# $\eta^4$-Coordination of Dienes and Heterodienes to the TripodCobalt(I) Template $[CH_3C(CH_2PPh_2)_3Co]^+$: Synthesis, Structure, and Dynamics

**Rolf Rupp,[a] Axel Frick,[a] Gottfried Huttner,*[a] Peter Rutsch,[a] Ute Winterhalter,[a] Annette Barth,[a] Peter Kircher,[a] and Laszlo Zsolnai[a]**

*Dedicated to Prof. Dirk Walther on the occasion of his 60th birthday*

**Keywords:** Tripol ligands / Dienes / Heterodienes / $\eta^4$-Coordination / Hindered rotation / Line-shape analysis

$CH_3C(CH_2PPh_2)_3CoCl$ (**1**) is easily accessible from $CH_3C(CH_2PPh_2)_3CoCl_2$ by reduction with activated zinc powder. Upon dehalogenation with $TlPF_6$, **1** reacts with dienes to give [*tripod*Co$^I$-($\eta^4$-diene)]$^+$ (**2**). The heterodienes acrolein and methyl vinyl ketone produce the analogous $\eta^4$-heterodiene compounds **3**. When crotonaldehyde is used as the potential $\eta^4$-diene ligand, decarbonylation is observed leading to [*tripod*Co$^I$-$(CO)_2$]$^+$ (**4**). Reaction of [*tripod*Co$_{aq}$]$(BF_4)_2$ with allyl mercaptan produces [*tripod*Co$^I$-($\eta^4$-thioacrolein)]$^+$ (**3a**) through dehydrogenation of the ligand precursor. 1,2-Diketones such as benzil and phenanthrenequinone do not coordinate in a $\eta^4$ fashion but rather generate $\eta^2$-coordinate enediolato ligands by an electron-transfer process, resulting in compounds of the type {*tripod*Co$^{III}$-[$\eta^2$-RC(O)=C(O)R]}$^+$ (**5**). All the compounds have been characterized by standard analytical and spectroscopic techniques, including X-ray analysis in some cases. Compounds **4** and **5** show trigonal-bipyramidal coordination in the solid state, whereas the coordination polyhedra in compounds **2** and **3** are better described as square-pyramidal. While a minimum of two phosphorus resonances might be expected for each of these coordination geometries, only one time-averaged signal is normally observed. Only with the $\eta^4$-coordinated heterodienes acrolein, methyl vinyl ketone, and thioacrolein present in **3** is there a resolution of the signals of the three chemically distinct phosphorus nuclei at low temperatures. By $^{31}$P-NMR line-shape analysis, the activation barriers for the rotational reorientation of the heterodienes are found to be around $\Delta H^{\neq} = 47$ kJmol$^{-1}$ for all three compounds **3**.

## Introduction

The chemistry of *tripod*cobalt templates $[CH_3C(CH_2Ph_2)_3Co]$ has been extensively studied. Largely due to the efforts of Sacconi and his group, the very special properties of this kind of template have been documented through the isolation of many types of compounds that are not accessible with any other type of $[L_3Co]$ template.[1] However, the chemistry of this highly valuable template $[CH_3C(CH_2PPh_2)_3Co]$ is hampered by the fact that the initial oxidation state of cobalt is generally Co$^{II}$ and the [*tripod*Co] compounds are formed by addition of the *tripod* ligand and an appropriate coligand to the inorganic salt. The products of such reactions may well contain cobalt in the oxidation states of Co$^I$, Co$^{II}$, and Co$^{III}$, depending on the coligand and the reaction conditions.[2−4]

A systematic approach to the chemistry of the $[CH_3C(CH_2PPh_2)_3Co]^+$ template containing cobalt in the oxidation state (+I) has not yet been developed, even though a 14-electron species such as [*tripod*Co]$^+$ might be expected to provide a highly promising access to a novel type of coordination chemistry of the [*tripod*Co] entity. This expectation arises, in part, from consideration of the chemistry of the CpCo template, which has rapidly developed since the generation of this template by reductive decyclopentadienylation was reported by Jonas.[5][6] Moreover, since there are relatively few methods available for the generation of 14-electron species with late 3d transition metals, the development of suitable methods for the generation of a [*tripod*Co]$^+$ reagent would seem particularly worthwhile.

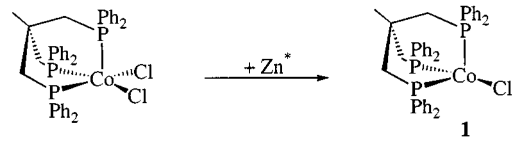
In this paper, we report on several methods for the in situ generation of [*tripod*Co]$^+$ and its reactions with unsaturated compounds.

## Results and Discussion

Amongst the compounds containing the $[CH_3C(CH_2PPh_2)_3Co^I]$ template, the chloride $CH_3C(CH_2PPh_2)_3CoCl$ (**1**) appeared to be the most logical starting material for probing the chemistry of the $[CH_3C(CH_2PPh_2)_3Co]^+$ entity. **1** has been known for a long time and its preparation by $NaBH_4$ reduction of $CH_3C(CH_2PPh_2)_3CoCl_2$ has been reported by Sacconi et al.[2a] Its structure and its complicated equilibrium with respect to the starting material $CH_3C(CH_2PPh_2)_3CoCl_2$ have recently been described.[2b] While it is possible to prepare **1** by the method described by Sacconi et al., the accompanying formation of $\{[CH_3C(CH_2PPh_2)_3Co]_2H_3\}^+$ complicates this procedure and a simpler, cleaner preparation pathway remains desirable.[2a,2c,3a] We have found that $CH_3C(CH_2PPh_2)_3CoCl_2$ undergoes a clean reduction to **1** when treated with activated zinc powder in THF (Scheme 1).

---

[a] Anorganisch-Chemisches Institut der Universität Heidelberg,
Im Neuenheimer Feld 270, D-69120 Heidelberg, Germany
Fax: (internat.) + 49-(0)6221/545707
E-mail: g.huttner@indi.aci.uni-heidelberg.de



1

Scheme 1

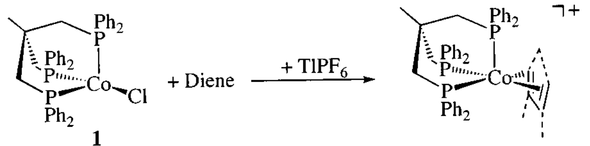
After filtration and evaporation of the THF, **1** is obtained as a microcrystalline beige powder in almost quantitative yield. While freshly prepared **1** dissolves in $CH_2Cl_2$ to produce a clear orange-brown solution, dissolution of samples of **1** left at room temperature for more than 6 h leads to green solutions, indicating different degrees of decomposition. The nature of the green products has not yet been established.

## [TripodCo$^I$] Derivatives of Dienes

Freshly prepared **1** reacts with dehalogenating agents in the presence of 4-electron donors $L_2$ such as conjugated dienes to produce the corresponding [*tripod*Co$^I$-$L_2$]$^+$ species **2**. When **1** was treated with $(CH_3)_3SiOSO_2CF_3$, a colour change from orange-brown to red-brown was observed. Addition of 2,3-dimethyl-1,3-butadiene resulted in a colour change to orange and, after evaporation of the solvent, an orange microcrystalline powder was obtained. By comparison with authentic spectroscopic data for the corresponding compound [*tripod*Co$^I$-($\eta^4$-2,3-dimethyl-1,3-butadiene)]$^+$ (**2b**; see below), the data obtained following this reaction clearly showed that the $\eta^4$-diene derivative had been formed. The product obtained this way was, however, found to be contaminated with some paramagnetic impurities, which could not be separated. While the $^{31}$P-NMR spectrum of the product clearly showed the characteristic signals of **2b**, the $^1$H-NMR spectrum featured only very broad signals, as befits the presence of some paramagnetic contamination. Mass spectra of the product showed the characteristic fragmentation pattern of **2b** as the dominant pattern, as well as the characteristic *m*/*z* peak of [*tripod*Co$^I$-(triflate)]. It is thus probable that the paramagnetic contamination was, in fact, due to [*tripod*Co$^I$-(triflate)] which, in analogy to [*tripod*Co$^I$-(formate)]$^+$, should be a 16-electron paramagnetic species.[2d] If this interpretation is correct, the coordinative power of the triflate anion is evidently still too high to allow for its complete exchange by the diene under the applied conditions.[7]

When a solution of **1** in $CH_2Cl_2$ was treated with an equimolar amount of $GaCl_3$, a colour change from orange-brown to red-brown was observed. When this solution was treated with 2,3-dimethyl-1,3-butadiene, a further colour change to orange was observed. Mass spectra showed the fragmentation pattern of **2b**. In contrast to the product obtained by dehalogenation with $(CH_3)_3SiOSO_2CF_3$ (see above), no paramagnetic contamination was apparent and both the $^1$H- and $^{31}$P-NMR spectra of the product were in complete agreement with those obtained for authentic **2b** (see below). While it is clear from these results that **2b** was indeed formed under the described conditions, elemental analysis data for the product were less than satisfactory. Carbon and hydrogen values were too low, indicating that the anionic part of the salt was not in fact $GaCl_4^-$, which had been assumed to constitute the counteranion.

$AgBF_4$ and $AgPF_6$, while also acting as dehalogenating agents, proved not to be appropriate for this reaction since they led to concomitant oxidation. The problems were finally overcome by using $TlPF_6$ as the dehalogenating agent (Scheme 2).



1

| Nr. | Diene |
|---|---|
| **2a** | 2-Methylbutadiene |
| **2b** | 2,3-Dimethylbuta-1,3-diene |
| **2c** | Cyclopentadiene |

Scheme 2

The orange $PF_6$ salts of **2a**−**2c** were obtained in good yields after purification by chromatography (Table 1, Table 4, Table 9). *Tripod*Co$^I$ derivatives of conjugated dienes of type **2** are known.[2e] [*Tripod*Co$^I$-($\eta^4$-butadiene)]$^+$, [*tripod*Co$^I$-($\eta^4$-isoprene)]$^+$ (**2a**), [*tripod*Co$^I$-($\eta^4$-1,3-cyclohexadiene)]$^+$, [*tripod*Co$^I$-($\eta^4$-1,3,5,7-cyclooctatetraene)]$^+$, and [*tripod*Co$^I$-($\eta^4$-1,3,5-cycloheptatriene)]$^+$ have previously been obtained by treating solutions of *tripod*Co$^{II}$ precursors with propan-2-ol as the reductant in the presence of the appropriate olefinic ligand.[2e] A standard procedure for reactions of this type has not yet been established, nor have the products been completely characterized, although the structures of the products are known from a reported X-ray analysis of [*tripod*Co$^I$-($\eta^4$-1,3,5-cycloheptatriene)]$ClO_4$.[2e] The type of coordination observed in this $\eta^4$-coordinated triene derivative remains essentially unchanged when dienes are coordinated to the [*tripod*Co]$^+$ entity. The general features already described by Sacconi et al. for the cycloheptatriene derivative apply equally well to the structure of **2c**, which has been determined in the case of its $PF_6$ salt (Figure 1, Figure 6; Table 5, Table 10).

The $^{31}$P-NMR spectra of compounds **2**, besides the characteristic septet due to the $PF_6$ counteranion, show one sharp signal, the shape of which does not change significantly on cooling from 303 K to 193 K (Table 1). Irrespective of the specific coordination geometry (trigonal bipyramidal *vs.* square pyramidal), for a static structure arising from the combination of an entity with constitutional $C_3$-symmetry (*tripod*Co) and a coligand with at most $C_{2v}$-symmetry, a minimum of two different $^{31}$P-NMR signals can be expected. This expectation is indeed borne out by the spectroscopic behaviour of the related compounds [$L_3Co^I$-($\eta^4$-diene)]$^+$ (L = $PMe_3$, $PMe_2Ph$, $PPh_2H$) containing three isolated phosphane donors, where − depending on the symmetry of the diene coligand and the temperature of observation − up to three $^{31}$P-NMR signals are observed.[8−10]

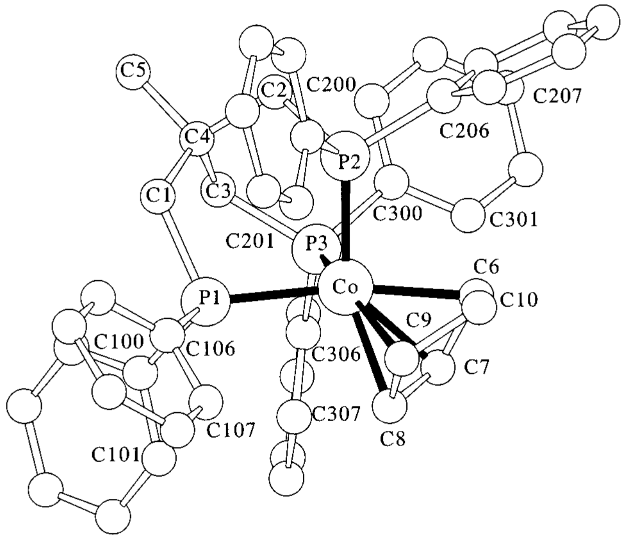


Figure 1. X-ray structure of **2c**

The fact that **2a**−**2c** show only one sharp signal for the three phosphorus nuclei of the coordinated ligand can only be rationalized by assuming that some dynamic process is operative, which renders the time-averaged environments of the phosphorus nuclei equivalent. This process must have a rather low activation energy, since not even a broadening of this $^{31}$P-NMR signal is observed on cooling to 193 K. The most easily envisaged dynamic process is a tumbling of the diene coligands about the idealized $C_3$-axis of the [*tripod*Co] template. Such a tumbling motion would, of course, involve the transition of idealized square-pyramidal and idealized trigonal-bipyramidal coordination geometries. The $^1$H-NMR spectra (Table 1) are in full agreement with the assigned constitutions, as are the mass spectra, which show the molecular ions as the most prominent peaks (Table 4). High-resolution mass spectra (**2a**−**2c**) and microanalytical data (**2b**) are also in agreement with the given formulae (Table 1).

When the procedure for the dehalogenation of **1** was performed in the presence of ethylene instead of a conjugated diene, [*tripod*Co$^I$-(ethylene)$_2$]$^+$ was formed, as was evident from the $^{31}$P-NMR spectrum and mass spectroscopic data (see Experimental Section). However, it was not possible to purify the compound by chromatography, nor was it possible to obtain an analytically pure specimen by crystallization.

When non-conjugated dienes such as bicyclo[2.2.1]hepta-2,5-diene (2,5-norbornadiene) or 1,5-cyclooctadiene were used, $PF_6$ salts containing [*tripod*Co$^I$-(diene)]$^+$ as the cationic part were formed in high yields. Again, the compounds could not be purified by chromatography without significant decomposition (see Experimental Section). Even though the aforementioned compounds incorporating non-conjugated dienes or two ethylene ligands were invariably obtained with contamination by minor amounts of paramagnetic impurities, they were the only detectable products by $^{31}$P-NMR and mass spectrometry. The species [*tripod*Co$^I$-(ethylene)$_2$]$^+$ is found to be thermodynamically far more stable than its isoelectronic equivalent CpCo(ethylene)$_2$.[5][6] While this latter compound starts to decompose at 323 K, [*tripod*Co(ethylene)$_2$]$PF_6$ is indefinitely stable at 343 K under an inert atmosphere.

On the other hand, the reactions of **1** described above show that, upon activation with $TlPF_6$, this compound constitutes a clean source for the intermediate generation of [*tripod*Co]$^+$. With regard to ease of handling, a method involving in situ reduction of [*tripod*Co]$^{2+}$ to [*tripod*Co]$^+$ would be desirable. It is in fact observed that a solution of $Co_{aq}(BF_4)_2$ and *tripod* in ethanol/$CH_2Cl_2$ reacts with conjugated dienes when treated with activated zinc powder in an ultrasonic bath. Compounds **2a**−**2c** are also accessible by this method (Scheme 3). They may be isolated as $PF_6$ salts by metathesis with $KPF_6$ in acetone following workup as described.

The yields of **2a**−**2c** achieved using this method were somewhat lower than those obtained starting from **1** (Table 9).

## [TripodCo$^I$] Derivatives of Heterodienes

It has been observed that treatment of $Co_{aq}(BF_4)_2$ with 2-propene-1-thiol (allyl mercaptan) in the presence of $NaBPh_4$ and *tripod* produces the thioacrolein compound **3a** (Scheme 4).[2f]

In order to obtain this compound in a reproducible manner, it is necessary to keep the reaction mixture in a Schlenk tube sealed with a rubber stopper, presumably to keep the oxygen concentration at a very low but significant level. The $BPh_4$ salt of **3a** was obtained as a spectroscopically and analytically pure, dark-green, crystalline material consisting of single crystals suitable for X-ray analysis (Figure 2, Figure 5; Table 4, Table 5, Table 10).

When $Co_{aq}(BF_4)_2$ was treated with 2-propen-1-ol (allyl alcohol) instead of 2-propene-1-thiol (allyl mercaptan), a smooth colour change was again observed, leading to a red-brown solution. Evaporation of the solvent afforded a red-brown powder, the mass spectrum of which showed the molecular ion of the acrolein derivative **3b** as the most prominent peak. The $^{31}$P-NMR data of the product were also identical with the data obtained for the analytically pure $\eta^4$-acrolein compound **3b** (see below). However, it proved impossible to obtain an analytically pure compound using this reaction procedure.

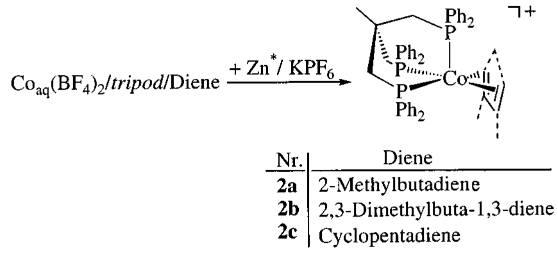
Based on the observation that **1** reacts with dienes in an almost quantitative manner, the procedure used for the activation of **1** in the presence of dienes was applied with heterodienes as the potential coligands. It was found that 2-propenal (acrolein) and its methylated derivative 3-buten-2-one (methyl vinyl ketone) became $\eta^4$-coordinated at the [*tripod*Co]$^+$ template in the same way as observed for carbon-centred diene ligands (Scheme 5).

Compounds **3b** and **3c** were produced in yields comparable to those obtained in the synthesis of **2** (Table 9). Chromatographic workup of the $PF_6$ salts of **3b** and **3c** resulted in claret microcrystalline powders, which proved to be analytically and spectroscopically pure (Table 2, Table 4).

Table 1. Analytical data for compounds **2a** to **2c**

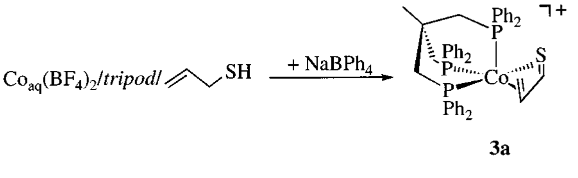
| Compound | **2a**·$PF_6^-$ | **2b**·$PF_6^-$ | **2c**·$PF_6^-$ |
|---|---|---|---|
| $^1H$ NMR | $CD_3NO_2$ | $CD_2Cl_2$ | $CD_2Cl_2$ |
| *tripod*-$CH_3$ | 1.17–1.95 m, 3 H | 1.33–1.99 m, 3 H | 1.93 br., 3 H |
| *tripod*-$CH_2$ | 2.74 br., 6 H | 2.57 br., 6 H | 2.62 br., 6 H |
| arom. H | 7.26–7.61 m, 30 H | 7.09–7.41 m, 30 H | 7.16–7.78 m, 30 H |
| $CH{=}CH_2$ | 1.17–1.95 m, 2 H | – | – |
| $C_q{=}CH_2$ | 1.17–1.95 m, 2 H | 1.33–1.99 m, 4 H | – |
| $CH_2{=}CH$ | 5.71 br., 1 H | – | – |
| *ligand*-$CH_3$ | 1.17–1.95 m, 3 H | 1.33–1.99 m, 6 H | – |
| $CH{-}CH_2$ | – | – | 3.12 br., 2 H |
| $CH{=}CH$ | – | – | 6.70 br., 2 H |
| $=CH{-}CH_2$ | – | – | 2.62 br., 3.74 br., 2 H |
| $^{31}P\{^1H\}$ NMR | $CD_2Cl_2$ | $CD_2Cl_2$ | $CD_2Cl_2$ |
| $PPh_2$ | 22.2 s | 19.1 s | 25.9 s |
| $PF_6$ | −144.2, $^1J_{PF}$ = 713 Hz | −144.2, $^1J_{PF}$ = 713 Hz | −144.2, $^1J_{PF}$ = 713 Hz |
| $^{13}C\{^1H\}$ NMR[a] | $CD_2Cl_2$ | $CD_2Cl_2$ | $CD_2Cl_2$ |
| *tripod*-$CH_3$ | 35.7 m | 37.5 m | 35.9 m |
| *tripod*-$CH_2$ | 34.5 m | 35.4 m | 34.4 m |
| *tripod*-$C_q$ | 37.5 s | 37.7 s | 37.6 s |
| arom. C | 129.2–132.3 | 128.8–134.9 | 129.3–135.8 |
| *ligand*-$CH_3$ | 20.3 s | 18.2 s | – |
| $CH{=}CH_2$ | 42.0 s | – | – |
| $C_q{=}CH_2$ | 43.1 s | 43.5 s | – |
| *ligand*-$C_q$ | 108.8 | 104.6 | – |
| $CH{-}CH_2$ | – | – | 43.3 s |
| $CH{=}CH$ | – | – | 93.3 s |
| $=CH{-}CH_2$ | – | – | 150.9 s |
| elemental analysis: (calcd./found) | –[b] | C: 61.99/61.08<br>H: 5.42/5.64 | –[b] |
| HR-FAB (m/z): (calcd./found) | 751.2223/751.2236 | 765.2379/765.2394 | 749.2067/749.2039<br>748.1988/748.1973 |

[a] $CH_3$, $CH_2$, CH, and C carbons were assigned by means of a 135° DEPT experiment. – [b] Satisfactory microanalytical data could only be obtained for **2b**. The problems encountered with **2a** and **2c** may be traced to inappropriate handling of these air-sensitive compounds during microanalytical workup.



| Nr. | Diene |
|---|---|
| **2a** | 2-Methylbutadiene |
| **2b** | 2,3-Dimethylbuta-1,3-diene |
| **2c** | Cyclopentadiene |

Scheme 3



**3a**

Scheme 4

The reaction that was found to proceed cleanly in the case of acrolein and methyl vinyl ketone, leading to the $\eta^4$-coordinate heterodiene compounds **3b** and **3c**, could not be carried out with 2-butenal (crotonaldehyde) as the heterodiene. Reaction of this specific unsaturated aldehyde with **1** in the presence of $TlPF_6$ was found to produce the dicarbonyl compound **4** (Scheme 6).

The dicarbonyl compound **4** was isolated as its $BPh_4$ salt. **4** itself has previously been described by Ellermann et al. as

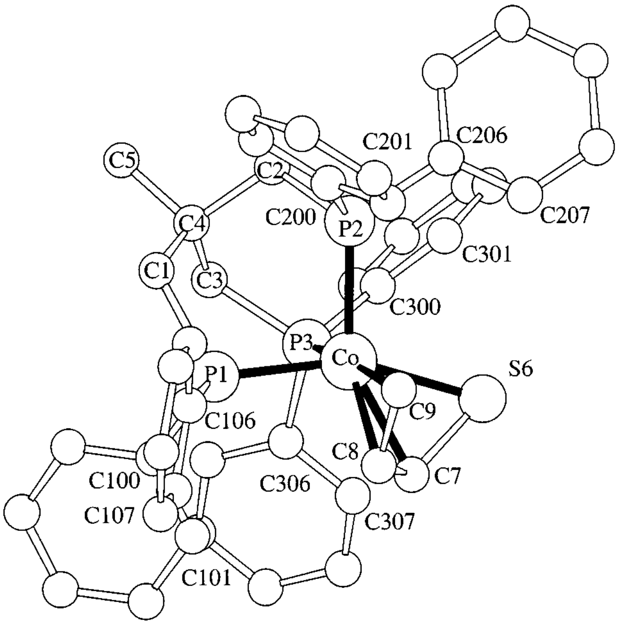
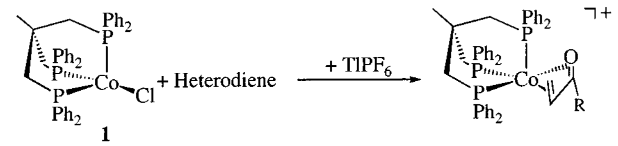


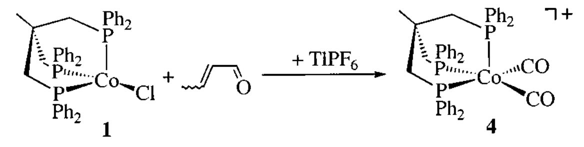
Figure 2. X-ray structure of **3a**; here, a consistent numbering scheme for all the compounds is used for the sake of easier comparison, which differs from that used for the deposited structure

the product of the reaction of *tripod* with $Co_2(CO)_8$.[2g] **4** could also be obtained from **1** in the presence of $TlPF_6$ and CO (see Experimental Section). The structure of **4**·$(BPh_4)^-$,



| Nr. | Heterodiene |
|---|---|
| **3b** | Acrolein |
| **3c** | Methyl vinyl ketone |

Scheme 5



Scheme 6

as determined by X-ray analysis, is shown in Figure 3 (Table 6, Table 10).

The approximate idealized trigonal-bipyramidal coordination is evident from Figure 3, as well as from the data in Table 6.

In view of the clean reactions giving **3b** and **3c** as compounds with $\eta^4$-coordinated heterodienes, the comparatively clean reaction of the linear $C_4$-heterodiene crotonaldehyde to produce the dicarbonyl compound **4** is remarkable. It appears that decarbonylation of α,β-unsaturated aldehydes is the predominant reaction pathway when allylic intermediates can be formed, which is possible by a simple hydrogen migration process with crotonaldehyde, thereby producing **4**, but cannot occur with the heterodienes leading to **3b** and **3c**.

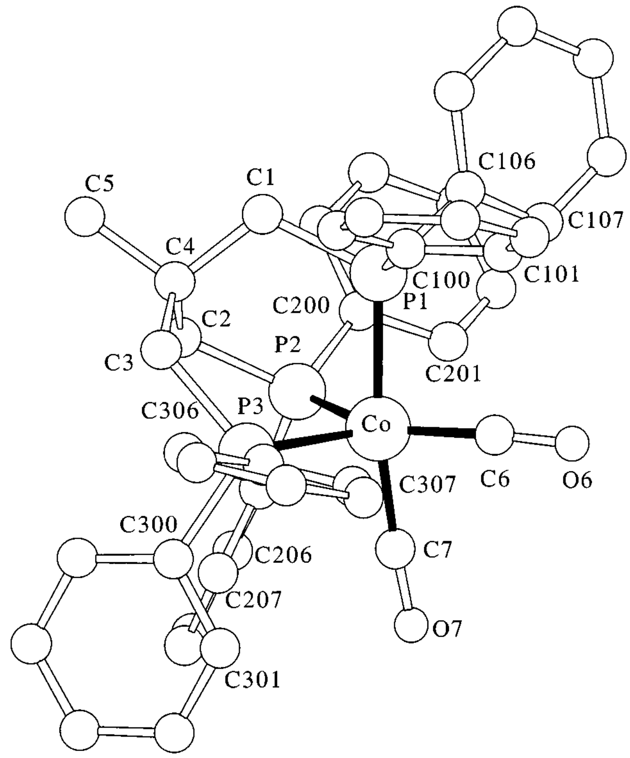


Figure 3. X-ray structure of **4**

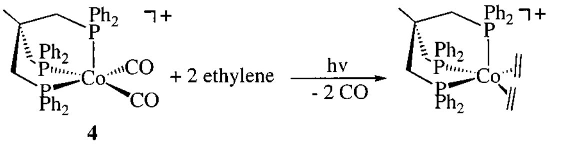
**4** itself might represent a precursor for the generation of the [*tripod*Co]$^+$ species if its carbonyl groups could be dis-

Table 2. Analytical data for compounds **3a** to **3c**

| Compound | **3a**$\cdot BPh_4^-$ | **3b**$\cdot PF_6^-$ | **3c**$\cdot PF_6^-$ |
|---|---|---|---|
| $^1$H NMR | [D$_6$]acetone | $CD_2Cl_2$ | $CD_2Cl_2$ |
| *tripod*-$CH_3$ | 1.93 m, 3 H | 1.99 br., 3 H | 1.88 m, 3 H |
| *tripod*-$CH_2$ | 2.39−2.72 m, 6 H | 2.39−2.96 m, 6 H | 2.63−2.82 m, 6 H |
| arom. H | 7.18−7.74 m, 50 H | 7.08−7.91 m, 30 H | 6.79−7.60 m, 30 H |
| *ligand*-$CH_2$-*i*[a] | 1.45 m, 1 H | 1.12 m, 1 H | 1.24 m, 1 H |
| *ligand*-$CH_2$-*a*[a] | 2.39−2.72 m, 1 H | 2.39−2.96 m, 1 H | 2.63−2.82 m, 1 H |
| $CH_2=CH$ | 6.24 s, 1 H | 6.25 m, 1 H | 5.88 m, 1 H |
| X=CH[d] | 7.18−7.74 m, 1 H | 8.57 br., 1 H | − |
| *ligand*-$CH_3$ | − | − | 2.34 m, 3 H |
| $^{31}P\{^1H\}$ NMR[b] | $CD_2Cl_2$ | $CD_2Cl_2$ | [D$_8$]THF |
| $PF_6$ | − | −144.2, $^1J_{PF} = 713$ Hz | −144.2, $^1J_{PF} = 713$ Hz |
| $^{13}C\{^1H\}$ NMR[c] | $CD_2Cl_2$ | $CD_2Cl_2$ | $CD_2Cl_2$ |
| *tripod*-$CH_3$ | 38.8 m | 36.4 m | 36.5 m |
| *tripod*-$CH_2$ | 34.3 m | 31.6 m | 32.6 m |
| *tripod*-$C_q$ | 37.9 s | 37.3 s | 38.4 s |
| arom. C | 131.1−134.5 | 129.2−143.1 | 128.9−133.0 |
| *ligand*-$CH_2$ | 54.0 s | 45.7 s | 44.4 s |
| *ligand*-$CH_3$ | − | − | 22.6 s |
| $CH_2=CH$ | 102.1 s | 89.4 s | 78.3 s |
| X=C[c,d,e] | 108.9 s | 129.2−143.1 | 153.7 s |
| elemental analysis (calcd./found) | −[f] | C: 59.74/59.33<br>H: 4.90/5.75 | C: 60.14/59.16<br>H: 5.05/5.32 |
| HR-FAB (m/z): (calcd./found) | 755.1630/755.1679 | − | − |

[a] ligand-*i*: *endo*-H of the diene; ligand-*a*: *exo*-H of the diene. − [b] See also Table 7. − [c] $CH_3$, $CH_2$, CH, and C carbons were assigned by means of a 135° DEPT experiment. − [d] X = S: **3a**; X = O: **3b**, **3c**. − [e] In **3b**, this resonance appears in the aromatic region and is obscured by the arene carbon signals. − [f] Satisfactory microanalytical data could only be obtained for **3b** and **3c**. The sensitivity of **3a** coupled with the nature of the handling during microanalytical workup did not allow precise analysis.

placed. Considering the cationic [*tripod*Co]$^+$ template to which the carbonyl groups are coordinated, the cobalt−CO bonds should not be prohibitively strong. Indeed, the $\nu_{CO}$ IR absorptions of **4** are observed at rather high energies (2025 cm$^{-1}$, 1965 cm$^{-1}$; Table 4), indicating that the CO bond order is high with the consequence that the Co−C$_{CO}$ bond order should be low. With this in mind, **4** was irradiated in the presence of ethylene, whereupon complete replacement of its CO groups by ethylene ligands was observed (Scheme 7).

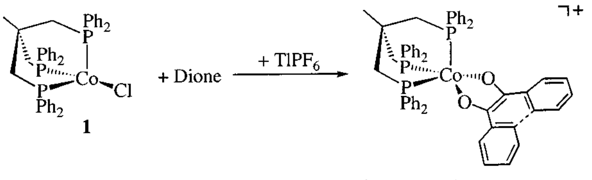


Scheme 7

Although the product formed in this reaction could not be obtained in analytically pure form, its mass spectrum and $^{31}$P-NMR data leave no doubt as to its identity. The spectroscopic data obtained were in quantitative agreement with the data found for the same cation prepared from **1** (see Experimental Section).

The fact that not only carbon-centred dienes but also conjugated mono-heterodienes coordinate to the [*tripod*Co]$^+$ template in a η$^4$ fashion indicates that this template is ideally suited for the coordination of ligands containing a 4-centre 4π-system. In this respect, the template behaves as expected for an isoelectronic equivalent of Fe(CO)$_3$ and CpCo. The Fe(CO)$_3$ template is known to form stable derivatives with dienes, and is the only known template that also allows the η$^4$-coordination of heterodienes.[11−13] In fact, to the best of our knowledge, η$^4$-coordination of dienes and thioacrolein has hitherto only been achieved using this type of iron-centred template.[14]

By generating [*tripod*Co]$^+$ in the presence of 1,2-diketones, the question was addressed whether these 4-centre 4π-systems would bind in a η$^4$-coordination mode or whether, by electron-transfer processes, they would be transformed into η$^2$-coordinating enediolato-type ligands. The coordination of a dialdehyde to the Cp*Co template, in a fashion where at least one CO group of the ligand forms a π-bond with the other one acting as a σ-donor, has recently been reported by Brookhart et al., and hence the η$^4$-coordination of 1,2-diketones cannot a priori be excluded.[15] However, reaction of benzil or phenanthrenequinone with **1** in the presence of TlPF$_6$ produces the enediolato derivatives **5** (Scheme 8).



| Nr. | Dione |
|---|---|
| **5a** | Benzil |
| **5b** | 9,10-Phenanthrenequinone |

Scheme 8

Formal oxidation of Co$^I$ to Co$^{III}$ thus took place, with a corresponding formal two-electron reduction of the diketones to produce enediolato ligands. It appears that the propensity of the [*tripod*Co]$^+$ template to acquire an 18-electron configuration − which it would have if the dione were to have bound as a η$^4$-diene ligand − is not sufficiently strong to counterbalance the formation of the stable five-membered cycles present in **5** accompanied by a 16-electron configuration at the cobalt centre. Many compounds showing the same type of bonding of 1,2-dioxo ligands as found in **5** are known, and an alternative synthesis of **5b** has been mentioned in the literature.[4a−4c] A characteristic feature of such compounds is that they show a prominent long-wavelength absorption at around 800 nm, which has been interpreted in terms of an LMCT band.[4c] This type of band is also seen for compounds **5** (Table 4). The η$^4$-binding mode of the dienes present in **2** and **3** gives rise to a distinctly different electronic absorption pattern (Table 4).

The η$^2$-bonding mode of the ligands in **5**, which, as outlined above, could be established on the basis of the electronic spectra, was further corroborated by the observation that the $^{13}$C resonances of the carbon atoms in the 2,3-positions of the unsaturated ligands are at distinctly different δ values for the η$^4$-coordinated dienes (**2**, **3**) as compared to the corresponding shifts for the η$^2$-coordinated ligands in **5** (Table 1, Table 2, Table 3). Moreover, the $^{31}$P resonances of **5** (Table 3) appear in a range characteristic of [*tripod*Co(diolato)]$^+$ compounds (δ = 30−36), which is again distinctly different from the range in which the corresponding resonances for the η$^4$-diene derivatives **2** and **3** are seen (Table 1, Table 2).[4a−4c]

Compounds **5** were obtained in microcrystalline form as the intense cornflower-blue PF$_6$ salt (**5a**) or as the blue-green BPh$_4$ salt (**5b**). The results of an X-ray structure analysis of single crystals of **5b** were in complete agreement with the constitution established on the basis of spectroscopic data, clearly showing the η$^2$-binding mode of the enediolato ligand (Figure 4; Table 6, Table 10).

## Structure and Dynamics

While the structure of **5b** needs no further comment since it is in very good agreement with the many well-documented and discussed structures of the [*tripod*Co-(enediolato)]$^+$ type, the structures of the compounds containing η$^4$-coordinated dienes merit further discussion.[4a−4c]

If the geometries of these compounds (Figure 1, Figure 2, Figure 5, Figure 6; Table 5) are described as square-pyramidal, then the axial Co−P bond lengths (Co−P2) might be expected to be different from the equatorial distances. However, it is found that in all the compounds mentioned in this paper, **2c**, **3a**, and in the literature, [*tripod*Co$^I$-(η$^4$-C$_7$H$_8$)]$^+$ (**A**, **B**, Figure 6; Table 5), [(Me$_3$P)$_3$Co$^I$-(η$^4$-C$_7$H$_8$)]$^+$ (**C**, Figure 6; Table 5), the Co−P bonds are of approximately equal length.[2e,10] In **2c**, the equatorial bond Co−P1 [228.5 (1) pm] is some 7 pm longer than the Co−P2 [221.2

Table 3. Analytical data for compounds **4** and **5**

| | **4**·$BPh_4^-$ | **5a**·$PF_6^-$ | **5b**·$BPh_4^-$ |
|---|---|---|---|
| $^1H$ NMR | $CD_2Cl_2$ | $CD_3NO_2$ | $CD_2Cl_2$ |
| *tripod*-$CH_3$ | 1.91 br., 3 H | 1.94 br., 3 H | 1.80 m, 3 H |
| *tripod*-$CH_2$ | 2.70 br., 6 H | 2.81 br., 6 H | 2.68 m, 6 H |
| arom. H | 7.21−7.31 m, 50 H | 7.15−7.93 m, 40 H | 6.92−8.90 m, 38 H |
| $^{31}P\{^1H\}$ NMR | $CD_2Cl_2$ | $CD_3NO_2$ | $CD_2Cl_2$ |
| $PPh_2$ | 23.8 s | 32.7 s | 36.8 s |
| $PF_6$ | − | −144.2, $^1J_{PF}$ = 713 Hz | − |
| $^{13}C\{^1H\}$ NMR[a] | $CD_2Cl_2$ | $CD_3NO_2$ | $CD_2Cl_2$ |
| *tripod*-$CH_3$ | 36.7 m | 35.5 m | 36.8 m |
| *tripod*-$CH_2$ | 33.7 m | 30.9 m | 32.0 m |
| *tripod*-$C_q$ | 37.4 s | 38.2 s | 38.6 s |
| arom. C | 129.3−140.2 | 128.8−140.1 | 122.1−136.4 |
| CO | 206.1 s | 172.1 s | 165.0 s |
| elemental analysis[b] | C: 75.99/75.31 | C: 63.59/62.83 | C: 78.35/75.18 |
| (calcd./found) | H: 5.62/5.55 | H: 4.75/5.03 | H: 5.58/5.78 |
| HR-FAB (m/z): | 739.1495/739.1497 | 893.2278/893.2316 | 891.2121/891.2157 |
| (calcd./found) | 711.1545/711.1562 | | |

[a] $CH_3$, $CH_2$, CH, and C carbons were assigned by means of a 135° DEPT experiment. − [b] The rather poor data obtained for **5b**·$BPh_4^-$ may be attributed to inappropriate handling of this sensitive compound during microanalytical workup. Moreover, with the equipment used, carbon values tend to be too low in the presence of boron.

(1) pm] and Co−P3 [221.4 (1) pm] bonds. An explanation for this difference might be found in the interaction between the phenyl groups at P1 and the cyclopentadiene ligand. A comparison of the structures shown in Figure 5 and Figure 6 shows that the orientation of these phenyl groups is distinctly different in **2c** (Figure 6) from the observed orientations in **3a** (Figure 5) and **A**, **B** (Figure 6). The torsion angles given in Table 5 quantify this difference. Comparing the positions of the diene ligands relative to the [*tripod*Co] entities in Figure 5 and Figure 6, it can be seen that the diene ligand in **2c** is positioned such as to reduce this interaction. In all the compounds examined (Figure 5, Figure 6; Table 5, Table 10), the cobalt−carbon bonds to the central carbon atoms of the diene systems are shorter than those to the terminal carbon atoms. This corresponds to a general rule.[9,10,16]

The cobalt−sulfur bond to the sulfur atom of the thioacrolein ligand in **3a** measures 231.3(4) pm. Since the heterodiene is approximately planar (C9−C8−C7−S6: 5°), this indicates a shift of the diene ligand relative to the [*tripod*Co] entity (Figure 5; Table 5, Table 10). The bond lengths within the diene ligands are as expected, as are the angles and torsion angles within the [*tripod*Co] cages (Table 5, Table 10).

The description of the compounds as idealized square-pyramidal is perhaps rather too simplistic. The rotational positions of the diene ligands relative to a pseudo $C_3$-axis of the [*tripod*Co] entity, vertical in relation to the P1−P2−P3 plane and centred at the cobalt atom, are rather

Table 4. Analytical data for compounds **2** to **5**

| Compound | IR: $\tilde{\nu}$ [$cm^{-1}$] | UV/vis: nm [$L\ mol^{-1}cm^{-1}$][a] | CV potential[a] | MS (*m*/*z*) |
|---|---|---|---|---|
| **2a**·$PF_6^-$ | PF: 837 vs | 355 (1190); 440 (450) | $E_{1/2}$ = 888 mV, $\Delta E$ = 150 mV;<br>$E_p^A$ = 1680 mV; $E_p^C$ = −1530 mV<br>$\Delta E_{Fc}$ = 125 mV | FAB: 751 [$M^+$];<br>683 [$M^+$ − isoprene] |
| **2b**·$PF_6^-$ | PF: 839 vs | 410 (1140); 460 (570) | $E_{1/2}$ = 885 mV, $\Delta E$ = 290 mV;<br>$E_p^C$ = −1770 mV<br>$\Delta E_{Fc}$ = 120 mV | FAB: 765 [$M^+$];<br>683 [$M^+$ − 2,3-dimethylbutadiene] |
| **2c**·$PF_6^-$ | PF: 839 vs | 340 (1190); 440 (310) | $E_p^A$ = 900 mV;<br>$E_p^C$ = −1200 mV | FAB: 749 [$M^+$]; 748 [$M^+$ − H];<br>683 [$M^+$ − cyclopentadiene] |
| **3a**·$BPh_4^-$ | | 444 (1810); 590 (1230) | $E_p^A$ = 360 mV; $E_p^A$ = 1300 mV<br>$E_p^C$ = −830 mV | FAB: 755 [$M^+$];<br>683 [$M^+$ − thioacrolein] |
| **3b**·$PF_6^-$ | PF: 841 vs | 420 (1105); 530 (890) | $E_p^A$ = 1350 mV;<br>$E_p^C$ = −950 mV | FAB: 739 [$M^+$];<br>683 [$M^+$ − acrolein] |
| **3c**·$PF_6^-$ | PF: 841 vs | 390 (1870); 580 (1250) | $E_p^A$ = 1180 mV;<br>$E_p^C$ = −840 mV | FAB: 753 [$M^+$];<br>683 [$M^+$ − methyl vinyl ketone] |
| **4**·$BPh_4^-$ | CO: 1965, 2025 vs | | $E_{1/2}$ = 1120 mV, $\Delta E$ = 155 mV[b]<br>$E_p^C$ = −1500 mV;<br>$\Delta E_{Fc}$ = 125 mV | FAB: 739 [$M^+$]; 711 [$M^+$ − CO]<br>683 [$M^+$ − 2 CO] |
| **5a**·$PF_6^-$ | PF: 837 vs | 390 (2590); 590 (3140);<br>730 (2540) | $E_p^C$ = −850 mV;<br>$E_p^A$ = 760 mV; | FAB: 893 [$M^+$]; 683 [$M^+$ − benzil]<br>683 [$M^+$ − benzil] |
| **5b**·$BPh_4^-$ | | 390 (6920); 640 (5190);<br>810 (1380) | $E_{1/2}$ = −610 mV, $\Delta E$ = 110 mV;<br>$E_p^A$ = 840 mV;<br>$\Delta E_{Fc}$ = 135 mV | FAB: 891 [$M^+$];<br>683 [$M^+$ − phenanthrenequinone] |

[a] All measurements were performed in $CH_2Cl_2$ solution at scan speeds of 200 $mVs^{-1}$. − [b] Quasi-reversible oxidation.

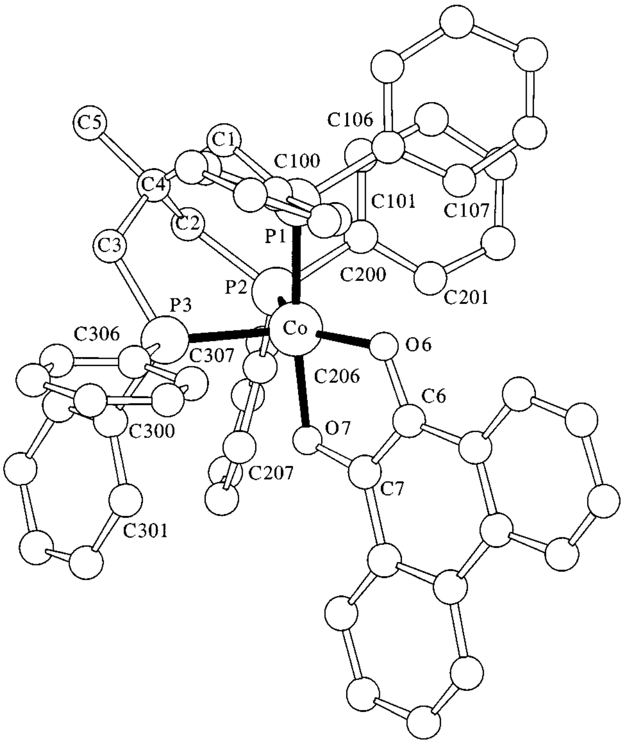


Figure 4. X-ray structure of **5b**

different. As a point of reference for describing this rotation with respect to the diene system, the midpoint of the central bond C7−C8 of this system was chosen. The point of reference with respect to the [*tripod*Co] template was chosen as P1. The angle φ describing the rotation of these reference points with respect to the pseudo axis was found to lie between 27° and 84° in the *tripod* derivatives and to be 40° in the $PMe_3$ derivative (Figure 5, Figure 6; Table 5, Table 10). It thus appears that the rotational position is rather flexible.

If the rotational positions were fixed, the phosphorus nuclei would reside in different environments even in solution, such that, depending on the symmetry of the arrangement, three or at least two different phosphorus signals could be expected to be observed by $^{31}$P-NMR spectroscopy. In fact, it is observed that compounds **2** give rise to only one $^{31}$P-NMR signal in $CD_2Cl_2$ solution, which shows no broadening even on cooling to 193 K. Since it is improbable that all three nuclei − given a static structure − are isochronous, it must be concluded that the all-carbon diene ligands in **2** are free to rotate even at low temperatures, such that a time-averaged $^{31}$P-NMR signal is observed. This is in contrast to observations made for other compounds of the type [$L_3M(\eta^4$-diene)].[8−10,17] In these cases, the ligands L were non-chelating phosphorus donors. For compounds of this type, rotation − even at temperatures close to ambient − is generally sufficiently slow to result in resolution into dis-

Table 5. Bond lengths [pm], bond angles [°], and torsion angles [°] in **2c**, **3a**, **A**, **B**, and **C**

| Compound[a] | **2c**·$PF_6^-$ | **3a**·$BPh_4^-$ | [*tripod*Co($\eta^4$-$C_7H_8$)]$^+$ **A**, **B**[b,c] | [$(Me_3P)_3Co(\eta^4$-$C_7H_8$)]$^+$ **C**[b] |
|---|---|---|---|---|
| Co−P1 | 228.50(13) | 221.4(4) | 224.1(8)/223.1(8) | 222.1(2) |
| Co−P2 | 221.23(12) | 224.2(3) | 223.7(7)/226.9(7) | 223.4(2) |
| Co−P3 | 221.40(13) | 224.4(3) | 224.8(7)/226.0(8) | 224.9(2) |
| Co−C6/Co−S6[d] | 209.8(4) | 231.3(4) | 213(3)/208(2) | 211.7(8) |
| Co−C7 | 205.6(5) | 205.3(14) | 213(3)/197(3) | 203.9(8) |
| Co−C8 | 206.0(4) | 206.9(12) | 209(3)/204(2) | 203.6(8) |
| Co−C9 | 212.4(4) | 211.3(12) | 224(2)/213(2) | 213.6(9) |
| C7−C6/C7−S6[d] | 141.2(6) | 173.9(15) | 150(4)/143(3) | 142(1) |
| C7−C8 | 143.0(7) | 138.2(2) | 140(4)/140(3) | 138(1) |
| C8−C9 | 139.8(7) | 142.5(17) | 148(4)/139(3) | 143(1) |
| C8−C7−C6/S6[d] | 106.5(4) | 119.1(12) | 114.6(26)/121.1(2) | 119.2(8) |
| C7−C8−C9 | 106.9(4) | 118.9(12) | 126.2(25)/114.7(20) | 120.3(8) |
| P1−Co−P2 | 93.71(5) | 93.80(13) | 95.5(3)/91.6(3) | 100.87(8) |
| P2−Co−P3 | 89.12(5) | 87.45(13) | 90.8(3)/90.5(3) | 95.49(9) |
| P1−Co−P3 | 91.71(5) | 95.17(13) | 872(3)/87.7(3) | 97.91(9) |
| C9−C8−C7−C6/S6[d] | −1.1 | 5 | −2.7/1.6 | −0.3 |
| C4−C1−P1−Co | 34.4 | 36.3 | 18.3/28.8 | − |
| C4−C2−P2−Co | 32.9 | 32.7 | 14.8/32.6 | − |
| C4−C3−P3−Co | 29.6 | 21.8 | −2.0/32.7 | − |
| Hz−P1−C100−C101[e] | 8.5 | −14.6 | 24.6/−23.7 | − |
| Hz−P1−C106−C107[e] | −6.2 | −59.6 | 52.1/−53.6 | − |
| Hz−P2−C200−C201[e] | −40.4 | 14.1 | 25.9/2.5 | − |
| Hz−P2−C206−C207[e] | −62.7 | 7.7 | 65.8/−15.1 | − |
| Hz−P3−C300−C301[e] | 14.0 | −68.1 | 33.3/−46.8 | − |
| Hz−P3−C306−C307[e] | 50.0 | −23.3 | 28.6/−34.5 | − |
| φ[f] | 84 | 27 | 78/57 | 40 |

[a] Standard deviations in units of the least significant digit are given in each case. − [b] Here, a consistent numbering scheme for all the complexes is used for the sake of easier comparison, which differs from that used for the deposited structures. − [c] Two independent molecules. − [d] In **3a**, S6. − [e] In order to define the rotation of the phenyl groups with respect to the idealized $C_3$ axis of the [tripodCo] entity, the following procedure was adopted: a vector vertical in relation to the P1−P2−P3 plane and pointing towards the observer with respect to the projections shown in Figure 5 and Figure 6 was fixed at the individual phosphorus atoms. Its end point was designated as Hz. The given torsion angles refer to this convention. − [f] The rotational position of the diene systems was characterized by the torsion angle φ. φ is measured as the rotation about an axis vertical with respect to the P1−P2−P3 plane and fixed to the cobalt atom. As a fixed point in the diene system, the midpoint between the two central carbon atoms (C7−C8) was chosen. The torsion angle about the pseudo axis between P1 and this point is defined as φ.

Table 6. Bond lengths [pm], bond angles [°], and torsion angles [°] in **4** and **5b**

| Compound | **4**·$BPh_4^-$[a] | **5b**·$BPh_4^-$[a] |
|---|---|---|
| Co−P1 | 222.57(8) | 219.5(8) |
| Co−P2 | 223.47(6) | 222.1(3) |
| Co−P3 | 226.02(7) | 221.5(4) |
| Co−X1[b] | 175.4(2) | 185.7(8) |
| Co−X2[b] | 177.6(2) | 186.7(8) |
| X1−Y1[b] | 115.5(3) | 129.9(12) |
| X2−Y2[b] | 113.7(2) | 129.3(12) |
| X1−Co−X2[b] | 86.94(9) | 82.2(3) |
| P1−Co−P2 | 88.24(3) | 91.26(12) |
| P2−Co−P3 | 96.01(3) | 92.34(12) |
| P1−Co−P3 | 90.07(3) | 91.57(13) |
| P1−Co−X1[b] | 87.86(7) | 88.0(3) |
| P2−Co−X1[b] | 141.87(8) | 136.5(3) |
| P3−Co−X1[b] | 121.90(8) | 131.2(3) |
| P1−Co−X2[b] | 169.63(7) | 169.9(3) |
| P2−Co−X2[b] | 90.32(7) | 97.6(3) |
| P3−Co−X2[b] | 100.30(7) | 93.0(3) |
| Co−X1−Y1[b] | 175.54(18) | 115.7(7) |
| Co−X2−Y2[b] | 176.51(18) | 113.3(8) |
| C4−C1−P1−Co | 17.0 | 17.8 |
| C4−C2−P2−Co | 28.7 | 15.3 |
| C4−C3−P3−Co | 16.7 | 19.2 |
| Hz−P1−C100−C101[c] | 30.8 | 21.4 |
| Hz−P1−C106−C107[c] | 29.8 | 40.0 |
| Hz−P2−C200−C201[c] | 7.2 | 18.4 |
| Hz−P2−C206−C207[c] | 84.0 | 57.0 |
| Hz−P3−C300−C301[c] | 7.8 | 18.9 |
| Hz−P3−C306−C307[c] | 24.2 | 31.4 |

[a] Standard deviations in units of the least significant digit are given in each case. − [b] X, Y refer to the residues at the [*tripod*Co] template in the sequence Co−X−Y. For compound **4**, the meaning of these symbols is thus X1, X2 = C6, C7 and Y1, Y2 = O6, O7. For compound **5**, it is X1, X2 = O6, O7, and Y1, Y2 = C6, C7. − [c] In order to define the rotation of the phenyl groups with respect to the idealized $C_3$ axis of the [*tripod*Co] entity, the following procedure was adopted: a vector vertical in relation to the P1−P2−P3 plane and pointing towards the observer with respect to the projections shown in Figure 5 and Figure 6 was fixed at the individual phosphorus atoms. Its end point was designated as Hz. The given torsion angles refer to this convention.

crete signals in the $^{31}$P-NMR spectra as well as in the $^1$H-NMR spectra for the groups which are symmetrically non-equivalent in a static arrangement.[8−10,17]

At first glance, it is difficult to understand why this type of rotation of the diene ligands should have a lower associated activation energy in the [*tripod*Co] compounds as compared to the non-chelate [$L_3$Co] derivatives. Comparing the structure of $[(Me_3P)_3Co^I\text{-}(\eta^4\text{-}C_7H_8)]^+$ (Figure 6; Table 5, Table 10) with those of the [*tripod*Co] compounds (Figure 5, Figure 6; Table 5, Table 10), it appears that the P−Co−P angles in the *tripod* derivatives are somewhat smaller than those in the $[(Me_3P)_3Co]$ compound. This would leave more space between the coordinated diene and the phosphorus nuclei in the *tripod* compounds as compared to that in the $[(Me_3P)_3Co]$ derivative (Figure 6; Table 5, Table 10). However, it would appear that the dominant repulsive interactions between the *tripod* ligand and the dienes are those between the substituents on phosphorus and the dienes and not those between the dienes and the phosphorus nuclei. Space-filling models of $[\textit{tripod}Co^I\text{-}(\eta^4\text{-}C_7H_8)]^+$ (**A**) and $[(Me_3P)_3Co^I\text{-}(\eta^4\text{-}C_7H_8)]^+$ (**C**) are shown in Figure 7.[2e,9] For the *tripod* compound **A**, no $^{31}$P-NMR data are available, but in view of the findings for compounds **2** it is probable that the diene ligand is free to rotate in this compound as well.[2e]

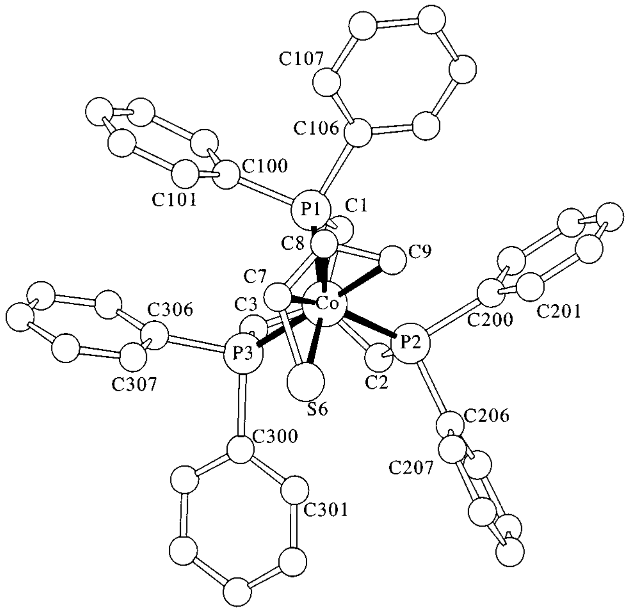
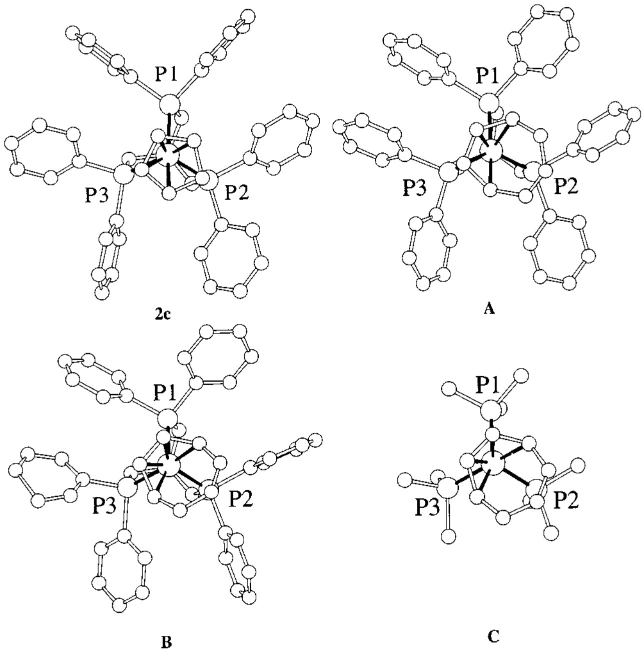


Figure 5. X-ray structure of **3a**; here, a consistent numbering scheme for all the compounds is used for the sake of easier comparison, which differs from that used for the deposited structure



**2c** **A** **B** **C**

Figure 6. X-ray structures of compounds **2c**, **A**, **B**, and **C**; here, a consistent numbering scheme for all the compounds is used for the sake of easier comparison, which differs from that used for the deposited structures

For $[(Me_3P)_3Co^I\text{-}(\eta^4\text{-}C_7H_8)]^+$, the NMR data reveal a static structure even at room temperature.[10] Figure 6 and Figure 7 suggest that the incorporation of methyl substituents at the phosphorus donors in $[(Me_3P)_3Co^I\text{-}(\eta^4\text{-}C_7H_8)]^+$ leads to a more congested steric situation than that in [*tri-*

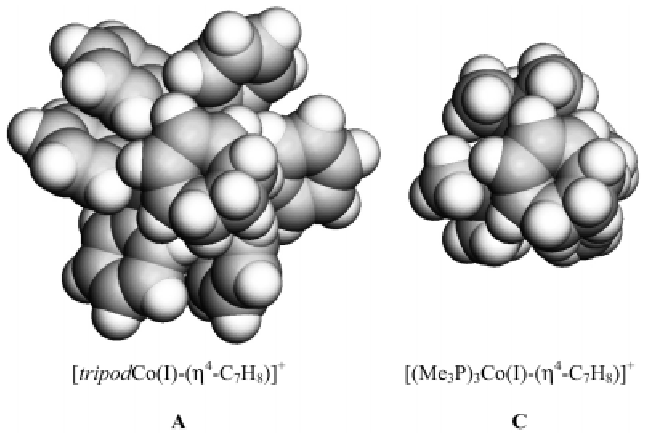


Figure 7. Space-filling models of **A** [*tripod*$\mathrm{Co^{I}}$-($\eta^4$-$C_7H_8$)]$^+$ and **C** [$(Me_3P)_3Co^{I}$-($\eta^4$-$C_7H_8$)]$^+$

*pod*$\mathrm{Co^{I}}$-($\eta^4$-$C_7H_8$)]$^+$, where a rotation of the phenyl groups may open up an almost unimpeded rotational pathway for the diene ligand.

The finding that there is still free rotation of the diene ligands in **2** at 193 K must mean that the electronic contribution to this barrier is rather low and hence the electronic preference for one orientation over the other must be small. This electronic contribution to the barrier might be expected to be higher with heterodiene ligands and indeed it is found that the heterodiene compounds **3** show three different phosphorus signals in their low-temperature $^{31}$P-NMR spectra (Table 7). On warming to 303 K, exchange processes become apparent such that for **3a** and **3b** only one time-averaged $^{31}$P-NMR signal is observed. In the case of **3c**, coalescence remains incomplete at 303 K. The spectra obtained at different temperatures have been analysed by line-shape analysis.[18] The quality of fit obtained by this procedure is shown for **3a** as a representative example, as is the Eyring plot obtained from the individual line-fitting procedures (Figure 8).

An activation enthalpy of 47 kJmol$^{-1}$ was determined for **3a** (Table 8). The activation enthalpies similarly derived for **3b** and **3c** were 46 kJmol$^{-1}$ and 48 kJmol$^{-1}$ (Table 8).

The activation entropies were found to be negative throughout the series of compounds **3a**−**3c** (Table 8). While the entropy value derived for **3b** ($-22 \pm 6$ Jmol$^{-1}$K$^{-1}$) was not too accurate, the activation entropy found for **3c** was definitely negative, more so than that determined for **3a** (Table 8). The entropy data thus suggest that the transition state associated with the rotational process is sterically more

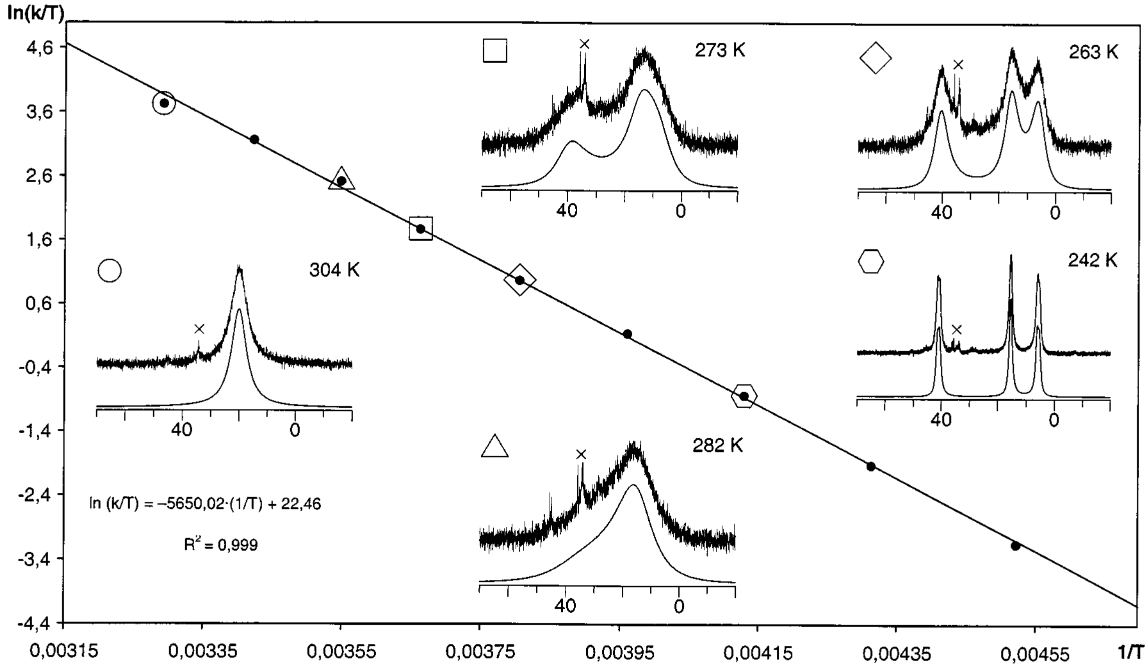


Figure 8. Eyring plot and examples of experimental (top) and simulated (bottom) spectra for compound **3a**; × denotes impurities

Table 7. $^{31}$P-NMR data for compounds **3a** to **3c**

| Compound | $T$ [K] | $P_a$ [ppm] | $P_b$ [ppm] | $P_c$ [ppm] | $J_{ab}$ [Hz] | $J_{ac}$ [Hz] | $J_{bc}$ [Hz] |
|---|---|---|---|---|---|---|---|
| **3a** | 221.13 | 41.1 | 15.3 | 6.2 | 16 | 64 | 8 |
| | 303.80 | – | 9.6 | – | | | |
| **3b** | 221.13 | 47.5 | 15.0 | −3.0 | 10 | 68 | 6 |
| | 303.80 | – | 18.0 | – | | | |
| **3c** | 241.70 | 47.7 | 14.3 | −3.4 | 16 | 67 | 13 |
| | 303.80 | 46.6 | 14.9 | −3.9 | | | |

Table 8. Calculated rotational barriers and thermodynamic parameters from line-shape analysis

| $T$ [K] | **3a**; $k$ [s$^{-1}$] | **3b**; $k$ [s$^{-1}$] | **3c**; $k$ [s$^{-1}$] |
|---|---|---|---|
| 221.13 | 9.5 | 4 | − |
| 231.88 | 34 | − | − |
| 241.70 | 105 | − | 8 |
| 252.55 | 290 | − | 25 |
| 262.82 | 690 | 215 | 145 |
| 273.06 | 1600 | − | 320 |
| 281.83 | 3500 | − | 640 |
| 292.27 | 6900 | − | 1200 |
| 303.80 | 12600 | 5300 | 2700 |
| Thermodynamic data[a] | $\Delta H^{\neq} = 47.0 \pm 0.5$ kJmol$^{-1}$<br>$\Delta S^{\neq} = -11 \pm 2$ Jmol$^{-1}$K$^{-1}$<br>$\Delta G^{\neq}_{298} = 50.2 \pm 0.5$ kJmol$^{-1}$ | $\Delta H^{\neq} = 46.3 \pm 1.5$ kJmol$^{-1}$<br>$\Delta S^{\neq} = -22 \pm 6$ Jmol$^{-1}$K$^{-1}$<br>$\Delta G^{\neq}_{298} = 53.0 \pm 2.9$ kJmol$^{-1}$ | $\Delta H^{\neq} = 47.9 \pm 0.7$ kJmol$^{-1}$<br>$\Delta S^{\neq} = -27 \pm 3$ Jmol$^{-1}$K$^{-1}$<br>$\Delta G^{\neq}_{298} = 56.0 \pm 0.1$ kJmol$^{-1}$ |

[a] Error estimates from linear regression; for a discussion concerning the estimation of the error in $\Delta G^{\neq}_{298}$, see ref.[24]

congested than the ground state. The activation enthalpies were found to be approximately equal for all three compounds **3a**−**3c**, despite the fact that the ligand in **3a** contains sulfur as the heteroatom while the ligands in **3b** and **3c** contain oxygen.

## Conclusion

Simple and straightforward procedures for the synthesis of [*tripod*Co$^{I}$-L$_2$]$^+$ have been described, where L$_2$ is a diene (isoprene, 2,3-dimethylbuta-1,3-diene, cyclopentadiene) (**2**) or heterodiene (acrolein, methyl vinyl ketone, thioacrolein) (**3**), coordinated in a $\eta^4$ fashion. While the idealized square-pyramidal coordination geometry observed for **2** and **3** in the solid state might be expected to give rise to chemically different phosphorus nuclei, only one sharp time-averaged $^{31}$P-NMR signal is observed for **2**. Only with **3** is the rotational reorientation process sufficiently slow to allow the observation of three different $^{31}$P-NMR signals at low temperatures. Line-shape analysis has allowed the estimation of $\Delta H^{\neq}$ in these cases, for which values close to 47 kJmol$^{-1}$ have been obtained for all the compounds analysed (**3a** thioacrolein, **3b** acrolein, **3c** methyl vinyl ketone).

## Experimental Section

**General Remarks:** Unless noted otherwise, all manipulations were carried out under argon using standard Schlenk techniques. All solvents were dried by standard methods and distilled under argon.[19] The zinc powder (Merck) used in some of the reactions was activated by stirring it under argon by means of a magnetic bar for 12 h. The solvents $CD_3NO_2$, [D$_6$]acetone, [D$_8$]THF, and $CD_2Cl_2$ used for NMR spectroscopic measurements were degassed by three successive ”freeze-pump-thaw” cycles and dried with 4 Å molecular sieves. − Photochemical reactions were carried out with a Hanau TQ high-pressure mercury lamp in a Duran glass 50 irradiation apparatus equipped with a cooling system. − NMR: Bruker Avance DPX 200 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 (residual protons in) $CD_3NO_2$ ($^1$H: δ = 4.33; $^{13}$C: δ = 62.8), [D$_6$]acetone ($^1$H: δ = 2.05; $^{13}$C: δ = 29.8, 206.2), [D$_8$]THF ($^1$H: δ = 1.72, 3.57; $^{13}$C: δ = 25.3, 67.4), and $CD_2Cl_2$ ($^1$H: δ = 5.32; $^{13}$C: δ = 53.8) as internal standards. $^{31}$P chemical shifts (δ) in ppm with respect to 85% $H_3PO_4$ ($^{31}$P: δ = 0) as external standard. − IR: Bruker IFS-66; KBr discs. − UV/vis: Perkin−Elmer Lambda 19 − Fast-atom bombardment (FAB) MS: Finnigan MAT 8230; xenon atom beam; 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: Gallenkamp MFB-595 010; uncorrected values. − 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 substrate in 0.1 M $n$Bu$_4$NPF$_6$/CH$_2$Cl$_2$.

**Preparation of *Tripod*CoCl (1):** 1 mmol (130 mg) of $CoCl_2$ and 1 mmol (624 mg) of $CH_3C(CH_2PPh_2)_3$ (*tripod*) were dissolved in 25 mL of THF to give a blue-green solution of *tripod*CoCl$_2$.[2b] An excess of activated zinc powder was then added to the solution, and the mixture was treated for 10 min. in an ultrasonic bath. When the reaction was complete, the mixture had become orange-beige in colour. The solvent was evaporated and the residue was redissolved in $CH_2Cl_2$. The solution was filtered to remove $ZnCl_2$ and excess zinc powder. The solvent was then evaporated once more to leave *tripod*CoCl (**1**) in analytically pure form. − $C_{41}H_{39}ClCoP_3$ calcd. C 68.48, H 5.47; found C 68.57, H 5.61.

**A: General Procedure for the Synthesis of [*Tripod*Co$^{I}$-($\eta^4$-diene)]$^+$ Complexes or [*Tripod*Co$^{III}$-diolato]$^+$ Compounds from 1,3-Dienes and Heterodienes [Diene = Isoprene (2a), 2,3-Dimethylbuta-1,3-diene (2b), Cyclopentadiene (2c), Acrolein (3b), Methyl Vinyl Ketone (3c), Benzil (5a), Phenanthrenequinone (5b)]:** 1 mmol (718 mg) of freshly prepared *tripod*CoCl (**1**) and 1 mmol (349 mg) of $TlPF_6$ were suspended in 20 mL of THF to give a yellow solution, from which a fine white precipitate was deposited. 1 mmol of the appropriate ligand (Table 9) was then added to this suspension and the reaction mixture was treated in an ultrasonic bath for 10 min. During the course of this procedure, the reaction mixture underwent a colour change to orange in the case of the carbon-centred dienes, to claret in the case of acrolein and methyl vinyl ketone, to cornflower blue with benzil, and to blue-green with phenanthrenequinone. The solvent was subsequently evaporated in vacuo and the residue was redissolved in $CH_2Cl_2$. This solution was filtered to remove the TlCl produced. The solvent was then evaporated once more and the residue (except in the case of **5b**) was purified by chromatography on silica gel (ICN Biomedicals, 32−63 µm, 60 Å),

Table 9. Analytical data for compounds **2** to **5**

| Compound | Coligand | Eluent mixture | Colour | Yield [%] (method) | m.p. [°C][a] |
|---|---|---|---|---|---|
| **2a** | 68 mg (1 mmol)<br>isoprene | $Et_2O/CH_2Cl_2$<br>(2:1) | orange | 78 (A)<br>64 (B) | 141 (dec.) |
| **2b** | 82 mg (1 mmol)<br>2,3-dimethylbutadiene | $Et_2O/CH_2Cl_2$<br>(2:1) | orange | 71 (A)<br>61 (B) | 150 (dec.) |
| **2c** | 66 mg (1 mmol)<br>cyclopentadiene | $Et_2O/CH_2Cl_2$<br>(2:1) | orange | 76 (A)<br>69 (B) | 155 (dec.) |
| **3a** | 108 mg (1.5 mmol)<br>2-propenethiol | – | brown-green | 35 | 130 (dec.) |
| **3b** | 56 mg (1 mmol)<br>acrolein | $Et_2O/CH_2Cl_2$<br>(3:1) | claret | 81 | 125 (dec.) |
| **3c** | 70 mg (1 mmol)<br>methyl vinyl ketone | $Et_2O/CH_2Cl_2$<br>(3:1) | claret | 78 | 130 (dec.) |
| **4** | 116 mg (2 mmol)<br>2-butenal | $Et_2O/CH_2Cl_2$<br>(3:1) | orange | 76 | 175 (dec.) |
| **5a** | 210 mg (1 mmol)<br>benzil | $Et_2O/CH_2Cl_2$<br>(4:1) | cornflower blue | 85 | 180 (dec.) |
| **5b** | 208 mg (1 mmol)<br>phenanthrenequinone | – | blue-green | 91 | 185 (dec.) |

[a] dec. = decomposition.

eluting with the solvent mixture indicated in Table 9, to afford the $PF_6$ salts of **2a**–**c**, **3b**, **3c**, and **5a**. In order to obtain the crystalline $BPh_4$ salt of **5b**, a solution of **5b**·$PF_6$ in THF was treated with a three-fold excess of $NaBPh_4$. The solvent was evaporated, the residue was redissolved in $CH_2Cl_2$, and this solution was filtered to remove $NaPF_6$ and excess $NaBPh_4$. Removal of the solvent afforded **5b**·$BPh_4$. For analytical data of the compounds, see Table 1, Table 2, Table 3, Table 4.

**B: General Procedure for the Synthesis of [*Tripod*Co$^I$-($\eta^4$-diene)]$PF_6$ Complexes [Diene = Isoprene (2a), 2,3-Dimethylbutadiene (2b), Cyclopentadiene (2c)]:** 1 mmol (342 mg) of $Co_{aq}(BF_4)_2$ and 1 mmol (624 mg) of *tripod* were dissolved in 30 mL of $CH_2Cl_2$/ethanol (1:1) to give a brown-red solution. 1 mmol of the appropriate diene (Table 9) and a five-fold excess of zinc powder were then added. The reaction mixture was treated in an ultrasonic bath for 5 min. The solvent was then removed in vacuo, the residue was redissolved in $CH_2Cl_2$, and this solution was filtered to remove $ZnCl_2$ and excess zinc powder. The filtrate was then concentrated to dryness, the residue was redissolved in THF, and treated with a three-fold excess of $KPF_6$. The solvent was again removed in vacuo, the residue was redissolved in $CH_2Cl_2$, and this solution was filtered to remove excess $KPF_6$ and $KBF_4$. The filtrate was concentrated to dryness and the residue was purified by chromatography on silica gel (ICN Biomedicals, 32–63 µm, 60 Å), eluting with the solvent mixture indicated in Table 9. After workup of the appropriate fractions, the $PF_6$ salts of **2a**–**c** were obtained as microcrystalline powders. For analytical data of the compounds, see Table 1, Table 4.

**Preparation of [*Tripod*Co$^I$-($\eta^4$-thioacrolein)]$BPh_4$ (3a·$BPh_4^-$):** 1 mmol (342 mg) of $Co_{aq}(BF_4)_2$ and 1 mmol (624 mg) of *tripod* were dissolved in 30 mL of THF/ethanol (1:1) to give a brown-red solution. Addition of 1.5 mmol (108 mg) of allyl mercaptan and 3 mmol (1026 mg) of $NaBPh_4$ led to an immediate colour change to dark brown. After filtration through silanized silica gel (Merck), the filtrate was concentrated in vacuo to a volume of 20 mL. The Schlenk tube was then flushed with argon and sealed with a rubber stopper. After 3 days, a brown-green precipitate had been deposited, which was washed with $Et_2O$ (3 × 10 mL). The product, which could reproducibly be obtained, was identified as analytically and spectroscopically pure **3a**·$BPh_4$ (Table 2, Table 4).

**Preparation of [*Tripod*Co$^I$-$(CO)_2$]$BPh_4$ (4·$BPh_4^-$): (a) From 2-Butenal:** 1 mmol (718 mg) of freshly prepared *tripod*CoCl (**1**) and 1 mmol (349 mg) of $TlPF_6$ were suspended in 20 mL of THF to give a yellow solution, from which a fine white precipitate was deposited. 2 mmol (116 mg) of 2-butenal (commercial *E*/*Z* mixture) was added to this suspension and the reaction mixture was treated in an ultrasonic bath for 10 min. During the course of this procedure, the reaction mixture underwent a colour change to orange. The solvent was then evaporated in vacuo and the residue was redissolved in $CH_2Cl_2$. This solution was filtered to remove the TlCl produced. After concentration of the filtrate, the residue was redissolved in THF and this solution was treated with a three-fold excess of $NaBPh_4$. The solvent was evaporated, the residue was redissolved in $CH_2Cl_2$, and this solution was filtered to remove $NaPF_6$ and excess $NaBPh_4$. Concentration of the filtrate and purification of the residue by chromatography on silica gel (ICN Biomedicals, 32–63 µm, 60 Å), eluting with the solvent mixture indicated in Table 9, gave the $BPh_4$ salt of [*tripod*Co$^I$-$(CO)_2]^+$. For analytical data of the compound, see Table 3, Table 4.

**(b) From CO:** 1 mmol (718 mg) of freshly prepared *tripod*CoCl (**1**) and 1 mmol (349 mg) of $TlPF_6$ were suspended in 20 mL of THF to give a yellow solution, from which a fine white precipitate was deposited. CO was then bubbled through this solution for 10 min., leading to a colour change to orange. The solvent was then evaporated in vacuo and the residue was redissolved in $CH_2Cl_2$. This solution was filtered to remove the TlCl produced. After concentration of the filtrate, the residue was redissolved in THF and this solution was treated with a three-fold excess of $NaBPh_4$. The solvent was evaporated, the residue was redissolved in $CH_2Cl_2$, and this solution was filtered to remove $NaPF_6$ and excess $NaBPh_4$. Concentration of the filtrate and purification of the residue by chromatography on silica gel (ICN Biomedicals, 32–63 µm, 60 Å), eluting with the solvent mixture indicated in Table 9, gave the $BPh_4$ salt of [*tripod*Co$^I$-$(CO)_2]^+$. For analytical data of the compound, see Table 3, Table 4.

**Preparation of [*Tripod*Co$^I$-(norbornadiene)]$PF_6$ and [*Tripod*Co$^I$-(1,5-cyclooctadiene)]$PF_6$:** 1 mmol (718 mg) of freshly prepared *tripod*CoCl (**1**) and 1 mmol (349 mg) of $TlPF_6$ were suspended in 20 mL of THF to give a yellow solution, from which a fine white precipitate was deposited. 1 mmol of the appropriate ligand was then added to this suspension and the reaction mixture was treated in an ultrasonic bath for 10 min. During the course of this procedure, the reaction mixture underwent a colour change to brown-

Table 10. Crystal data for compounds **2c**, **3a**, **4**, and **5b**

| Compound | **2c**·$PF_6^-$ | **3a**·$BPh_4^-$ | **4**·$BPh_4^-$ | **5b**·$BPh_4^-$ |
|---|---|---|---|---|
| Formula | $C_{46}H_{45}CoF_6P_4$ | $C_{68}H_{63}BCoP_3S$ | $C_{67}H_{59}BCoO_2P_3$ | $C_{79}H_{67}BCoO_2P_3$ |
| Molecular mass | 894.630 | 1074.890 | 1058.790 | 1210.98 |
| Crystal system | monoclinic | monoclinic | monoclinic | monoclinic |
| Space group | $P2_1/n$ (No. 14)[22] | $C2/c$ (No. 15)[22] | $P2_1/c$ (No. 14)[22] | $C2/c$ (No. 15)[22] |
| Lattice constants | $a$ = 1051.7(2) pm | $a$ = 3809(1) pm | $a$ = 1323.5(3) pm | $a$ = 2450.8(5) pm |
| | $b$ = 1745.5(4) pm | $b$ = 909.0(2) pm | $b$ = 2071.2(4) pm | $b$ = 1620.3(4) pm |
| | $c$ = 2239.9(5) pm | $c$ = 3277(1) pm | $c$ = 1990.3(4) pm | $c$ = 3652.0(7) pm |
| | $\beta$ = 90.99(3)° | $\beta$ = 96.61(3)° | $\beta$ = 98.50(3)° | $\beta$ = 100.02(1)° |
| Cell volume | $4111 \times 10^6$ pm$^3$ | $11564 \times 10^6$ pm$^3$ | $5396 \times 10^6$ pm$^3$ | $14281 \times 10^6$ pm$^3$ |
| Molecular units per cell | $Z = 4$ | $Z = 8$ | $Z = 4$ | $Z = 8$ |
| Density (calculated) | 1.445 g cm$^{-3}$ | 1.235 g cm$^{-3}$ | 1.303 g cm$^{-3}$ | 1.126 g cm$^{-3}$ |
| Temperature | 200 K | 293 K | 200 K | 290 K |
| Measuring device | Nonius-Kappa CCD | Siemens Nicolet-Syntex | Nonius-Kappa CCD | SiemensNicolet-Syntex |
| No. reflns. for cell refinement | – | 81 | – | 25 |
| Scan range | 3.6° < 2θ < 50.0° | 4.2° < 2θ < 46.1° | 2.9° < 2θ < 52.1° | 3.6° < 2θ < 48.0° |
| Method | ω-scan, Δω = 1.0° | ω-scan, Δω = 0.75° | ω-scan, Δω = 1.0° | ω-scan, Δω = 0.54° |
| Scan speed | 15 sec/frame | 2.2 < dω/dt < 29.3° min$^{-1}$ | 25 sec/frame | 12° min$^{-1}$ |
| Measured reflections | 16197 | 8166 | 126963 | 11305 |
| Unique reflections | 7247 | 8049 | 10664 | 11011 |
| Observed reflections ($I \geq 2\sigma$) | 5191 | 4383 | 8672 | 4632 |
| No. of parameters refined | 519 | 549 | 672 | 733 |
| Max. residual electron density | $2.89 \times 10^{-6}$ e pm$^{-3}$ | $2.55 \times 10^{-6}$ e pm$^{-3}$ | $0.93 \times 10^{-6}$ e pm$^{-3}$ | $1.67 \times 10^{-6}$ e pm$^{-3}$ |
| Agreement factors | $R_1 = 0.058$ | $R_1 = 0.122$ | $R_1 = 0.038$ | $R_1 = 0.127$ |
| ($F^2$ refinement) | $R_w = 0.160$ | $R_w = 0.328$ | $R_w = 0.103$ | $R_w = 0.406$ |

orange. The solvent was evaporated in vacuo and the residue was redissolved in $CH_2Cl_2$. This solution was filtered to remove TlCl. Evaporation of the solvent from the filtrate afforded the $PF_6$ salts as dark-orange powders. – $^{31}$P NMR ($CD_2Cl_2$): [*tripod*Co$^I$-(norbornadiene)]$^+$: δ = 23.8 (s), −144.2 (sept, $^1J_{PF}$ = 713 Hz); [*tripod*Co$^I$-(1,5-cyclooctadiene)]$^+$: δ = 24.1 (s), −144.2 (sept, $^1J_{PF}$ = 713 Hz). – IR (KBr): [*tripod*Co$^I$-(norbornadiene)]$^+$: ṽ (PF): 849 cm$^{-1}$ vs; [*tripod*Co$^I$-(1,5-cyclooctadiene)]$^+$: ṽ (PF): 837 cm$^{-1}$ vs. – FAB-MS: [*tripod*Co$^I$-(norbornadiene)]$^+$: $m/z$ = 775 [M$^+$]; [*tripod*Co$^I$-(1,5-cyclooctadiene)]$^+$: $m/z$ = 792 [M$^+$].

**Preparation of [*Tripod*Co$^I$-(ethylene)$_2$]PF$_6$:** 1 mmol (718 mg) of freshly prepared *tripod*CoCl (**1**) and 1 mmol (349 mg) of $TlPF_6$ were suspended in 20 mL of THF to give a yellow solution, from which a fine white precipitate was deposited. Ethylene was then bubbled through this solution for 15 min., leading to a colour change to brown-orange. The solvent was subsequently evaporated in vacuo and the residue was redissolved in $CH_2Cl_2$. This solution was filtered to remove the TlCl produced. Evaporation of the solvent from the filtrate afforded the $PF_6$ salt as a brown-orange powder. – $^{31}$P NMR ($CD_2Cl_2$): δ = 22.5 (br. s), −144.2 (sept, $^1J_{PF}$ = 713 Hz). – IR (KBr): ṽ (PF): 839 cm$^{-1}$ vs. – MS-FAB: $m/z$ = 739 [M$^+$].

The $BPh_4$ salt of [*tripod*Co$^I$-(ethylene)$_2$]$^+$ could also be obtained by irradiation of [*tripod*Co$^I$-(CO)$_2$]BPh$_4$ (**4**) while bubbling ethylene through the reaction mixture for 1 h. – $^{31}$P NMR ($CD_2Cl_2$): δ = 22.5 (br. s). – MS-FAB: 739 [M$^+$].

**X-ray Crystallographic Study:** The measurements were made on a Siemens P4 four-circle diffractometer (**3a** and **5b**) or on a Nonius-Kappa CCD diffractometer (**2c** and **4**), using graphite-monochromated Mo-$K_\alpha$ radiation throughout. In the case of the measurements on the Siemens P4 four-circle diffractometer, the intensities of three check reflections (measured every 100 reflections) remained constant throughout the data collection, thus indicating crystal and electronic stability. The data collected on this instrument were corrected in the usual manner, including an experimental absorption correction. The data from the Nonius-Kappa CCD device were processed using the standard Nonius software.[20] All calculations were performed using the SHELXT-PLUS software package. Structures were solved by direct methods using the SHELXS-97 program and refined with SHELXL-97.[21][22] Graphical handling of the structural data during solution and refinement was performed with XPMA.[23] Atomic coordinates and anisotropic thermal parameters of the non-hydrogen atoms were refined by full-matrix least-squares calculations. Data relating to the structure determinations are compiled in Table 10. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-127496 to CCDC-127498. Copies of data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [Fax: (internat.) +44 (0)1223/336033; E-mail: deposit@ccdc.cam.ac.uk].

## Acknowledgments

We are indebted to the Deutsche Forschungsgemeinschaft (SFB 247) and the Fonds der Chemischen Industrie for financial support. One of us (R.R.) is indebted to the Graduiertenkolleg "Selektivität in der organischen und metallorganischen Synthese und Katalyse" for a scholarship. The unselfish cooperation of Dr. J. Groß and Mr. T. Jannack (mass spectrometric measurements), Mr. D. Günauer (cyclic voltammetry), and Mrs. A. Dittes, Mrs. C. Vetter, Mrs. E. Weiß and Mr. F. Liebscher (elemental analysis) is gratefully acknowledged.

---

[1] L. Sacconi, F. Mani, *Trans. Met. Chem.* **1982**, *8*, 179.

[2] Cobalt(I): [2a] L. Sacconi, S. Midollini, *J. Chem. Soc., Dalton Trans.* **1972**, 1213–1216. – [2b] K. Heinze, G. Huttner, L. Zsolnai, P. Schober, *Inorg. Chem.* **1997**, *36*, 5457–5469. – [2c] V. Sernau, G. Huttner, J. Scherer. L. Zsolnai, T. Seitz, *Chem. Ber.* **1995**, *128*, 193–195. – [2d] V. Sernau, G. Huttner, J. Scherer, O. Walter, *Chem. Ber.* **1996**, *129*, 243–245. – [2e] C. Bianchini, P. Dapporto, A. Meli, L. Sacconi, *J. Organomet. Chem.* **1980**, *193*, 117–126. – [2f] A. Barth, Ph. D. Dissertation, Universität

Heidelberg, **1990**. – [2g] J. Ellerman, J. F. Schindler, *Z. Naturforsch*. **1975**, *30b*, 914–919. – [2h] J. Ellermann, J. F. Schindler, *Chem. Ber*. **1976**, *109*, 1095–1105. – [2i] J. Ellermann, J. F. Schindler, *J. Organomet. Chem.* **1975**, *94*, 201–212. – [2j] C. A. Ghilardi, C. Mealli, S. Midollini, V. I. Nefedov, A. Orlandini, L. Sacconi, *Inorg. Chem*. **1980**, *19*, 2454–2462. – [2k] D. L. DuBois, D. W. Meek, *Inorg. Chem*. **1976**, *15*, 3076–3088. – [2l] M. Di Vaira, L. Sacconi, *Angew. Chem*. **1982**, *94*, 338–351; *Angew. Chem. Int. Ed. Engl.* **1982**, *27*, 330. – [2m] A. Barth, G. Huttner, M. Fritz, L. Zsolnai, *Angew. Chem.* **1990**, *102*, 956–958; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 929.

[3] Cobalt(II): see, for example ref.[1,2b,2f] – [3a] P. Dapporto, S. Midollini, L. Sacconi, *Inorg. Chem.* **1975**, *14*, 1643–1650. – [3b] S. Vogel, A. Barth, G. Huttner, T. Klein, L. Zsolnai, R. Kremer, *Angew. Chem*. **1991**, *103*, 325–327; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 303. – [3c] S. Vogel, G. Huttner, C. Emmerich, *Z. Naturforsch*. **1993**, *48b*, 353–362.

[4] Cobalt(III): see, for example, literature cited in: [4a] C. Bianchini, D. Masi, C. Mealli, *Inorg. Chem*. **1987**, *26*, 3683–3693. – [4b] S. Vogel, G. Huttner, L. Zsolnai, *Z. Naturforsch*. **1993**, *48b*, 641–652. – [4c] K. Heinze, G. Huttner, L. Zsolnai, A. Jacobi, P. Schober, *Chem. Eur. J.* **1997**, *3*, 732–743.

[5] K. Jonas, C. Krüger, *Angew. Chem*. **1980**, *92*, 513–531; *Angew. Chem. Int. Ed. Engl.* **1980, 19**, 520.

[6] K. Jonas, *Angew. Chem*. **1985**, *97*, 292–307; *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 295.

[7] G. A. Lawrance, *Chem. Rev.* **1986**, *86*, 17–33.

[8] M. Bressan, R. Ettorre, P. Rigo, *J. Organomet. Chem*. **1978**, *144*, 215–223.

[9] L. C. A. de Carvalho, Y. Pérès, M. Dartiguenave, Y. Dartiguenave, A. L. Beauchamp, *Organometallics* **1985**, *4*, 2021–2028.

[10] L. C. A. de Carvalho, M. Dartiguenave, Y. Dartiguenave, *J. Organomet. Chem*. **1989**, *367*, 187–195.

[11] A. Guinot, P. Cadiot, *J. Organomet. Chem*. **1980**, *194*, 357–365.

[12] D. C. Dittmer, K. Takahashi, M. Iwanami, *J. Am. Chem. Soc*. **1976**, *98*, 2795–2803.

[13] R. L. Harlow, C. E. Pfluger, *Acta Cryst*. **1973**, *B29*, 2633–2635.

[14] STNeasy search 1 Jun 30, 07:49:04, **1999**.

[15] C. P. Lenges, M. Brookhart, P. S. White, *Angew. Chem*. **1999**, *111*, 535–538, *Angew. Chem. Int. Ed. Engl.* **1999**, *38*, 552.

[16] F. A. Cotton, V. W. Day, B. A. Frenz, K. I. Hardcastle, J. M. Troup, *J. Am. Chem. Soc.* **1973**, *95*, 4522–4528.

[17] S. Komiya, H. Minato, T. Ikariya, T. Yamamoto, A. Yamamoto, *J. Organomet. Chem*. **1983**, *254*, 83–88.

[18] [18a] G. Binsch, *J. Am. Chem. Soc.* **1969**, *91*, 1304–1309. – [18b] WIN-Dynamics 1.0 Release 951220, NMR Dynamic Spectra Simulation and Iteration, Bruker-Fanzen Analytik GmbH and K. Ill′yasow, O. Nedopekin, Bremen, Germany.

[19] *Organikum*, Deutscher Verlag der Wissenschaften, Berlin, **1990**.

[20] DENZO-SMN, Data processing software, Nonius **1998**; http://www.nonius.com.

[21] [21a] G. M. Sheldrick, *SHELXS-97, Program for Crystal Structure Solution*, University of Göttingen, **1997**; http://shelx.uni-ac.gwdg.de/shelx/index.html. – [21b] G. M. Sheldrick, *SHELXL-97, Program for Crystal Structure Refinement*, University of Göttingen, **1997**; http://shelx.uni-ac.gwdg.de/shelx/index.html.

[22] *International Tables for X-ray Crystallography*, vol. 4, Kynoch Press, Birmingham, U.K., **1974**.

[23] L. Zsolnai, G. Huttner, *XPMA, http://www.rzuser.uni-heidelberg.de/~v54/xpm.html*, Universität Heidelberg, **1994**.

[24] G. Binsch, H. Kessler, *Angew. Chem*. **1980**, *92*, 445–463; *Angew. Chem. Int. Ed. Engl.* **1980**, *92*, 440.

Received August 12, 1999
[I99300]