Coordination Compounds of *tripod*Co^{II} and *tripod*Co^{I} − Selective Substitution and Redox Behaviour

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Dedicated to Prof. Jürgen Wolfrum on the occasion of his 60th birthday

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The five-coordinate *tripod*Cobalt(II) compound [*tripod*Co^{II}Cl$_2$] (**2**) [*tripod* = $CH_3C(CH_2PPh_2)_3$] undergoes selective substitution of its chlorine groups on activation with KPF$_6$ in the first substitution step and by TlPF$_6$ in the second. Compounds of the type [*tripod*Co^{II}LL′]$^{2+}$ with two nitrile (**3**$^{2+}$) or isonitrile (**5**$^{2+}$) ligands are obtained by this route. Compounds [*tripod*Co^{II}L$_2$] containing two equal ligands L are also accessible from Co$^{II}_{aq}$ as the starting material. The syntheses of [*tripod*Co^{II}(CNR)$_2$]$^{2+}$ (**5**$^{2+}$) and [*tripod*Co^{II}X$_2$] (X = CN, NCO, NCS) (**6**) are reported. Different routes to *tripod*Co^{I} derivatives are described. Depending on the nature of the co-ligands, four-coordinate − [*tripod*Co^{I}NCO] (**7**) − or five-coordinate − [*tripod*Co^{I}(CNR)$_2$]$^{+}$ (**5**$^{+}$) − compounds are obtained. Several high-yield syntheses of [*tripod*Co^{I}-alkyne]$^{+}$ (**8**$^{+}$) compounds are reported. The compounds are characterised by the usual analytical and spectroscopic techniques including X-ray analysis of selected examples.

Introduction

An extensive chemistry has been described for the *tripod*cobalt template [$CH_3C(CH_2PPh_2)_3Co$]$^{n+}$ (n = 0−3).[1−4] Stable compounds [*tripod*CoL$_m$]$^{n+}$ have been characterised with cobalt in all four of its formal oxidation states of Co^0 to Co^{III}.[1−4] The standard entry into *tripod*cobalt chemistry is by reaction of the *tripod* ligand with cobalt(II) salts in the presence of co-ligands L, which will generally produce the five-coordinate species [*tripod*Co^{II}L$_2$]. In specific cases, due to electron transfer between the co-ligand and the metal centre, *tripod*cobalt(I) derivatives e.g. [(*tripod*cobalt(I) iodide][2a] or *tripod*cobalt(III) derivatives e.g. [*tripod*cobalt(III) catecholate]$^{+}$ [4] may also be accessible by this route. While many compounds [*tripod*cobalt(II)L$_2$]$^{n+}$ and a number of compounds [*tripod*cobalt(I)L$_2$]$^{+}$ or [*tripod*cobalt(I)L] are known, almost nothing is known about the possible exchange of co-ligands in such species by selective substitution reactions.

Exchange of the η^2-acetato ligand in [*tripod*cobalt(II) acetate]$^{+}$ [3a] with an allylic ligand and the substitution of one chloride ligand in [*tripod*cobalt(II)Cl$_2$][2b,3b] by neutral donor ligands[2b,3c] appear to be the only examples of selective substitution reactions in *tripod*cobalt(II) chemistry. As far as *tripod*Co^{I} chemistry is concerned, the extensive work of J. Ellermann et al. has shown that the carbonyl groups in [*tripod*Co^{I}(CO)$_2$]$^{+}$ − which is obtained from Co$_2$(CO)$_8$ as the starting material − undergo substitution reactions under photolytic conditions.[2c−2e] The possibility of exchanging the chloride ligand in [*tripod*Co^{I}Cl] has only recently been reported as a selective entry into *tripod*Co^{I} chemistry.[2f]

It is apparent that in order to further develop the chemistry of the *tripod*cobalt template, it is necessary to develop more general methods of substitution processes. In view of the many cases where reversible reductions or oxidations of [*tripod*Co^{II}L$_2$]$^{n+}$ compounds have been documented by cyclic voltammetry, it is also necessary to find preparative methods which allow selective change in the oxidation state of the metal centre. Such methods would be especially useful with respect to *tripod*Co^{I} chemistry since *tripod*Co^{II} compounds are more easily accessible than the corresponding *tripod*Co^{I} species.

We report here on the stepwise selective subsitution of the chloro ligands in [*tripod*CoCl$_2$] (**1**) by two different donor ligands L and L′ to produce [*tripod*Co^{II}LL′]$^{n+}$ (n = 0, 2). Compounds of the type [*tripod*Co^{II}L$_2$]$^{n+}$, on the other hand, are easily accessible by standard methods, with the synthesis of such compounds [L = RNC, RCN (n = 2); CN^{-}, OCN^{-}, SCN^{-} (n = 0)] being reported. Upon reduction, these compounds [*tripod*Co^{II}L$_2$] produce [*tripod*Co^{I}L$_2$] or [*tripod*Co^{I}L] depending on the nature of L. With nitriles as co-ligands L, the cobalt(I) species [*tripod*Co^{I}(NCR)$_2$]$^{+}$ are highly reactive and react with alkynes to produce [*tripod*Co^{I}(η^2-alkyne)]$^{+}$, which may also be obtained from [*tripod*Co^{I}Cl] and alkyne upon activation with TlPF$_6$.[2f]

Results and Discussion

Stepwise Substitution Leading to [tripodCo^{II}LL′]

[*tripod*CoCl$_2$] (**1**)[2b,3b] undergoes selective substitution of one of its two chloro ligands by neutral two-electron donors upon activation with KPF$_6$[2b] or NaBPh$_4$.[3c]

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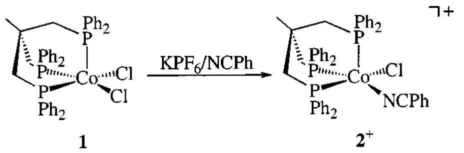
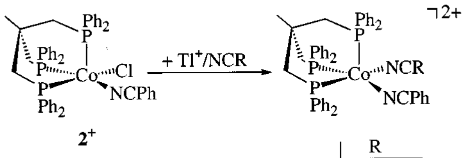


Scheme 1

The benzonitrile derivative 2^+ (Scheme 1) is obtained by a procedure analogous to the one reported for the synthesis of [*tripod*Co^{II}(Cl)(NCMe)]$^+$.[2b] Analytical and spectroscopic data (Tables 3 and 4) confirm its identity. The remaining chloride group in 2^+ may be replaced in a second substitution step upon activation with TlPF$_6$.

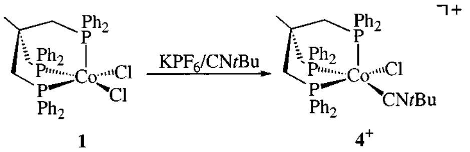
While compounds such as $3a^{2+}$, with two identical nitrile substituents, might also be obtained by more standard methods[3d], the synthesis of compound $3b^{2+}$, containing two different nitrile donors relies on the selective stepwise substitution process described (Scheme 2). Both compounds are fully characterised (Tables 3 and 4).



	R
$3a^{2+}$	Phenyl
$3b^{2+}$	Methyl

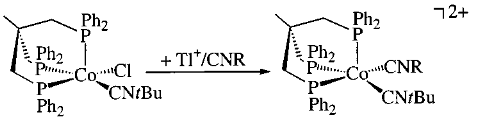
Scheme 2

It had been found by L. Sacconi et al. that **1** undergoes selective substitution of one chloro group by cyclohexyl isocyanide upon activation with NaBPh$_4$.[3c] Analogously, in the presence of KPF$_6$, **1** reacts with *t*BuNC to produce the monosubstituted product 4^+ (Scheme 3, for analytical and spectroscopic data see Tables 3 and 4).



Scheme 3

Only when activated with TlPF$_6$ will the remaining chloride group in 4^+ undergo substitution, producing 5^{2+} (Scheme 4, for analytical and spectroscopic data see Tables 3 and 4).



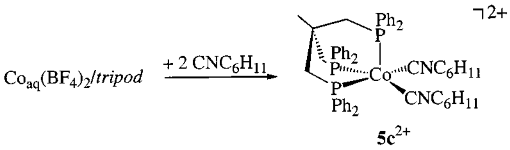
	R
$5a^{2+}$	*t*Bu
$5b^{2+}$	Cyclohexyl

Scheme 4

Compounds such as $5a^{2+}$, containing two identical isonitrile ligands, may directly be obtained from **1** by using a 2:1 molar ratio of TlPF$_6$/**1** in the presence of two equivalents of the corresponding isonitrile. An excess of isonitrile has to be avoided since it leads to partial decoordination of the *tripod* ligand. Decomplexation is apparent from the corresponding ^{31}P-NMR spectra, which generally, even for the necessarily paramagnetic *tripod*Co^{II} compounds, show well resolved signals for the coordinated phosphorus donors around δ = 34 and the signal of a decoordinated *tripod* phosphorus donor at δ = −27.

One Step Formation of [tripodCo^{II}L$_2$]

Compounds such as $5a^{2+}$ are easily accessible by the standard procedure of treating a mixture of Co$^{II}_{aq}$(BF$_4$)$_2$/*tripod* in EtOH/CH$_2$Cl$_2$ with two equivalents of an isonitrile. Since no single crystals suitable for X-ray analysis had been obtained for the PF$_6^-$ salts of either $5a^{2+}$ or $5b^{2+}$, this synthetic procedure was applied with cyclohexyl isocyanide as the co-ligand to give the salt of $5c^{2+}$, in the hope it would produce crystals suitable for X-ray analysis (Scheme 5).



Scheme 5

The formation of $5c^{2+}$ under these reaction conditions is clear from the mass spectrum of its salt, which shows a prominent peak for [*tripod*Co(CNC$_6$H$_{11}$)$_2$]$^+$ (*m*/*z* = 901) independent of the anion used. Crystals were obtained after metathesis with KPF$_6$ in acetone and crystallisation of the metathesis product from acetone by vapour phase diffusion of Et$_2$O. Structural analysis of these crystals clearly reveals the structure of $5c^{2+}$ (Figure 1 and 2; Table 1 and 6).

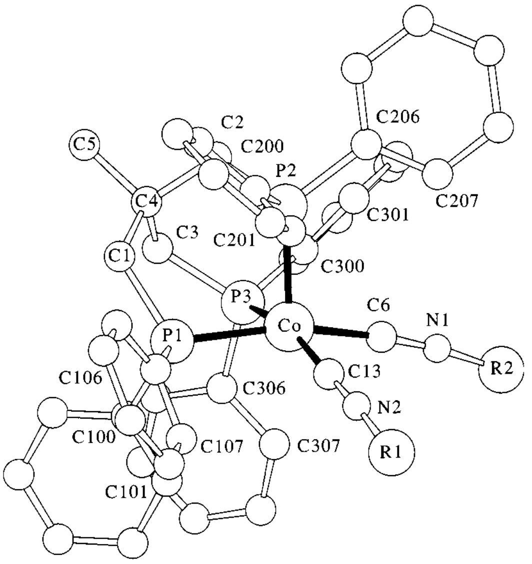


Figure 1. X-ray structure of $5c^{2+}$ ($R^1 = R^2 = C_6H_{11}$)

The crystal structure was unexpectedly found to contain PO$_2$F$_2^-$ counterions. Formation of this type of counterion from PF$_6^-$ has been reported in several cases.[5] The water necessary for this hydrolysis reaction may come from the cobalt(II)$_{aq}$ starting material as well as from water in the acetone solvent used for crystallisation. There are two crys-

Table 1. Bond lengths [pm], bond angles [°] and torsion angles [°] for the [*tripod*CoL$_n$]$^{m+}$ compounds **5c**$^{2+}$[(PF$_2$O$_2$)$^-$]$_2$, **5a**$^+$(PF$_2$O$_2$)$^-$, **6a**, **6c**, and **7a** (standard deviations in units of the least significant digit given in each case)

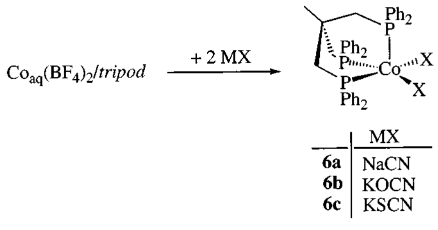
Compound[b]	**5a**$^+$(PF$_2$O$_2$)$^-$ [a] L = CN*t*Bu $n = 2; m = 1$	**5c**$^{2+}$[(PF$_2$O$_2$)$^-$]$_2$ L = CNC$_6$H$_{11}$ $n = 2; m = 2$	**6a** L = CN $n = 2; m = 0$	**6c** L = NCS $n = 2; m = 0$	**7a** [a] L = NCO $n = 1; m = 0$
Co−P1	219.9(2)	224.1(2)	221.3(2)	219.8(4)	223.2(1)
Co−P2	222.1(2)	229.5(2)	228.9(2)	229.4(4)	221.9(1)
Co−P3	219.9(2)	224.1(2)	224.1(2)	220.5(4)	221.8(1)
Co−L1	184.4(7)	187.1(7)	188.6(1)	190.6(1)	192.8(2)
Co−L2	182.6(6)	187.5(7)	191.1(1)	190.8(1)	−
P1−Co−P2	88.24(3)	88.7(7)	90.8(1)	92.84(1)	91.6(3)
P2−Co−P3	96.01(3)	95.8(8)	90.4(1)	91.10(1)	92.9(3)
P1−Co−P3	90.07(3)	87.4(7)	89.2(1)	89.58(2)	90.7(4)
P1−Co−L1	90.2(5)	93.2(3)	87.4(3)	92.7(3)	124.9(2)
P1−Co−L2	161.7(5)	165.7(3)	167.1(3)	151.4(3)	−
P2−Co−L1	110.6(5)	100.6(3)	116.2(3)	99.1(3)	121.9(2)
P2−Co−L2	106.1(5)	105.2(2)	101.5(3)	115.3(3)	−
P3−Co−L1	154.5(4)	163.6(2)	153.3(3)	169.4(3)	125.2(2)
P3−Co−L2	90.2(4)	87.7(3)	94.4(3)	85.5(3)	−
L1−Co−L2	84.5(3)	87.8(3)	83.86(4)	87.6(3)	−
C4−C1−P1−Co	31.4	24.9	26.6	13.3	28.4
C4−C2−P2−Co	32.0	37.9	26.7	12.9	30.0
C4−C3−P3−Co	22.1	21.9	27.9	10.3	29.8
Hz−P1−C100−C101[c]	−17.6	−8.0	−8.2	21.1	−34.7
Hz−P1−C106−C107[c]	−42.4	−26.8	59.3	70.2	−0.5
Hz−P2−C200−C201[c]	−27.6	−2.6	9.9	16.9	−27.3
Hz−P2−C206−C207[c]	−9.2	13.2	5.8	27.4	1.6
Hz−P3−C300−C301[c]	−63.4	−80.0	−41.0	40.4	−46.8
Hz−P3−C306−C307[c]	−11.5	−5.8	−2.0	17.3	5.5

[a] For the sake of comparison the structure was inverted with respect to the deposited data. − [b] For **5a**$^+$, **5c**$^{2+}$ the designators L1 and L2 refer to the ligands labelled by R1 and R2 respectively in Figures 2 and 3. For **6a** and **6c** L1 refers to the ligand designated by C6N6 and L2 to the one designated by C7N7 in each case (Figures 2 and 3). − [c] In order to define the rotation of the phenyl groups with respect to the idealised C_3 axis of the [*tripod*Co] entity the following procedure was adopted: a vector vertical to the P1−P2−P3 plane and pointing towards the observer with respect to the projections given in Figures 2 and 3 is fixed at the individual phosphorus atoms. Its end point is called Hz. The torsion angles given refer to this convention.

tallographically independent anions in the unit cell of **5c**$^{2+}$, both of which show disorder (see Experimental Section). In contrast to the anions, the cations of **5c**$^{2+}$ are not affected by disorder problems. The idealised square pyramidal structure of **5c**$^{2+}$ is apparent from Figure 1 and 2 and Table 1. It is assumed that **5a**$^{2+}$ and **5b**$^{2+}$ adopt the same type of geometry.

Compound **5c**$^{2+}$ can only obtained by the described route if the amount of isonitrile used does not exceed the stoichometric limit. If an excess of isonitrile is used, mixtures of compounds are obtained having at least partial replacement of the phosphorus donors by isonitrile ligands.

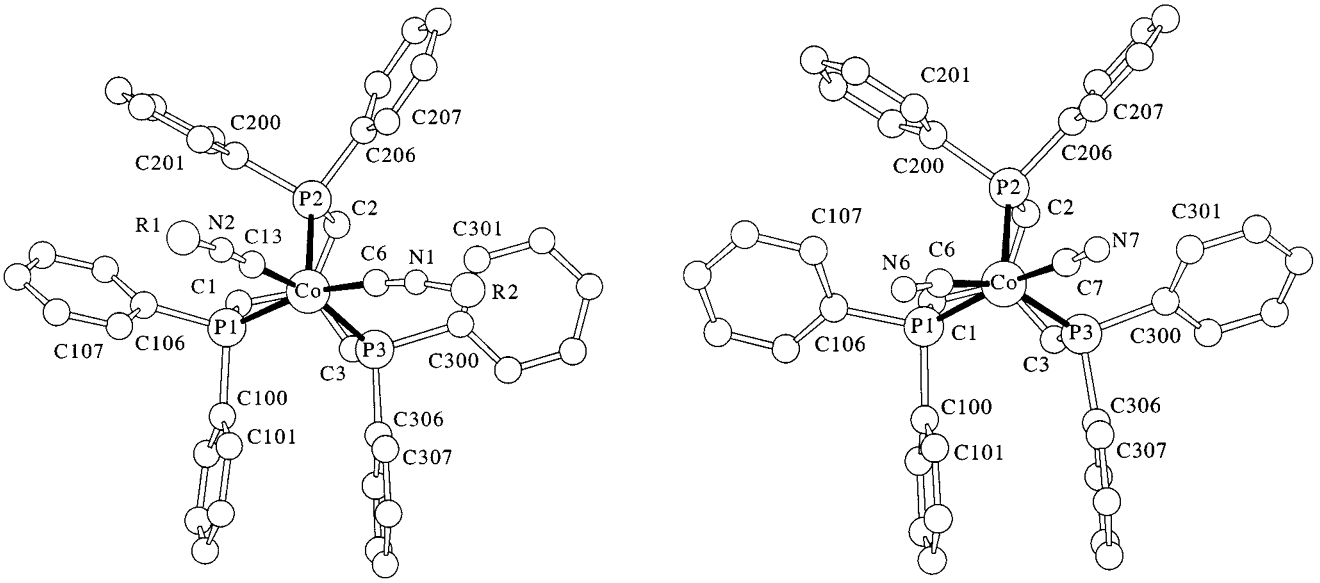
With cyanide as an isoelectronic anionic equivalent of RNC, the risk of replacing the phosphorus donors by cyanide ligands is even higher as it has been found that aqueous solutions of NaCN may completely replace the *tripod* and the co-ligands in [*tripod*CoL$_2$].[3e,6] Nevertheless, under controlled conditions, the cyano derivative **6a** is accessible by the standard procedure (Scheme 6).



Scheme 6

The cyanide ligands in **6a** may be viewed as isoelectronic equivalents of isonitriles analogous to compounds such as **5**$^{2+}$; they may also be seen as pseudo-halide ligands analogous to **1**. This latter classification leads to the question of whether other pseudo-halide derivatives may be accessible by the same type of procedure. It is in fact found that NCO$^-$ and NCS$^-$ form the corresponding pseudo-halide derivatives **6b** and **6c**. The compounds are isolated as microcrystalline powders (**6b**: green; **6c**: brown) with the analytical and spectroscopic data being in agreement with the assigned formulations (Table 3 and 4). The structures of **6a** and **6c** have been solved by X-ray crystallography (Figure 2 and Figure 3; Tables 1; 6 and 7).

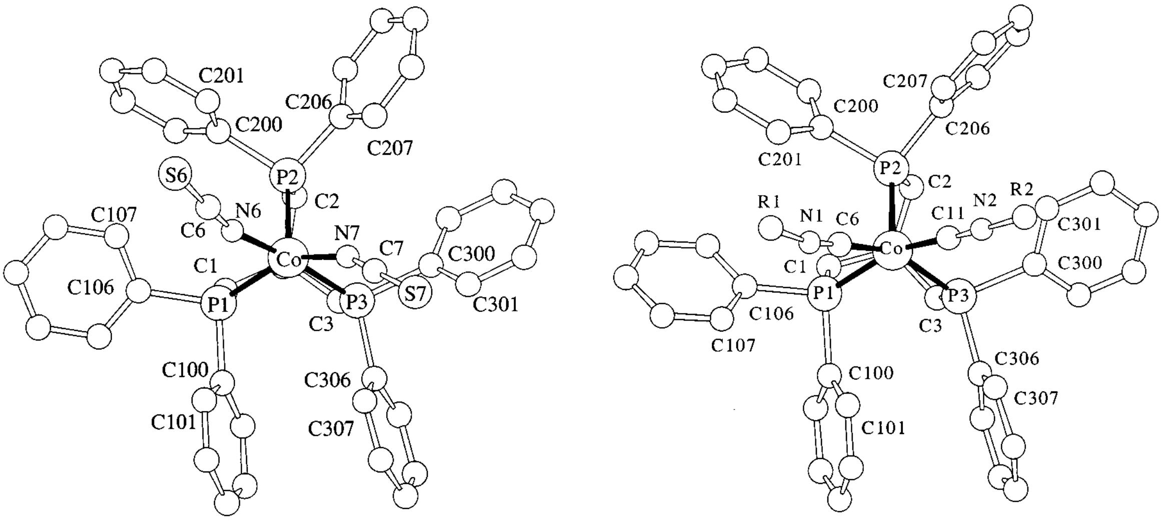
Both compounds show an idealised square-pyramidal coordination of the cobalt centre with one of the phosphorus donors (P2, Figure 2 and 3; Table 1) occupying the apical position and with the other two phosphorus donors and the two co-ligands forming the base of the pyramid. Comparison of the three structures of the type [*tripod*Co^{II}L$_2$] reported in this paper (**5c**$^{2+}$, **6a**, **6c**; Table 1; Figure 2 and 3) shows that the apical Co−P bond is longer (229 pm) than the equatorial Co−P bonds (220−224 pm). The P−Co−P angles are, by virtue of being part of the chelate cage, close to 90° in each case. The L−Co−L angles spanned by the coordinated atoms of the co-ligands are found in the narrow range of 84−88° (Table 1). The P−Co−L angles fall into two classes. The angles referring to ligands which are in an idealised *trans* position to each other show values be-



$5c^{2+}$

6a

Figure 2. X-ray structure of compounds $5c^{2+}$ ($R^1 = R^2 = C_6H_{11}$) and **6a**; projection onto the P1−P2−P3 plane



6c

$5a^+$

Figure 3. X-ray structure of compounds **6c** and $5a^+$ ($R^1 = R^2 = t$Bu); projection onto the P1−P2−P3 plane.

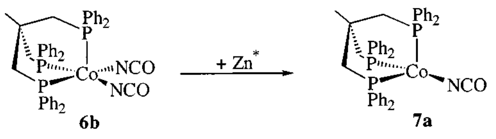
tween 151° and 169° (Table 1) while angles referring to mutual idealised *cis* positions are in a range between 86° and 116°. The deviations from the idealised square-pyramidal geometry are thus substantial. Nevertheless the Co−P bond described as axial is definitely the longest one in each case. The scheme used to label the atoms refers to the standard used in many other publications referring to the structure of *tripod*Co compounds.[7] It is such that the torsion angles of the chelate scaffolding (C4−Ci−Pi−Co; Table 1; Figure 2 and 3) are positive throughout. The rotational position of the phenyl groups (Hz−Pi−Cj−Ck; Table 1; Figure 2 and 3) shows a common trend for all three compounds $5c^{2+}$, **6a**, **6c**. Two of the phenyl groups at P1 and P3 (labels C100 and C306, Figure 2 and 3, Table 1) are oriented such that they are almost parallel to the idealised C_3 axis of the *tripod*Co fragment, while the other two phenyl groups at these phosphorus atoms are tilted with respect to this axis. The phenyl groups at the axial phosphorus centre P2 tilt to a lesser degree (Figure 2 and 3; Table 1) and may well be close to being parallel to the idealised C_3 axis.

tripodCo^I Complexes

Starting from Co^{II} Precursors

*tripod*Co^I complexes should be accessible from *tripod*Co^{II} compounds, irrespective of whether their cyclovoltammetric reduction is reversible or not. In the case of a reversible reduction one would expect the reduction product to have the same composition as the Co^{II} starting material as well as a similar structure. An irreversible reduction, on the other hand, does not necessarily mean that the compound decomposes to a complex mixture of products, it only means that the product will have a structure and possibly constitution which is different from the starting material. Preparative reduction has therefore been conducted for [*tripod*CoL$_2$] species whose cyclovoltammograms show reversible reductions, such as **5a**$^{2+}$ and **6a**, as well as those which show irreversible ones, such as **6b/c** (Tables 3 and 4).

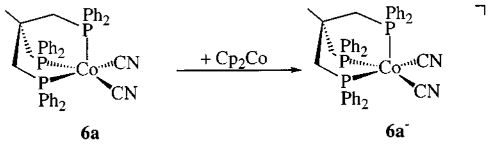
An example of a [*tripod*Co^{II}L$_2$] compound which undergoes irreversible reduction but still selectively produces a specific *tripod*Co^{I} compound is [*tripod*Co^{I}Cl$_2$] (**1**) which is preparatively reduced to [*tripod*Co^{I}Cl].[2a,2b,2f] With this in mind the pseudo-halide derivatives **6b/c**, which show an irreversible reduction step in their cyclovoltammograms, may well be expected to selectively produce [*tripod*Co^{I}] derivatives upon preparative reduction. This expectation is born out by the successful synthesis of **7a** from **6b** using activated zinc powder as the reductant (Scheme 7).



Scheme 7

Brown **6b** produces green **7a** which is obtained as a microcrystalline powder (analytical and spectroscopic data in Tables 3 and 4). Crystals of **7a** are obtained by vapour diffusion of petroleum ether (boiling range 40−60 °C) into its CH$_2$Cl$_2$ solutions. The coordination around the Co^{I} centre of **7a** can be described as a trigonally distorted tetrahedron (Figure 4; Table 1) as is characteristic of compounds [*tripod*Co^{I}L].[2a,2b,2n] Compound **7a** is found to be paramagnetic with two unpaired electrons per formula unit. This is to be expected if the coordination environment around the d^8-Co^{I} centre of **7a** is an idealised tetrahedron. Two of the P−Co−P angles are about 90°; the P−Co−L angles are found to be around 120°. The rotational position of the phenyl groups closely correspond to a C_3-symmetric arrangement with three of these groups being almost parallel to the idealised C_3 axis and the three other ones (Figure 4; Table 1) being inclined in similar extents in this direction in a propeller type arrangement.

Since the five-coordinate Co^{II} compound **6b** forms the four-coordinate Co^{I} species **7a** it is clear why the cyclovoltammetric reduction is irreversible. Clearly, a rapid ligand dissociation process is initiated when **6b** undergoes one-electron reduction. With **6a** the electrochemical behaviour is the reverse of the one found for **6b**. Compound **6a** undergoes reversible reduction while its oxidation is irreversible whereas **6b** is reversibly oxidised with the reduction being irreversible. Reduction of **6a** by Cp$_2$Co is predicted to produce the five-coordinate compound [*tripod*Co^{I}(CN)$_2$]$^-$, **6a**$^-$ (Scheme 8).



Scheme 8

The salt containing **6a**$^-$ as the anion and Cp$_2$Co$^+$ as the cation is obtained as a microcrystalline red-brown material. It has not been possible to obtain it in an analytically pure form. On the other hand FAB-MS spectra clearly demonstrate its composition from [*tripod*Co^{I}(CN)$_2$]$^-$ (m/z = 737) and Cp$_2$Co$^+$ (m/z = 189). The presence of cyano ligands is indicated by a weak IR absorption at 2100 cm^{-1}. The corresponding broad and weak absorption is not shifted by much compared to the starting compound **6a**. The observed bands should be composed of an envelope of two vibration modes (sym. and antisym.) which are not individually resolved. The ^{31}P-NMR spectra of **6a**$^-$ show a signal characteristic for an η^3-coordinated *tripod* ligand at δ = 31.

Since the Cp$_2$Co$^+$ salt of **6a**$^-$ could not be isolated as an analytically pure compound an alternative synthesis of **6a**$^-$ was tested. [*tripod*^{I}Co(CO)$_2$]$^+$, which is known to undergo carbonyl substitution under photochemical activation[2c−2e] reacts with NaCN to also produce **6a**$^-$. The reaction is,

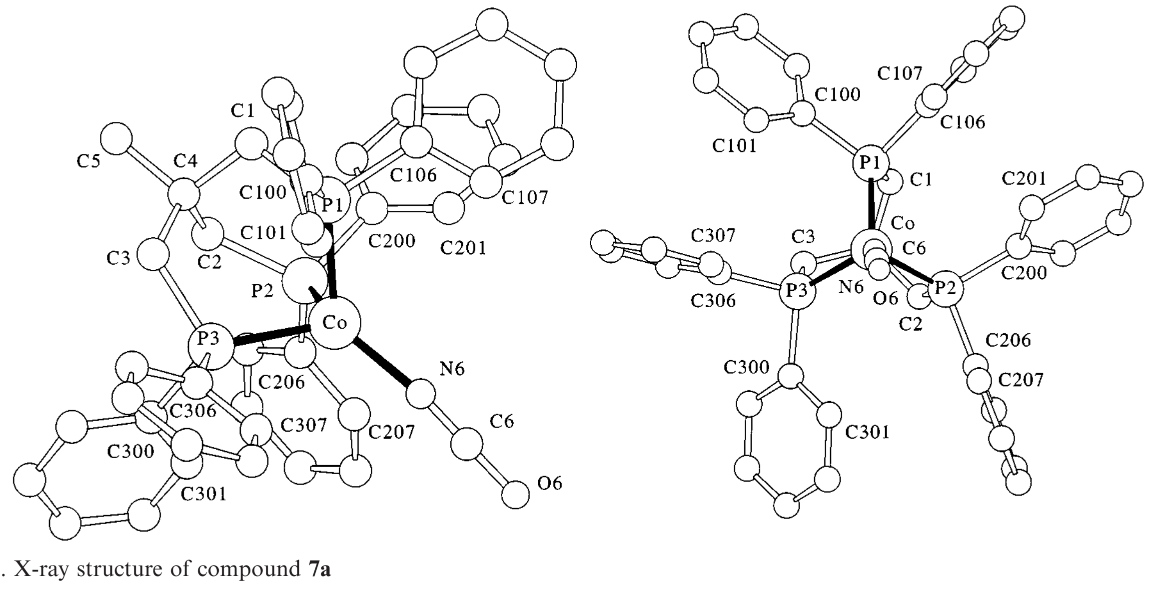
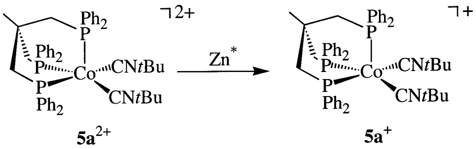


Figure 4. X-ray structure of compound **7a**

however, not as clean as the one starting from **6a**. The product obtained from [*tripod*$Co^I(CO)_2$]$^+$, while showing the FAB^- signal of **6a**$^-$ (m/z = 737), is found to be contaminated by species in which the ligand groups of the *tripod* ligand are partially decoordinated (^{31}P NMR: $\delta = -27$).

If cyanide is viewed as a pseudo-halide species, the five-coordination of **6a**$^-$ is in contrast to the four-coordination of **7a**. In view of the backbonding properties of the cyanide ligand the five-coordination of **6a**$^-$ corresponds to the five-coordination of [*tripod*$Co^I(CO)_2$]$^+$. This latter view leads to the expectation that the reduction of the isonitrile derivatives **5**$^{2+}$ might produce stable Co^I derivatives, since isonitrile ligands have more in common with carbonyl ligands than their isoelectronic relatives CN^-.[8] The reversible cyclovoltammetric reduction of **5a**$^{2+}$ is mirrored by the straightforward preparative reduction of **5a**$^{2+}$ to **5a**$^+$ by activated zinc powder (Scheme 9).



Scheme 9

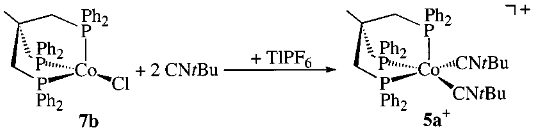
Compound **5a**$^+$ is isolated as its PF_6^- salt after chromatography on SiO_2 as a microcrystalline powder with almost the same orange yellow colour as characteristic for starting material **5a**$^{2+}[(PF_6)^-]_2$. The cyclovoltammogram observed for **5a**$^+$ is the same as the one observed for **5a**$^{2+}$ with the reduction wave of **5a**$^{2+}$ corresponding to the oxidation wave of **5a**$^+$ (Table 3, Experimental Section). Compound **5a**(PF_6) is a diamagnetic salt showing well-resolved NMR spectra (Experimental Section). This may be taken as a further proof of the five-coordination of its cobalt centre since four-coordination would lead to paramagnetism (see **7a**). Single crystals were grown by dissolving **5a**(PF_6) in CH_2Cl_2 and allowing Et_2O to diffuse into this solution. After several trials, a few crystals suitable for X-ray crystallography could be obtained. These crystals were found to contain a $PF_2O_2^-$ counterion instead of the PF_6^- counterion of the starting material due to hydrolysis during the crystallisation experiments. While the counterion shows disorder, in the crystal the cation **5a**$^+$ is completely ordered (see Experimental Section).

The structure of the cation of **5a**$^+$ is very similar to the structure of **5c**$^{2+}$ (not taking into account the different substituents of the isonitrile ligands: **5c**$^{2+}$: $C_6H_{11}NC$; **5a**$^+$: C_4H_9NC), Figure 2 and 3). The idealised square-pyramidal coordination around the cobalt centres is evident from Figure 2 as well as from the data in Table 1. Co−P and Co−L bond lengths are longer in the Co^{II} compound **5c**$^{2+}$ as compared to those in the Co^I species **5a**$^+$. Arguments based on ionic radii would lead one to expect the contrary. Models based on covalent bonding characterise **5a**$^+$ as an electron-precise 18-electron compound with the maximum number of valence electrons involved in bonding whereas **5c**$^{2+}$ has a 17-electron configuration and thus one bonding electron less than **5a**$^+$. The observed shortening of the bond lengths when going from the 17-electron compound **5c**$^{2+}$ to the 18-electron species **5a**$^+$ is thus easily understood. There is only one other pair of *tripod*Co derivatives for which the structure of the Co^I and the Co^{II} form is known. [*tripod*Co(η^3-allyl]$^{m+}$ (m = 0, 1) exists in the two different oxidation states Co^I and Co^{II}.[2n,3b] [With modified tripodal ligands such as $P(CH_2CH_2PPh_2)_3$ other structurally characterised pairs of Co^I/Co^{II} redox couples are known.][3l,3k] The same regularities observed for **5a**$^+$/**5c**$^{2+}$ are found for [*tripod*Co(η^3-allyl]$^{m+}$ (m = 0, 1).[2n,3b] The Co−P bonds in the Co^{II} species are some 8 pm longer than the ones in the Co^I derivative. The difference between the lengths of the basal and apical Co−P bonds is apparent for the cobalt(II) species ($Co-P_{apical}$: 230 pm; $Co-P_{basal}$: 221 pm) while these bonds are almost equal for the Co^I compound (215−217 pm).[2n,3b] A similar trend is evident when comparing the Co−P distances of **5c**$^{2+}$ and **5a**$^+$ (Table 1).

While isonitriles RNC are strongly backbonding ligands, nitriles RCN are far less so.[8] While the isonitrile derivative [*tripod*$Co^{II}(CNR)_2$]$^{2+}$ (**5a**$^{2+}$) produces the stable five-coordinate Co^I reduction product **5a**$^+$, the corresponding nitrile derivatives [*tripod*$Co^{II}(RCN)_2$]$^{2+}$ (**3**$^{2+}$) are expected to produce less stable Co^I species since charge delocalisation into the nitrile ligand will not help to stabilise these compounds to a great extent. Nevertheless, compounds **3**$^{2+}$ have been found to undergo reversible reduction[3d] indicating that relatively long lived five-coordinate species **3**$^+$ are produced. One-electron reduction is not immediately followed by a ligand-dissociation step. This is in contrast to the behaviour of the five-coordinate isocyanate derivative [*tripod*$Co^{II}(NCO)_2$] (**6b**) which produces the four-coordinate [*tripod*$Co^I(NCO)$] (**7a**) upon reduction. When [*tripod*$Co^{II}(NCMe)_2](BF_4)_2$[3d] is treated with activated zinc powder, a blue solution is immediately obtained from the green solution of the starting material. When the excess zinc powder is filtered off, this solution turns brown. No single compound could be isolated from these solutions and it remains speculative whether the blue or brown colour is due to [*tripod*$Co^I(RCN)_2$]$^+$.

Starting from Co^I Precursors

It was felt that starting from appropriate Co^I compounds might solve the problem of producing nitrile derivatives of *tripod*Co^I. The corresponding synthetic procedure was tested with the synthesis of the isonitrile compound **5a**$^+$ from [*tripod*Co^ICl] (**7b**) (Scheme 10).

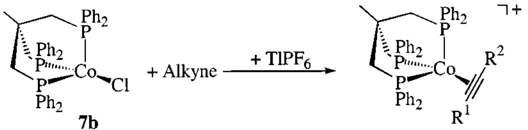


Scheme 10

Since it is known that **5a**$^+$ is a stable compound (see above) one should be able to isolate it if the procedure works. When a beige suspension of **7b** in THF is treated with $TlPF_6$, a white precipitate of TlCl forms leading to a yellow solution of [*tripod*Co^IL_n]$^+$ where L should be a THF ligand. When this mixture is treated with two equivalents of *t*BuNC, an immediate colour change is observed and **5a**$^+$(PF$_6$)$^-$ is obtained in good yield. The analytical and spectroscopic data of the product correspond to those obtained when **5a**$^+$ is prepared from **5a**$^{2+}$ by reduction (see above). The propensity of [*tripod*CoCl] to produce compounds [*tripod*CoL$_2$]$^+$ when activated by Tl$^+$ had already been used for the synthesis of such compounds where L$_2$ is a diene or a heterodiene ligand.[2f] The reaction principle therefore appears to be quite general and the reaction of **7b** with nitriles should produce nitrile derivatives of *tripod*Co^I (**3**$^+$). On addition of nitriles to the suspensions prepared from **7b** and TlPF$_6$ (see above), an immediate colour change from yellow to brown is observed. The brown products could, however, not be isolated and their formulation as **3**$^+$ may be erroneous. An argument for this formulation is the observation that such brown solutions are also obtained when **3**$^{2+}$ is reduced by activated zinc powder (see above).

The fact that the brown compounds cannot be isolated as such shows that they are reactive species which by themselves should be able to undergo ligand substitution processes. As a test for this hypothesis the brown solutions were treated with tolane since it is known that [*tripod*Co^I(η^2-alkyne)] compounds are stable isolable species.[2g,2h] The salt of **8a**$^+$ is obtained by this procedure in yields around 90% (Table 2 and 5). Compound **8a**$^+$ had been obtained by L. Sacconi et al.[2g] who used the in situ reduction of Co^{II} salts by 2-propanol in the presence of *tripod* and tolane as their preparative method. The yields obtained by this procedure are not given in the literature but reproduction of these syntheses resulted in yields around 30%.[2i]

The sequence of **7b** → **3b**$^+$ → **8a**$^+$ is successful. It shows that alkynes are excellent probes for trapping kinetically labile *tripod*Co^I intermediates (Scheme 11). Such intermediates are of course also formed when solutions of **7b** are treated with Tl$^+$ and, as expected, such solutions react with alkynes to produce the corresponding [*tripod*Co^I(η^2-alkyne)] complexes **8**$^+$ as well.



	R^1	R^2
8a$^+$	Ph	Ph
8b$^+$	Ph	H
8c$^+$	*t*Bu	H
8d$^+$	H	CH$_2$OH

Scheme 11

The reaction is also tolerant to terminal alkynes (**8b**$^+$, **8c**$^+$) and OH substituents on the alkyne ligand (**8d**$^+$).

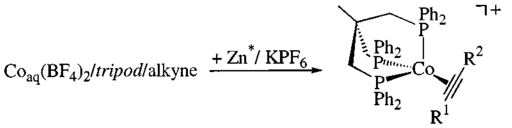
Based on the observation made by L. Sacconi et al.[2g] that compounds **8a**$^+$ and **8b**$^+$ are obtained from a mixture of Co(ClO$_4$)$_{2aq}$/*tripod*/alkyne with 2-propanol as the reductant it is reasonable to test this type of reaction by using a more conventional reductant instead of 2-propanol. A mixture of Co$^{II}_{aq}$(BF$_4$)$_2$ and *tripod* reacts with alkynes when treated with activated zinc powder as reductant (Scheme 12).

It is found that this synthetic procedure works well, with apparently almost quantitative formation of **8**$^+$; yields of the isolated pure compounds are only reduced by loss during chromatographic work up. This simple reaction protocol is also tolerant to terminal alkynes (**8b**$^+$, **8c**$^+$) while alcoholic groups are not tolerated. The 18-electron compounds **8**$^+$ show well-resolved NMR spectra (Table 5). All groups of signals in their ^{1}H-, ^{13}C-, and ^{31}P-NMR spectra

Table 2. Syntheses, yields and properties of compounds **2**–**8** (see Experimental Section)

Compound	Method	Co-ligand	Colour	Yield [%]	Melting point [°C][a]
2PF$_6$		104 mg benzonitrile	orange-brown	75	170
3a(PF$_6$)$_2$	A	208 mg benzonitrile	dark-green	85	170
	B	208 mg benzonitrile	dark-green	79	
3b(PF$_6$)$_2$	A	43 mg acetonitrile	green	74	165
4PF$_6$		84 mg *tert*-butyl isonitrile	green	82	185
5a(PF$_6$)$_2$	A	84 mg *tert*-butyl isonitrile	red-orange	76	210
	B	168 mg *tert*-butyl isonitrile	red-orange	82	
5b(PF$_6$)$_2$	A	110 mg cyclohexyl isonitrile	red-orange	70	200
5aPF$_6$	C	168 mg *tert*-butyl isonitrile	red-orange	59	180
	D	168 mg *tert*-butyl isonitrile	red-orange	51	
6a		98 mg NaCN	claret	94	
6b		164 mg KOCN	brown	71	175
6c		196 mg KSCN	beige	59	170
7a			brown-green	89	170
8PF$_6$	G	178 mg diphenylethyne	dark-green	91	175
	H	178 mg diphenylethyne		88	
8PF$_6$	G	102 mg phenylethyne	green	77	161
	H	102 mg phenylethyne		61	
8PF$_6$	G	82 mg 2,3-dimethylbutyne	green	59	155
	H	82 mg 2,3-dimethylbutyne		51	
8PF$_6$	G	57 mg propynol	dark-green	66	140

[a] Decomposition.



	R^1	R^2
8a$^+$	Ph	Ph
8b$^+$	Ph	H
8c$^+$	*t*Bu	H

Scheme 12

can be unequivocally assigned (Table 5). The coordination of both of the carbon atoms of the alkyne ligand is clear from the ^{13}C-NMR signals relating to these atoms. The η^2 coordination of the alkynes in compounds of the type **8**$^+$ is also indicated by comparison with a structurally analysed example.[2n] There is only one ^{31}P-NMR signal for each compound **8**$^+$. In any static structure with a C_2-symmetric alkyne, the juxtaposition of the C_3-symmetric P3−Co entity and the C_2-symmetric alkyne with the coinciding C_2 and C_3 axes give a minimum of two different phosphorus environments, and generally three different types of environment for the phosphorus atoms will exist. A single ^{31}P-NMR peak, observed for all compounds **8**$^+$, indicates that the alkynes rotate around the constitutional C_3 axis of the *tripod*Co template such that all the different environments are averaged in the time domain of the NMR experiment. Rapid rotation of the co-ligands around the idealised C_3 axis of the *tripod*Co template with only one ^{31}P-NMR signal being apparent − where a static structure would lead to at least two signals − is often observed.[2f]

Compounds **8**$^+$ are diamagnetic, which means that the alkyne acts as a 4-electron donor ligand, so that **8**$^+$ are 18-electron compounds. Oxidation of **8**$^+$ occurs at potentials above 1000 mV (vs. SCE, Table 5) and is irreversible throughout. This means that the formal oxidation products **8**$^{2+}$ are unstable. Reduction, on the other hand, is reversible or at least quasireversible for all compounds **8**$^+$ (Table 5) occurring between −600 and −800 mV (vs. SCE). The neutral reduction products **8** are formal 19-electron compounds. Their stability is thus unexpected. This may be explained by the argument that alkynes are known to act as rather flexible donor molecules, which may supply between two and four electrons.[8] In this sense the extra electron would be localised on the alkyne ligands. Any attempts to isolate the neutral compounds **8** have been unsuccessful so far.

No distinct reaction product could be obtained from Co$^{II}_{aq}$(BF$_4$)$_2$/*tripod* with HC≡C−CH$_2$OH as the alkyne and activated zinc powder as the reductant, while the reaction based on **7b** as the starting material gave the corresponding alkyne derivative **8d**$^+$ in high yield. When Me$_3$SiC≡CH is used as the alkyne, both types of reaction failed to produce an isolable η^2-alkyne compound of the type **8**$^+$. By the appropriate colour change (yellow to green with **7b** as the starting material and red-brown to green with Co$^{II}_{aq}$ as the starting compound) the production of an η^2-alkyne derivative **8**$^+$ is indicated in each case. However, on evaporation of the solvent the green-brown species decomposes to produce a grey residue from which no compounds can be extracted showing any indication (MS, ^{31}P NMR) of the presence of species of the type **8**$^+$. With TMSC≡CTMS the observations are again different. Independent of which reaction methodology is applied, no colour change is observed. With its TMS substituents, the alkyne is too bulky to enter the reaction pocket of the *tripod*cobalt template. If the alkyne substituents were to bend backwards as they do with coordinated alkynes (C≡C−R = 140°[2h]) TMSC≡CTMS might possibly fit into the pocket. However, bending will only start to occur when the coordinatively unsaturated metal and the alkyne triple bond are close enough to each other. This appears to be impossible with the small [*tripod*M]$^+$ reaction pocket and the bulky TMSC≡CTMS alkyne. If the *tripod*Co entity is seen as a protective group for protecting alkynes from undergoing standard organic transformations the observed selective response to the bulkiness of the alkyne substituents might find its application in organic synthesis.

Conclusion

The chlorine groups of [*tripod*Co^{II}(Cl)$_2$] (**1**) may be substituted in a stepwise manner by two different donor ligands to produce [*tripod*Co^{II}LL′]$^{2+}$. A broader range of preparative methods exists for the synthesis of compounds [*tripod*Co^{II}L$_2$]$^{n+}$ (n = 0, 2) with two equal donor ligands (L = RCN, RNC, CN$^-$, OCN$^-$, SCN$^-$).

Cobalt(II) derivatives [*tripod*Co^{I}L$_2$] (L = RNC) or [*tripod*Co^{I}L] (L = NCO$^-$, alkyne) are available by different routes starting from the *tripod*Co^{I} precursors [*tripod*Co^{I}(CO)$_2$]$^+$ or [*tripod*Co^{I}Cl]. They are also accessible from Co^{II} precursors using Co$^{II}_{aq}$ under reducing conditions.

Experimental Section

General Remarks: Unless otherwise noted, all manipulations were carried out under argon by means of standard Schlenk techniques. All solvents were dried by standard methods and distilled under argon (PE 40/60 = petroleum ether, boiling range 40−60 °C).[9] The zinc powder (Merck) used in some of the reactions was activated by stirring it under argon with a magnetic bar for 12 h. For ultrasonic activation of reaction mixtures an ultrasonic bath (Bender & Hobein, Laboson 200) was used. *tripod*Co^{II}Cl$_2$ was prepared in accordance with a literature procedure.[3i] All other chemicals were obtained from commercial suppliers and used without further purification. The solvents [D$_6$]acetone, CDCl$_3$, and CD$_2$Cl$_2$ used for NMR-spectroscopic measurements were degassed by three successive freeze-pump-thaw cycles and dried over 4-Å molecular sieves. − NMR: Bruker Avance DPX 200 operating at 200.12 MHz (^{1}H), 50.323 MHz (^{13}C{^{1}H}), 81.015 MHz (^{31}P{^{1}H}) T = 303 K, unless stated otherwise; chemical shifts (δ) in ppm with respect to [D$_6$]acetone (^{1}H: δ = 2.05; ^{13}C: δ = 29.8, 206.2), CDCl$_3$ (^{1}H: δ = 7.27; ^{13}C: δ = 77.0) and CD$_2$Cl$_2$ (^{1}H: δ = 5.32; ^{13}C: δ = 53.8) as internal standards. ^{31}P chemical shifts (δ) are in ppm with respect to 85% H$_3$PO$_4$ (^{31}P: δ = 0) as external standard. − IR: Bruker IFS-66, KBr disks. − EPR: Bruker ESP 300E (X-band, external standard diphenylpicrylhydrazyl). All measurements were carried out at 20 °C in a standard cavity ER 4102St. − Magnetic measurements: Sherwood Scientific Magnetic Susceptibility Balance MSB, MK I, JM Alfa # 9997 (Sherwood Scientific Ltd.), calibration with $HgCo(SCN)_4$. All measurements were carried out at 20 °C. − UV/Vis: Perkin−Elmer Lambda 19. − Fast-atom bombardment (FAB): Finnigan MAT 8230, xenon, matrix: 4-nitrobenzyl alcohol. − HR-MS (FAB): JEOL JMS 700, matrix: 4-nitrobenzyl alcohol. − Elemental analyses: Microanalytical Laboratory of the Organisch-Chemisches Institut, Universität Heidelberg. − Melting points (not corrected): Gallenkamp MFB-595 010. − Photochemical activation: mercury high-pressure lamp (Hanau, TQ 150), Duran glass apparatus. − Cyclic voltammetry: Metrohm Universal Meß- und Titriergefäß, Metrohm GC electrode RDE 628, platinum electrode, SCE electrode, Princeton Applied Research potentiostat Model 273, 10^{-3} M in 0.1 M nBu_4NPF_6/CH_2Cl_2. Reactions described as reversible show a square-root dependence of current versus scan speed in the range of 50 to 800 mVs^{-1}.

General Procedure for the Synthesis of [*tripod*Co^{II}(Cl)(L)]PF_6 Complexes (L = NCPh: 2; L = CN*t*Bu: 4): [*tripod*$CoCl_2$] (**1**) (753 mg, 1 mmol) was dissolved in acetone (15 mL) to give a green-blue solution. The appropriate co-ligand (Table 2, 1 mmol) and KPF_6 (185 mg, 1 mmol) was added to the solution. While stirring the reaction mixture for 15 min, a colour change was observed − orange-brown in the case of nitriles and green in the case of isonitriles. The solvent was evaporated in vacuo and the residue dissolved in CH_2Cl_2. The solution was filtered to remove KCl. The solvent was evaporated again and the residue washed with Et_2O (5 × 5 mL). Removal of the solvent afforded **2**PF_6 and **4**PF_6. For analytical data of the compounds see Table 3 and Table 4.

General Procedure for the Synthesis of [*tripod*Co^{I}LL′]$(PF_6)_2$ Complexes from Compounds [*tripod*Co^{II}(Cl)(L)]PF_6

Method A [L = L′ = NCPh ($3a^{2+}$); L = NCPh, L′ = NCMe ($3b^{2+}$); L = CN*t*Bu ($5a^{2+}$); L = CN*t*Bu, L′ = CNCy ($5b^{2+}$)]: The appropriate [*tripod*Co^{II}(Cl)(L)]PF_6 compound (L = NCPh: **2**PF_6; L = CN*t*Bu: **4**PF_6, 1 mmol) and $TlPF_6$ (349 mg, 1 mmol) were dissolved in THF (20 mL). The appropriate co-ligand L′ (Table 2, 1 mmol) dissolved in THF (5 mL) was added to the suspension and the reaction mixture treated in an ultrasonic bath for 5 min. During this time the reaction mixture changed its colour − orange-brown to green in the case of nitriles, green to red-orange in the case of isonitriles. The solvent was evaporated in vacuo and the residue dissolved in CH_2Cl_2. The solution was filtered to remove TlCl. The solvent was evaporated again, the residue dissolved in THF (1 mL) and precipitated with Et_2O (5 × 5 mL). Removal of the solvent afforded **3a**$(PF_6)_2$, **3b**$(PF_6)_2$, **5a**$(PF_6)_2$, and **5b**$(PF_6)_2$. For analytical data of the compounds see Table 3 and 4.

Method B [L = NCPh ($3a^{2+}$); L = CN*t*Bu ($5a^{2+}$)]: 1 mmol (753 mg) of [*tripod*Co(Cl)$_2$] (**1**) and 2 mmol (700 mg) of $TlPF_6$ were dissolved in 20 mL of THF. 2 mmol of the appropriate ligand L (Table 2), dissolved in 5 mL of THF, was added to the reaction mixture which was then treated in an ultrasonic bath for 15 min. During this procedure the reaction mixture changed its colour − blue-green to green in the case of the nitrile and to red-orange in the case of the isonitrile. The solvent was evaporated in vacuo and the residue dissolved in CH_2Cl_2. The solution was filtered to remove the TlCl produced. The solvent was evaporated again, the residue dissolved in 1 mL of THF and precipitated with 5 mL of Et_2O five times. Removal of the solvent afforded **3a**$(PF_6)_2$ and **5a**$(PF_6)_2$. For analytical data of the compounds see Table 3 and 4.

Preparation of [*tripod*Co^{I}(CN*t*Bu)$_2$]PF_6 {[5a(PF_6)]}

Method C: Freshly prepared [*tripod*CoCl][2f] (**1**) (718 mg, 1 mmol) and $TlPF_6$ (349 mg, 1 mmol) were suspended in THF (20 mL) to give a yellow solution while a fine white powder precipitated. *tert*-Butyl isocyanide (168 mg, 2 mmol), dissolved in THF (5 mL), was added dropwise to the suspension and the reaction mixture treated in an ultrasonic bath for 10 min. During this time the reaction mixture changed its colour from brown-orange to red-orange. The solvent was evaporated in vacuo and the residue dissolved in CH_2Cl_2. The solution was filtered to remove $TlPF_6$. The solvent was evaporated and the residue purified by chromatography on SiO_2 (ICN 32-63, 60 Å) with a solvent mixture of Et_2O/CH_2Cl_2 (5:1) to give the PF_6 salt of [*tripod*Co(CN*t*Bu)$_2$]$^+$. − MS-FAB: 849 [*tripod*Co(CN*t*Bu)$_2$]$^+$. − ^1H NMR ($CDCl_3$): 1.37 (s, 18 H, *ligand*-CH_3), 1.58 (br., 4 H, *tripod*-CH_3), 2.77 (br., 6 H, CH_2), 7.16−7.74 (m, 30 H, aromatic H). − ^{13}C NMR ($CDCl_3$): 25.9 (s, *ligand*-CH_3), 30.5 (m, CH_2), 38.6 (s, *ligand*-C_q), 38.9 (m, *tripod*-CH_3), 39.3 (s,

Table 3. Analytical data for compounds 2^+ to **7**

Compound	IR: $\tilde{\nu}$ [cm^{-1}]	EPR[a]	$\mu_{eff.}$ [B. M.][b]	Cyclovoltammetry potential [mV][a]
2PF_6	PF: 840 vs NC: 2255 w	$g_1 = 2.14$ ($A_1 \approx 24$ G) $g_2 = 2.10$ ($A_2 \approx 30$ G)	2.0	−
3a$(PF_6)_2$	PF: 840 vs NC: 2325 w	$g \approx 2.1$	2.0	−
3b$(PF_6)_2$	PF: 840 vs NC: 2320, 2285 w	$g \approx 2.1$	2.0	−
4PF_6	PF: 840 vs CN: 2185 vs	$g \approx 2.1$	1.9	−
5a$(PF_6)_2$	PF: 840 vs CN: 2120, 2190 vs	$g \approx 2.1$	2.0	$E_{1/2} = 120$, $\Delta E = 150$ $E_p^a = 1600$; $\Delta E_{Fc} = 140$
5b$(PF_6)_2$	PF: 840 vs CN: 2110 vs	$g \approx 2.1$	1.9	−
6a	CN: 2096, 2101 w	$g = 2.10$ ($A = 22$ G)	1.8	$E_{1/2} = -1076$, $\Delta E = 110$ $E_p^a = 840$; $\Delta E_{Fc} = 105$
6b	OCN: 2230, 2210 s	$g_1 = 2.12$ ($A_1 \approx 23$ G) $g_2 = 2.10$ ($A_2 \approx 30$ G)	2.1	$E_{1/2} = 325$, $\Delta E = 120$ $E_p^c = -1255$; $\Delta E_{Fc} = 140$
6c	SCN: 2100, 2070 s	$g_1 = 2.14$ ($A_1 \approx 24$ G) $g_2 = 2.11$ ($A_2 \approx 31$ G)	2.1	$E_{1/2} = 500$, $\Delta E = 120$ $E_p^c = -995$; $\Delta E_{Fc} = 210$
7a	OCN: 2200 s	−	2.9	−

[a] All measurements were performed in CH_2Cl_2 solutions at 20 °C at scan speeds of 200 mVs^{-1}. − [b] Magnetic balance MSB MK I, 20 °C, see Experimental Section.

Table 4. Analytical data for compounds **2^+** to **7**

Compound	Mass spectrometry (*m*/*z*)	HR-FAB (*m*/*z*) calculated/*found*	Elemental analysis calculated/*found*
2PF_6	821 [M^+] 718 [M^+ − NCPh]	–	C: 55.94/*56.28* H: 4.41/*4.97* N: 1.33/*0.71*[a]
3a$(PF_6)_2$	683 [*tripod*Co^+]	–	C: 55.99/*56.13* H: 4.19/*4.23* N: 2.37/*2.35*
3b$(PF_6)_2$	683 [*tripod*Co^+]	–	C: 50.93/*51.22* H: 4.11/*4.67* N: 2.33/*2.52*[a]
4PF_6	767 [M^+ − Cl] 718 [M^+ − CN*t*Bu]	–	C: 58.33/*58.80* H: 5.12/*5.93* N: 1.48/*2.41*
5a$(PF_6)_2$	849 [M^+] 766 [M^+ − CN*t*Bu]	849.3006/*849.3085*	[b]
5b$(PF_6)_2$	875 [M^+] 792 [M^+ − CN*t*Bu] 767 [M^+ − CNCy]	875.3223/*875.3244*	[b]
6a	736 [M^+] 709 [M^+ − CN] 683 [M^+ − 2 CN]	–	C: 70.21/*70.34* H: 5.39/*5.52* N: 3.81/*3.93*
6b	767 [M^+]	–	C: 67.27/*65.99* H: 5.12/*5.07* N: 3.64/*3.54*
6c	799 [M^+]	–	C: 59.73/*58.17* H: 4.67/*4.50* N: 3.16/*3.11*[a]
7a	726 [M^+]	–	C: 69.52/*69.54* H: 5.42/*5.54* N: 1.93/*1.93*

[a] One CH_2Cl_2 solvate molecule per formula unit. − [b] Due to varying contents of solvent molecules in the crystals elemental analysis was not satisfactory.

tripod-C_q), 123.4−133.8 (aromatic C), 156.1 (s, CN). − ^{31}P NMR ([D$_6$]acetone): δ = −144.2, (sept, $^1J_{PF}$ = 713 Hz), 32.4. − IR: ṽ [cm^{-1}] = 840 (vs, PF_6), 2140 (vs, CN). − HR-FAB (calculated/*found*): 849.30066/*849.3085*. − Cyclovoltammetry (CH_2Cl_2): $E_{1/2}$ = 125 mV, ΔE = 140 mV; E_p^a = 1600 mV, ΔE_{Fc} = 110 mV. − Elemental analysis [calculated for composition as found by X-ray analysis of the same batch **5a**$(PF_2O_2^-)\cdot 0.4\ Et_2O \cdot 0.25\ CH_2Cl_2$]: calcd. C 61.57, H 5.77, N 2.82; found C 60.22, H 6.14, N 3.62.

Method D: $Co_{aq}(BF_4)_2$ (342 mg, 1 mmol) and *tripod* (624 mg, 1 mmol) were dissolved in CH_2Cl_2/ethanol (1:1, 30 mL) to give a brown-red solution. A five-fold excess of zinc powder and *tert*-butyl isocyanide (168 mg, 2 mmol), dissolved in THF (5 mL), were added dropwise. The reaction mixture was treated in an ultrasonic bath for 5 min. The solvent was removed in vacuo, the residue dissolved in CH_2Cl_2 and filtered to remove $ZnCl_2$ and excess zinc powder. The solvent was evaporated, the residue dissolved in THF and treated with a three-fold excess of KPF_6. The solvent was removed in vacuo, the residue dissolved in CH_2Cl_2 and filtered to remove excess KPF_6 and KBF_4. The solvent was evaporated and the residue purified by chromatography on SiO_2 (ICN) with a solvent mixture of Et_2O/CH_2Cl_2 (5:1) to give the PF_6 salt of [*tripod*Co^I(CN*t*Bu)$_2$]$^+$ (**5a**PF_6). For analytical data see above.

Preparation of [*tripod*$Co^{II}(CN)_2$] (6a): $Co_{aq}(BF_4)_2$ (342 mg, 1 mmol) and *tripod* (624 mg, 1 mmol) were dissolved in CH_2Cl_2/EtOH (1:2, 30 mL) to give a brown-red solution. NaCN (98 mg, 2 mmol), dissolved in ethanol/water (1:1, 20 mL), was added dropwise to give a claret solution. The solvent was removed in vacuo, the residue dissolved in CH_2Cl_2 and filtered to remove $NaBF_4$. Concentration afforded **6a** as claret powder. Single crystals suitable for X-ray analysis were obtained by vapour diffusion of Et_2O into a CH_2Cl_2 solution of **6a**.

Generation of [*tripod*$Co^I(CN)_2$]$^-$ ($6a^-$). − Method E: Compound **6a** (739 mg, 1 mmol) and Cp_2Co (189 mg, 1 mmol) were dissolved in 20 mL of THF. The colour of the solution changed from claret to brown. The solvent was evaporated and the residue washed with Et_2O (5 × 5 mL). − MS-FAB: FAB-positive: 189 [Cp_2Cp^+]; FAB-negative: 739 [*tripod*$Co^I(CN)_2$]$^-$. − ^{31}P NMR (CD_2Cl_2): δ = 32.4. − IR: ṽ [cm^{-1}] = 2100 (w, CN).

Method F: [*tripod*$Co^I(CO)_2$]PF_6[2c] (885 mg, 1 mmol) and NaCN (98 mg, 2 mmol) were suspended in THF (50 mL). The suspension was irradiated for 3 h. During this time a colour change from claret to brown was observed. The solvent was removed in vacuo and the brown residue washed Et_2O (5 × 5 mL). MS-FAB: FAB-negative: 739 [*tripod*$Co(CN)_2$]$^-$. − ^{31}P NMR (CD_2Cl_2): δ = 32.4. − IR: ṽ [cm^{-1}] = 2100 (w, CN).

General Procedure for the Synthesis of [*tripod*$Co^{II}(NCX)_2$] Complexes [X = O (6b); X = S (6c)]: $Co_{aq}(BF_4)_2$ (342 mg, 1 mmol) and *tripod* (624 mg, 1 mmol) were dissolved in CH_2Cl_2/ethanol (1:2, 30 mL) to give a brown-red solution. The appropriate salt KX (Table 2, 2 mmol), dissolved in solvent (methanol in the case of **6b**, Et_2O in the case of **6c**, 20 mL), was added. The solvent was removed in vacuo, the residue dissolved in CH_2Cl_2 and filtered to remove KBF_4. The solvent was evaporated and the residue washed with Et_2O at 0 °C (5 × 5 mL). For analytical data of the compounds see Table 3 and 4.

Preparation of [*tripod*Co^INCO] (7a): [*tripod*$Co^{II}(NCO)_2$] (**6b**) (767 mg, 1 mmol) was dissolved in THF (20 mL) and a five-fold excess of zinc powder added. The reaction mixture was treated in an ultrasonic bath for 5 min. The solvent was removed in vacuo, the residue dissolved in CH_2Cl_2 and filtered. After concentration, **7a** was obtained as microcrystalline brown-green powder. Single crystals suitable for X-ray analysis were obtained by vapour diffusion of Et_2O into a solution of **7a** in CH_2Cl_2. For analytical data of the compound see Table 3 and 4. The product corresponds in all its properties to the one obtained by an independent method.[2d]

General Procedure for the Synthesis of the PF_6 Salts of [*tripod*Co^I(η^2-alkyne)]$^+$ (8a$^+$−8d$^+$). − Method G: Freshly prepared [*tripod*CoCl][2f] (**1**) (718 mg, 1 mmol) and $TlPF_6$ (349 mg, 1 mmol) were suspended in THF (20 mL) to give a yellow solution while a fine white precipitate was formed. The appropriate alkyne (Table 2, 1 mmol) was added to the suspension and the reaction mixture treated in an ultrasonic bath for 10 min. During this procedure the reaction mixture changed its colour to green. The solvent was evaporated in vacuo and the residue dissolved in CH_2Cl_2. The solution was filtered to remove TlCl. The solvent was evaporated again and the residue (except **8d**$^+$) purified by chromatography on SiO_2 (ICN 32-63, 60 Å) with a solvent mixture of Et_2O/CH_2Cl_2 (5:1) to produce the PF_6 salts of **8a**$^+$−**8c**$^+$. In the case of **8d**$^+$ the solvent was evaporated and the residue was washed with Et_2O (5 × 5 mL). For analytical data of the compounds see Table 5.

Method H: $Co_{aq}(BF_4)_2$ (342 mg, 1 mmol) and *tripod* (624 mg, 1 mmol) were dissolved in CH_2Cl_2/EtOH (1:1, 30 mL) to give a brown-red solution. The appropriate alkyne (Table 2, 1 mmol) and a five-fold excess of zinc powder were added. The reaction mixture was treated in an ultrasonic bath for 5 min. The solvent was removed in vacuo, the residue dissolved in CH_2Cl_2 and filtered to remove $ZnCl_2$ and excess zinc powder. The solvent was evaporated, the residue dissolved in THF and treated with a three-fold excess of KPF_6. The solvent was removed in vacuo, the residue dissolved in CH_2Cl_2 and filtered to remove excess KPF_6 and KBF_4. The solvent was evaporated again and the residue purified by chromatography on SiO_2 (ICN 32-63, 60 Å) with a solvent mixture of Et_2O/CH_2Cl_2 (5:1) to produce the PF_6 salts of **8a**$^+$−**8c**$^+$. Analytical data of the compounds: Table 5.

X-ray Crystallographic Study: The measurements were carried out with a Siemens P4 four-circle diffractometer (**6a**) or a Nonius−Kappa CCD diffractometer (**5c**$^{2+}$, **5a**$^+$, **6b**, and **7a**), all using graphite-monochromated Mo-K_α radiation. In case of the Siemens P4 four-circle diffractometer measurements, the intensities of three reference reflections (measured every 100 reflections) remained constant throughout the data collection, thus indicating crystal and electronic stability. The data collected with the Siemens P4 diffractometer were corrected by standard methods including experimental absorption correction. The data from the Nonius−Kappa CCD device were processed by the standard Nonius software.[10] All calculations were performed using the SHELXT PLUS software package. Structures were solved by direct methods with the SHELXS-97 program and refined with the SHELXL-97 program.[11,12] Graphical handling of the structural data during solution and refinement was performed with XPMA.[13] Atomic coordinates and anisotropic thermal parameters of the non-hydrogen atoms were refined by full-matrix least-squares calculations. Table 6 and Table 7 compile the data for the structure determinations. The geometry of the counterion $PO_2F_2^-$ of **5c**$^{2+}$[$(PO_2F_2)^-$]$_2$ as found in this analysis is rather inaccurate due to disorder problems but is in overall agreement with the literature data.[5] This disorder could be resolved by the split-atom technique such that at one of these positions two different rotational positions were sufficient, whereas at the other position three to four rota-

Table 5. Analytical data for compounds **8a**$^+$ to **8d**$^+$

Compound	**8a**PF_6	**8b**PF_6	**8c**PF_6	**8d**PF_6
^{1}H{^{31}P} NMR	[D$_6$]acetone	CD_2Cl_2	$CDCl_3$	CD_2Cl_2
tripod-CH_3	1.83 br., 3 H	1.93 br., 3 H	1.89 br., 3 H	1.92 br., 3 H
tripod-CH_2	2.90 br., 6 H	2.64 br., 6 H	2.57 br., 6 H	2.60 br., 6 H
aromat. H	7.03−7.57 m, 40 H	7.06−7.59 m, 35 H	7.01−7.65 m, 30 H	7.04−7.52 m, 30 H
≡C−H	−	10.38 q, J_{PH} = 6 Hz, 1 H	9.84 br., 1 H	9.84 br., 1 H
ligand-CH_3	−	−	1.40 br. s, 9 H	−
≡C−CH_2	−	−	−	2.35 br., 2 H
^{31}P NMR	[D$_6$]acetone	CD_2Cl_2	$CDCl_3$	CD_2Cl_2
PPh_2	38.9 s	40.0 s	37.8 s	42.3 s
PF_6	−144.2, $^1J_{PF}$ = 713 Hz	−144.2, $^1J_{PF}$ = 713 Hz	−144.2, $^1J_{PF}$ = 713 Hz	−144.2, $^1J_{PF}$ = 713 Hz
^{13}C {^{1}H } NMR[a]	CD_2Cl_2	CD_2Cl_2	[b]	CD_2Cl_2
tripod-CH_3	36.9 m	36.6 br.	−	36.7 br.
tripod-CH_2	33.7 m	33.4 p-t, J = 13 Hz	−	33.9 p-t, J = 12 Hz
tripod-C_q	39.5 s	40.1 s	−	40.4 s
aromat. C	123.6−137.5 m	129.1−135.2 m	−	129.1−133.8 m
C≡*C*−C	178.3 s	174.6 s	−	177.9 s
C≡*C*−H	−	165.8 s	−	159.5 bs
≡C−*C*H_2	−	−	−	65.1 b
IR: $\tilde{\nu}$(PF) [cm^{-1}]	845	845	845	835
Mass spectrometry (*m*/*z*)	861 [M$^+$]	785 [M$^+$]	765 [M$^+$]	737 [M$^+$]
Cyclovoltammetry:	$E_{1/2} = -610$ $\Delta E = 195$	$E_{1/2} = -715$[d] $\Delta E = 150$	$E_{1/2} = -790$ $\Delta E = 65$	$E_{1/2} = -730$ $\Delta E = 90$
Potential [mV][c]	E_p^a =1210 ΔE_{Fc} = 130	E_p^a = 1110 ΔE_{Fc} = 140	E_p^a =1110 ΔE_{Fc} = 100	E_p^a =1025 ΔE_{Fc} = 120
UV/Vis [nm] (lmol^{-1}cm^{-1})[c]	370 (2260) 460 (1010) 590 (760)	370 (930) 610 (580)	470 (460) 600 (580)	350 (6710) 440 (1980) 580 (1105)
Elemental analysis: calculated/*found*	C: 65.61/*65.36* H: 4.91/*5.21*	C: 63.24/*63.12* H: 4.87/*5.16*	C: 57.90/*57.29*[e] H: 5.16/*5.41*	C: 59.74/*59.42* H: 4.90/*5.41*
HR-FAB (*m*/*z*): calculated/*found*	861.2379/*861.2366*	− −	765.2379/*765.2426*	− −

[a] CH_3, CH_2, CH, and C carbon atoms were determined in a 135° DEPT experiment. − [b] No satisfying ^{13}C-NMR spectra could be obtained due to disintegration of the compound during the measurement. − [c] All measurements were performed in CH_2Cl_2 at 20 °C. − [d] Quasi-reversible reduction. − [e] Calculated for one CH_2Cl_2 solvate per formular unit.

Table 6. Crystal data for compounds **5**$^{2+}$, **5**$^+$, and **6a**

Compound	**5a**$^+$(PF$_2$O$_2$)$^-$ [a]	**5c**$^{2+}$[(PF$_2$O$_2$)$^-$]$_2$[b]	**6a** [c]
Empirical formula	$C_{51}H_{57}CoF_2N_2O_2P_4$	$C_{55}H_{61}CoN_2O_4F_4P_5$	$C_{43}H_{39}CoN_2P_3$
Molecular mass	950.85	1103.89	735.60
Crystal system	monoclinic	orthorhombic	orthorhombic
Space group	*P*2$_1$ (No. 4)[12]	*Pbcn* (No. 60)[12]	*Pbca* (No. 61)[12]
Lattice constants	a = 1256.9(3) pm	a = 3676.6(7) pm	a = 1684.3(5) pm
	b = 1657.6(3) pm	b = 1449.3(3) pm	b = 1903.4(6) pm
	c = 1285.2(3) pm	c = 2057.7(4) pm	c = 2221.5(8) pm
	β = 99.50(3)°	β = 90°	β = 90°
Cell volume	3561 × 10^6 pm^3	10938 × 10^6 pm^3	7122 × 10^6 pm^3
Molecular units per cell	Z = 2	Z = 8	Z = 8
Density (calculated)	1.260 g cm^{-3}	1.358 g cm^{-3}	1.372 g cm^{-3}
Temperature	200 K	200 K	200 K
Measuring device	Nonius Kappa CCD	Nonius Kappa CCD	Siemens Nicolet-Syntex
Number of reflections for cell refinement			25
Scan range	4.1 ° < 2φ < 50.0 °	3.0 ° < 2φ < 50.0 °	3.7 ° < 2φ < 45.1 °
Method	ω scan, Δω = 1.0 °	ω scan, Δω = 1.0 °	ω scan, Δω = 0.6 °
Scan speed	15 s/frame	12 s/frame	6 < dω/dt < 29.3 ° min^{-1}
Measured reflections	47755	163249	4708
Unique reflections	9294	9628	4678
Observed reflections ($I \geq 2\sigma$)	7768	6005	2479
Number of parameters refined	602	625	361
Maximum of residual electron density	1.18 × 10^{-6} e pm^{-3}	1.27 × 10^{-6} e pm^{-3}	0.59 × 10^{-6} e pm^{-3}
Agreement factors	R_1 = 0.070	R_1 = 0.086	R_1 = 0.082
(F^2 refinement)	R_w = 0.200	R_w = 0.285	R_w = 0.199

[a] Anions are disordered (see X-ray Crystallographic Study). The crystal specimen analysed was found to contain 0.25 CH_2Cl_2 and 0.4 Et_2O per **5a$^+$**.These solvate molecules as a whole occupy distinct positions within the crystal, but show rotational disorder. – [b] About disorder of the anions see X-ray Crystallographic Study. The crystal specimen analysed was found to contain 0.5 EtOH per **5c^{2+}**. – [c] One of the CN ligands shows disorder with respect to the Co−C−N bond angle.

Table 7. Crystal data for compounds **6c** and **7a**

Compound	**6c**[a]	**7a**
Empirical formula	$C_{43}H_{39}CoN_2P_3S_2$	$C_{42}H_{39}CoNOP_3$
Molecular mass	799.78	725.63
Crystal system	monoclinic	monoclinic
Space group	*P*2$_1$/*n* (No. 14) [12]	*Cc* (No. 9) [12]
Lattice constants	a = 928.6(2) pm	a = 1212.3(2) pm
	b = 2698.0(5) pm	b = 1639.4(3) pm
	c = 1701.4(3) pm	c = 1822.6(4) pm
	β = 100.97(3)°	β = 100.51(3)°
Cell volume	4185 × 10^6 pm^3	3562 × 10^6 pm^3
Molecular units per cell	Z = 4	Z = 4
Density (calculated)	1.368 g cm^{-3}	1.353 g cm^{-3}
Temperature	200 K	200 K
Measuring device	Nonius Kappa CCD	Nonius Kappa CCD
Scan range	3.9 ° < 2φ < 50.0 °	4.2 ° < 2φ < 52.0 °
Method	ω scan, Δω = 1.0 °	ω scan, Δω = 2.0 °
Scan speed	30 s/frame	5 s/frame
Measured reflections	45160	24740
Unique reflections	7133	7017
Observed reflections ($I \geq 2\sigma$)	1788	6245
Number of parameters refined	226	437
Maximum of residual electron density	1.17 × 10^{-6} e pm^{-3}	0.43 × 10^{-6} e pm^{-3}
Agreement factors	R_1 = 0.093	R_1 = 0.035
(F^2 refinement)	R_w = 0.250	R_w = 0.072

[a] The crystal specimen analysed was found to contain 0.75 CH_2Cl_2 per molecule **6c**.

tional positions had to be taken into account in order to reproduce the electron-density distribution. The $PO_2F_2^-$ counterion in **5a**$^+$(PO$_2$F$_2$)$^-$ is also disordered. Refinement in a split-atom model with the phosphorus atom, the two oxygen atoms, and one fluorine atom in just one position and the second fluorine atom equally distributed over two positions gave a satisfactory agreement. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-135321 to -135325. Copies of data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge, Cambridge CB2 1EZ, UK [Fax: (internat. code) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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