Synthesis and π-Tweezer Properties of *tripod*Cobalt-Bisalkynyl Compounds [$CH_3C(CH_2PPh_2)_3Co(C{\equiv}CR)_2$] − Application to the Oxidative Coupling of Alkynyl Groups

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Dedicated to Prof. Peter Paetzold on the occasion of his 65th birthday

Keywords: Tripod ligands / Cobalt / π-Tweezers / Oxidative Coupling / Alkyne complexes

tripod$CoCl_2$ [$CH_3C(CH_2PPh_2)_3CoCl_2$] (**1**) reacts with alkynyllithium reagents RC≡CLi to produce *tripod*Co($C{\equiv}CR)_2$ (**2**). The neutral paramagnetic Co^{II} species **2** can be reduced to the anionic diamagnetic Co^{I} compounds **2**$^-$, which can also be obtained by treating *tripod*CoCl (**3**) with two equivalents of LiC≡CR. Compounds **2** contain an M($C{\equiv}CR)_2$ group with the alkynyl substituents in *cis*-positions to each other. The expectation that they might therefore act as π-tweezer ligands is born out by the characterisation of *tripod*Co($C{\equiv}CR)_2$–NiCO (**4**). The *cis*-position of the alkynyl groups in **2** should also facilitate their oxidative coupling. This type of reaction is, in fact, observed when compounds **2** are treated with one-electron oxidants. Reaction of **2** with Cp_2Fe^+ leads to [*tripod*Co(η^2-R*C*≡*C*C≡CR)]$^+$ **(5)** in which one of the triple bonds of the diyne acts as a four-electron donor ligand while the other one remains uncoordinated. One-electron oxidation of **2** thus initiates a two-electron oxidative coupling of the alkynyl groups with concomitant one-electron reduction of Co^{II} (**2**) to Co^{I} (**5**). All compounds were characterised by the usual analytical and spectroscopic techniques including EPR spectroscopy. The structure of compounds **5** is exemplified by an X-ray analysis of [*tripod*Co(η^2-*t*Bu*C*≡*C*C≡C*t*Bu)](PF_6) (**5b**).

Introduction

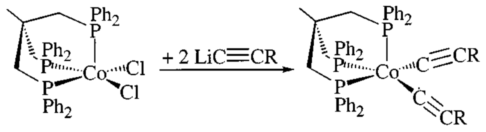
The coordination chemistry of the [*tripod*cobalt] template [$CH_3C(CH_2PPh_2)_3Co$] is characterised by the persistent pentacoordination in [*tripod*CoL_2]$^{n+}$ compounds, regardless of the oxidation state (Co^{III}: d^6, Co^{II}: d^7, Co^{I}: d^8).[1,2] While only pentacoordination is known for d^6- and d^7-electron configurations, lower oxidation states allow for pseudo-tetrahedral coordination.[2a,2b,3−8] With the geometric constraint imposed by the facial η^3-coordination of the *tripod* ligand, the co-ligands L in [*tripod*CoL_2] are necessarily *cis* to each other.

With this in mind, the synthesis of *cis*-bisalkynyl derivatives [*tripod*Co($C{\equiv}CR)_2$]$^{n+}$ is a rewarding goal in view of the particular reactivity patterns documented for some specific *cis*-[$L_nM(C{\equiv}CR)_2$] *cis*-bisalkynyl compounds such as [$Cp_2M(C{\equiv}CR)_2$] (M = Ti, Zr, Hf).[9] It is shown in this paper how the compounds [*tripod*Co($C{\equiv}CR)_2$]$^{n+}$ (n = −1, 0) **2** are accessible, and how these bisalkynyl species may be used as π-tweezers in derivatives such as [*tripod*Co($C{\equiv}CR)_2$−NiCO] (**4**). Compounds **2** may also serve as reagents for the oxidative coupling of the alkynyl ligands.

Results and Discussion

Cobalt(II) Derivatives

[*tripod*$CoCl_2$] (**1**)[2b] reacts with two equivalents of the alkynyllithium compound LiC≡CR (R=Ph, *t*Bu, TMS) to give the corresponding bisalkynyl derivatives **2a**−**c**.[2a,2b]



1

	R
2a	Phenyl
2b	tert. Butyl
2c	Trimethylsilyl

In order to produce **2** in high yields, the reaction has to be performed at −80 °C in THF. Even at this low temper-

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ature, the reactions are spontaneous and an immediate colour change from blue (**1** in THF[2b]) to brown (**2**) is observed. After changing the solvent from THF to toluene, with subsequent filtration, compounds **2** are obtained, by evaporation of the solvent, as microcrystalline black-brown powders. Derivatives of **1** that have only one alkynyl substituent and one remaining chloro substituent are not accessible by this procedure. If only one equivalent of $LiC\equiv CR$ is used, a mixture of **1** and **2** results. This is in agreement with the observation that a 1:1 mixture of the clean compounds **1** and **2** does not result in alkynyl−chloro exchange.

While single crystals of **2** suitable for X-ray analysis could not be obtained, analytical data unequivocally established the structure as shown for **2**. Osmometric determination of the molecular mass of **2a** shows that compounds **2** are monomeric (see Experimental Section). Mass spectrometry shows the molecular ion in each case (Table 1). The $C\equiv C$ bonds of **2** give rise to a characteristic ν(CC) absorption band in each case (Table 1). Compounds **2** are paramagnetic with an effective magnetic moment of 1.8 BM measured for **2a** at 25 °C (see Experimental Section).

Table 1. Analytical data for compounds **2**

Compound	**2a**	**2b**	**2c**
EPR (298 K, THF)[a]	$g_1 = 2.13, A_1 = 44$ G $g_2 = 2.04, A_2 = 45$ G	$g_1 = 2.13, A_1 = 45$ G $g_2 = 2.04, A_2 = 47$ G	$g_1 = 2.13, A_1 = 44$ G $g_2 = 2.04, A_2 = 45$ G
EPR (298 K, powder)	$g \approx 2.05$	$g \approx 2.05$	$g \approx 2.05$
EPR (100 K, powder)	$g \approx 2.05$	$g \approx 2.05$	$g \approx 2.05$
IR: $\tilde{\nu}$ CC [cm^{-1}]	2068 (w)	2068 (w)	2082 (w)
MS-EI: *m/z* [frag.]	885 [M$^+$]	845 [M$^+$]	877 [M$^+$]
CV: $E_{1/2}$ (ΔE) [mV][b]	−570 (90)	−670 (95)	−550 (80)
E_p^A [mV]	390	345	270
ΔE_{Fc} [mV]	130	155	125
elemental analysis calculated/*found*	C: 80.17/*80.30* H: 6.23/*5.82*[c]	C: 75.26/*74.27* H: 6.79/*7.03*	C: 69.77/*68.71* H: 6.54/*6.58*

[a] The *g* factors and hyperfine splitting constants were obtained by simulation of the experimental spectra. – [b] All measurements were performed in CH_2Cl_2 solutions; the potentials are given relative to the SCE electrode. – [c] Calculated for **2a**·2.5 toluene.

All compounds show an EPR pattern characteristic of pentacoordinated [*tripod*$Co^{II}L_2$] species (Table 1).[2c] Solution EPR spectra at 25 °C (Figure 1, top) revealed the presence of two species with individual *g* factors and hyperfine splitting constants (Figure 1, middle spectra) which, by analogy to literature data, were interpreted as being due to idealised square pyramidal and idealised trigonal bipyramidal coordination modes.[2c] Powder EPR spectra (25 °C and −173 °C) show only one broad resonance with no resolved coupling to the ^{57}Co ($I = {}^7/_2$) nucleus (Table 1).

Cobalt(I) Derivatives

Cyclovoltammetric studies of **2a** in CH_2Cl_2 indicated that compounds **2** should undergo one-electron reduction to produce the corresponding anionic Co^I species [*tripod*$Co(C\equiv CR)_2]^-$ (Table 1). Reversible reduction of **2a** is observed at −574 mV with reference to a SCE (Table 1). Treating **2a** with an equimolar amount of Cp_2Co in toluene led to a brown powder similar to **2a** in colour. FAB-negative mass spectra of this powder show a signal for **2a**$^-$ (*m/z* = 885), while FAB-positive mass spectra demonstrate the presence of $CpCo^+$ (*m/z* = 189).

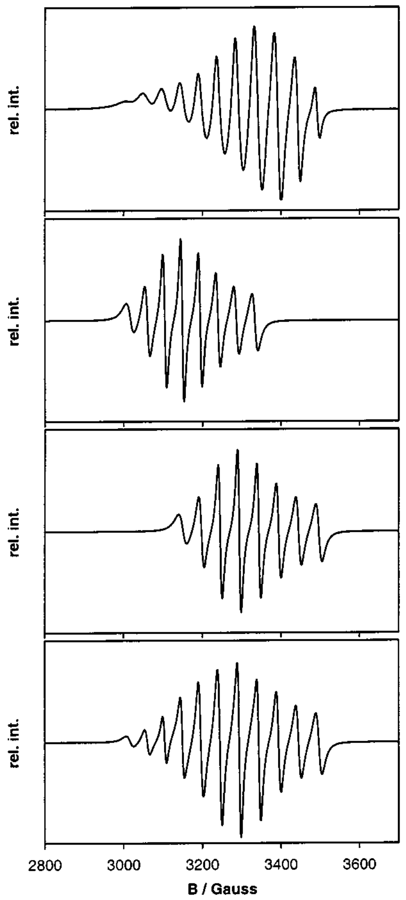
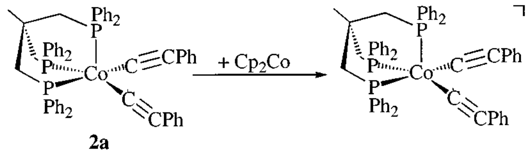
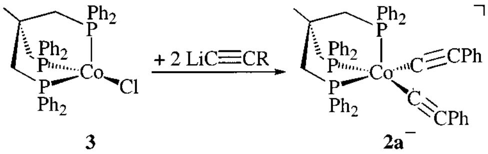


Figure 1. EPR spectrum of **2b** in THF at 298 K (top), simulations of the two individual components (middle) and composed simulated spectrum (bottom)



2a

Due to difficulties in the purification of the [Cp_2Co][*tripod*$Co(C\equiv CPh)_2$] salt, a different preparative strategy to produce **2a**$^-$ was used. The cobalt(I) compound [*tripod*CoCl] (**3**)[2a,2b] was reacted with two equivalents of $LiC\equiv CPh$ to produce the cobaltate(I) compound **2a**$^-$, which was isolated as its PPh_4^+ salt.



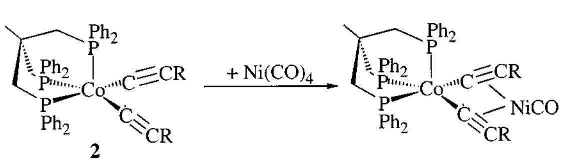
3 **2a**$^-$

Elemental analysis and mass spectra are in agreement with the assigned structure (see Experimental Section). The ν(CC) vibration of **2a**$^-$ at 2049 cm^{-1} (see Experimental Section) is shifted to a lower wave number than that of **2a**

(2068 cm^{-1}) (Table 1), as would be expected if some charge is delocalised into the π-system of the ligand. Owing to the prolonged measuring time required, ^{13}C NMR spectra of the sensitive PPh_4^+**2a**$^-$ could not be obtained. A sharp ^{31}P NMR signal at δ = 32.1 and a well-resolved ^1H NMR spectrum clearly show that **2a**$^-$ is a diamagnetic Co^I compound. Anion **2a**$^-$ conforms to the 18-electron rule, and this may be one of the reasons for the observation that, regardless of the stoichiometry of LiC≡CPh and **3** (2:1 or 1:1), **2a**$^-$ is inevitably obtained and there is no indication of the formation of [*tripod*CoC≡CPh].

Reactions of the Bisalkynyl Compounds 2

The propensity of **2** to act as a π-tweezer compound is seen by the reaction of **2** with $Ni(CO)_4$ to give compounds **4**. A NiCO moiety is retained in the π-tweezer entity of **2**.



	R
4a	Phenyl
4b	tert. Butyl
4c	Trimethylsilyl

The structure of compounds **4** is in agreement with their analytical and spectroscopic data. Mass spectra of **4** show a prominent peak for [M$^+$ − CO] in each case (Table 2). The presence of the coordinated carbonyl group is evident from the corresponding ν(CO) IR bands for all compounds **4** (Table 2). This prominent band is observed at about 2000 cm^{-1}, which is in good agreement with the observation of the corresponding bands in π-tweezer compounds $[(RCp)_2M(C{\equiv}CR)_2{-}NiCO]$ (M = Ti, Zr, Hf) at about the same wavenumbers.[9] This indicates that direct metal−nickel interactions are not really very important for the stability of this type of compound; if they were, the CO group would be sensitive to the presence of different types of L_nM entities to which the alkynyl groups are bound in $[L_nM(C{\equiv}CR)_2]$.[9] In agreement with this interpretation is the observation that cyclovoltammetric reduction of **4b** (−605 mV vs. SCE, see Experimental Section) occurs at about the same potential as that of **2a** (−574 mV vs. SCE, Table 1). Compounds **4** are paramagnetic as are the parent compounds **2** from which they are derived. The EPR spectra of compounds **4** (Table 2) closely resemble those of **2** (Table 1) with only minor changes in *g* values and coupling constants. With **4c**, the hyperfine structure is not resolved and one broad resonance is observed at $g \approx 2.05$. The fact that two overlapping signals are observed for **4**, with the spectral pattern being similar to that observed for the parent compounds **2**, may be explained by the same type of reasoning as discussed for **2**. With **4**, it is of course necessary to assume that the bisalkynyl-Ni moiety changes place as a single unit such that the idealised trigonal bipyramidal and idealised square pyramidal coordination geometries may interchange.

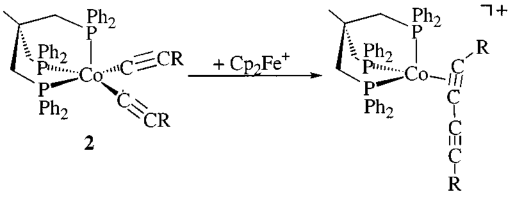
Table 2. Analytical data for compounds **4**

Compound	**4a**	**4b**	**4c**
EPR (298 K, THF))	$g_1 = 2.11, A_1 = 45$ G $g_2 = 2.02, A_2 = 48$ G	$g_1 = 2.11, A_1 = 48$ G $g_2 = 2.02, A_2 = 49$ G	$g \approx 2.005$
IR: $\tilde{\nu}$ CO [cm^{-1}]	1999 (s)	2001 (s)	2000 (s)
MS-FAB: *m*/*z* [frag.]	885 [M$^+$ − NiCO] 944 [M$^+$ − CO]	845 [M$^+$ − NiCO] 904 [M$^+$ − CO]	936 [M$^+$ − CO]
elemental analysis calculated/*found*	C: 71.63/*72.97* H: 5.08/*5.50*	C: 69.55/*67.49* H: 6.16/*6.31*	C: 60.14/*58.20* H: 5.70/*5.81*[a]

[a] Calculated for **4c** · 2 CH_2Cl_2.

In the chemistry of π-tweezer ligands, Cu^I and Ag^I have been found to be specifically prone to engage in bonding with π-tweezers.[9c] When solutions of **2** are treated with salts of these cations, however, the reaction is complicated by the propensity of **2** towards oxidation. Cyclovoltammetry of **2a** shows that the compound is irreversibly oxidised (Table 1) and this is what presumably happens when compounds **2** are treated with potentially oxidising metal ions.

Preparative oxidation of **2** with Cp_2Fe^+ results in a transformation of **2** into **5**.



	R
5a	Phenyl
5b	tert. Butyl
5c	Trimethylsilyl

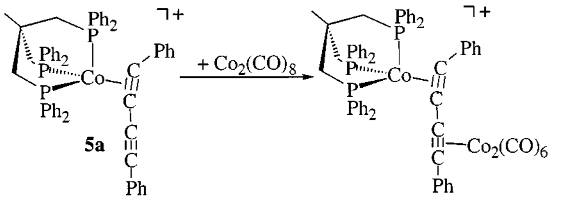
The alkynyl groups of **2** undergo oxidative coupling to result in 1,3-diyne ligands with one of the two triple bonds being coordinated to the cobalt centre. The process is brought about by a single-electron transfer-step such that, while the alkyne groups are oxidised in a formal two-electron oxidation, the cobalt centre is reduced from Co^{II} in **2** to Co^I in **5**. The coupling of σ-bonded alkynyl compounds is not without precedent: with rhodium as the central atom in $[Rh^{III}(C{\equiv}C{-}Ph)_2(SnPh_3)(PiPr_3)_2]$, oxidative coupling by I_2 to give *trans*-$[Rh^I(\eta^2\text{-}PhC{\equiv}CC{\equiv}CPh)(PiPr_3)_2I]$ is formally similar to the transformation of **2** into **5**, since reduction of the central metal (in this case reduction of Rh^{III} to Rh^I) necessarily accompanies the oxidative coupling of the alkynyl ligands.[10,11]

The salts **5**·PF_6 are obtained as analytically and spectroscopically pure green powders (Table 3) which show the peak for the molecular ion in their FAB mass spectra in each case. They are diamagnetic and show well-resolved NMR spectra. Their ^{31}P NMR resonances are observed in the range δ = 35 to 38 (Table 3). ^1H and ^{13}C NMR spectra reveal the signals of each constitutional group in the expected range (Table 3). The presence of one coordinated and one uncoordinated triple bond is evident from the corresponding ^{13}C NMR signals (Table 3). The presence of an uncoordinated triple bond is also indicated by a weak ν(CC) IR band at 2100−2200 cm^{-1} (Table 3). Chemical proof for the existence of an uncoordinated reactive triple bond is found in the reaction of **5a** with [$Co_2(CO)_8$].

Table 3. Analytical data for compounds **5**

Compound	**5a**	**5b**	**5c**
^{1}H NMR[a]			
tripod-**CH$_3$**	1.96 b, 3 H	1.83 b, 3H	1.95 b, 3 H
tripod-**CH$_2$**	2.68 b, 6 H	2.53 b, 6H	2.60 b, 6 H
aromat. H	7.07–7.54 m, 40 H	7.06–7.85 m, 30 H	7.01–7.30 m, 30 H
*t*Bu/SiMe$_3$[b]		1.36 br. s, 9 H 1.50 br. s, 9 H	0.11 s, 18 H
^{31}P NMR			
PPh$_2$	37.8 s	35.4 s	37.3 s
PF$_6$	−144.2 sept, $^1J_{PF}$ = 713 Hz	−144.2 sept, $^1J_{PF}$ = 713 Hz	−144.2 sept, $^1J_{PF}$ = 713 Hz
^{13}C{^{1}H } NMR			[c]
tripod-CH$_3$	36.6 m	36.6 m	
tripod-CH$_2$	32.6 m	33.3 m	
tripod-**C$_q$**	39.5 s	37.8	
aromat. C	123.8–133.6	128.8–133.9	
CH$_3$(*t*Bu)		30.5 s	
C$_q$(*t*Bu)		41.0 s	
C≡C	86.7 s; 100.8 s	77.3 s; 100.6 s	
Co η^2–**C≡C**	163.3 s; 181.6 s	164.0 s; 200.9 s	
MS-FAB: *m/z* [frag.]	885 [M$^+$]	845 [M$^+$]	877 [M$^+$]
IR: ν̃ PF [cm^{-1}]	846 (s)	843 (s)	840 (s)
IR: ν̃ CC [cm^{-1}]	2155 (w)	2218 (w)	2121 (w)
elemental analysis: calculated/*found*	C: 66.42/65.89 H: 4.79/5.01	C: 64.24/*63.69* H: 5.80/*6.21*	C: 59.88/*60.13* H: 5.62/*5.90*
HR-FAB: *m/z* calculated/*found*		683.1597/*683.1547* 845.3006/*845.2968*	

[a] All NMR measurements were performed in CD_2Cl_2. – [b] *t*Bu for **5b**, SiMe$_3$ for **5c**. – [c] No ^{13}C NMR data could be obtained owing to decomposition of the compound during the measurement.



5a

This reaction, as performed under standard conditions, gives [*tripod*Co(η^2-Ph*C*≡*C*C≡CPh−$Co_2(CO)_6$)]$^+$ as the main product.[12] This is apparent from the FAB mass spectra of its PF_6 salt which show the molecular ion (*m/z* = 1171, see Experimental Section) together with the peaks corresponding to the consecutive loss of up to five CO groups. The last CO group is lost together with the Co_2 entity, which was part of the coordinated $Co_2(CO)_6$ unit, apparently in one step leading to the mass peak of [*tripod*Co(η^2-Ph*C*≡*C*C≡CPh)]$^+$ **5a**. The IR data of the $Co_2(CO)_6$ adduct of **5a** are also in agreement with its formulation as **5a**·$Co_2(CO)_6$ (see Experimental Section).[12] The ^{31}P NMR resonance of this compound is found at δ = 36.9 (see Experimental Section). Under carbonylating conditions, the carbonyl derivative [*tripod*Co(CO)$_2$]$^+$ is formed as a minor side-product, as indicated by its ^{31}P NMR resonance at δ = 24.1 (see Experimental Section) and by the FAB-MS signal of the molecular ion (*m/z* = 739, see Experimental Section).[2f] This observation also shows that the diyne, once it has been formed as a ligand at the [*tripod*Co] template, can be set free from the metal by extensive carbonylation.[13] The presence of the PF_6 counterion is corroborated by a strong ν(PF) vibration and by the corresponding ^{31}P NMR signal in each case (Table 3).

The structure of **5** is confirmed by an X-ray analysis of the PF_6 salt of **5b** (Table 4 and 5). A general view of **5b** is given in Figure 2 (left), as well as a projection of the structure onto the plane of the three phosphorus atoms (right).

Table 4. Bond lengths [pm], bond angles [°] and torsion angles [°] for **5b**

Co–P1	218.91 (15)
Co–P2	216.19 (14)
Co–P3	223.53 (17)
Co–C6	187.5 (5)
Co–C7	186.4 (5)
C6–C7	131.3 (8)
C7–C8	140.0 (8)
C8–C9	120.0 (8)
P1–Co–P2	84.57 (6)
P1–Co–P3	96.31 (6)
P2–Co–P3	92.48 (6)
C14–C6–C7	134.5 (5)
C6–C7–C8	140.1 (5)
C7–C8–C9	178.6 (6)
C8–C9–C10	177.8 (6)
C4–C1–P1–Co	12.5
C4–C2–P2–Co	34.9
C4–C3–P3–Co	31.0
Hz1–P1–C100–C101[a]	–18.6
Hz1–P1–C106–C107[a]	–6.1
Hz2–P2–C200–C201[a]	–2.4
Hz2–P2–C206–C207[a]	–2.9
Hz3–P3–C300–C301[a]	–34.1
Hz3–P3–C306–C307[a]	–74.0

[a] These torsion angles are defined with respect to auxiliary vectors Hz_x–P_x (x = 1–3) orthogonal to the plane spanned by the three P atoms and pointing towards the observer with respect to the orientation shown in Figure 2 (right): Hz_x–P_x–C_{ipso}–C_{ortho}.

Table 5. Crystal data for compound **5b**

Formula	$C_{53}H_{57}CoF_6P_4$ · 0.5 THF
Molecular mass	1026.85
Crystal system	triclinic
Space group (no.)	*P*1bar (2)
a [pm]	1241.37 (2)
b [pm]	1469.37 (2)
c [pm]	1632.39 (1)
α [°]	84.1010 (0)
β [°]	77.268 (1)
γ [°]	69.723 (0)
Cell volume [10^6 pm^3]	2723.20(6)
Molecular units per cell	*Z* = 2
Density (calcd) [g cm^{-3}]	1.252
T [K]	296
Scan range	4.0° ≤ 2Θ ≤ 54.4°
Scan speed	10 sec/frame
Measured reflections	21864
Unique reflections	9137
Obs. reflections ($I \geq 2\sigma$)	4903
Parameters refined	614
Max. of residual electron density [10^{-6} e pm^{-3}]	0.69
Agreement factors (F^2 refinement)	R_1 = 7.2% R_w = 20.6%

From this second view in Figure 2, it becomes clear that there are at least two sets of chemically different phosphorus nuclei in **5b**. The fact that only one ^{31}P NMR signal

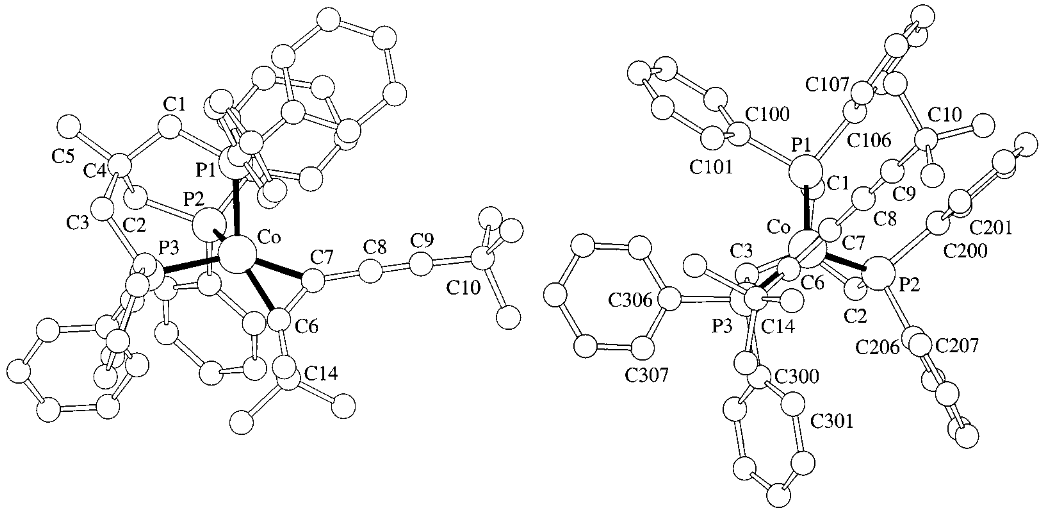


Figure 2. General view and projection of the structure of the cation of **5b**

is observed means that the coordinated alkyne group is free to adopt different rotational positions relative to the [*tripod*Co] scaffolding, with the vector radiating from the cobalt centre to the midpoint of the coordinated alkyne bond (C6−C7) interpreted as the axis of this rotation. With the coordinated alkyne bond seen as just one donor ligand, the coordination geometry around the cobalt may be described as idealised tetrahedral.

The *t*Bu substituent of the alkyne in **5b** makes the coordinated triple bond a rather bulky one. The rotational position of the alkyne ligand is such that the *t*Bu substituent (C14, Figure 2) of the coordinated alkyne ligand (C6−C7, Figure 2) is in an eclipsed position with respect to the Co−P3 bond. It follows that the *t*Bu−C≡C substituent (C8−C9−C10, Figure 2) at the other carbon centre of the coordinated alkyne (C7, Figure 2) is in a staggered position with respect to the Co−P1 and Co−P2 bonds (Figure 2). The steric strain imposed by the orientation of the alkyne ligand is mirrored by the geometric parameters of the Co−P_3 part of the compound. The distance Co−P3 (224 pm) is distinctly larger than the Co−P1 (220 pm) and Co−P2 (216 pm) distances. The P3−Co−P2 (92.5°) and P3−Co−P1 (96.3°) angles are definitely larger than the angle between the Co−P1 and Co−P2 bonds (84.6°). The rotational positions of the "phenyl-petals" also respond to this steric strain; the phenyl groups at P3 show distinctly larger rotation angles than those at P1 and P2 (Figure 2, Table 5).

The coordinated triple bond (C6−C7: 131.3 pm, Table 4 and 5) is approximately 11 pm longer than the uncoordinated one (C8−C9: 120.0 pm, Table 4 and 5). As expected, the coordination around the carbon atoms of the free triple bond is linear (C7−C8−C9: 176.6°; C8−C9−C10: 177.8°, Table 4 and 5), but the bond angles at the carbon atoms of the coordinated triple bond (C14−C6−C7: 134.5°; C6−C7−C8: 140.1°, Table 4 and 5) are distinctly different from 180°. The degree of this bending and the lengthening of the coordinated bond are indicative of a strong interaction between the alkyne and the metal.[15]

Based on the formalism of electron counting, the alkynes in **5** should act as four-electron donors since the compounds are diamagnetic and behave as 18-electron compounds,[14] while a 16-electron species [*tripod*CoL]$^+$ with L acting as a two-electron donor should be paramagnetic.[4−7] This follows from simple crystal-field-type arguments as well as from experience.[4−7,14] Assuming that the alkyne ligands in **5** act as four-electron donor moieties is in good agreement with the established rules correlating the ^{13}C NMR resonances of coordinated alkyne groups with the number of electrons which these groups donate to the metal.[15] The signals of the carbon atoms of the coordinated alkyne group in **5a** are observed at approximately $\delta = 160-180$ and those of **5b** occur at $\delta = 164-200$ (Table 3). The uncoordinated triple bonds give rise to signals between $\delta = 77$ and $\delta = 101$ in these compounds (Table 3). These latter shift values compare favourably with the ^{13}C NMR shifts reported for uncoordinated 1,3-diynes. In cobalt(I) compounds in which alkyne ligands can only act as two-electron donors (due to the electron count), ^{13}C NMR resonances of $\delta \approx 100$ are generally observed.[16] The C−C bond lengths in these compounds are found to be about 127 pm, which is definitely shorter than the C6−C7 distance (131 pm, Table 5) in **5b** where the alkyne acts as a four-electron donor.[16b]

The bonding of acetylenes at [*tripod*Co]$^+$ fragments has previously been reported, although no NMR spectroscopic data were given.[17]

Conclusion

*tripod*Co-bisalkyne compounds are easily prepared by the reaction of *tripod*Co-halides with LiC≡CR. Starting from [*tripod*CoCl_2] (**1**), neutral Co^{II} derivatives [*tripod*Co(C≡CR)$_2$] **(2)** are obtained. Anionic Co^{I} derivatives [*tripod*Co(C≡CR)$_2$]$^-$ **(2$^-$)** are found when [*tripod*CoCl] **(3)** is used as the starting material. The bisalkynyl compounds **2** are found to act as π-tweezer ligands with Ni(CO). It is observed that they undergo one-electron oxidation which results in oxidative coupling of the alkynyl ligands to produce 1,3-diynes and concomitant reduction of Co^{II} to Co^{I} to produce [*tripod*Co(η^2-R*C*≡*C*C≡CR)]$^+$ **(5)**.

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.[18] The CD_2Cl_2 used for NMR spectroscopic measurements was degassed by three successive "freeze-pump-thaw" cycles and dried with 4 Å molecular sieves. − EPR: Bruker ESP 300 E, X-band, standard cavity ER 4102, temperature control unit Eurotherm B-VT 2000, external standard dipenylpicrylhydrazyl (DPPH); Simulation: XSophe Computer Simulation Software Suite, Version 1.0.4b, 1993−1999; XEPRView, Version 1.0, 1999; Bruker Analytik, Rheinstetten, Germany. − NMR: Bruker Avance DPX 200 at 200.12 MHz (^{1}H), 50.323 MHz ($^{13}C\{^1H\}$), 81.015 MHz ($^{31}P\{^1H\}$), T = 303 K; chemical shifts (δ) are given in ppm with respect to CD_2Cl_2 (^{1}H: δ = 5.32; ^{13}C: δ = 53.8) as internal standard. ^{31}P chemical shifts (δ) are given in ppm with respect to 85% H_3PO_4 (^{31}P: δ = 0) as external standard. − IR: Bruker IFS-66, KBr disks. − MS: Finnigan MAT 8230; Fast-atom bombardment (FAB) xenon, matrix: 4-nitrobenzyl alcohol. − HR-MS (FAB) JEOL JMS 700, matrix: 4-nitrobenzyl alcohol. − Magnetic measurements: Faraday balance with a Bruker electromagnet B-E 15 C8, Bruker Field Controller B-H 15, Sartorius vacuum-microbalance M25 D-S, Oxford Temperature Control Unit ITC-4; calibration with $K_3[Fe(CN)_6]$. − Molecular weight determinations: Knauer vapor-pressure osmometer No. 7311100000; calibration with dibenzil. − Elemental analyses: Microanalytical Laboratory of the Organisch-Chemisches Institut, Universität Heidelberg. − Melting points: Gallenkamp MFB-595 010, melting points are not corrected. − Cyclic voltammetry: Metrohm "Universal Meß- und Titriergefäß", Metrohm GC electrode RDE 628, platinum electrode, SCE electrode, Princeton Applied Research potentiostate Model 273, 10^{-3} M in 0.1 M nBu_4NPF_6/CH_2Cl_2.

General Procedure for the Synthesis of Compounds 2: Alkyne (2 mmol) was dissolved in Et_2O (5 mL) and deprotonated with *n*BuLi (0.8 mL, 2.5 M in *n*-hexane) at −80 °C. After 5 min, the reaction mixture was allowed to warm to room temperature. [*tripod*$CoCl_2$] (1 mmol, 753 mg) was dissolved in THF (25 mL) and cooled to −80 °C. The acetylide was added at −80 °C with a syringe, and a brown solution was immediately formed. After 10 min at −80 °C, the reaction mixture was allowed to warm to room temperature and the solvent was removed under reduced pressure. The resulting black-brown residue was dissolved in toluene and filtered to remove LiCl. After evaporation of the solvent, compounds **2** were obtained as microcrystalline black-brown powders. Attempts to obtain crystals suitable for X-ray crystallography were unsuccessful. Compounds **2** are highly soluble in organic solvents such as hexane, toluene, Et_2O, and methanol such that crystallisation by diffusion is unfeasible; slow evaporation of the solvent leaves them as microcrystalline powders only. Cooling the solutions down to −80 °C also did not result in single crystals.

μ_{eff} (**2a**, 25 °C) = 1.8 BM; osmometric determination of the molecular mass of compound **2a**: calcd./found: 885/887.

Preparation of PPh_4[*tripod*Co^I-(C≡CPh)$_2$], $PPh_4{}^+$2a$^-$: [*tripod*CoCl] **(3)** (1 mmol, 718 mg) was suspended in THF (20 mL). LiC≡CPh (2 mmol) in Et_2O (5 mL) was added at −80 °C. The reaction mixture was stirred for 10 min at this temperature and then allowed to warm to 25 °C resulting in a colour change from beige to red-brown. The solvent was evaporated and the residue dissolved in CH_2Cl_2. Ph_4PCl (1 mmol, 375 mg) was added and the reaction mixture stirred for 20 min. After removal of the solvent under reduced pressure, the residue was redissolved in toluene and filtered to remove LiCl. Evaporation of the solvent produced $PPh_4{}^+$**2a**$^-$ as a red-brown, air-sensitive powder. − ^{1}H NMR (CD_2Cl_2): δ = 1.28 (br. s, 3 H, C*H*$_3$), 2.46 (br. s, 6 H, C*H*$_2$), 7.07−7.48 (m, 60 H, *H*$_{ar}$). − ^{31}P NMR (CD_2Cl_2): δ = 26.8 (s, *P*Ph$_4{}^+$), 32.1 (s, CH$_2$−*P*). − IR (KBr): ν(CC) = 2049 (w) cm^{-1}. − MS (FAB-negative): *m*/*z* = 885 [M$^-$]. − $C_{81}H_{69}CoP_4$ (1225.27): calcd. C 79.40, H 5.68; found C 78.21, H 5.82. − M.p. 145 °C (dec.).

General Procedure for the Synthesis of Compounds 4: Compound **2** (1 mmol) was dissolved in toluene and treated with a threefold excess of $Ni(CO)_4$. The reaction mixture was stirred for 2 h. No colour change took place, but a slow gas evolution was observed. The solvent was removed under reduced pressure and the residue recrystallised from CH_2Cl_2. After evaporation of the solvent, compounds **4** were obtained as black-brown microcrystalline powders.

CV (**4b**, CH_2Cl_2, vs. SCE): $E_{1/2}$ = 605 mV (rev.), Δ*E* = 90 mV.

General Procedure for the Synthesis of Compounds 5: Compound **2** (1 mmol) was dissolved in acetone (25 mL) and treated with $(Cp_2Fe)PF_6$ (1 mmol, 332 mg). The colour immediately changed from black-brown to green. The solvent was removed under reduced pressure and the resulting green residue was purified by chromatography on SiO_2 (ICN 32−63, 60 Å) with PE (boiling range 40−60 °C)/CH_2Cl_2 (5:1). After evaporation of the solvent, the PF_6 salts **5a−c** were obtained as fine black-green powders. Single crystals of compound **5b** suitable for X-ray diffraction were obtained after three months by diffusion of PE (boiling range 40−60 °C) into a solution of **5b** in THF.

Preparation of 5a·$Co_2(CO)_6$: Compound **5a** (0.1 mmol, 103 mg) was dissolved in acetone (10 mL). [$Co_2(CO)_8$] (0.15 mmol, 52 mg) was added and the reaction mixture was stirred for 1.5 h. A darkening of the solution was evident after a few minutes. The solvent was removed under reduced pressure and the residue was washed three times with Et_2O. After evaporation of the solvent, the $Co_2(CO)_6$ adduct of **5a** was obtained as a black microcrystalline powder.

^{31}P NMR (CD_2Cl_2): δ = 36.9 (s, CH$_2$−*P*). − IR (KBr): ν(CO) = 2100 (s), 2083 (s), 2054 (s), 2034 (s) cm^{-1}. − MS (FAB): *m*/*z* = 1171 [M$^+$], 1143 [M$^+$ − CO], 1115 [M$^+$ − 2CO], 1087 [M$^+$ − 3CO], 1059 [M$^+$ − 4CO], 1031 [M$^+$ − 5CO], 885 [M$^+$ − $Co_2(CO)_6$].

X-ray Crystallographic Study: The measurement was carried out on a Siemens AXS Smart CCD diffractometer using graphite-monochromated Mo-K_α radiation. All calculations were performed using the SHELXT PLUS software package. The structure was solved by direct methods with the SHELXS-97 program and refined with the SHELXL-97 program.[19] Graphical handling of the structural data during solution and refinement was performed with XPMA.[20] Atomic coordinates and anisotropic thermal parameters of the non-hydrogen atoms were refined by full-matrix least-squares calculations. Table 5 lists the data for the structure determination.

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-133001. Copies of data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge, Cambridge CB2 1EZ, UK [Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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