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Examples of Different Reactions of Benzylsulfanyl-Substituted Alkynes with Selected Complexes of Ti^{II} and Co^{I}

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Reactions of the group 4 metallocene alkyne complexes $[Cp_2M(L)(btmsa)]$ (Cp = η^5 -cyclopentadienyl = η^5 -C₅H₅, btmsa = η^2 -Me₃SiC₂SiMe₃; **1**: M = Ti, L = none; **2**: M = Zr, L = pyridine) and of the $[(triphos)Co^{I}]$ moiety [triphos = 1, 1, 1tris(diphenylphosphanylmethyl)ethane] with the benzylsulfanyl-substituted acetylenes PhCH₂S-C₂-SCH₂Ph (3) and $PhCH_2S-C_2-SFmoc$ (4) (Fmoc = fluorenylmethoxycarbonyl) have been investigated. Complex 1 reacted with 3 to give a mixture of a violet solid and $[Cp_2Ti(SCH_2Ph)_2]$ (5). Subsequently, the violet solid transformed in toluene at 70 °C into the dinuclear complex $[(Cp_2Ti)_2(\mu-\kappa^2-\kappa^2-BnSC_4SBn)]$ (6) displaying two [Cp₂Ti] moieties bridged by a 1,4-bis(benzylsulfanyl)-1,3-butadiyne in the trans configuration. Complex 6 was further degraded in toluene at 100 °C to the tetranuclear cluster [CpTiS]₄ (7). Similar reactivity was deduced indirectly for the reaction partners 1/4 and 2/3. For Co^I, the side-on

Introduction

In general, the isolation of small unsaturated all-carbon metallacycles (Scheme 1, A–C, X = CH₂, CMe₂) is challenging due to their high ring strain,^[1–5] although an essential stabilisation effect has been attributed to interactions of metal d orbitals with remote π bonds. The formal substitution of ring CR₂ moieties by heteroatom groups leads to a variety of new species, the synthesis of which are motivated by their prospective preparative potential as well as an interest in investigating their stability. The first examples of stable type **B** metallapent-3-ynes with X = SiMe₂ and type **C** metallacycloallenes with X = NR appeared recently.^[6–8] However, examples of type **B** with X = NR or S have so

alkyne complexes [(triphos)Co(3)](PF₆) (9-PF₆) and [(triphos)-Co(4)](PF₆) (10-PF₆) were obtained. Reductive removal of the benzyl groups in $9-PF_6$ and subsequent coordination of the [Cp(PPh₃)Ru^{II}]⁺ moiety led to the dinuclear complex [(triphos)Co(μ - η^2 - κ^2 -C₂S₂)RuCp(PPh₃)] (13)displaying acetylene dithiolate (acdt²⁻) in a side-on carbon-sulfur chelate coordination mode. In contrast, the reaction of 10-PF₆ with piperidine under very mild conditions resulted in the thio-alkyne complex [(triphos)Co(PhCH₂SC₂S)] (11) bearing a terminal sulfur substituent at the coordinated alkyne. However, a subsequent rearrangement reaction led to the Co^{III} dithiolene complex $[(triphos)Co{S_2C_2(NC_5H_{10})(CH_2Ph)}]$ - (PF_6) (14-PF₆). The intricate rearrangement very likely involves a dinuclear Co species with a η^2 - κ^2 coordination of the C₂S₂ moiety.

far only been isolated as dinuclear complexes, which were formed by coordination of a second metal at the distal side of the metallaheterocyclopent-3-yne (Scheme 1, **E** and **F**). Complexes of this type show a remarkable versatility of bonding modes and canonical forms. According to Lentz et al., the dinuclear Mo complex **E** is best described as a *cis*diazabutatriene complex formed by the C–C coupling of $CF_3NC.^{[9]}$ The corresponding sulfur congeners **F** are related to acetylene dithiolate, but the precise description is dependent on the oxidation state of the metals.^[10]

In addition, Hessen et al. observed an interesting alternative *trans*-diazabutatriene complex **D** (Scheme 1).^[11] The obvious structural flexibility of the heterometallacycles mirrors that of the prototype all-carbon metallacyclocumulenes and -cyclopentynes (Scheme 2). Although the *trans* configuration was observed for group 4 metallocenes and diazametallacycles, dinuclear complexes with $acdt^{2-}$ (acetylenedithiolato) and group 6/group 8 transition metals show predominantly a *cis* configuration.

To gain a deeper insight into the existence and stability of such five-membered, unsaturated ring systems with different heteroatoms, the coordination chemistry of neutral donor-substituted acetylenes like $R_2N-C_2-NR_2$, R_2P-C_2-



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Scheme 1. Strained five-membered metallacycles and examples of dinuclear complexes of metallaheterocyclopent-3-ynes.



Scheme 2. Observed *cis* and *trans* dinuclear complexes of all-carbon metallacyclocumulenes or metallacyclopentynes.

PR₂ and RS–C₂–SR as well as the corresponding anionic ligands like $[S-C_2-S]^{2-}$ (acdt²⁻) is of high interest. We were particularly interested in whether the *cis* and *trans* configuration is forced either by a particular type of transition metal or the nature of the donor heteroatom. Therefore we have investigated the behaviour of exclusively sulfur-substituted alkynes with group 4 metallocenes on the one hand and electron-rich late-transition-metal complexes on the other. Because acetylenedithiol is intrinsically unstable, the bis(sulfanyl)alkynes were furnished with potential thiol protecting groups like benzyl and fluorenylmethoxycarbonyl (Fmoc). With respect to the electron/hole formalism, the d² metallocenes are the inverse of the Co^I d⁸ system. Therefore, in this contribution we compare the diverse reactivity of selected Ti^{II} metallocenes and the [(triphos)Co^I]⁺ moiety

[triphos = 1,1,1-tris(diphenylphosphanylmethyl)ethane] with the alkynes PhCH₂S–C₂–SCH₂Ph (**3**) and FmocS–C₂– SBn (**4**). Different reaction patterns and coordination modes of the stable final products were uncovered. As a result we present the full characterisation and X-ray crystal structure analyses of a dinuclear titanocene complex with a bridging C–C-coupled butadiyne derivative, a dinuclear Co/ Ru complex with a bridging acdt^{2–} and an intricate rearrangement reaction of a Co thioalkyne complex resulting in a Co^{III} dithiolene complex.

Results and Discussion

The reactions of group 4 metallocene alkyne complexes $[Cp'_2M(L)(btmsa)]$ (1: M = Ti, Cp' = Cp = η^5 -cyclopentadienyl, L = none; 2: M = Zr, Cp' = Cp, L = pyridine) and more sterically hindered complexes [M = Ti, Zr; L =none; Cp'₂ = *rac*-(ebthi) = *rac*-ethylenebis(tetrahydroindenyl), Cp*₂ = (η^5 -pentamethylcyclopentadienyl)₂] with the alkynes PhCH₂S–C₂–SCH₂Ph (3) and FmocS–C₂–SBn (4) were investigated. The alkyne 4, which is furnished with a potential *S*-protecting group, was synthesised by a standard procedure.^[12] However, with the metallocenes 1 and 2, only the symmetrically substituted alkyne 3 led to isolable compounds.

Complex 1 reacted with 3 in diethyl ether at room temperature to give a mixture of a violet solid and $[Cp_2Ti(SCH_2Ph)_2]$ (5), which is already known^[16] (Scheme 3). The violet solid, which is insoluble in diethyl ether, thf, *n*-hexane and toluene, was separated by filtration. Complex 5 was obtained from the filtrate by fractionated crystallisation using *n*-hexane. These crystals of 5 were suitable for X-ray crystallography. The violet solid was suspended in toluene and stirred at 70 °C for several hours, yielding [(Cp₂Ti)₂(μ - κ ²- κ ²-BnSC₄SBn)] (6) as a dark-green solid, which is poorly soluble in thf and toluene and insoluble in diethyl ether and n-hexane. When 6 was suspended in toluene and stirred at 100 °C for several hours, the solution turned dark brown and contained brown solids, which were recrystallised from toluene to yield 7 as dark-brown crystals. This multistep reaction is summarised in Scheme 3.

Furthermore, 2 was treated with 3 in diethyl ether under the same conditions as described above for 1. This procedure yielded a brown complex reaction mixture from which only a few crystals of $[Cp_2Zr(SBn)_2]$ (8) could be iso-



Scheme 3. Pathway for the reaction of 1 with 3.



lated by crystallisation from n-hexane. The reactions of the more sterically hindered titano- and zirconocenes under the same conditions led to black, very complex reaction mixtures from which no defined product could be isolated.

When one benzyl residue in the starting alkyne was substituted by an Fmoc protecting group (alkyne 4) and the reaction with 1 was carried out under the same conditions as described above, a very complex reaction mixture was obtained from which a small amount of a red solid was isolated and identified as 5. This led us to conclude that a similar C_{sp} -S bond activation occurred. Unfortunately, a complex related to 6 was not isolated.

Based on the isolated complexes and reaction steps, a reaction mechanism is proposed for the synthesis of complex 6 (Scheme 4). First, the starting material 1 generates in a typical dissociation of $Me_3SiC_2SiMe_3$ the titanocene

fragment [Cp₂Ti], which reacts with 3 to give the metallacyclopropene [$Cp_2Ti(\eta^2-BnSC_2SBn)$]. From this presumed intermediate both a dinuclear and mononuclear reaction pathway are possible (Scheme 4, left and right side, respectively). The latter would involve the oxidative addition of the C_{sp}-S bond to yield a σ-bonded acetylide and benzylthiolate directly attached to Ti in [Cp₂Ti(SBn)(C₂SBn)]. Similar reactions have been reported for other acetylenes like PhC₂Ph and Me₃SiC₂SiMe₃ with the formation of the acetylide moieties [M(Ph)(C₂Ph)] or [M(SiMe₃)(C₂SiMe₃)], respectively.^[13] The rearrangement of [Cp₂Ti(SBn)(C₂SBn)] to 5 and the tweezer compound $[Cp_2Ti(C_2SBn)_2]$, and the subsequent reaction of the latter Ti^{IV} complex with $[Cp_2Ti]$ should give a σ,π -acetylide-bridged Ti^{III} complex. Related dinuclear complexes have been extensively investigated for the combination of titanocene and late transition metals by



Scheme 4. Suggested pathways for the formation of complexes 5 and 6.

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Lang and co-workers.^[14] C–C coupling of the acetylides in such compounds is very typical and gives the product 6.

The alternative dinuclear mechanism (Scheme 4, left side) includes the coordination of both sulfur atoms in the metallacyclopropene $[Cp_2Ti(\eta^2-BnSC_2SBn)]$ by $[Cp_2Ti]$, which results in a dinuclear structure derived from **B** (X = SBn, Scheme 1). This compound could dissociate to give $[Cp_2Ti(SBn)]$ and $[Cp_2Ti(C_2SBn)]$, both as Ti^{III} complexes with the typical tendency of such compounds to dimerise. The acetylide gives the σ,π -acetylide-bridged Ti^{III} complex and, after C–C coupling of the acetylides, the product **6**. The Ti^{IV} -dithiolate complex **5** is formed after rearrangement and dissociation of $[Cp_2Ti]$ from the dinuclear Ti^{III} species $[Cp_2Ti(SBn)]_2$.

The molecular structure of **6** is depicted in Figure 1 and selected bond lengths and angles are given in Table 1. The central bond between C1–C1A has a length of 1.468(3) Å, consistent with a C_{sp^2} – C_{sp^2} single bond. The C1–C2 (C1A–C2A) bond has a length of 1.325(3) Å, in the typical range of a double bond. Therefore the Lewis representation of **6** in Scheme 4 can be regarded as appropriate. The Ti–C distances [2.078(2) and 2.117(2) Å] are not equal, resulting in an asymmetric coordination with respect to the Ti1–C1 axis. The central C₄ moiety lies in one plane with the titanium atoms. Angles C2–C1–C1A of 127.3(2)° and C1–C2–S1 of 123.3(2)° were observed.



Figure 1. Molecular structure of 6 in the crystal form with thermal ellipsoids set at the 50% probability level. Hydrogen atoms have been omitted for clarity.

The structural parameters of **6** are very similar to those of the related complex $[(Cp_2Ti)_2\{\mu-\kappa^2(1,3),\kappa^2(2,4)-tBu-C_4-tBu\}]$ (**6**-*t*Bu) bearing two terminal *tert*-butyl groups (Table 1).^[15] Only the angle C1–C2–S1 [123.3(2)°] in **6** devi-

Table 1. Selected bond lengths [Å] and angles [°] of compound 6 and 6-tBu.

6		6 - <i>t</i> Bu ^[a]	
C1–C2	1.325(3)	C1C2	1.325(5)
C1–C1A	1.468(3)	C2–C2A	1.494(6)
Til-C2	2.078(2)	Ti-C1	2.093(4)
Til-C1A	2.117(2)	Ti-C2A	2.142(3)
C1A-C1-C2	127.3(2)	C2A-C2-C1	128.2(4)
C1C2S1	123.3(2)	C2C1C3	132.0(3)

[a] See ref.^[15]. The corresponding bond lengths and angles are displayed on the same line. The original labelling scheme was retained.

ates by about 9° from the corresponding angle in 6-tBu [132.0(3)°]. Significant differences within the Ti₂C₄ core are solely observed for the bond lengths Ti1–C1A (corresponding to Ti–C2A in 6-tBu), being somewhat shorter in the sulfide derivative 6. In summary, the terminal substituents at the coordinated butadiyne chain exert a marginal influence on the structural parameters.

The side-product **5** has already been described in the literature,^[16] but its molecular structure has not been published until now. Red crystals of **5** suitable for X-ray crystallography were obtained from *n*-hexane solution. The molecular structure and selected parameters of **5** are depicted in Figure 2. It shows a tetrahedral geometry, with two SBn and two Cp moieties occupying the coordination sites. The heavier congener $[Cp_2Zr(SBn)_2]$ (**8**) shows a significantly larger S1–M–S2 angle of 99.52(2)°.^[17]



Figure 2. Molecular structure of **5** in the crystal form with thermal ellipsoids set at the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected bond lenghts [Å] and angles [°]: Ti1–S1 2.4085(5), Ti1–S2 2.3822(5), S1–Ti1–S2 95.42(2).

The cubic compound 7, which was obtained after thermolysis of **6**, was recrystallised from toluene to yield crystals suitable for X-ray analysis (Figure 3). The molecular structure shows a distorted cube composed of four [CpTi] units and four sulfur atoms with obtuse angles at titanium and acute ones at sulfur. Furthermore, the bond lengths and angles around the titanium atom are not equal: the Ti– S distances vary from 2.3508(8) to 2.4199(8) Å, the S–Ti–S angles are in the range of 97.84(3) to 105.42(3)° and the Ti–S–Ti angles range from 74.38(2) to 79.40(3)°. A similar structure with comparable bond lengths and angles was published for [Cp*TiS]₄ by Mach and co-workers.^[18] Re-



lated uncharged metal–sulfur cubane structures [CpMS]₄ have also been reported for other transition metals like vanadium,^[19] iron,^[20] chromium^[21] and cobalt.^[22]



Figure 3. Molecular structure of 7 in the crystal fom with thermal ellipsoids set at the 50% probability level. Cp rings are displayed as grey spheres for clarity. Selected bond lenghts [Å] and angles [°]: Ti1–S2 2.3508(8), Ti1–S1 2.3839(8), Ti1–S2A 2.4091(8), Ti2–S1 2.3537(8), Ti2–S2 2.3828(8), Ti2–S1A 2.4199(8), S2–Ti1–S1 97.89(3), S2–Ti1–S2A 100.63(3), S1–Ti1–S2A 105.42(3), S1–Ti2–S2 97.84(3), S1–Ti2–S1A 100.74(3), S2–Ti2–S1A 105.12(3), Ti2–S1–Ti1 79.32(2), Ti2–S1–Ti2A 77.70(2), Ti1–S1–Ti2A 74.38(2), Ti1–S2–Ti2 79.40(3), Ti1–S2–Ti1A 77.79(3), Ti2–S2–Ti1A 74.60(2).

The cleavage of C_{sp}-S bonds is in fact a frequent concomitant reaction in alkynyl thiolato and alkynyl sulfide coordination chemistry.^[23] However, the facile cleavage in bis(benzylsulfanyl)acetylene is surprising as the benzyl group usually serves as a protecting group in the preparation of alkyne complexes with acetylene dithiolate ($acdt^{2-}$) still bearing two terminal sulfur atoms.^[24] This strategy led successfully to a variety of heterobimetallic complexes with acdt²⁻ bridges, the side-on carbon-bound metals being either W^{II} (d⁴) or Co^I (d⁸).^[10] With respect to the targeted metalladithiacyclopentynes (\mathbf{B} , $\mathbf{X} = \mathbf{S}$, Figure 1), we chose at first the latter transition metal Co, which is thiophilic on the one hand and forms stable side-on carbon π complexes on the other. In addition, we decided to test the fluorenylmethoxycarbonyl (Fmoc) group as an S-protecting group, which can be removed by solvolysis under milder conditions compared with the benzyl group. Following the procedure of Dartiguenave and co-workers,^[25] the reaction of the symmetrical alkyne 3 as well as FmocS-C2-SBn (4) with [(triphos)CoBr] in the presence of KPF₆ in CH₃CN led to the alkyne complexes $[(triphos)Co(3)](PF_6)$ (9-PF₆) and $[(triphos)Co(4)](PF_6)$ (10-PF₆). The dark-green complexes were characterised as four-electron donor alkyne complexes by the ¹³C NMR resonances of the Co-bound C atoms (195.0 and 190.8 ppm for 10-PF₆). In addition, the identity of 10-PF₆ was proven by X-ray crystal structure analysis. The molecular structure of the cation $[10]^+$ is depicted in Figure 4 and selected parameters are given in the caption. The complex cation $[10]^+$ forms a distorted tetrahedral coordination sphere with the alkyne considered as occupying one coordination site. The bonding parameters are in the expected range and match those of related Co^I alkyne complexes.[10c,26]

A two-step reductive removal of the benzyl groups in 9- PF_6 using C_8K led to the anionic target complex K-12 (Scheme 5). The intermediate complex [(triphos)-



Figure 4. Molecular structure of the cation $[10]^+$ in the crystal of 10-PF₆·1.25CH₂Cl₂ with thermal ellipsoids set at the 40% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Co1–C1 1.846(5), Co1–C2 1.872(5), Co1–P2 2.149(1), Co1–P3 2.203(2), Co1–P4 2.163(2), C1–C2 1.288(7), C1–C2–S2 146.7(5), C2–C1–S1 144.4(5).

 $CoC_2(S)(SBn)$] (11), which was obtained (by a different procedure) and characterised previously,^[10c] must be isolated between the two reduction steps. Complex K-12 is difficult to characterise due to its limited stability. However, trapping experiments with K-12 and [CpRu(PPh₃)₂Cl] gave the neutral dinuclear complex 13 in moderate yields. Complex 13 shows a large low-field shift of the ¹³C NMR resonance for the Co-bound C atoms to 267.4 ppm.



Scheme 5. Synthesis of K-12 and trapping as dinuclear complex 13. Reagents and conditions: (i) C_8K , thf; (ii) [CpRu(PPh₃)₂Cl], thf.

The molecular structure of **13**, which was determined by X-ray diffraction analysis, is depicted in Figure 5 and selected parameters are given in the caption. Complex **13** displays a side-on carbon–sulfur chelate coordination of $acdt^{2-}$ bridging Ru and Co and representing a type F alkyne complex (Scheme 1) of a cycloruthenadithiapentyne. The μ - η^2 - κ^2 -coordination mode of $acdt^{2-}$ is caused by a substantial decrease in the alkyne bend back angles. Although the C_{sp}–S angles in **10**-PF₆ of 146.7(5) and 144.4(5)° are typical of 4e-donor alkyne complexes, these angles are 124.7(4) and 123.8(4)° in **13**. Interestingly, this change is not reflected in the Co–C1/C2 bond lengths, which are very similar in **10**-PF₆ and **13**. Another striking feature of the structure of **13** is the folding about the S–S axis. The plane angles SRuS and SCCS of the crystallographically independent mole-



cules in the X-ray structure solution of **13** range from 14.78 to 20.28°, which indicates the flat energy profile of the fold-ing.



Figure 5. Molecular structure of a selected crystal of 13 in $13 \cdot 0.5C_4H_8O_2$ with thermal ellipsoids set at the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Co1–C1A 1.850(5), Co1–C2 1.859(4), Co1–P1 2.169(1), Co1–P2 2.165(1), Co1–P3 2.165(1), C1A–C2 1.362(6), Ru1A–S1A 2.404(1), Ru1A–S2A 2.394(1), Ru1A–P4 2.257(1), C1A–C2–S2A 124.7(4), C2–C1A–S1A 123.8(4), S1A–Ru1A–S2A 85.71(4).

The reaction of 10-PF₆ with an excess of piperidine in thf solution led to the fast removal of the Fmoc group and formation of neutral [(triphos)CoC₂(S)(SBn)] (11), which is indicated by a distinct colour change from intense green to dark blue (Scheme 6). The identity of compound 11 displaying one terminal sulfur atom could be proven by ³¹P NMR and UV/Vis absorption spectroscopy (see Figures S1 and S2 in the Supporting Information). Surprisingly, pure 11 could not be isolated by the Fmoc method; the solutions turned green while evaporating the excess piperidine. According to ³¹P NMR spectroscopy, the crude product consisted of different species with partially free CH₂PPh₂ arms of triphos. Finally, from a solution of the mixture in either thf or toluene we were able to crystallise in up to 27% yield a new complex showing an unexpected connectivity. The result of the X-ray crystal structure analysis is depicted in Figure 6 and selected parameters are given in the caption.

The isolated complex cation $[14]^+$ is a dithiolene complex. The alkyne ligand has formally flipped over and two thiolato groups are coordinated to the Co centre. The free valences at the former triple bond are now substituted by a piperidinyl and a benzyl group. Owing to the positive overall charge, cobalt is reasonably regarded as Co^{III}. Hence, an oxidation has occurred on going from 10-PF₆ to 14-PF₆ with the oxidation equivalents coming from protons of piperidine (now attached to carbon) and piperidinium (formed in the essential deprotonation of the Fmoc group). The overall coordination polyhedron is best described as square pyramidal with a τ value of 0.11. However, the bonding of the donor atom P1 is rather restricted apical



Scheme 6. Reaction of 10-PF₆ with piperidine to give 14-PF₆ including a proposed mechanism via intermediate I.



Figure 6. Molecular structure of the cation $[14]^+$ in the crystal of 14-PF₆·2.25toluene with thermal ellipsoids set at the 40% probability level. Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Co1–S1 2.159(2), Co1–S2 2.146(2), Co1–P1 2.188(2), Co1–P2 2.236(2), Co1–P3 2.242(2), C1–C2 1.348(8), C1–C2–S2 119.7(5), C2–C1–S1 117.9(5), S1–Co1–S2 88.13(7).

due to the constraint of the triphos ligand. All bonding parameters are in the expected range. On average, the Col– P bond lengths are clearly longer in $[14]^+$ than those in $[10]^+$ and 13, which reflects the different physical oxidation states (Co^{III} vs. Co^I). The Co–S bond lengths are similar to those found in related dithiolato complexes. The values of



2.159(2) and 2.146(2) Å for Co1-S1 and Co1-S2 determined for [14]⁺ are somewhat shorter than the values of and 2.164(2) Å found 2.174(2)in [(triphos)Co- $(S_2C_6H_4)^{+}$,^[27] which can be attributed to the more pronounced dithiolene character in the ethylene derivative. Interestingly, the related alkyldithiolato complexes show τ values between 0.29 and 0.42, leading to two distinctively different Co-S bond lengths (2.155 and 2.197 Å, the latter being close to a *trans* phosphorus position),^[27a] whereas the dithiolene complexes are characterised by small τ values (avoiding a trans phosphorus position) and, accordingly, have comparable Co-S bond lengths.

The formation of the dithiolene complex $14-PF_6$ from the side-on alkyne complex 10-PF₆ raises the question as to whether the formal flipping of the alkyne ligand indeed involves only the mononuclear complex species or whether, in contrast, the dinuclear complex I shown in Scheme 6 is an essential intermediate. Insights into the mechanism were sought by reactivity studies, ³¹P NMR investigations and DFT calculations. The thio-alkyne complex 11, formed from [(triphos)Co(η^2 -BnS–C₂–SC₂H₄TMS)]PF₆ (15-PF₆) by reaction with [NBu₄]F is indefinitely stable in solution with hydrocarbons and ethers in an inert atmosphere. Complex 11 had been fully characterised and its molecular structure was elucidated by X-ray diffraction.^[10c] The reaction of pure 11 with an excess of piperidine in thf did not lead to [14]⁺ according to NMR spectroscopic evidence. However, ³¹P NMR studies indicated the existence of different species in solution including the starting material 11. Finally, the addition of a small amount of trifluoroacetic acid led to the formation of $14-CO_2CF_3$. It is instructive that none of the NMR spectroscopic investigations gave any evidence for any paramagnetic species. In addition, the ³¹P NMR spectra display resonances of the CH₂PPh₂ arms of free triphos (see Figure S1). DFT calculations with 11^{Me} (methyl instead of the benzyl substituent) using the B3IYP functional and a 6-311G(d,p) standard basis set revealed the in-plane lone pair at the terminal sulfur atom to be the HOMO (Figure S4). According to a natural bond order (NBO) analysis, the negative charges are located in the thioalkyne (-0.234 e⁻ at the terminal sulfur atom), which supports coordination of a second metal ion. In turn, positive charges are found on the CoP₃ moiety. However, the central Co atom is sterically protected by six phenyl groups. Any nucleophilic attack at Co requires the dissociation of one (diphenylphosphanyl)methyl arm, which is indeed observed in the NMR spectra.

In summary, a plausible reaction mechanism is suggested in Scheme 6 for the synthesis of 14-PF₆. First, the concerted mechanism with a dinuclear intermediate I could explain why no paramagnetic species was observed. Secondly, the dinuclear complex [(triphos)Co(C₂S₂)Co(triphos)], which is closely related to the cationic intermediate suggested, had recently been isolated and structurally characterised.^[28] The formation of the necessary [(triphos)Co]⁺ species even in catalytic amounts by dissociation of the alkyne BnS–C₂–SH from 11 could be provoked by protonation by the piperidinium cation. The final dissociation of the [(triphos)Co]⁺ species from the alkyne bond must involve a concerted reaction, or at least a preceding nucleophilic attack, because DFT calculations ruled out a minimum for the hypothetical cobaltadithiacyclopentyne complex [(triphos)CoS(SBn)C₂]. Geometry optimizations led always to a standard κ^1 -alkynethiolato complex with a terminal BnS group. The observation of free arms of the triphos ligand by ³¹P NMR might indicate that piperidine is already coordinated to the cobalt in the position of the dangling triphos arm ready to move to the carbon if the [(triphos)Co]⁺ moiety binds to the sulfur atoms. An alternative mechanism based on a mononuclear transformation is discussed in the Supporting Information (Figure S5). Unfortunately, further kinetic studies to prove the different mechanisms were seriously hampered by side-reactions.

Conclusion

Complexes of transoid butadiynes coordinated by two titanium atoms are usually obtained either from butadiynes and Ti^{II} precursors^[29–31] or from acetylides and Ti^{III} halides.^[32] In the latter case, C–C coupling of two phenylacetylide moieties in a titanocene complex was observed.

The facile synthesis of **6** from the Cp_2Ti^{II} complex **1** and $BnSC_2SBn$ (**3**) is unprecedented in so far as the cleavage of an alkyne carbon-heteroatom bond, with SBn as the leaving group, and the subsequent C–C coupling of the formed acetylide moieties leading to the zig-zag butadiyne complex **6** proceed consecutively.

In contrast, Co^I in the [Co(triphos)] η^2 -alkyne moiety allows the removal of thiol protective groups in order to derive coordinated alkynes with terminal sulfur atoms. However, the 1,3-shift of a Bn group in an alkyne complex with a distal BnS substituent and the subsequent rearrangement of the C_2S_2 moiety in the formation of 14-PF₆ is exceptional. Interestingly, for both transformations a change in the (metal) oxidation state is involved. For the early transition metals Ti and Zr the high d-orbital energies and the corresponding strong bias to oxidative addition may be crucial for the initial reaction step. For cobalt, the balance between π -donor ability to stabilise the alkyne complex and the thiophilicity of the final CoIII centre might be the determining factor. Nevertheless, the contrasting behaviour of alkynyl sulfides with Ti^{II} and Co^I sheds light on the versatile reactivity of sulfur-substituted alkynes.

Experimental Section

General: All experiments were conducted with exclusion of oxygen and moisture. All operations were carried out under argon using standard Schlenk techniques. Prior to use, *n*-hexane and toluene were distilled from sodium tetraethylaluminate and stored under argon. thf and diethyl ether were dried with sodium, then distilled from sodium tetraethylaluminate and stored under argon. [Cp₂Ti(btmsa)] (1), [Cp₂Zr(py)(btmsa)] (2) and the bis(benzylsulfanyl)acetylene (3) were prepared according to literature procedures.^[12,33] The following spectrometers were used: Mass spectra: MAT 95-XP (Thermo Electron); NMR spectra: Bruker AV250 and



AV300. ¹H and ¹³C chemical shifts are referenced to the solvent signals: [D₆]toluene ($\delta_{CH3} = 2.09 \text{ ppm}$, $\delta_{CH3} = 20.4 \text{ ppm}$), [D₈]thf ($\delta_{O-CH2} = 3.58 \text{ ppm}$, $\delta_{O-CH2} = 67.57 \text{ ppm}$) and CDCl₃ ($\delta_{H} = 7.26 \text{ ppm}$, $\delta_{C} = 77.16 \text{ ppm}$). IR: Nicolet 6700 FT-IR spectrometer with a smart endurance attenuated total reflection (ATR) device. Melting points: MP70, Mettler Toledo. Melting points were measured in sealed capillaries.

S-(4-Phenyl-3-thiabut-1-ynyl) O-Fluorenylmethyl Thiocarbonate (4): At -78 °C a solution of benzylethynyl sulfide (0.5 g, 3.38 mmol) in diethyl ether (80 mL) was treated with n-butyllithium (1.6 M solution in n-hexane, 2.1 mL). After 15 min of stirring, sulfur (108.3 mg, 3.38 mmol, dried in vacuo overnight) was added. After stirring at -78 °C for a further 15 min, the mixture was warmed to room temperature and stirred until the sulfur was consumed. The light-orange solution was cooled again to -20 °C and solid fluorenylmethoxycarbonyl chloride (874 mg, 3.38 mmol) was added in small portions. After stirring at -20 °C for a further 15 min, the solution was warmed to room temperature and stirred overnight. The orange suspension was filtered and the clear filtrate concentrated in vacuo. Finally, the crude product was purified by column chromatography (silica, n-hexane/ethyl acetate, 20:1) to obtain 4 as an orange oil, yield 1.02 g (75%). ¹H NMR (300 MHz, CDCl₃, 297 K): δ = 7.72–7.18 (m, 13 H, Ph), 4.45 (d, $J_{H,H}$ = 7.55 Hz, 2 H, OCH_2), 4.18 (t, $J_{H,H}$ = 7.55 Hz, 1 H, Fmoc-CH), 3.95 (s, 2 H, SCH₂) ppm. ¹³C NMR (75 MHz, CDCl₃, 297 K): δ = 142.7 (CO), 142.9, 141.3 (Fmoc-Cipso), 135.9 (Ph-Cipso), 129.1, 128.7, 128.1, 128.0, 127.3, 125.2, 120.2 (Ph-CH), 95.7 (BnSC-C-SCO), 78.3 (BnSC-CSCO), 71.1 (OCH₂), 46.6 (CH), 41.3 (BnSCH₂) ppm. C₂₄H₁₈O₂S₂ (402.53): calcd. C 71.61, H 4.51, S 15.93; found C 70.99, H 4.55, S 15.79.

[(Cp₂Ti)₂(BnSC₄SBn)] (6): A solution of 3 (135 mg, 0.5 mmol, 1 equiv.) in diethyl ether (20 mL) was added at room temp. to a stirred solution of 1 (267 mg, 0.75 mmol, 1.5 equiv.) in diethyl ether (20 mL). After stirring for 2.5 d at room temp., a black solution and a black-violet solid were formed. The solid was filtered off and washed once with thf (25 mL) and diethyl ether (2×20 mL). The resulting violet solid [m.p. 189-193 °C (dec.)] was too insoluble for NMR studies or recrystallisation. It was suspended in toluene and heated at 70 °C for 4 d to give a light-green solution and darkgreen (almost black) rhombic crystals of 6. After filtration, washing with toluene and drying in vacuo, pure 6 was obtained. In addition, the byproduct $[Cp_2Ti(SBn)_2]$ (5) was isolated from the filtrate and the washing solutions as red crystals by recrystallisation from toluene/n-hexane (ca. 1:2). 6: Yield 71 mg (44%), m.p. 122-124 °C (dec.). ¹H NMR (300 MHz, $[D_8]$ thf, 297 K): $\delta = 4.38$ (s, 4 H, CH₂), 5.53 (s, 20 H, Cp), 7.21-7.28 (m, 2 H, Ph), 7.31-7.39 (m, 4 H, Ph), 7.47–7.56 (m, 4 H, Ph) ppm. ¹³C NMR (300 MHz, [D₈]thf, 297 K): δ = 107.8 (Cp) ppm. Further signals were not observed due to low solubility. MS spectra showed only the thermolysis product 7, which could originate from the sample being heated in a steel crucible after introducing it into the spectrometer. $C_{38}H_{34}S_2Ti_2$ (650.57): calcd. C 70.16, H 5.27; found C 66.63, H 5.48. The data obtained for 5 were in accordance with ref.^[16].

Thermolysis of Complex 6: Complex 6 (20 mg, 0.03 mmol) was suspended in [D₈]toluene (0.7 mL) and transferred into a Young's tube. After heating to 100 °C for 1 d, the colour changed from green to brown. Small dark-brown crystals were also observed. X-ray analysis of these crystals identified the product as compound 7, m.p. 172–174 °C (dec.). ¹H NMR (300 MHz, [D₈]toluene, 297 K): δ = 5.87 (s, Cp) ppm. ¹³C NMR (300 MHz, [D₈]toluene, 297 K): δ = 109.7 (Cp) ppm. MS (EI, 70 eV): *m*/*z* (%) = 580 (92) [M]⁺, 515 (15), 450 (14), 385 (7). Further analytical data were unobtainable due to very poor yields and therefore insufficient amounts of substance.

Reaction of [Cp₂Zr(btmsa)(pyridine)] (2) with Alkyne 3: A solution of **3** (270 mg, 0.5 mmol, 1 equiv.) in toluene (30 mL) was added at -78 °C to a stirred solution of **2** (471 mg, 0.5 mmol, 1 equiv.) in toluene (30 mL). The solution was warmed to room temperature and stirred for 2 h. After removal of the solvent and all volatiles in vacuo the resulting yellow-brownish solid was extracted with *n*-hexane (5 × 20 mL). The solvent of the extracts was removed in vacuo and the resulting yellow solid was recrystallised from toluene to yield a few yellow crystals. X-ray analysis of these crystals identified the product as the previously reported complex [Cp₂Zr-(SBn)₂] (8). All the obtained data are in agreement with ref.^[17].

Reaction of [Cp₂Ti(btmsa)] (1) with Alkyne 4: A solution of 4 (201 mg, 0.5 mmol, 1 equiv.) in diethyl ether was added at $-20 \,^{\circ}$ C to a stirred solution of 1 (178 mg, 0.5 mmol, 1 equiv.) in diethyl ether. The solution instantly turned dark brown. Removal of the volatiles at room temp. in vacuo resulted in a brown solid. This solid was extracted with *n*-hexane (20 mL), the extract reduced in vacuo to 10 mL and then filtered again. The filtrate was stored at $-78 \,^{\circ}$ C to yield a small amount of a red solid, which was identified by NMR spectroscopy as [Cp₂Ti(SBn)₂] (5).^[16]

[(Triphos)Co(η²-BnSC₂SBn)](PF₆) (9-PF₆): A mixture of **3** (2.0 g, 7.4 mmol) and 1,1,1-tris(diphenylphosphanylmethyl)ethanecobalt(I) bromide (2.1 g, 2.75 mmol) was dissolved in CH₃CN (30 mL). A solution of KPF₆ (0.5 g, 2.75 mmol) in CH₃OH (10 mL) was added. The dark-green solution obtained was stirred overnight and subsequently concentrated to dryness in vacuo. Column chromatography (silica, thf) yielded an oily product, which was crystallised by gas-phase diffusion of Et₂O into a thf solution of **9-**PF₆, yield 1.09 g (41%). ¹H NMR (300 MHz, CDCl₃, 297 K): δ = 7.40–6.90 (m, 40 H, Ph), 4.20 (s, 2 H, CH₂), 2.50 (br. s, 6 H, PCH₂), 1.80 (br. s, 3 H, CH₃) ppm. ³¹P NMR (121 MHz, CDCl₃, 297 K): δ = 35.90 (PCH₂), -144.50 (PF₆) ppm. MS (MALDI-TOF): *m*/*z* = 953 [M]⁺, 683 [M – **3**]⁺. C₅₇H₅₃CoF₆P₄S₂ (1098.98): calcd. C 62.30, H 4.86, S 5.84; found C 62.17, H 4.76, S 5. 62.

[(Triphos)Co(η²-BnSC₂SFmoc)](PF₆) (10-PF₆): A solution of 4 (369 mg, 0.92 mmol) in acetonitrile (15 mL) was added to a suspension of 1,1,1-tris(diphenylphosphanylmethyl)ethanecobalt(I) bromide (350 mg, 0.46 mmol) in acetonitrile (15 mL). After stirring for 15 min, solid KPF₆ (84.4 mg, 0.46 mmol) was added. The mixture was stirred overnight at room temperature. Subsequently, the green solution was concentrated in vacuo and finally purified by column chromatography (silica, dichloromethane/methanol, 30:1). Crystals were obtained by slow evaporation of a solution of 10-PF₆ in dichloromethane (5 mL) and toluene (0.5 mL), yield 485 mg (86%). ¹H NMR (300 MHz, CDCl₃, 297 K): $\delta = 7.73-6.88$ (m, 43 H, Ph), 4.61 (d, $J_{H,H}$ = 7.36 Hz, 2 H, OCH₂), 4.30 (s, 2 H, CH₂), 4.26 (t, $J_{\text{H,H}} = 7.55 \text{ Hz}, 1 \text{ H}, \text{ CH}, 2.44 \text{ (br. s, 6 H, PCH}_2), 1.78 \text{ (br. s, 3)}$ H, CH₃) ppm. ¹³C NMR (75 MHz, CDCl₃, 297 K): δ = 195.0, 190.8 (C=C), 142.7, 141.3 (Fmoc- C_{ipso}), 136.9 (Ph- C_{ipso}), 131.7, 131.6, 131.5, 130.1, 129.1, 128.8, 128.5, 128.2, 127.6, 127.3, 124.89 (Ph-CH), 70.5 (OCH2), 46.7 (CH), 41.9 (BnSCH2), 39.3 (triphos-C_{quart}), 36.3 (CH₃), 33.3 (PCH₂) ppm. ³¹P NMR (121 MHz, CDCl₃, 297 K): δ = 39.03 (PCH₂), -144.14 (PF₆) ppm. C₆₅H₅₇Co-F₆O₂P₄S₂ (1231.10): calcd. C 63.41, H 4.67, S 5.21; found C 63.10, H 4.66, S 5.03.

[(Triphos)(η^2 -*C*,*C'*-acetylenedithiolato)cobaltate- κ^2 -*S*,*S'*-ruthenium-(cyclopentadienyl)(triphenylphosphane)] (13): At -78 °C, C₈K (44 mg, 0.325 mmol) was added to a green solution of 9-PF₆ (275 mg, 0.25 mmol) in thf (50 mL). The mixture was stirred overnight and subsequently evaporated to dryness under reduced pressure. Extraction with toluene (3 × 20 mL) resulted in a blue solution, which was filtered to remove graphite and KPF₆. Finally, the



toluene was evaporated to yield 11, which was sufficiently pure to be used in the next step. Again at -78 °C, C₈K (31 mg, 0.23 mmol) was added to a solution of crude 11 (110 mg, 0.127 mmol) in thf (20 mL). After 2 h of stirring at ambient temperature, $[(C_5H_5)-$ Ru(PPh₃)₂Cl] (93 mg, 0.128 mmol) was added. Subsequently the mixture was heated at reflux for 2 h to give an intense green solution. After evaporation of the solvent, the residue was washed with CH₃CN to remove PPh₃. Finally, the crude product 13 was subjected to chromatographic purification (SiO2, ethyl acetate/n-hexane, 4:1). Crystals of 13 were obtained by vapour diffusion of npentane into an ethyl acetate solution, yield 35 mg (23%). ¹H NMR (400 MHz, C_6D_6): $\delta = 7.95$, 7.61, 7.12–6.77 (m, 45 H, Ph-H), 4.50 (s, 5 H, C₅H₅), 1.96 (br. s, 6 H, PCH₂), 1.13 (br. s, 3 H, CH₃) ppm. ¹³C NMR (100 MHz, C_6D_6): $\delta = 267.4$ (CoC₂), 141– 128 (8 signals, Ph-C), 78.1 (C₅H₅), 37.5 (q, CH₃), 36.7 (q, CCH₃), 34.3 (m, PCH₂) ppm. ³¹P NMR (161.9 MHz, C₆D₆): δ = 54.18 (PPh_3) , 36.44 (PCH_2) ppm. MS (ESI-TOF, CH₃OH): m/z =1200.1383 [M]⁺, 938.0473 [M - PPh₃]⁺. C₆₆H₅₉CoP₄RuS₂· 0.5C₄H₈O₂ (1244.25): calcd. C 65.64, H 5.10, S 5.15; found C 65.93, H 5.03, S 5.12.

[(Triphos)(1-piperidinyl-2-benzylethene-1,2-dithiolato)cobaltate(lll)]-(PF₆) (14-PF₆): At -78 °C, piperidine (2 mL) was added to a green solution of 9-PF₆ (30 mg, 0.024 mmol) in thf (20 mL). An immediate colour change to deep blue was observed. The solution was warmed to room temperature and stirred for further 2 h. Subsequently, the solvent was evaporated in vacuo and the black residue was dissolved in toluene (5 mL). The resulting black-green suspension was filtered through Celite and the filtrate was concentrated in vacuo. Finally, crystals were obtained by evaporation of a solution of 14-PF₆ in toluene (5 mL) under argon, yield 7.2 mg (27%). ¹H NMR (500 MHz, [D₈]thf, 297 K): $\delta = 7.28-6.85$ (m, 35 H, Ph), 4.08 (s, 2 H, Ph-C H_2), 2.98 [t, J(H,H) = 5.23 Hz, 4 H, NCH₂], 2.72 (br. s, 6 H, PCH₂), 1.80 (s, 3 H, CH₃), 1.67 (m, 6 H, piperidine-CH₂) ppm. ¹³C NMR (125 MHz, [D₈]thf, 297 K): δ = 133.6 (Ph-Cipso), 132.5, 129.9, 128.8, 128.2, 126.06 (Ph-CH), 55.0 (NCH₂), 42.9 (CH₂-Ph), 35.3 (CH₃), 29.6 (PCH₂), 26.3 (piperidine-CH₂), 23.8 (piperidine-p-CH₂) ppm. ³¹P NMR (121 MHz, [D₈]thf, 297 K): δ = 32.66 (PCH₂), -144.11 (PF₆) ppm. C₅₅H₅₆CoF₆NP₄S₂ (1091.99): calcd. C 60.49, H 5.17, N 1.28, S 5.87; found C 61.02, H 5.22, N 1.26, S 5.73.

Crystal Structure Determination: Diffraction data were collected with a Bruker–Nonius Apex X8 CCD and a Bruker Kappa Apex II Duo diffractometer using graphite-monochromated Mo- K_{α} radiation. Structure solutions were found by direct methods (SHELXS-97) and refined by full-matrix least-squares procedures on F^2 (SHELXL-97).^[34] All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were included at calculated positions with fixed thermal parameters.

CCDC-912589 (for 3), -911894 (for 5), -911895 (for 6), -911896 (for 7), -912590 (for 10-PF₆), -927145 (for 13) and -912591 (for 14-PF₆) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Crystal Data for 5: $C_{24}H_{24}S_2$ Ti, M = 424.45, monoclinic, space group P_{2_1}/n , a = 12.8348(2), b = 9.7228(2), c = 16.4166(3) Å, $\beta = 91.030(1)^\circ$, V = 2048.30(6) Å³, T = 150(2) K, Z = 4, 30727 measured reflections, 5077 unique reflections ($R_{int} = 0.0354$), final R values [$I > 2\sigma(I)$]: $R_1 = 0.0290$, $wR_2 = 0.0670$, final R values (all data): $R_1 = 0.0432$, $wR_2 = 0.0742$, 244 parameters.

Crystal Data for 6: $C_{38}H_{34}S_2Ti_2$, M = 650.57, monoclinic, space group C2/c, a = 26.6277(6), b = 8.9374(2), c = 15.8971(3) Å, $\beta =$

125.653(1)°, V = 3074.11(11) Å³, T = 150(2) K, Z = 4, 29652 measured reflections, 3548 unique reflections ($R_{int} = 0.0342$), final R values [$I > 2\sigma(I)$]: $R_1 = 0.0360$, $wR_2 = 0.0869$, final R values (all data): $R_1 = 0.0454$, $wR_2 = 0.0931$, 178 parameters.

Crystal Data for 7: $C_{20}H_{20}S_4Ti_4$, M = 580.20, monoclinic, space group C2/c, a = 18.1469(5), b = 8.2013(2), c = 15.9455(4) Å, $\beta = 115.287(1)^\circ$, V = 2145.74(10) Å³, Z = 4, 27784 measured reflections, 2656 unique reflections ($R_{int} = 0.0230$), final R values [$I > 2\sigma(I)$]: $R_1 = 0.0345$, $wR_2 = 0.0787$, final R values (all data): $R_1 = 0.0366$, $wR_2 = 0.0795$, 119 parameters.

Crystal Data for 10-PF₆: $C_{65}H_{57}CoF_6O_2P_4S_2 \cdot 1.25CH_2Cl_2$, M = 1337.19, green plates, monoclinic, space group C2/c, a = 40.370(3), b = 13.6487(8), c = 25.1746(14) Å, $\beta = 116.215(5)^{\circ}$, V = 12444.6(13) Å³, $\rho = 1.427$ g cm⁻³, $\mu = 0.616$ mm⁻¹, Z = 8, 74925 measured reflections, 11059 unique reflections ($R_{int} = 0.1121$), 5875 observed reflections, 722 parameters, final *R* values [$I > 2\sigma(I)$]: $R_1 = 0.0790$, $wR_2 = 0.1829$, largest peak/hole 1.417/-0.862 e⁻Å⁻³.

Crystal Data for 13: C₆₆H₅₉CoP₄RuS₂·0.5C₄H₈O₂, M = 1244.18, green plates, triclinic, space group *P*1, a = 11.4343(6), b = 13.4639(7), c = 20.1101(10) Å, a = 101.7250(10), $\beta = 100.1630(10)$, $\gamma = 102.0140(10)^{\circ}$, V = 2886.6(3) Å³, $\rho = 1.431$ gcm⁻³, $\mu = 0.777$ mm⁻¹, Z = 2, 33830 measured reflections, 29916 unique reflections ($R_{int} = 0.0205$), 23024 observed reflections, 1424 parameters, final *R* values [$I > 2\sigma(I)$]: $R_1 = 0.0517$, $wR_2 = 0.1076$, largest peak/hole 0.587/-0.751 e⁻Å⁻³.

Crystal Data for 14-PF₆: $C_{55}H_{56}CoF_6NP_4S_2 \cdot 2.25C_7H_8$, M = 1299.24, blue blocks, monoclinic, space group $P2_1/n$, a = 23.319(3), b = 11.6992(11), c = 23.504(3) Å, $\beta = 104.423(3)^\circ$, V = 6210.3(12) Å³, $\rho = 1.390$ gcm⁻³, $\mu = 0.509$ mm⁻¹, Z = 4, 42571 measured reflections, 10897 unique reflections ($R_{int} = 0.1445$), 4685 observed reflections, 687 parameters, final R values [$I > 2\sigma(I)$]: $R_1 = 0.0736$, $wR_2 = 0.1393$, largest peak/hole 0.562/-0.470 e⁻Å⁻³.

Supporting Information (see footnote on the first page of this article): Mechanism studies, reaction control for the formation of 14- PF_6 by ³¹P NMR and UV/Vis spectroscopy, additional structure data for 3 and 13, computational details, Kohn-Sham molecular orbitals of 11.

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