1480, 1433, 1097, 747, 693 (Ph). − ^{1}H NMR ($CDCl_3$): δ = −17.66 [t, $^1J(^{195}Pt-^1H)$ = 991 Hz, $^2J(^{31}P-^1H)$ = 26.7 Hz, 1H], 7.24−7.64 (m, 30H, Ph). − ^{31}P NMR ($CHCl_3$, capillary containing D_2O): δ = 27.92 [s, $^1J(^{195}Pt-^{31}P)$ = 3015 Hz]. − ^{13}C NMR ($CDCl_3$): δ = 109.11 (s, CN), 109.08 (s, CN), 111.3 (s, methanide-C), 130.0 [dd, P-C-1, $^1J(^{31}P-^{13}C)$ = 28.9 Hz], 134.0 [dd, C-2,6, $^2J(^{31}P-^{13}C)$ = 7.0 Hz], 128.5 [dd, C-3,5, $^3J(^{31}P-^{13}C)$ = 5.5 Hz], 131.1 (s, C-4). − $C_{39}H_{31}N_3O_1P_2Pt$ (814.72): calcd. C 57.49, H 3.84, N 5.16; found C 57.34, H 4.13, N 5.01.

trans-(Hydrido)(1,1,3,3-tetracyano-2-azapropenido)bis(triphenylphosphane)platinum(II) (**4c**): Yellow crystals, yield 93%, m.p. 183°C (dec.). − IR: $\tilde{\nu}$ = 2223 cm^{-1}, 2197 [ν(CN)], 1586 [ν_{as}(C=N)], 1464 [ν_s(C=N)], 3055, 1476, 1433, 1097, 747, 690 (Ph). − ^{1}H NMR ($CDCl_3$): δ = −16.02 [t, $^1J(^{195}Pt-^1H)$ = 1133 Hz, $^2J(^{31}P-^1H)$ = 23.8 Hz, 1H_a], −16.23 [t, $^1J(^{195}Pt-^1H)$ = 1116 Hz, $^2J(^{31}P-^1H)$ = 24.6 Hz, 1H_b], H_a/H_b = 2:3, 7.24−7.61 (m, 30H, Ph). − ^{1}H NMR (C_6D_6): δ = −15.78 [t, $^1J(^{195}Pt-^1H)$ = 1129 Hz, $^2J(^{31}P-^1H)$ = 24.4 Hz, 1H_a], −16.07 [t, $^1J(^{195}Pt-^1H)$ = 1106 Hz, $^2J(^{31}$P-

Table 4. Crystal data and experimental details of X-ray structure determinations of compounds **4b**, **4c** and **4d**

	4b	**4c**	**4d**
Empirical formula	$C_{39}H_{31}N_3OP_2Pt$	$C_{42}H_{31}N_5P_2Pt$	$C_{44}H_{31}N_5P_2Pt$
Molecular mass [g mol^{-1}]	814.70	862.75	886.77
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/n$	$P2_1/n$
Lattice parameters			
a [Å]	11.942(1)	13.381(1)	9.971(1)
b [Å]	14.692(1)	14.105(1)	19.956(2)
c [Å]	20.021(2)	19.948(1)	20.185(2)
α [°]	90.0	90.0	90.0
β [°]	90.86(1)	96.19(1)	99.86(1)
γ [°]	90.0	90.0	90.0
V [Å^3]	3512.2(5)	3743.1(5)	3957.1(6)
Z	4	4	4
$F(000)$	1608	1704	1752
$D_{calc.}$ [g cm^{-3}]	1.541	1.531	1.488
μ (Mo K_α) [cm^{-1}]	41.20	38.71	36.64
Crystal dimensions [mm]	0.46 × 0.34 × 0.23	0.46 × 0.32 × 0.19	0.61 × 0.40 × 0.19
Check reflections	(300), (020), (006)	$(\bar{7}01)$, (060), $(00\bar{6})$	$(\bar{4}00)$, (004), $(\bar{1}\ 11\ 3)$
Intensity variation [%]	3.3	3.2	5.7
$2\theta_{max.}$ [°]	50.0	60.0	49.8
hkl range	±14, ±17, ±23	±18, ±19, ±28	±11, ±23, ±23
Measured reflections	12352	21776	13750
Unique reflections	6176	10888	6875
$R_{int.}$	0.0198	0.0433	0.0207
Obs. reflections [$I > 2\sigma(I)$]	4966	7730	4745
Refined parameters	419	455	473
Weight. coefficients a/b[a]	0.0220 / 1.0211	0.0151 / 0.1070	0.0306 / 0.6717
Absorption correction	empirical (Psi scans)	empirical (Psi scans)	empirical (Psi scans)
$T_{min.}$ / $T_{max.}$	0.2080 / 0.2447	0.1589 / 0.2764	0.1462 / 0.2611
$R1$ / $wR2$ / S (all data)	0.0357/0.0505/1.023	0.0547/0.0584/0.995	0.0493/0.0614/1.015
$R1$ / $wR2$ / S [$I > 2\sigma(I)$]	0.0216/0.0467/1.067	0.0261/0.0516/1.052	0.0242/0.0537/1.087
$(\Delta/\rho)_{max.}$ in last l.s. cycle	0.001	–0.002	–0.002
$\Delta\rho_{fin.}$ (min./max.) [e Å^{-3}]	–0.302 / 0.343	–0.411 / 0.866	–0.376 / 0.578

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

^{1}H) = 24.4 Hz, 1H$_b$], H$_a$/H$_b$ = 2.4:1, 7.04–7.52 (m, 30H, Ph). – ^{31}P NMR (CHCl$_3$, capillary containing D$_2$O): δ = 27.30 [s, ^1J(^{195}Pt-^{31}P) = 2912 Hz, P$_a$], 27.93 [s,^1J(^{195}Pt-^{31}P) = 2912 Hz, P$_b$], P$_a$/P$_b$ = 1.4:1. – ^{31}P NMR (C$_6$D$_6$): δ = 28.13 [s, ^1J(^{195}Pt-^{31}P) = 2905 Hz, P$_a$], 28.63 [s, ^1J(^{195}Pt-^{31}P) = 2913 Hz, P$_b$] P$_a$/P$_b$ = 2.3:1. – ^{13}C NMR (CDCl$_3$): δ = 77.2 (s, methanide-C), 110.6 (s, CN), 110.7 (s, CN), 116.4 (s, CN), 116.7 (s, CN), 130.0 [dd, P-C-1, ^1J(^{31}P-^{13}C) = 29.1 Hz], 133.9 [dd, C-2,6, ^2J(^{31}P-^{13}C) = 6.9 Hz, 129.0 [dd, C-3,5, ^3J(^{31}P-^{13}C) = 5.5 Hz], 131.6 (s, C-4). – $C_{42}H_{31}N_5P_2Pt$ (862.76): calcd. C 58.46, H 3.62, N 8.12; found C 57.62,H 3.95, N 7.90.

trans-(Hydrido)(1,1,2,3,3-pentacyanopropenido)bis(triphenylphosphane)platinum(II) (**4d**): Dark-yellow crystals, yield 99%, m.p. 179°C (dec.). – IR: $\tilde{\nu}$ = 2228 cm^{-1}, 2205 [ν(CN)], 1498 [ν(CC)], 3056, 1434, 750, 693 (Ph). – ^{1}H NMR (CDCl$_3$): δ = –16.13 [t, ^1J(^{195}Pt-^{1}H) = 1136 Hz, ^2J(^{31}P-^{1}H) = 23.1 Hz, 1H$_a$], –16.37 [s, ^1J(^{195}Pt-^{1}H) = 1148 Hz, ^2J(^{31}P-^{1}H) = 24.3 Hz, 1H$_b$], H$_a$/H$_b$ = 2.1:1, 7.24–7.61 (m, 30H, Ph). – ^{1}H NMR (C$_6$D$_6$): δ = –15.92 [t, ^1J(^{195}Pt-^{1}H) = 1130 Hz, ^2J(^{31}P-^{1}H) = 24.4 Hz], 7.04–7.49 (m, 30H, Ph). – ^{31}P NMR (CHCl$_3$, capillary containing D$_2$O): δ = 28.08 [s, ^1J(^{195}Pt-^{31}P) = 2905 Hz]. – ^{31}P NMR (C$_6$D$_6$): δ = 28.65 ^1J(^{195}Pt-^{31}P) = 2919 Hz]. – ^{13}C NMR (CDCl$_3$): δ = 63.5 (s, methanide-C), 135.4 (s, methanide-C), 111.7 (s, CN), 113.6 (s, CN), 114.4 (s, CN), 114.6 (s, CN), 118.9 (s, CN), 129.6 [dd, P-C-1, ^1J(^{31}P-^{13}C) = 28.9 Hz], 133.9 [dd, C-2,6, ^2J(^{31}P-^{13}C) = 5.9 Hz], 128.7 [dd, C-3,5, ^3J(^{31}P-^{13}C) = 5.5 Hz], 131.3 (s, C-4). – $C_{44}H_{31}N_5P_2Pt$ (886.79): calcd. C 59.60, H 3.52, N 7.90; found C 59.31, H 3.36, N 7.85.

X-Ray Crystal Structure Determination: A summary of crystal data along with details of the structure determination is given in Table 4[36]. All measurements were performed with a Stoe STADI 4 diffractometer using graphite-monochromated Mo-K_α radiation (λ = 0.71069 Å) in the ω-2Θ scanning mode at room temperature. Lattice constants were obtained by a least-squares treatment of the setting angles of 80 reflections in a 2Θ range of 10.1–12.8° (**4b**), 10.1–14.6° (**4c**), and 10.0–12.0° (**4d**). All three structures were solved by heavy-atom methods (program system SHELXS-86[37]). Structure refinement on F^2 was performed using the full-matrix least-squares techniques of SHELXL-93[38] with anisotropic displacement parameters for the non-H atoms. The hydrogen atoms were placed at their idealized positions with exception of the H atom bonded to the platinum atom in **4b** which was localized in a difference Fourier map and refined isotropically. The molecular structures in Figures 2–4 were plotted by use of the program XP/PC[39].

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* Dedicated to Professor *S. Engels* on the occasion of his 65th birthday.

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