# RSC Advances

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/advances

Dynamic Article Links ►

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

**ARTICLE TYPE**

# Investigation into the reactivity of 16-electron complexes $Cp^{\#}Co(S_2C_2B_{10}H_{10})$ ($Cp^{\#}$ = Cp, Cp*) towards methyl diazoacetate and toluenesulphonyl azide

**Wei Zhong,[a,b] Mingshi Xie,[a] Yizhi Li[a] and Hong Yan*[a]**

***Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX***
**DOI: 10.1039/b000000x**

A three-component reaction of 16-electron half-sandwich complex $Cp^*Co(S_2C_2B_{10}H_{10})$ (**2**) towards methyl diazoacetate (MDA) and toluenesulphonyl azide ($TsN_3$) gave di-inserted products $Cp^*Co(S_2C_2B_{10}H_{10})(C–CO_2Me)$ $(CHCO_2Me)(NHTs)$ (**3**) and $Cp^*Co(S_2C_2B_{10}H_{10})(CHCO_2Me)$ $(CHCO_2Me)(N_3Ts)$ (**4**), whereas MDA and $TsN_3$ in a mole ratio of 2:1 inserted into the Co–S bond to form a five-membered metallacyclic ring with different coordination model. Its two-component reaction with MDA affording complexes $Cp^*Co(S_2C_2B_9H_9)(CH_2CO_2Me)(CHCO_2Me)$ (**5**), $Cp^*Co(S_2C_2B_{10}H_{10})$ $(CH_2CO_2)$ (**6**) and $Cp^*Co(S_2C_2B_9H_9)(CH_2CO_2)$ (**7**) proved that above three-component reaction is not a simple stepwise reaction. For another 16-electron half-sandwich complex $CpCo(S_2C_2B_{10}H_{10})$ (**1**), two stepwise reaction routes were designed to achieve incorporation of these three components. Undergoing alkylidene-bridged adduct $CpCo(S_2C_2B_{10}H_{10})(CHCO_2Me)$ (**8**) or imido-bridged product $CpCo(S_2C_2B_{10}H_{10})(NTs)$ (**9**), complex $CpCo(S_2C_2B_{10}H_{10})(CHCO_2Me)(NTs)$ (**10**) was isolated as the sole product in moderate yield. In each route, one molecular of MDA and one molecular of $TsN_3$ insert into the two Co–S bonds of complex **1**, respectively, with the loss of $N_2$. All the new complexes were characterized by NMR spectroscopy, mass spectrometry, IR spectroscopy, elemental analysis and X-ray structural analysis.

## Introduction

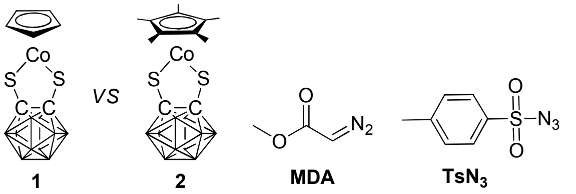
The interaction between metal complexes and organic small molecules has been studied extensively for the reason that it is the source for developing new catalytic reactions and catalysts.[1] Most of metal-catalyzed reactions undergo direct or indirect interaction between the metal centre and the substrate. In particular, some of these catalytic reactions involve the key step of inserting a M–X (X = C, N, S, O, etc.) bond with unsaturated organic substrates, such as alkenes,[2] alkynes,[3] allenes,[4] diazo compounds[5] and azides.[6] On the other hand, the successful isolation and characterization of some unstable metal-ligand complexes provides evidence for the existence of some intermediates in metal-induced catalytic cycles and help people to understand the catalytic mechanism well.[7]

As useful synthons, diazo compounds[5, 8] and azides[9] have been widely used in both organic and organometallic synthesis based on their various reactivities. For example, diazo compounds can be readily decomposed by transition-metal complexes to generate Fischer-type metal carbine intermediates, which can subsequently undergo various chemical transformations such as X–H (X = C, O, S, N, etc.) insertion,[10] cyclopropanation[11] and ylide formation.[12] Azides can be easily transformed into amines, isocyanates and other functional molecules and have more recently received an increasing interest as valuable and versatile reagents within the concept of “Click Chemistry”.[9b,9c,13] Furthermore, reactions of azides towards transition metal complexes afford various products including metal–organo azide complexes,[14] metal–imide complexes,[15] tetraazabutadiene complexes,[16] isocyanate derivatives[9e,15b] and triazenide complexes.[17]

For over 10 years, we are continually working to study the reaction chemistry of unsaturated 16-electron half-sandwich complexes $[CpM(E_2C_2B_{10}H_{10})]$ (Cp = cyclopentadienyl; M = Co; E = S, Se), $[Cp^*M(E_2C_2B_{10}H_{10})]$ (Cp* = pentamethylcyclopentadienyl; M = Co, Rh, Ir; E = S, Se) and [(p-cymene)$M(S_2C_2B_{10}H_{10})$] (M = Ru, Os) with organic small molecules.[18] In our previous work, we have reported the reactivity of 16-electron complex $CpCo(S_2C_2B_{10}H_{10})$ (**1**) with ethyl diazoacetate to afford a series of unpredictable products with Co−B bond formation.[18k] And very recently, we have systematically investigated the reaction of 16-electron complex **1** with various azides.[18m] On the basis of these results, we assume that the three-component reactions of such 16-electron species with diazo compounds and azides would lead to various chemical transformations. As part of our intensive studies in this field, herein we report our attempts on the three-component reactions of $Cp^{\#}Co(S_2C_2B_{10}H_{10})$ ($Cp^{\#}$ = Cp, **1**; $Cp^{\#}$ = Cp*, **2**) towards both methyl diazoacetate (MDA) and toluenesulphonyl azide ($TsN_3$) in one-spot.

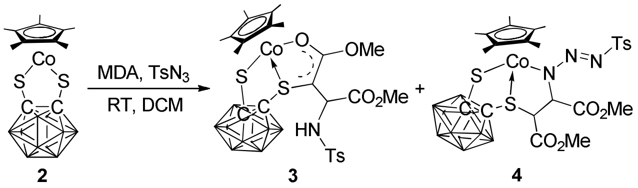
## Results and discussion

**Screening of substrates**. Our previous reports suggest that diazo compounds are very reactive towards 16-electron half-sandwich complex **1**,[18k] while azides are relatively inert which often performed in harsh reaction conditions such as reflux temperature.[18m] For the purpose of the three-component reaction of 16-electron species with both diazo compounds and azides, suitable substrates, including 16-electron species, diazo compounds and azides, need to be carefully screened. Considering the steric effect of Cp* ligand, which have been proved to decrease the reaction activity of its complexes towards alkynes,[18r] the 16-electron complex $Cp^*CoS_2C_2B_{10}H_{10}$ (**2**) may act as a good candidate to achieve this goal. Furthermore, we reduce the disparity of reactivity between diazo compounds and azides by choosing a relatively inert diazo compound (methyl diazoacetate, MDA) and a relatively reactive azide (toluenesulphonyl azide, $TsN_3$) (Scheme 1).



**Scheme 1**. Substrates for investigating.

**Three-component reaction of complex 2 with MDA and $TsN_3$**. The three-component reaction has been achieved by mixing 16-electron complex **2**, $TsN_3$ and MDA sequentially at ambient temperature, which afford products **3** and **4** in the yields of 52% and 22%, respectively, as shown in Scheme 2. It is worthwhile to note that the order of adding $TsN_3$ and MDA is very important for the formation of products **3** and **4**. $TsN_3$ should be added before MDA, otherwise many by-products derived from the reaction of complex **2** with MDA can be isolated. It is in agreement with the different reactivity of azides[18m, 18s] and diazo compounds[18k] towards 16-electron species.



**Scheme 2**. Three-component reaction of complex **2** with MDA and $TsN_3$ at ambient temperature.

Complexes **3** and **4** were characterized by elemental analysis, IR, NMR ($^1H$, $^{11}B$, $^{13}C$) and mass spectrometry. The most representative signals in the $^1H$ NMR spectrum of complex **3** are those due to Ts–NH and $CO_2Me$–CH groups, which appear as two doublets ($J$ = 5.0 Hz) at δ = 4.39 and 5.79 ppm. For complex **4**, the signals due to S–CH and N–CH groups also appear as two doublets ($J$ = 11.0 Hz) at δ = 4.23 and 4.78 ppm, respectively. The $^{13}C$ NMR spectra show the corresponding signals due to the N–C carbon atoms (δ = 56–59 ppm), and the ones assigned to S–C carbon atoms (δ = 71–78 ppm).

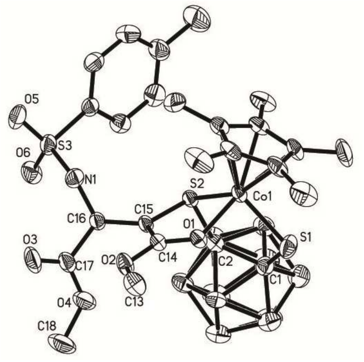


**Figure 1.** Molecular structure of complex **3.** Thermal ellipsoids are depicted at 30% probability. All hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Co(1)–S(1) = 2.2336(11), Co(1)–S(2) = 2.2454(9), Co(1)–O(1) = 1.969(2), S(1)–C(1) = 1.776(3), S(2)–C(2) = 1.824(3), S(2)–C(15) = 1.713(3), O(1)–C(14) = 1.282(3), C(1)–C(2) = 1.659(4), C(14)–C(15) = 1.384(4), C(15)–C(16) = 1.508(3), C(16)–N(1) = 1.454(3); S(1)–Co(1)–S(2) = 95.19(3), S(1)–Co(1)–O(1) = 94.52(6), S(2)–Co(1)–O(1) = 85.09(6), Co(1)–S(1)–C(1) = 105.71(11), Co(1)–S(2)–C(2) = 104.59(9), Co(1)–S(2)–C(15) = 96.84(10), C(2)–S(2)–C(15) = 107.02(13), Co(1)–O(1)–C(14) = 115.02(18), S(1)–C(1)–C(2) = 117.9(2), S(2)–C(2)–C(1) = 116.61(19), O(1)–C(14)–C(15) = 124.2(2), S(2)–C(15)–C(14)=114.37(19).

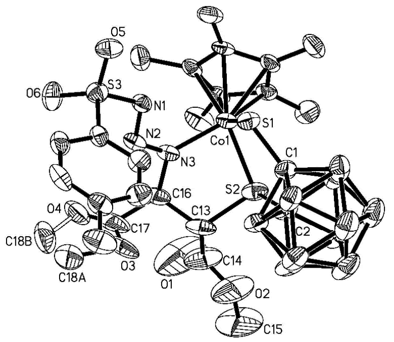
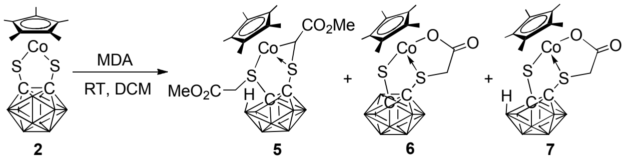


**Figure 2.** Molecular structure of complex **4.** Thermal ellipsoids are depicted at 30% probability. All hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Co(1)–S(1) = 2.2640(8), Co(1)–S(2) = 2.2090(8), Co(1)–N(3) = 1.937(2,) S(1)–C(1) = 1.770(3), S(2)–C(2) = 1.800(3), S(2)–C(13) = 1.845(3), N(1)–N(2) = 1.298(3), N(2)–N(3) = 1.288(3), N(3)–C(16) = 1.478(3), C(1)–C(2) = 1.685(4), C(13)–C(16) = 1.520(4); S(1)–Co(1)–S(2) = 93.99(3), S(1)–Co(1)–N(3) = 93.10(6), S(1)–Co(1)–C(3) = 127.83(7), S(2)–Co(1)–N(3) = 84.86(6), Co(1)–S(1)–C(1) = 104.60(9), Co(1)–S(2)–C(2) = 107.28(10), Co(1)–S(2)–C(13) = 101.71(9), C(2)–S(2)–C(13) = 103.37(13), S(3)–N(1)–N(2) = 110.09(17), N(1)–N(2)–N(3) = 114.0(2), Co(1)–N(3)–N(2) = 129.51(17), Co(1)–N(3)–C(16) = 118.63(16), N(2)–N(3)–C(16) = 111.8(2), S(1)–C(1)–C(2) = 117.83(18), S(2)–C(2)–C(1) = 114.44(18), S(2)–C(13)–C(16) = 110.72(18), N(3)–C(16)–C(13) = 108.4(2).

The absolute configurations of complexes **3** and **4** were further confirmed by X-ray crystallographic analysis. ORTEP representations of **3** and **4** with selected bond distances and angles are shown in Figure 1 and Figure 2, respectively. The molecular structure of **3** reveals that incorporation of one $TsN_3$ and two MDA ligands happen to construct a five-membered metallacyclic ring Co–O–C–C–S. In this process, both $TsN_3$ and two MDA ligands lose $N_2$ and then couple together to form a new "SSO" tridentate ligand. One feature that should be mentioned is that the coupling process makes the complex **3** unsymmetric and the $sp^3$ centre (C16) becomes a chiral centre, though complex **3** crystallizes in the achiral space group P2(1)/n as the R enantiomer. The distance of O(1)–C(14) (1.282(3) Å) is between that expected for carbon-oxygen single and double bonds. While the distance of C(14)–C(15) (1.384(4) Å), which is derived from the same MDA ligand, is also shorter than the usual C–C bond but longer than the normal C=C bond. This fact indicates that O1–C14–C15 is a conjugated $_3{}^4\pi$ system, where similar cases happened in our previous report.[18m] The distances of C(15)–C(16) (1.508(3) Å) and C(16)–N(1) (1.454(3) Å) are slight shorter than the normal C–C and C–N single bond, respectively. Different from complex **3**, the azido group of $TsN_3$ still exists in complex **4**, together with two molecules MDA losing $N_2$ to construct the other new "SSN" tridentate ligand, which features two chiral carbon atoms (C13 and C16). It is interesting to note that only one of the two possible diastereoisomer is formed. The average distance of N–N bonds of the $–N_3$ group (1.298(3) Å) is slight longer than the normal one. All other distances are in the expected range.

**Two-component reaction of complex 2 with MDA.** To insight into the mechanism for the formation of complexes **3** and **4**, two-component reaction of complex **2** with **MDA** was also investigated. The results showed that the above three-component reaction is a concerted reaction rather than a simple stepwise one. As shown in Scheme 3, the 16-electron complex **2** reacting with MDA led to the formation of complexes **5**–**7** in the yield of 9%, 53% and 7%, respectively. It has to be noted that complexes **5** and **7** are obtained in low yields. This is due to the generation of mixtures of complexes in the reaction, thus implying that the reaction products were purified by column chromatography, with the concomitant purification loss. It is totally different from the analogous reaction of complex **1** with ethyl diazoacetate (EDA), which gives interesting products featuring stable Co–B bond or selective B–H activation at carborane.[18k] In this new case, neither B–H activation nor Co–B bond formation happened. Such striking difference is possibly attributed to the steric effect of Cp* ligand in complex **2**.



**Scheme 3.** Two-component reaction of complex **2** with MDA at ambient temperature.

Complexes **5**–**7** have been fully characterized by IR, NMR, mass spectrometry and elemental analysis. The $^1H$ NMR spectra of these complexes show their most significant doublets due to the diastereotopic protons at the methylene group of the $–SCH_2$ branch with chemical shift in the range of 3.0~4.5 ppm ($J$ = 15.0~17.5 Hz). And for complexes **5** and **7**, another representative signals of $^1H$ NMR spectra is that due to the B–H–B hydride at the open face of the *nido*-$C_2B_9$ cluster, which appear as singlet at δ = –2.20 and –2.96 ppm, respectively. These observations are well agreement with their solid states.

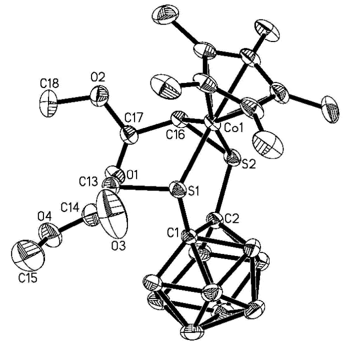


**Figure 3.** Molecular structure of complex **5.** Thermal ellipsoids are depicted at 30% probability. All hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Co(1)–S(1) = 2.2093(7), Co(1)–S(2) = 2.1757(8), Co(1)–C(16) = 1.976(3), C(16)–S(2) = 1.765(3), C(16)–C(17) = 1.468(4), C(2)–S(2) = 1.790(3), C(1)–C(2) = 1.552(4), C(1)–S(1) = 1.797(3), C(13)–S(1) = 1.814(3), C(13)–C(14) = 1.567(5); S(1)–Co(1)–S(2) = 93.37(3), C(16)–Co(1)–S(2) = 50.04(9), Co(1)–S(2)–C(16) = 59.09(9), Co(1)–S(2)–C(2) = 106.44(9), C(1)–C(2)–S(2) = 117.4(2), C(2)–C(1)–S(1) = 116.97(19), Co(1)–S(1)–C(1) = 105.52(9), Co(1)–C(16)–C(17) = 125.70(19), S(2)–C(16)–C(17) = 125.0(2), Co(1)–S(1)–C(13) = 113.23(10), C(1)–S(1)–C(13) = 102.44(13), S(1)–C(13)–C(14) = 108.39(2).

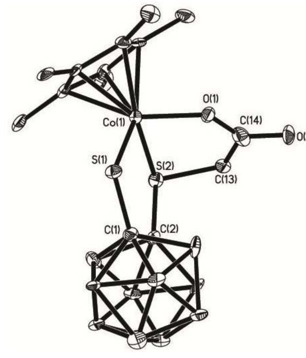


**Figure 4.** Molecular structure of complex **6.** Thermal ellipsoids are depicted at 30% probability. All hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Co(1)–S(1) = 2.248(2), Co(1)–S(2) = 2.234(2), Co(1)–O(1) = 1.960(4), S(1)–C(1) = 1.775(7), S(2)–C(2) = 1.786(7), S(2)–C(13) = 1.805(5), O(1)–C(14) = 1.278(8), O(2)–C(14) = 1.230(7), C(1)–C(2) = 1.658(9), C(13)–C(14) = 1.512(9); S(1)–Co(1)–S(2) = 93.46(7), Co(1)–S(1)–C(1) = 105.81(19), S(1)–Co(1)–O(1) = 94.99(12), Co(1)–S(2)–C(2) = 106.3(2), Co(1)–S(2)–C(13) = 95.5(2), C(2)–S(2)–C(13) = 103.1(3), Co(1)–O(1)–C(14) = 121.1(4), S(1)–C(1)–C(2) = 117.4(4), S(2)–Co(1)–O(1) = 86.78(13), S(2)–

C(13)–C(14) = 113.0(4), O(1)–C(14)–O(2) = 124.5(6), O(1)–C(14)–C(13) = 117.4(5), O(2)–C(14)–C(13) = 118.1(6).

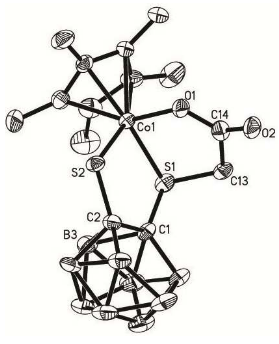
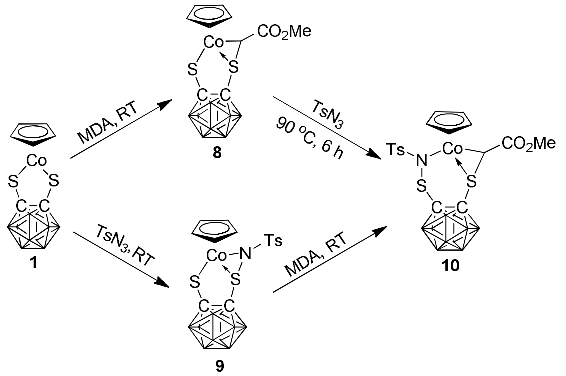


**Figure 5.** Molecular structure of complex **7.** Thermal ellipsoids are depicted at 30% probability. All hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Co(1)–S(1) = 2.2363(13), Co(1)–S(2) = 2.2530(14), Co(1)–O(1) = 1.901(4), S(1)–C(1) = 1.774(5), S(1)–C(13) = 1.809(5), S(2)–C(2) = 1.761(5), O(1)–C(14) = 1.316(6), O(2)–C(14) = 1.237(6), C(1)–C(2) = 1.591(7), C(13)–C(14) = 1.581(7); S(1)–Co(1)–S(2) = 92.21(5), S(1)–Co(1)–O(1) = 88.44(12), S(2)–Co(1)–O(1) = 90.65(13), Co(1)–S(1)–C(1) = 105.61(15), Co(1)–S(1)–C(13) = 99.24(17), C(1)–S(1)–C(13) = 103.0(2), Co(1)–S(2)–C(2) = 106.48(16), Co(1)–O(1)–C(14) = 121.4(3), S(1)–C(1)–C(2) = 118.6(3), S(2)–C(2)–C(1) = 116.8(3), S(1)–C(13)–C(14) = 109.6(3), O(1)–C(14)–C(13) = 119.5(4).

The molecular structures of complexes **5** and **7** (Figures 3 and 5) confirm that one of the apex BH close to the two carbon atoms of *o*-carborane has been lost, which present a *nido*-$C_2B_9$ cage instead of a *closo*-$C_2B_{10}$ unit. This phenomenon has been observed in many previous reports and the basic reaction environment or alcoholic solvent would be responsible for the loss of an apex BH in the *o*-carborane cage.[19] In our cases, the purification process by chromatography using silica may be the reason for such transformation. But in complex **6**, such case did not happen (Figure 4). In fact, reaction of complex **6** with silica for several hours at room temperature led to the formation of complex **7** in good yield. Interestingly, both complexes **6** and **7** present demethylation of the ester branch, which led to a carboxylate to coordinate the cobalt centre. A reasonable explanation for this may imply the presence of tiny amounts of water in the purification or work-up process, which is similar to recently described by Peris and co-workers for $Rh^{III}$ complexes.[20]

**Stepwise reaction of complex 1 with MDA and $TsN_3$.** As we discussed above, the 16-electron complex **1** shown so highly reactive to diazo compounds that three-component reaction of **1** with MDA and $TsN_3$ could not be achieved. But bearing an alternative approach in mind, the stepwise reaction of **1** with MDA and $TsN_3$ would aim to incorporate the three moieties into final product.

As shown in Scheme 4, there are two parallel routes to synthesize the target three-component adduct **10**. One is derived from the alkylidene-bridged adduct **8**, which was prepared according to our recent report.[18k] But in this new case, to get complex **8** with high yield and avoid further reaction with excess MDA, 1:1 mole ratio of raw material and 5 minutes for reaction time were optimized as reaction conditions. Another route undergoes an imido-bridged adduct **9**, whose formation and characterization has been reported in our previous study.[18m] Further reaction of complex **8** with $TsN_3$ at 90 °C or complex **9** with MDA at room temperature led to the formation of product **10** in moderate yield. While previous studies indicated that both alkylidene-bridged adduct and imido-bridged adduct shown comparative reactivity towards small organic molecules,[18k, 18m] the different reactivity presented here may be due to the nature of $TsN_3$ and MDA ligands.



**Scheme 4**. Two routes for stepwise reactions of complex **1** with MDA and $TsN_3$.

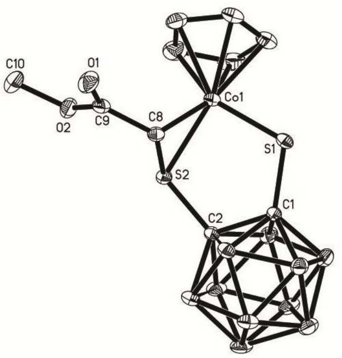


**Figure 6.** Molecular structure of complex **8.** Thermal ellipsoids are depicted at 30% probability. All hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°):Co(1)–S(1) = 2.265(10), Co(1)–S(2) = 2.174(10), Co(1)–C(8) = 1.970(3), C(8)–S(2) = 1.775(3), C(2)–S(2) = 1.803(3), C(1)–C(2) = 1.653(4), C(1)–S(1) = 1.771(3), C(8)–C(9) = 1.472(5); S(1)–Co(1)–S(2) = 95.15(3), C(8)–Co(1)–S(2) = 50.44(10), Co(1)–S(2)–C(8) = 58.84(11), Co(1)–S(2)–C(2) = 105.36(10), C(1)–C(2)–S(2) = 116.1(2), C(2)–C(1)–S(1) = 117.72(18), Co(1)–S(1)–C(1) = 102.84(10).

Good analytical data were obtained for complexes **8**–**10**, which were further supported by X-ray crystal structure determination (complex **9** was reported elsewhere[18m]). The ORTEP plots and selected bond parameters of complexes **8** and **10** are shown in Figures 6 and 7. Obviously, similar to other alkylidene-bridged and imido-bridged complexes,[18k, 18m, 21] MDA insert into one Co–S bond of complex **1** with the loss of $N_2$ to form a three-membered metallacyclic ring Co1−S2−C8. And in complex **10**, one $TsN_3$ and one MDA insert into the two Co–S bonds of complex **1**, respectively, to generate metallacyclic ring Co1−S1−C8 and Co1−S1−C1−C2−S2−N1. It is well-known that[22] alkylidene-adducts exist two geometrical isomers based on the position of R in –CHR group with respect to the iridadithiolene ring, namely *endo* and *exo* form, respectively. In our cases, both complexes **8** and **10** assign to *exo* form according to their $^1H$ NMR spectra. To our surprise, the second insertion reaction did not happen to either Co−C bond in complex **8** or Co−N bond in complex **9**, which have been proved as active sites for further insertion.[18k, 18m] We speculate that the high stability of complex **10** and the nature of carbene and nitrene derived from MDA and $TsN_3$ are responsible for such inserted mode.

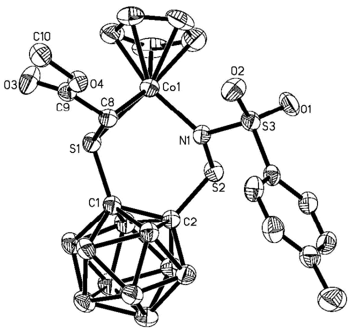


**Figure 7.** Molecular structure of complex **10.** Thermal ellipsoids are depicted at 30% probability. All hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Co(1)–S(1) = 2.1950(7), Co(1)–N(1) = 1.9661(18), Co(1)–C(8) = 1.970(2), S(1)–C(1) = 1.803(2), S(1)–C(8) = 1.768(2), S(2)–N(1) = 1.6923(18), S(2)–C(2) = 1.787(2), S(3)–N(1) = 1.6324(17), C(1)–C(2) = 1.690(3); S(1)–Co(1)–N(1) = 94.20(5), N(1)–Co(1)–C(8) = 89.89(8), S(1)–Co(1)–C(8) = 49.87(6), Co(1)–S(1)–C(1) = 116.42(7), Co(1)–S(1)–C(8) = 58.44(8), C(1)–S(1)–C(8) = 109.50(10), N(1)–S(2)–C(2) = 100.89(10), S(1)–C(1)–C(2) = 121.77(15), S(2)–C(2)–C(1) = 118.49(15), Co(1)–C(8)–S(1) = 71.69(9), Co(1)–N(1)–S(2) = 112.81(9), Co(1)–N(1)–S(3) = 122.20(10), S(2)–N(1)–S(3) = 113.60(10).

**Mechanistic implications.** According to our recent report,[18k] the alkylidene-bridged adduct **IT** may act as a key intermediate in these serial transformations. Due to the steric effect of Cp* ligand, intermediate **IT** is not stable even at low temperature. The same phenomena happened in the imido-bridged adduct, which features nucleophilic addition with $H_2O$ to break the Co–N bond.[18s, 23] Any attempt to isolate intermediate **IT** led to failure, but the evidence for its formation could be captured by *in situ* proton NMR experiment. As shown in Figure 8, mixing 1, 2-dichloroethane solution of MDA with complex **2** in the molar ratio of 1:1 in deuterated chloroform for 10 minutes presented three new proton signals with a ratio of 15:3:1 at $\delta$ = 1.57, 3.80 and 4.10 ppm ($\delta$ = 3.73 ppm is assigned to 1, 2-dichloroethane), which fit the formula of **IT** well. Furthermore, similar to other analogous alkylidene-bridged adducts featuring a characteristic peak of methenyl group,[18k, 24] the peak at $\delta$ = 4.10 ppm appeared while the peak at $\delta$ = 4.75 ppm attributed to $–CHN_2$ of MDA almost disappeared after conducting the reaction for 10 minutes (Figure 9). Based on the intermediate **IT**, the formation of complexes **3**–**7** can be illustrated in Scheme 5. For complexes **3**–**5**, insertion of ligand (MDA or both MDA and $TsN_3$) together with coupling reaction happened in these transformations. The existence of silica or water resulted in the loss of a BH vertex at carborane and the hydrolysis of an ester branch, which is responsible for the formation of complexes **5**–**7**.

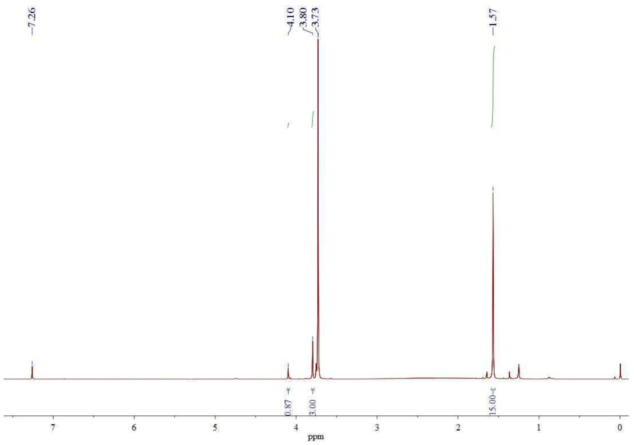


**Figure 8.** $^1H$ NMR spectra of **IT**

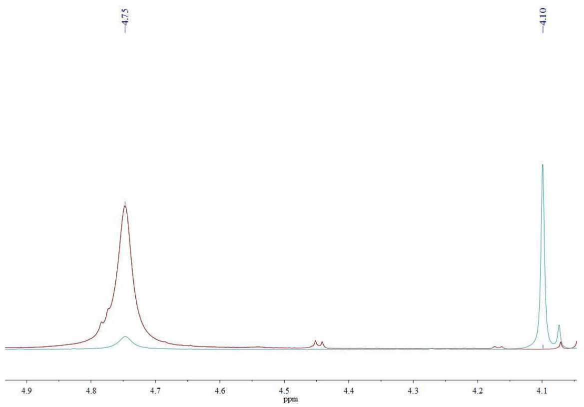
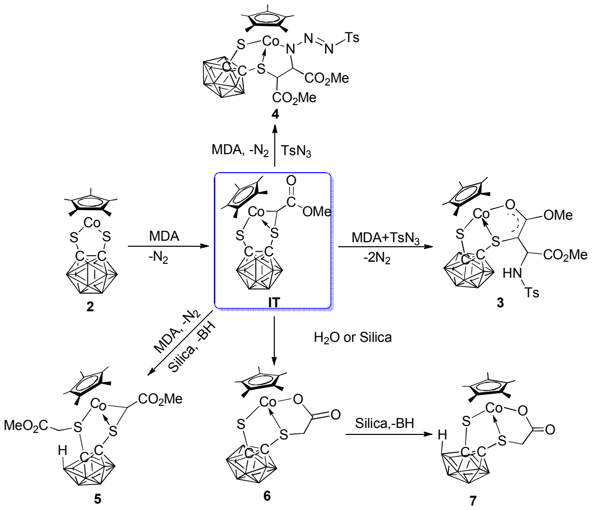


**Figure 9.** Comparison of characteristic peak of MDA and **IT**



**Scheme 5**. Proposed mechanism for the formation of complexes **3**–**7**

## Conclusions

In summary, a three-component reaction of 16-electron half-sandwich complex towards diazo compound and azide could be achieved by screening of proper reactant. That is complex **2** reacting with MDA and $TsN_3$, which afforded two novel products **3** and **4** with incorporation of these three components. For the mechanistic studies, two-component reaction of complex **2** and MDA have been also investigated, which gave the formation of complexes **5**–**7**. The significant disparities between these two reactions proved that the above three-component reaction is not a simple stepwise one. But for the analogous complex **1**, three-component reaction could be only conducted step by step rather than in one-spot. The di-inserted product **10** with MDA and $TsN_3$ moieties could be derived from alkylidene-bridged adduct **8** or imido-bridged adduct **9**. These diverse transformations presented in this work may be helpful for the design of catalysts in carbene and nitrene chemistries.

## Experimental

**General procedures.** $CpCoS_2C_2B_{10}H_{10}$,[25] $Cp^{*}CoS_2C_2B_{10}H_{10}$,[25] methyl diazoacetate[26] and toluenesulphonyl azide[27] were prepared by literature procedures. *Note: methyl diazoacetate is so reactive that it is stored as 1, 2-dichloroethane solution at low temperature (2.76 M)*. All reactions were carried out under argon by using standard Schlenk techniques. All solvents were dried and deoxygenated prior to use. Diethyl ether, tetrahydrofuran, and petroleum ether were refluxed and distilled over sodium/benzophenone under nitrogen. $CH_2Cl_2$ was distilled over $CaH_2$ under nitrogen. The NMR measurements were performed on a Bruker DRX 500 spectrometer. Chemical shifts were given with respect to $CHCl_3/CDCl_3$ (δ $^{1}$H = 7.26 ppm; δ $^{13}$C = 77.0 ppm) and external $Et_2O{\cdot}BF_3$ (δ $^{11}$B = 0 ppm). The IR spectra were recorded on a Bruker Vector 22 spectrophotometer with KBr pellets in the region of 4000–400 cm$^{-1}$. The C, H and N microanalyses were carried out with an Elementar Vario EL III elemental analyzer. Mass data were determined with the LCQ (ESI-MS, Thermo Finnigan) mass spectrometer.

**Synthesis of complexes 3 and 4.** The solution of **2** (120.0 mg, 0.30 mmol) in DCM (20 mL) was added with toluenesulphonyl azide (88.7 mg, 0.45 mmol) and methyl diazoacetate (2.76 M in solution of 1, 2-dichloroethane, 41.4 mg in 0.15 mL).The colour changed from dark yellow to blue quickly after mixing, then the colour slowly changed to dark green. The mixture was stirred for 5 hours at ambient temperature. After removing of all solvent under vacuum, the residue was chromatographically separated on silica, and elution with petroleum ether/DCM gave **3** (130.0 mg, 52%) and **4** (55.0 mg, 22%).

**3**: green solid. m.p. = 153 °C (dec.). $^{1}$H NMR ($CDCl_3$): δ 1.39 (s, 15H, Cp*), 2.45 (s, 3H, Ph–$CH_3$), 3.59 (s, 3H, O–$CH_3$), 3.70 (s, 3H, O–$CH_3$), 4.39 (d, 1H, *J* = 5.0 Hz, N–H), 5.79 (d, 1H, *J* = 5.0 Hz, CH–$CO_2$Me), 7.35 (d, 2H, *J* = 7.0 Hz, Ph), 7.88 (d, 2H, *J* = 7.5 Hz, Ph), $^{11}$B NMR ($CDCl_3$): δ −6.57 (3B), −5.31 (3B), −2.88 (4B), $^{13}$C NMR ($CDCl_3$): δ 9.39 (Cp*–$CH_3$), 21.57 (Ph–$CH_3$), 52.60 (O–$CH_3$), 53.70 (O–$CH_3$), 58.11 (N–C), 71.44 (S–C=), 94.99 (Cp*), 95.17 (Carborane), 103.46 (Carborane), 136.19 (Ph), 143.78 (2×Ph), 127.39 (Ph), 129.78 (2×Ph),170.77 (O=C), 175.28 (O=C). ESI−MS (70 eV): *m/z* 736.17 ([M+MeOH]$^{+}$, 95%). IR (KBr): ν (cm$^{-1}$) 1744 (C=O), 2582 (B−H). Anal. Calcd (%) for $C_{25}H_{40}B_{10}CoNO_6S_3$: C, 42.06; H, 5.65; N, 1.96. Found: C, 42.16; H, 5.92; N, 2.12.

**4**: green solid. m.p. = 168 °C (dec.). $^{1}$H NMR ($CDCl_3$): δ 1.54 (s, 15H, Cp*), 2.39 (s, 3H, Ph–$CH_3$), 3.84 (s, 3H, O–$CH_3$), 3.94 (s, 3H, O–$CH_3$), 4.23 (d, 1H, *J* = 11.0 Hz, S–CH), 4.78 (d, 1H, *J* = 11.0 Hz, N–CH), 7.22 (d, 2H, *J* = 8.0 Hz, Ph), 7.64 (d, 2H, *J* = 8.5 Hz, Ph), $^{11}$B NMR ($CDCl_3$): δ −8.96 (4B), −7.06 (3B), −5.18 (2B), −1.18 (1B), $^{13}$C NMR ($CDCl_3$): δ 10.12 (Cp*–$CH_3$), 21.50 (Ph–$CH_3$), 53.53 (O–$CH_3$), 54.35 (O–$CH_3$), 56.53 (N–C), 77.79 (S–C), 92.94 (Carborane), 98.49 (Cp*), 127.19 (2×Ph), 128.94 (2×Ph), 138.50 (Ph), 142.00 (Ph), 166.30 (O=C) ,167.92 (O=C). ESI−MS (70 eV): *m/z* 731.33 (M$^{+}$, 95%). IR (KBr): ν (cm$^{-1}$) 1745 (C=O), 2588 (B−H). Anal. Calcd (%) for $C_{25}H_{40}B_{10}CoN_3O_6S_3$: C, 40.48; H, 5.43; N, 5.66. Found: C, 40.33; H, 5.59; N, 5.39.

**Synthesis of complexes 5-7.** The solution of **2** (120.0 mg, 0.30 mmol) in DCM (20 mL) was added with methyl diazoacetate (2.76 M in solution of 1, 2-dichloroethane, 41.4 mg in 0.15 mL).The colour changed from dark yellow to blue quickly after mixing, then the colour slowly changed to dark green. The mixture was stirred for 10 hours at ambient temperature. After removing of all solvent under vacuum, the residue was chromatographically separated on silica, and elution with petroleum ether/DCM gave **5** (15.2 mg, 9%), **6** (85.5 mg, 53%) and **7** (8.1 mg, 5%).

**5**: red solid. m.p. = 169 °C (dec.). $^{1}$H NMR ($CDCl_3$): δ 1.66 (s, 15H, Cp*), 3.00 (d, 1H, *J* = 16.0 Hz, S–$CH_2$), 3.36 (s, 1H, S–CH), 3.81 (s, 3H, O–$CH_3$), 3.83 (s, 3H, O–$CH_3$), 4.12 (d, 1H, *J* = 16.0 Hz, S–$CH_2$), −2.20 (s, 1H, B–H–B), $^{11}$B NMR ($CDCl_3$): δ −31.09 (2B), −26.40 (2B), −14.42 (1B), −12.30 (2B), −5.97 (2B), ESI−MS (70 eV): *m/z* 558.25 ([M+Na]$^{+}$, 25%). IR (KBr): ν (cm$^{-1}$) 1631 (C=O), 2547 (B−H). Anal. Calcd (%) for $C_{18}H_{34}B_9CoO_4S_2$: C, 40.42; H, 6.41. Found: C, 40.30; H, 6.50.

**6**: green solid. m.p. = 186 °C (dec.). $^{1}$H NMR ($CDCl_3$): δ 1.45 (s, 15H, Cp*), 3.70 (d, 1H, *J* = 17.5 Hz, S–$CH_2$), 3.82 (d, 1H, *J* = 17.5 Hz, S–$CH_2$), $^{11}$B NMR ($CDCl_3$): δ −8.44 (1B), −6.80 (2B), −5.78 (1B), −3.60 (4B), −2.22 (2B), $^{13}$C NMR ($CDCl_3$): δ 9.61 (Cp*–$CH_3$), 29.28 (S–$CH_2$), 43.51 (S–$CH_2$), 90.87 (Carborane), 95.77 (Cp*), 97.32 (Carborane), 174.21 (O=C), ESI−MS (70 eV): *m/z* 490.75 ([M+MeOH]$^{+}$, 15%). IR (KBr): ν (cm$^{-1}$) 1639 (C=O), 2574 (B−H). Anal. Calcd (%) for $C_{14}H_{27}B_{10}CoO_2S_2{\cdot}H_2O$: C, 35.28; H, 6.13. Found: C, 35.50; H, 6.19.

**7**: red solid. m.p. = 189 °C (dec.). $^{1}$H NMR ($CDCl_3$): δ 1.56 (s, 15H, Cp*), 3.50 (d, 1H, *J* = 15.0 Hz, S–$CH_2$), 4.47 (d, 1H, *J* = 15.0 Hz, S–$CH_2$), −2.96 (s, 1H, B–H–B), $^{11}$B NMR ($CDCl_3$): δ −31.05 (1B), −25.46 (1B), −14.20 (2B), −12.06 (3B), −6.72 (2B), ESI−MS (70 eV): *m/z* 444.92 ([M]$^{-}$, 40%). IR (KBr): ν (cm$^{-1}$) 1645 (C=O), 2545 (B−H). Anal. Calcd (%) for $C_{14}H_{27}B_9CoO_2S_2$: C, 37.56; H, 6.08. Found: C, 37.70; H, 6.25.

**Synthesis of complex 8.** The solution of **1** (99.0 mg, 0.30 mmol) in DCM (20 mL) was added with methyl diazoacetate (2.76 M in solution of 1, 2-dichloroethane, 27.6 mg in 0.1 mL) in a molar ratio of about 1:1. The colour changed from red to blue rapidly after mixing, and the mixture was stirred for 5 minutes at ambient temperature. After removing of all solvent under vacuum, the residue was chromatographically separated on silica, and elution with petroleum ether/DCM gave **8** (88.6 mg, 69%).

**8**: blue solid. m.p. = 158 °C. $^1$H NMR (CDCl$_3$): δ 3.82 (s, 3H, O–CH$_3$), 4.37 (s, 1H, S–CH), 5.02 (s, 5H, Cp), $^{11}$B NMR (CDCl$_3$): δ −7.93 (2B), −6.55 (2B), −4.89 (1B), −2.20 (3B), −1.17 (2B), $^{13}$C NMR (CDCl$_3$): δ 45.03 (S–CH), 52.80 (O–CH$_3$), 85.01 (Cp), 88.49 (Carborane), 92.81 (Carborane), 175.19 (O=C). ESI−MS (70 eV): *m/z* 392.33 ([M]$^-$, 60%). IR (KBr): ν (cm$^{-1}$) 1697(C=O), 2596 (B–H). Anal. Calcd (%) for $C_{10}H_{19}B_{10}CoO_2S_2$: C, 29.85; H, 4.76. Found: C, 29.99; H, 4.95.

**Synthesis of 10**. *Method 1*. Toluenesulphonyl azide (59.1 mg, 0.3 mmol) was added to the blue solution of **8** (80.6 mg, 0.2 mmol) in toluene (20 mL). The mixture was heated at 90 °C for 6 h. The colour gradually turned from blue to purple. After removal of the solvent, the residue was chromatographically separated on silica, and elution with petroleum ether/DCM gave **10** (67 mg, 57%).

*Method 2*. Complex **9** was prepared according to our recent work.[18m] The solution of **9** (105.4 mg, 0.2 mmol) in DCM (20mL) was added with methyl diazoacetate (2.76 M in solution of 1, 2-dichloroethane, 41.4 mg in 0.15 mL). The mixture was stirred for 6 h at ambient temperature. The colour gradually turned from green to purple. After removal of the solvent, the residue was chromatographically separated on silica, and elution with petroleum ether/DCM gave **10** (69 mg, 59%).

**10**: purple solid. m.p. = 117 °C. $^1$H NMR (CDCl$_3$): δ 2.43 (s, 3H, Ph–CH$_3$), 3.91 (s, 3H, O–CH$_3$), 4.05 (s, 1H, S–CH), 5.14 (s, 5H, Cp), 7.29 (d, 2H, *J* = 8.0 Hz, Ph), 7.76 (d, 2H, *J* = 9.0 Hz, Ph), $^{11}$B NMR (CDCl$_3$): δ −12.25 (1B), −10.27 (1B), −9.01 (2B), −7.84 (1B), −6.07 (1B), −2.96 (1B), 0.87 (1B), 2.81 (2B), $^{13}$C NMR (CDCl$_3$): δ 21.48 (Ph–CH$_3$),43.27 (S–CH), 53.03 (O–CH$_3$), 57.38 (Carborane), 85.17 (Cp), 86.06 (Carborane), 127.84 (2×Ph), 129.32 (2×Ph), 137.69 (Ph), 143.01 (Ph), 175.59 (O=C). ESI−MS (70 eV): *m/z* 573 ([M+H]$^+$, 60 %), 595 ([M+Na]$^+$, 100%). IR (KBr): ν (cm$^{-1}$) 1707 (C=O), 2579 (B–H). Anal. Calcd (%) for $C_{17}H_{26}B_{10}CoNO_4S_3$: C, 35.72; H, 4.58; N, 2.45. Found: C, 35.88; H, 4.86; N, 2.59.

**X-ray Structure Determinations**. Crystals suitable for X-ray analysis were obtained by the slow evaporation of a solution in petroleum ether/dichloromethane. Diffraction data were collected on a Bruker SMART Apex II CCD diffractometer by means of graphitemonochromated Mo–Kα (λ = 0.71073 Å) radiation. During collection of the intensity data, no significant decay was observed. The intensities were corrected for Lorentz polarization effects and empirical absorption by using the SADABS program.[28] The structures were solved by direct methods with the SHELXS-97 program[29] and were refined on $F^2$ with SHELXTL (version 6.14).[30] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in calculated positions and were refined using a riding model. A summary of crystal data, data collection parameters, and structure refinement details is given in Tables 1 and 2. CCDC 1009704–1009710 for the complexes **3**–**8** and **10** 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.

## Acknowledgements

This work was supported by the National Basic Research Program of China (2013CB922101), the Natural Science Foundation of China (21271102 and 21301071).

## Notes and references

[a] *State Key Laboratory of Coordination Chemistry, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing, Jiangsu 210093, China. Tel: +86-25-83686724; E-mail: hyan1965@nju.edu.cn*
[b] *College of Biological, Chemical Sciences and Engineering, Jiaxing University, Jiaxing, Zhejiang 314001, China. Tel: +86-573-83640303*

1 (a) J. I. van der Vlugt, *Eur. J. Inorg. Chem.*, 2012, **2012**, 363-375; (b) L. Boisvert and K. I. Goldberg, *Acc. Chem. Res.* 2012, **45**, 899-910; (c) J. Zhang and X. Zhou, *C. R. Chim.*, 2010, **13**, 633-650; (d) S. Yao and M. Driess, *Acc. Chem. Res.* 2011, **45**, 276-287.
2 P. S. Hanley and J. F. Hartwig, *Angew. Chem. Int. Ed.*, 2013, **52**, 8510-8525.
3 (a) Y. Yamamoto, *Chem. Soc. Rev.*, 2014, **43**, 1575-1600; (b) V. P. Ananikov, K. A. Gayduk, N. V. Orlov, I. P. Beletskaya, V. N. Khrustalev and M. Y. Antipin, *Chem.–Eur. J.*, 2010, **16**, 2063-2071.
4 T. Bai, S. Ma and G. Jia, *Coord. Chem. Rev.*, 2009, **253**, 423-448.
5 Q. Xiao, Y. Zhang and J. Wang, *Acc. Chem. Res.* 2013, **46**, 236-247.
6 (a) B. M. Gardner and S. T. Liddle, *Eur. J. Inorg. Chem.*, 2013, **2013**, 3753-3770; (b) C.-M. Che, V. K.-Y. Lo, C.-Y. Zhou and J.-S. Huang, *Chem. Soc. Rev.*, 2011, **40**, 1950-1975.
7 (a) E. Poverenov, I. Efremenko, A. I. Frenkel, Y. Ben-David, L. J. W. Shimon, G. Leitus, L. Konstantinovski, J. M. L. Martin and D. Milstein, *Nature*, 2008, **455**, 1093-1096; (b) S. P. Sarish, D. Schaffner, Y. Sun and W. R. Thiel, *Chem. Commun.*, 2013, **49**, 9672-9674; (c) M. Tiberti, E. Papaleo, N. Russo, L. De Gioia and G. Zampella, *Inorg. Chem.*, 2012, **51**, 8331-8339; (d) G. Espino, A. Caballero, B. R. Manzano, L. Santos, M. Pérez-Manrique, M. Moreno and F. A. Jalón, *Organometallics*, 2012, **31**, 3087-3100; (e) S.-M. Yiu, W.-L. Man and T.-C. Lau, *J. Am. Chem. Soc.*, 2008, **130**, 10821-10827.
8 (a) N. R. Candeias and C. A. M. Afonso, *Curr. Org. Chem.*, 2009, **13**, 763-787; (b) C. Wentrup, *Acc. Chem. Res.* 2011, **44**, 393-404.
9 (a) H. Tanimoto and K. Kakiuchi, *Nat. Prod. Commun.*, 2013, **8**, 1021-1034; (b) N. V. Sokolova and V. G. Nenajdenko, *Rsc Adv.*, 2013, **3**, 16212-16242; (c) L. Y. Liang and D. Astruc, *Coord. Chem. Rev.*, 2011, **255**, 2933-2945; (d) S. Cenini, E. Gallo, A. Caselli, F. Ragaini, S. Fantauzzi and C. Piangiolino, *Coord. Chem. Rev.*, 2006, **250**, 1234-1253; (e) S. Cenini and G. La Monica, *Inorg. Chim. Acta*, 1976, **18**, 279-293.
10 (a) M. M. Díaz-Requejo and P. J. Pérez, *Chem. Rev.*, 2008, **108**, 3379-3394; (b) H. M. L. Davies and R. E. J. Beckwith, *Chem. Rev.*, 2003, **103**, 2861-2904; (c) H. M. L. Davies, X. Dai and M. S. Long, *J. Am. Chem. Soc.*, 2006, **128**, 2485-2490; (d) Z. Zhang and J. Wang, *Tetrahedron*, 2008, **64**, 6577-6605.
11 (a) F. Brackmann and A. de Meijere, *Chem. Rev.*, 2007, **107**, 4493-4537; (b) M. Lautens, W. Klute and W. Tam, *Chem. Rev.*, 1996, **96**, 49-92; (c) H.-U. Reissig and R. Zimmer, *Chem. Rev.*, 2003, **103**, 1151-1196.
12 (a) Y. Zhang and J. Wang, *Coord.Chem. Rev.*, 2010, **254**, 941-953; (b) X. Zhang, Z. Qu, Z. Ma, W. Shi, X. Jin and J. Wang, *J. Org. Chem.*, 2002, **67**, 5621-5625; (c) M. Ma, L. Peng, C. Li, X. Zhang and J. Wang, *J. Am. Chem. Soc.*, 2005, **127**, 15016-15017.
13 J. E. Hein and V. V. Fokin, *Chem. Soc. Rev.*, 2010, **39**, 1302-1315.
14 (a) M. G. Fickes, W. M. Davis and C. C. Cummins, *J. Am. Chem. Soc.*, 1995, **117**, 6384-6385; (b) G. Proulx and R. G. Bergman, *J. Am. Chem. Soc.*, 1995, **117**, 6382-6383; (c) M. Barz, E. Herdtweck and W. R. Thiel, *Angew. Chem. Int. Ed.*, 1998, **37**, 2262-2265; (d) G. Albertin, S. Antoniutti, D. Baldan, J. Castro and S. Garcia-Fontan, *Inorg. Chem.*, 2008, **47**, 742-748; (e) Y. Yu, A. R. Sadique, J. M. Smith, T. R. Dugan, R. E. Cowley, W. W. Brennessel, C. J. Flaschenriem, E. Bill, T. R. Cundari and P. L. Holland, *J. Am. Chem. Soc.*, 2008, **130**, 6624-6638; (f) W. J. Evans, C. A. Traina and J. W. Ziller, *J. Am. Chem. Soc.*, 2009, **131**, 17473-17481; (g) J. J. Curley, R. G. Bergman and T. D. Tilley, *Dalton Trans.*, 2012, **41**, 192-200.
15 (a) G. Guillemot, E. Solari, C. Floriani and C. Rizzoli, *Organometallics*, 2001, **20**, 607-615; (b) S. D. Brown, T. A. Betley and J. C. Peters, *J. Am. Chem. Soc.*, 2003, **125**, 322-323.
16 (a) R. I. Michelman, R. G. Bergman and R. A. Andersen, *Organometallics*, 1993, **12**, 2741-2751; (b) K. E. Meyer, P. J. Walsh and R. G. Bergman, *J. Am. Chem. Soc.*, 1995, **117**, 974-985; (c) A. F.

Heyduk, K. J. Blackmore, N. A. Ketterer and J. W. Ziller, *Inorg. Chem.*, 2005, **44**, 468-470; (d) G. Albertin, S. Antoniutti, A. Bacchi, A. Celebrin, G. Pelizzi and G. Zanardo, *Dalton Trans.*, 2007, 661-668.

17 (a) G. L. Hillhouse and J. E. Bercaw, *Organometallics*, 1982, **1**, 1025-1029; (b) G. L. Hillhouse and B. L. Haymore, *Inorg. Chem.*, 1987, **26**, 1876-1885.

18 (a) M. Herberhold, H. Yan, W. Milius and B. Wrackmeyer, *Angew. Chem. Int. Ed.*, 1999, **38**, 3689-3691; (b) M. Herberhold, H. Yan, W. Milius and B. Wrackmeyer, *Chem.–Eur. J.*, 2000, **6**, 3026-3032; (c) M. Herberhold, H. Yan, W. Milius and B. Wrackmeyer, *Z. Anorg. Allg. Chem.*, 2000, **626**, 1627-1633; (d) M. Herberhold, H. Yan, W. Milius and B. Wrackmeyer, *J. Chem. Soc.-Dalton Trans.*, 2001, 1782-1789; (e) B. Wrackmeyer, H. Yan, W. Milius and M. Herberhold, *Russ. Chem. Bull.*, 2001, **50**, 1518-1524; (f) B. H. Xu, D. H. Wu, Y. Z. Li and H. Yan, *Organometallics*, 2007, **26**, 4344-4349; (g) M. Herberhold, H. Yan, W. Milius and B. Wrackmeyer, *Chem.–Eur. J.*, 2002, **8**, 388-395; (h) B. H. Xu, X. Q. Peng, Y. Z. Li and H. Yan, *Chem.–Eur. J.*, 2008, **14**, 9347-9356; (i) B. H. Xu, J. C. Tao, Y. Z. Li, S. H. Li and H. Yan, *Organometallics*, 2008, **27**, 334-340; (j) Y. G. Li, Q. B. Jiang, X. L. Zhang, Y. Z. Li, H. Yan and V. I. Bregadze, *Inorg. Chem.*, 2010, **49**, 3911-3917; (k) G. F. Liu, J. R. Hu, J. L. Wen, H. M. Dai, Y. Z. Li and H. Yan, *Inorg. Chem.*, 2011, **50**, 4187-4194; (l) H.-D. Ye, G.-Y. Ding, M.-S. Xie, Y.-Z. Li and H. Yan, *Dalton Trans.*, 2011, **40**, 2306-2313; (m) W. Zhong, Q. Yang, Y. Shang, G. Liu, H. Zhao, Y. Li and H. Yan, *Organometallics*, 2012, **31**, 6658-6668; (n) J. R. Hu, X. Tang, G. F. Liu, Q. B. Jiang, D. D. Duanmu, Y. Z. Li and H. Yan, *J. Organomet. Chem.*, 2012, **721**, 36-41; (o) R. Zhang, L. Zhu, G. F. Liu, H. M. Dai, Z. Z. Lu, J. B. Zhao and H. Yan, *J. Am. Chem. Soc.*, 2012, **134**, 10341-10344; (p) R. Zhang, L. Zhu, Z. Z. Lu, H. Yan and V. I. Bregadze, *Dalton Trans.*, 2012, **41**, 12054-12063; (q) Z. J. Wang, H. D. Ye, Y. G. Li, Y. Z. Li and H. Yan, *J. Am. Chem. Soc.*, 2013, **135**, 11289-11298; (r) H.-D. Ye, G.-Y. Ding, M.-S. Xie, Y.-Z. Li and H. Yan, *Dalton Trans.*, 2011, **40**, 2306-2313; (s) W. Zhong, H. Yan and V. Bregadze, *Russ. Chem. Bull.*, 2014, **63**, 953-962.

19 (a) D. J. Crowther, N. C. Baenziger and R. F. Jordan, *J. Am. Chem. Soc.*, 1991, **113**, 1455-1457; (b) V. I. Bregadze, *Chem. Rev.*, 1992, **92**, 209-223; (c) D. J. Crowther, D. C. Swenson and R. F. Jordan, *J. Am. Chem. Soc.*, 1995, **117**, 10403-10404; (d) F. Teixidor, R. Benakki, C. Viñas, R. Kivekäs and R. Sillanpää, *Organometallics*, 1998, **17**, 4630-4633; (e) M. G. Davidson, M. A. Fox, T. G. Hibbert, J. A. K. Howard, A. Mackinnon, I. S. Neretin and K. Wade, *Chem. Commun.*, 1999, 1649-1650; (f) J.-Q. Wang, M. Herberhold and G.-X. Jin, *Organometallics*, 2006, **25**, 3508-3514.

20 M. Benítez, E. Mas-Marzá, J. A. Mata and E. Peris, *Chem.–Eur. J.*, 2011, **17**, 10453-10461.

21 (a) M. Nomura, T. Yagisawa, C. Takayama, T. Sugiyama, Y. Yokoyama, K. Shimizu, A. Sugimori and M. Kajitani, *J. Organomet. Chem.*, 2000, **611**, 376-385; (b) M. Nomura, C. Takayama, T. Sugiyama, Y. Yokoyama and M. Kajitani, *Organometallics*, 2004, **23**, 1305-1312.

22 M. Nomura, *Dalton Trans.*, 2011, **40**, 2112-2140.

23 H. Dou, W. Zhong, L. Yang, T. Wang, H. Yan and Y. Hou, *Biorg. Med. Chem.*, 2012, **20**, 4693-4700.

24 M. Sakurada, M. Kajitani, K. Dohki, T. Akiyama and A. Sugimori, *J. Organomet. Chem.*, 1992, **423**, 141-161.

25 D. H. Kim, J. J. Ko, K. Park, S. G. Cho and S. O. Kang, *Organometallics*, 1999, **18**, 2738-2740.

26 S. G. Alvarez and M. T. Alvarez, *Synthesis-Stuttgart*, 1997, 413-414.

27 L. McElwee-White and D. A. Dougherty, *J. Am. Chem. Soc.*, 1984, **106**, 3466-3474.

28 SADABS, *A Program for Empirical Absorption Correction,* G. M. Sheldrick, University of Göttingen (Germany), **1998**.

29 SHELXL-97, *Program for the Refinement of Crystal Structures,* G. M. Sheldrick, University of Göttingen (Germany), **1997**.

30 G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2008, **64**, 112-122.

Table 1 Crystallographic data for complexes **3**–**6**

| Compound | **3** | **4** | **5** | **6** |
|---|---|---|---|---|
| chemical formula | $C_{25}H_{40}B_{10}CoNO_6S_3$ | $C_{25}H_{40}B_{10}CoN_3O_6S_3$ | $C_{18}H_{34}B_9CoO_4S_2$ | $C_{14}H_{27}B_{10}CoO_2S_2\cdot H_2O$ |
| formula weight | 713.79 | 741.81 | 534.79 | 476.52 |
| crystal size (mm) | 0.15×0.13×0.12 | 0.18×0.14×0.11 | 0.25×0.22×0.18 | 0.20×0.16×0.12 |
| temperature (K) | 296(2) | 296(2) | 296(2) | 296(2) |
| radiation | Mo-Kα(0.71073Å) | Mo-Kα(0.71073Å) | Mo-Kα(0.71073Å) | Mo-Kα(0.71073Å) |
| crystal system | Monoclinic | Orthorhombic | Triclinic | Triclinic |
| space group | P2(1)/n | Pbca | P-1 | P-1 |
| $a$(Å) | 14.9811(14) | 15.4506(10) | 9.4239(11) | 7.504(4) |
| $b$(Å) | 12.0288(11) | 13.6578(9) | 9.8236(11) | 10.477(5) |
| $c$(Å) | 19.4267(18) | 34.644(2) | 15.0407(17) | 16.018(8) |
| $\alpha$(°) | 90.00 | 90.00 | 82.461(2) | 103.281(8) |
| $\beta$(°) | 97.9710(10) | 90.00 | 89.994(2) | 96.540(8) |
| $\gamma$(°) | 90.00 | 90.00 | 73.199(2) | 107.695(8) |
| V(Å$^3$) | 3467.0(6) | 7310.7(8) | 1320.4(3) | 1144.6(10) |
| Z | 4 | 8 | 2 | 2 |
| $\rho_{(calc)}$ (g/cm$^3$) | 1.368 | 1.348 | 1.345 | 1.383 |
| F (000) | 1480 | 3072 | 556 | 492 |
| absorp.coeff. (mm$^{-1}$) | 0.715 | 0.683 | 0.832 | 0.947 |
| θ range (deg) | 1.61 to 25.50 | 1.18 to 26.00 | 2.19 to 26.00 | 2.12 to 25.00 |
| reflns collected | 19970 ($R_{int}$ = 0.0502) | 41674 ($R_{int}$ = 0.1417) | 10038 ($R_{int}$ = 0.0212) | 6910 ($R_{int}$ = 0.0528) |
| indep. reflns | 6407 | 7187 | 5163 | 3839 |
| Refns obs. [$I > 2\sigma(I)$] | 4341 | 3015 | 4429 | 2496 |
| data/restr/paras | 6407/1/423 | 7187/86/449 | 5163/0/357 | 3839/0/276 |
| GOF | 1.012 | 0.986 | 1.036 | 0.996 |
| $R_1$/w$R_2$ [$I > 2\sigma(I)$] | 0.0473/0.1117 | 0.0489/0.0736 | 0.0436/0.1328 | 0.0658/0.1515 |
| $R_1$/w$R_2$ (all data) | 0.0770/0.1216 | 0.1490/0.0820 | 0.0506/0.1385 | 0.1132/0.1654 |
| larg peak and hole(e/Å$^3$) | 0.382/–0.381 | 0.450/–0.371 | 0.810/–0.443 | 0.992/–0.553 |

Table 2 Crystallographic data for complexes **7**, **8** and **10**

| Compound | **7** | **8** | **10** |
|---|---|---|---|
| chemical formula | $C_{14}H_{27}B_9CoO_2S_2$ | $C_{10}H_{19}B_{10}CoO_2S_2$ | $C_{17}H_{26}B_{10}CoNO_4S_3$ |
| formula weight | 447.70 | 402.40 | 571.60 |
| crystal size (mm) | 0.28×0.24×0.22 | 0.30×0.23×0.18 | 0.27×0.24×0.20 |
| temperature (K) | 291(2) | 296(2) | 296(2) |
| radiation | Mo-Kα(0.71073Å) | Mo-Kα(0.71073Å) | Mo-Kα(0.71073Å) |
| crystal system | Orthorhombic | Monoclinic | Triclinic |
| space group | P2(1)2(1)2(1) | P2(1)/c | P-1 |
| *a*(Å) | 10.3728(8) | 6.5496(8) | 7.6763(6) |
| *b*(Å) | 13.1268(10) | 12.0999(15) | 10.9331(8) |
| *c*(Å) | 16.7553(11) | 22.472(3) | 16.1145(12) |
| *α*(°) | 90.00 | 90.00 | 94.3150(10) |
| *β*(°) | 90.00 | 94.648(2) | 92.6730(10) |
| *γ*(°) | 90.00 | 90.00 | 95.6580(10) |
| V($Å^3$) | 2281.4(3) | 1775.1(4) | 1340.03(17) |
| Z | 4 | 4 | 2 |
| $\rho_{(calc)}$ ($g/cm^3$) | 1.303 | 1.506 | 1.417 |
| F (000) | 924 | 816 | 584 |
| absorp.coeff. ($mm^{-1}$) | 0.943 | 1.202 | 0.900 |
| θ range (deg) | 1.97 to 26.00 | 1.82 to 26.00 | 1.88 to 26.00 |
| reflns collected | 10510 ($R_{int}$ = 0.0492) | 11610 ($R_{int}$ = 0.0863) | 7376 ($R_{int}$ = 0.0398) |
| indep. reflns | 4482 | 3461 | 5174 |
| Refns obs. [$I > 2\sigma(I)$] | 3394 | 2561 | 4087 |
| data/restr/paras | 4482/0/258 | 3461/0/230 | 5174/0/367 |
| GOF | 1.085 | 0.945 | 1.038 |
| $R_1/wR_2$ [$I > 2\sigma(I)$] | 0.0564/0.1121 | 0.0511/0.1063 | 0.0355/0.0808 |
| $R_1/wR_2$ (all data) | 0.0686/0.1153 | 0.0657/0.1109 | 0.0447/0.0837 |
| larg peak and hole($e/Å^3$) | 0.624/–0.381 | 0.832/–0.580 | 0.285/–0.234 |