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# Alkyne Dicobalt Carbonyl Complexes with Sulfide Ligands. Synthesis, Crystal Structure, and Dynamic Behavior

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Hexacarbonyl dicobalt complex of bis(*tert*-butylsulfonylethyne) [$Co_2(\mu\text{-}Bu^tSO_2C)_2(CO)_6$, **3**] experiences a thermally induced ligand exchange process with methyl *p*-tolyl sulfide, dibenzyl sulfide, and diethyl sulfide to give the corresponding stable sulfide complexes [$Co_2(\mu\text{-}Bu^tSO_2C)_2(CO)_5SR_2$] **4**, **5**, and **6**, respectively, in good yield (59−65%). The reaction with tetrahydrothiophene gives a disubstituted complex **7** in 74% yield. Oxathiane **9**, derived from (+)-(2*R*)-10-mercaptoisoborneol, also reacts with **3** to generate a chiral sulfide complex **8** (58%). The solid-state structures of **5** and **8** have been established by X-ray crystallography and reveal the preference of the incoming sulfur ligand to occupy an equatorial coordination site. Further structural studies on **5** have been performed by low-temperature $^1H$ NMR analysis and by theoretical procedures at the PM3(tm) level of theory. Analysis of the low-temperature $^1H$ NMR spectrum of **5** shows a signal splitting consistent with the freezing of an equilibrium between two equatorially coordinated sulfides, and the computational study of the different isomers of **5** shows that the equatorially coordinated complex is 3.9 kcal $mol^{-1}$ lower in energy than the most stable axially coordinated one, in agreement with solid-state and solution studies. Finally, ligand exchange experiments have been performed in order to provide an explanation for the Pauson−Khand reactivity of alkynes containing ancillary sulfide ligands and were found to support the experimentally observed rate enhancements.

## Introduction

Since its discovery in 1973, the Pauson−Khand reaction has gained a major role in the synthetic chemist toolbox.[1] This reaction consists of the carbonylative cycloaddition between an alkene and an alkyne to yield a cyclopentenone. In the noncatalytic versions of this reaction the first step is the formation of the dicobalthexacarbonyl complex of the alkyne, which can be either isolated or generated in situ. From the very beginning, the development of an asymmetric version of this process became of great interest to chemists. Up to date, to turn this reaction enantioselective several approaches have been tested.[2−5] One of such methodologies, developed by our group, is based on the use of chiral auxiliaries in the asymmetric Pauson−Khand reaction,[4,5] and it has been applied to the enantioselective synthesis of complex molecules.[6] While we first investigated conventional auxiliaries, whose effectiveness is based on a pronounced conformational bias,[4] a second generation of chelating chiral controllers also

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10.1021/om9903036 CCC: $18.00

**Scheme 1**

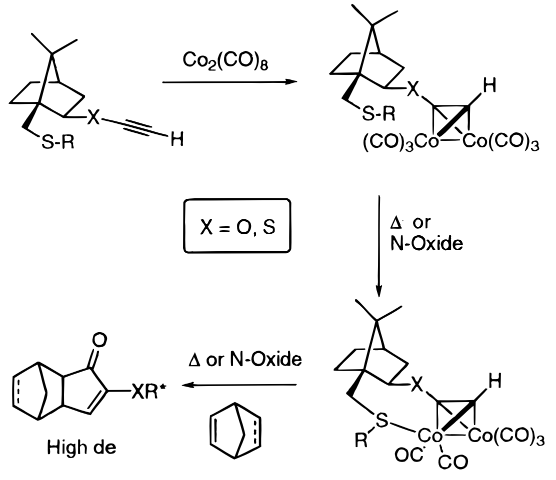
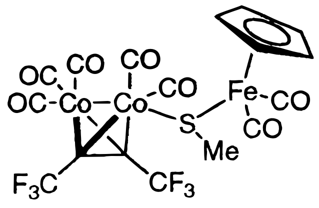


**Chart 1**



**1**

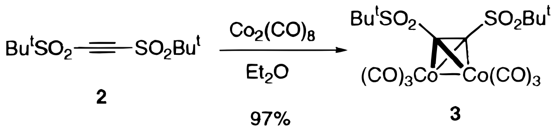
proved to be very effective.[5] In these studies, we have demonstrated that the occurrence of an intramolecular sulfide coordination to the $Co_2$–alkyne core results in an enhanced reactivity and diastereoselectivity in the intermolecular cycloaddition process (Scheme 1), much in the same way as the regioselectivity of the reaction is controlled by a sulfide ligand present in the alkyne.[7]

Therefore, it would be of great interest to study dicobalt complexes having sulfide ligands that do not form a part of the original alkyne molecule, toward designing new catalysts for an enantioselective version of the Pauson–Khand reaction.

In clear contrast with group V ligands, there are very few examples in the literature of sulfide coordination to alkyne dicobalt complexes.[7–9] In fact, there is only one example of such type of complexes with a monodentate sulfide ligand not covalently bonded to the alkyne: the bis(trifluoromethyl)acetylene derivative **1** (Chart 1), described by Petillon and co-workers.[8]

Upon analysis of the structural features of **1**, we concluded that a main contribution to its stability could be the effect of the electron-withdrawing trifluoromethyl groups on the cobalt cluster. Bis(*tert*-butylsulfonyl)ethyne **2**,[10a] a strongly electron-deficient alkyne introduced a few years ago by our group as a general acetylene synthon in the Diels–Alder reaction,[10b–d] could be an excellent probe to study the coordination chemistry of simple alkyl sufides to alkyne–dicobalt hexacarbonyl complexes. We describe herein the synthesis and a detailed structural study of the cobalt carbonyl complexes of bis(*tert*-butylsulfonyl)ethyne with sulfide ligands.

**Scheme 2**



## Results and Discussion

**(A) Synthesis of Cobalt Carbonyl Complexes with Sulfide Ligands, $Co_2(\mu\text{-}Bu^tSO_2C_2)_2(CO)_5SRR'$.** Bis(*tert*-butylsulfonyl)ethyne **2** was prepared in two steps from $Bu^tSH$ and trichloroethene using the previously described procedure.[10a] Although the complexation of alkynes bearing electron-withdrawing groups has often proved difficult, after a few trials we found that formation of the hexacarbonyl complex **3** could be conveniently performed by treating a freshly crystallized sample of **2** with $Co_2(CO)_8$ in dry ether. In this way **3** was obtained as an air-stable red crystalline solid in 97% yield (Scheme 2).

With **3** in our hands we proceeded to investigate its reactions with methyl *p*-tolyl sulfide as a test ligand. It is known that amine *N*-oxides oxidize metal-coordinated CO ligands, providing in this manner a free coordination site for the incoming ligand.[11] Consequently, we first checked the *N*-oxide-induced formation of sulfide complexes, in a fashion similar to what had been successfully done for the preparation of the pentacarbonyl complexes of chelating auxiliaries.[5] Addition of a slight excess of *N*-methyl morpholine *N*-oxide (NMO) to a solution of **3** and of methyl *p*-tolyl sulfide (2 equiv) in dichloromethane resulted in rapid color change from bright red to brown. Simultaneously, a new, brown spot could be observed on TLC. However, upon solvent removal, no clean sulfide complex could be isolated. We reasoned that the *N*-methyl morpholine formed as a byproduct hampered the purification of the target complex. To avoid this, we switched to an *N*-oxide of a volatile amine, i.e., trimethylamine *N*-oxide (TMANO). On using 2 equiv of TMANO in $CH_2Cl_2$, we were able to isolate the corresponding monosulfide complex **4**,

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(7) (a) Krafft, M. E.; Juliano, C. A.; Scott, I. L.; Wright, C.; McEachin, M. D. *J. Am. Chem. Soc.* **1991**, *113*, 1693–703. (b) Krafft, M. E.; Scott, I. L.; Romero, R. H. *Tetrahedron Lett.* **1992**, *33*, 3829–3832. (c) Krafft, M. E.; Scott, I. L.; Romero, R. H.; Feibelmann, S.; Vanpelt, C. E. *J. Am. Chem. Soc.* **1993**, *115*, 7199–7207.

(8) Rumin, R.; Manojlovic-Muir, L.; Muir, K. W.; Petillon, F. Y. *Organometallics* **1988**, *7*, 375–383.

(9) There is one example of a sulfide–phosphine bidentate ligand coordinated to a dicobaltcarbonyl acetylene complex: Edwards, A. J.; Mack, S. R.; Mays, M. J.; Mo, C.-Y.; Raithby, P. R.; Rennie, M.-A. *J. Organomet. Chem.* **1996**, *519*, 243–252.

(10) (a) For a convenient preparation of **2** see: Riera, A.; Marti, M.; Moyano, A.; Pericàs, M. A.; Santamaria, J. *Tetrahedron Lett.* **1990**, *31*, 2173–6. (b) Riera, A.; Marti, M.; Moyano, A.; Pericàs, M. A.; Santamaria, J. *Tetrahedron Lett.* **1990**, *31*, 2173–6. (c) Virgili, M.; Belloc, J.; Moyano, A.; Pericàs, M. A.; Riera, A. *Tetrahedron Lett.* **1991**, *32*, 4583–4586. (d) Belloc, J.; Virgili, M.; Moyano, A.; Pericàs, M. A.; Riera, A. *Tetrahedron Lett.* **1991**, *32*, 4579–4582.

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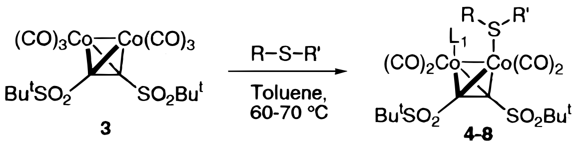
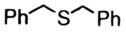
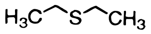
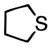
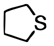
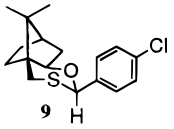
**Table 1. Synthesis of Dicobaltpentacarbonyl Complexes with Sulfide Ligands under Thermal Conditions**



| Sulfide | Time | $L_1$ | Sulfide complex | $\Delta\bar{\nu}$ (cm$^{-1}$)[a] | Yield(%) |
|---|---|---|---|---|---|
| *p*-Tolyl-S-CH$_3$ | 36h | CO | 4 | 31 | 59 |
|  | 24h | CO | 5 | 33 | 65 |
|  | 24h | CO | 6 | 36 | 63 |
|  | 5h |  | 7 | 56 | 74 |
|  | 36h | CO | 8 | 32 | 58[b] |

[a] $\Delta\bar{\nu} = \bar{\nu}(\mathbf{3}) - \bar{\nu}(\mathbf{X})$, $\bar{\nu}$ = mean IR carbonyl frequency. [b] 1 equiv of oxathiane **9** was employed.

albeit in a moderate 24% yield.[12] Complex **4** showed a $^1$H NMR spectra consistent with the complexation of a methyl *p*-tolyl sulfide unit. The $-SCH_3$ group, initially at $\delta$ 2.04 ppm ($C_6D_6$) in the free ligand, underwent a downfield shift and appeared at $\delta$ 2.39 ppm in **4**. Along with that, the average carbonyl frequencies ($\bar{\nu}$) in the IR spectrum of **4** shifted 31 cm$^{-1}$ with respect to the parent hexacarbonyl complex, in accordance with the exchange from a carbonyl to a more electron-releasing ligand. Similar values of $\Delta\bar{\nu}$ are found in the literature for monophosphine-substituted pentacarbonyldicobalt complexes.[13]

To improve the chemical yield obtained when employing *N*-oxides, thermal activation was also investigated. Thus, hexacarbonyl complex **3** and methyl *p*-tolyl sulfide in excess were heated at 65 °C in toluene under nitrogen. To facilitate ligand exchange, CO was periodically removed through evacuation and refilling with nitrogen. After 36 h, this treatment produced a brown solution of **4**, which, upon solvent evaporation, extraction with hexane, and crystallization, afforded **4** as an analytically pure, brown microcrystalline solid in 59% yield. Following this general procedure, a series of sulfide-substituted cobalt complexes **4**−**8** were synthesized and characterized (Table 1).

Reaction with dibenzyl sulfide and diethyl sulfide led to the corresponding monosubstituted sulfide complexes **5** and **6**, respectively, in 65% and 63% yield. When the highly nucleophilic tetrahydrothiophene was used in excess in the reaction, the initial formation of the brown-colored monosubstituted sulfide complex was soon followed by the appearance of a new complex characterized by a green spot on TLC. At the end, a green solid insoluble in hexane was obtained in 74% yield. $^1$H NMR, mass spectroscopy, and a $\Delta\bar{\nu} = 56$ cm$^{-1}$ shift in the carbonyl IR spectrum confirmed the green solid was a bis(tetrahydrothiophene) complex, **7**. Analysis of the IR spectrum in the 1990−2100 cm$^{-1}$ zone indicated that this compound is most probably the isomer with both tetrahydrothiophene ligands in axial position ($C_{2v}$ symmetry) since **7** shows only three stretching CO, while four such signals, due to symmetry considerations, should be expected for any other isomer.[14] Finally, the reaction of **3** with the chiral oxathiane **9**, obtained from (+)-10-mercaptoisoborneol and *p*-chlorobenzaldehyde,[15] afforded an optically active complex **8** (Table 1). $^1$H NMR of **8** ($C_6D_6$) showed two different Bu$^t$ singlets, consistent with the new diastereotopic nature of the *tert*-butylsulfonyl groups attached to the carbon−cobalt core, as expected for the coordination of a chiral ligand.

Unlike the preceding examples, reaction attempts with diphenyl sulfide and di(*tert*-butyl) sulfide under either thermal or oxidative conditions were not successful. The two *tert*-butylsulfonyl groups probably impose large steric requirements too difficult to meet for a sterically encumbered sulfide such as $Bu^t_2S$. In the case of $Ph_2S$ the problem is probably of electronic nature; conjugation with two phenyl groups lowers significantly the Lewis basicity of sulfur, thus preventing coordination.

**(B) Crystal Structure of $Co_2(\mu\text{-}Bu^tSO_2C_2)_2(CO)_5$-$SBn_2$ (5).** Dibenzyl sufide complex **5** could be isolated in two different crystalline forms. This behavior, however, does not seem to involve any structural change at the molecular level since both types of crystals display in solution the same $^1$H NMR spectra. When **5** was crystallized from cold hexane, red fragile needles, not suitable for X-ray diffraction, were obtained (mp 125 °C). Crystallization from hot hexane, however, yielded dark red crystals (mp 129 °C), suitable this time for X-ray analysis. The relevant crystal and structure refinement data are shown in Table 2. Selected atomic distances and angles are provided in Table 3, and the corresponding ORTEP drawing is shown in Figure 1.

The interatomic cluster distances found in **5** are similar to those found in other alkyne−dicobalt complexes.[16] The metal−metal bond length found (2.488 Å) is among the longest for this class of compounds, and

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[12] The possibility of sulfide oxidation by the amine *N*-oxide has been ruled out. Treatment of methyl *p*-tolyl sufide with an excess of TMANO in $DCCl_3$ at room temperature for 2 h did not yield any oxidized sulfur compound, as monitored by $^1$H NMR.

[13] (a) Chia, L. S.; Cullen, W. R.; Franklin, M.; Manning, A. R. *Inorg. Chem.* **1975**, *14*, 2521−2525. (b) Varadi, G.; Vizi-Orosz, A.; Vastag, S.; Palyi, G. *J. Organomet. Chem.* **1976**, *108*, 225−233. (c) Bradley, D. H.; Khand, M. A.; Nicholas, K. M. *Organometallics* **1992**, *11*, 2598−2607.

[14] There are six possible isomers for compound **7**: one diaxially substituted, belonging to the $C_{2v}$ symmetry group, three diequatorially substituted ($C_2$, $C_s$ with both ligands in the same cobalt and $C_s$ with one ligand in each cobalt), and two axial−equatorially susbtituted (both belonging to the $C_1$ group). For all of them, except for the diaxial one, four CO stretchings are expected. It is worth noting than in the other cobalt complexes prepared in this article the number of carbonyl signals is in good agreement with the theoretical prediction based on their symmetry. For a detailed explanation of the procedure see: Cotton, F. A. *Chemical Applications of Group Theory*; John Wiley & Sons: New York, 1990.

[15] Aggarwal, V. R.; Ford, J. G.; Fonquerna, S.; Adams, H.; Jones, R. V. H.; Fieldhouse, R. *J. Am. Chem. Soc.* **1998**, *120*, 8328−8339.

[16] (a) Jeffery, J. C.; Pereira, R. M. S.; Vargas, M. D.; Went, M. J. *J. Chem. Soc., Dalton Trans.* **1995**, 1805−1811. (b) Bonnet, J. J.; Mathieu, R. *Inorg. Chem.* **1978**, *17*, 1973−1976. (c) Bradley, D. H.; Khand, M. A.; Nicholas, K. M. *Organometallics* **1989**, *8*, 554−556. (d) D'Agostino, M. F.; Frampton, C. S.; McGlinchey, M. J. *Organometallics* **1990**, *9*, 2745−2753. (e) Gelling, A.; Went, M. J.; Povey, D. C. *J. Organomet. Chem.* **1993**, *455*, 203−210.

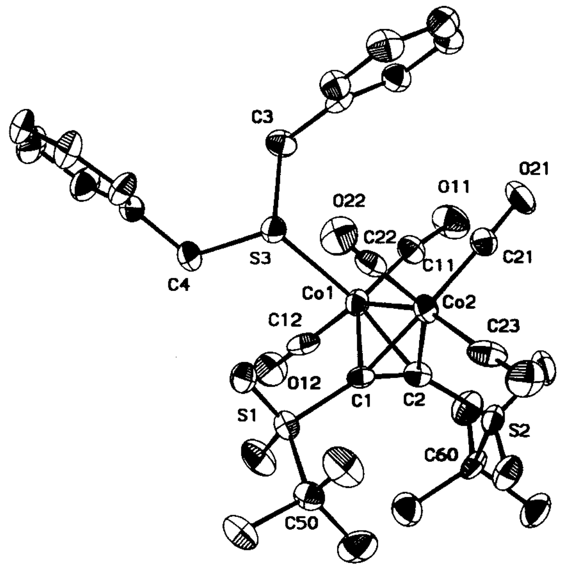

**Figure 1.** ORTEP drawing of **5** showing 30% probability ellipsoids. H atoms have been omitted for clarity.

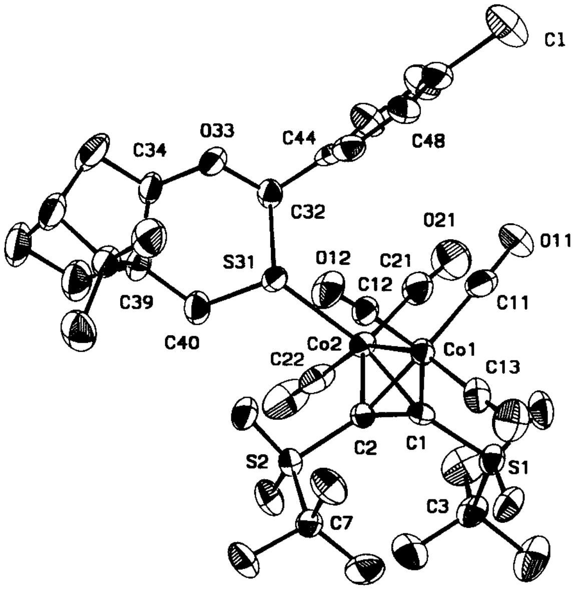

**Figure 2.** ORTEP drawing of **8** showing 30% probability ellipsoids. H atoms have been omitted for clarity.

**Table 2. Crystal Data and Structure Refinement Parameters for 5 and 8**

| parmeter | 5 | 8 |
|---|---|---|
| empirical formula | $C_{29}H_{32}Co_2O_9S_3$ | $C_{32}H_{39}ClCo_2O_{10}S_3$ |
| fw | 738.59 | 833.12 |
| temperature (K) | 293(2) | 293(2) |
| wavelength (Å) | 0.71069 | 0.71069 |
| crystal system | monoclinic | orthorhombic |
| space group | *C*1 2/*c* 1 | *P* $2_1$ $2_1$ $2_1$ |
| *a* (Å) | 28.52(2) | 11.098(5) |
| *b* (Å) | 10.364(4) | 14.210(6) |
| *c* (Å) | 24.658(13) | 24.271(4) |
| α (deg) | 90 | 90 |
| *β* (deg) | 114.99(6) | 90 |
| *γ* (deg) | 90 | 90 |
| volume (Å$^3$) | 6607(7) | 3828(2) |
| *Z* | 8 | 4 |
| density (calc) (Mg/m$^3$) | 1.485 | 1.446 |
| absorption coeff (mm$^{-1}$) | 1.243 | 1.151 |
| *F*(000) | 3040 | 1720 |
| crystal size (mm) | 0.22 × 0.18 × 0.07 | 0.43 × 0.32 × 0.20 |
| *θ* range (deg) | 1.58 to 24.99 | 1.68 to 24.97 |
| index ranges | $-33 \leq h \leq 30$ | $0 \leq h \leq 13$ |
|  | $0 \leq k \leq 12$ | $0 \leq k \leq 16$ |
|  | $0 \leq l \leq 29$ | $0 \leq l \leq 28$ |
| no. of unique reflns | 5786 | 3357 |
| absorption correction | empirical | empirical |
| max. and min. transmn | 0.992 and 0.713 | 1.000 and 0.953 |
| refinement method | full-matrix least-squares on $F^2$ |  |
| no. of data/restrains/params | 5786/15/388 | 3357/27/433 |
| goodness of fit on $F^2$ | 0.718 | 0.891 |
| final *R* indices [$I > 2\sigma(I)$] | $R(F) = 0.0550$ | $R(F) = 0.0433$ |
|  | $R_w(F^2) = 0.0830$ | $R_w(F^2) = 0.0994$ |
| *R* indices (all data) | $R(F) = 0.1899$ | $R(F) = 0.0781$ |
|  | $R_w(F^2) = 0.0936$ | $R_w(F^2) = 0.1083$ |
| absolute struct param |  | 0.04(3) |
| $\Delta\rho_{max}$ and $\Delta\rho_{min}$ (e A$^{-3}$) | 0.304/−0.314 | 0.408/−0.413 |

the C−C distance of the formerly acetylenic bond is 1.35(1) Å. Interestingly, the cluster bond Co(1)−C(2) = 1.900(5) is slightly shorter than Co(1)−C(1) = 1.964(5), probably due to the trans effect that the sulfide ligand exerts. The cobalt−sulfur distance in **5** (Co(1)−S(3) = 2.279(2) Å) is remarkably similar to that found in **1** (2.270 Å). Upon coordination, the alkyl−alkyl angle in the thioether ligand (C(3)−S(3)−C(4) = 100.2°) remains practically untouched and matches exactly the free sulfide mean angle[17] of 100.8°.

Besides this, two significant features present in the crystal structure of **5** should be stressed: (a) the coordination of $Bn_2S$ to a pseudoequatorial site and (b) the synclinal conformation of both *tert*-butyl groups with respect to the C−C bond of the cluster, the torsion angles being C(1)−C(2)−S(2)−C(60) = −94.8° and C(2)−C(1)−S(1)−C(50) = 76.2°. In addition, to further accommodate the bulky sulfide, the torsion angle S(1)−C(1)−C(2)−S(2) = 48° deviates also from planarity. In such a twisted conformation of the bis-*tert*-butylsulfonylethyne backbone, the ligand is placed at one of the two equatorial sites free of the steric repulsion exerted by the *tert*-butyl groups. The pseudoequatorial position of the sulfide group can be clearly apreciated in the eclipsing of this group with one of the carbonyl groups [C(22)−O(22)] in the cobalt tricarbonyl fragment, the corresponding torsion angle being nearly zero (see Table 3).

**(C) Crystal Structure of Chiral Complex 8.** The X-ray diffraction of a single crystal of **8**, obtained by slow cooling of a warm hexane solution, showed the existence in the unit cell of four molecules of a single enantiomer, which is depicted in Figure 2. The most relevant crystallographic and geometrical parameters of the X-ray structure can be found in Tables 2 and 3.

The similarity between structures **5** and **8** is striking. The geometries of both metal clusters are almost coincident, and the two most important features of **5** are also present in **8**: the synclinal conformation of both *tert*-butyl groups and the coordination of the sulfide ligand to an equatorial coordination site on cobalt. With respect to the ligand itself, the oxathiane ring adopts the expected chairlike conformation and the sulfur atom is coordinated through the equatorial lone pair to the metal center.

The coordination of the sulfide to an equatorial position in both cases is somewhat surprising since it is commonly accepted for this class of compounds that

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(17) Obtained from a Cambridge Data Base search.

**Table 3. Selected Bond Lengths (Å) and Bond Angles (deg) for X-ray Structures 5 and 8**

| complex **5** | | complex **8** | |
|---|---|---|---|
| Co(1)−Co(2) | 2.488(1) | Co(1)−Co(2) | 2.479(2) |
| Co(1)−C(1) | 1.964(5) | Co(2)−C(2) | 1.948(7) |
| Co(1)−C(2) | 1.900(5) | Co(2)−C(1) | 1.926(8) |
| Co(2)−C(1) | 1.935(6) | Co(1)−C(2) | 1.937(7) |
| Co(2)−C(2) | 1.957(7) | Co(1)−C(1) | 1.953(7) |
| C(1)−C(2) | 1.35(1) | C(1)−C(2) | 1.37(1) |
| Co(1)−S(3) | 2.279(2) | Co(2)−S(31) | 2.281(2) |
| Co(1)−C(11) | 1.796(6) | Co(2)−C(21) | 1.84(1) |
| Co(1)−C(12) | 1.811(7) | Co(2)−C(22) | 1.80(1) |
| C(12)−Co(1)−S(3) | 96.1(2) | C(22)−Co(2)−S(31) | 95.1(3) |
| C(11)−Co(1)−S(3) | 105.7(2) | C(21)−Co(2)−S(31) | 107.8(4) |
| C(11)−Co(1)−C(12) | 99.0(3) | C(21)−Co(2)−C(22) | 96.4(5) |
| S(3)−Co(1)−Co(2) | 96.6(1) | Co(1)−Co(2)−S(31) | 96.71(7) |
| Co(1)−S(3)−C(3) | 110.6(2) | Co(2)−S(31)−C(32) | 114.4(3) |
| Co(1)−S(3)−C(4) | 110.4(2) | Co(2)−S(31)−C(40) | 110.8(3) |
| C(3)−S(3)−C(4) | 100.2(3) | C(32)−S(31)−C(40) | 94.6(4) |
| C(2)−C(1)−S(1) | 146.8(5) | C(1)−C(2)−S(2) | 146.8(6) |
| C(1)−C(2)−S(2) | 145.6(5) | S(1)−C(1)−C(2) | 145.8(6) |
| C(11)−Co(1)−Co(2)−C(21) | −12.3(3) | C(11)−Co(1)−Co(2)−C(21) | 11.0(5) |
| S(3)−Co(1)−Co(2)−C(22) | −8.0(2) | C(12)−Co(1)−Co(2)−S(31) | 6.2(3) |
| C(12)−Co(1)−Co(2)−C(23) | −40.2(7) | C(13)−Co(1)−Co(2)−C(22) | 33(1) |
| C(11)−Co(1)−S(3)−C(3) | −5.8(3) | C(21)−Co(2)−S(31)−C(32) | 9.6(5) |
| C(12)−Co(1)−S(3)−C(4) | −14.6(3) | C(22)−Co(2)−S(31)−C(40) | 16.6(5) |
| S(1)−C(1)−C(2)−S(2) | 48(1) | S(1)−C(1)−C(2)−S(2) | −38(2) |
| C(2)−C(1)−S(1)−C(50) | −76.2(1) | C(1)−C(2)−S(2)−C(7) | 78.8(1) |
| C(1)−C(2)−S(2)−C(60) | −94.8(1) | C(3)−S(1)−C(1)−C(2) | 81.8(1) |

poor $\pi$-acceptor ligands prefer coordination to pseudo-axial sites. There are many examples of axially coordinated monodentate phosphine ligands. Regarding the sulfide ligands, in the only monodentate case decribed so far of a sulfide not covalently bonded to the alkyne, Petillon and co-workers[8] have reported that it is axially coordinated to the metal. Only in the case of bidentate ligands,[9] for obvious structural restrictions, do these occupy two equatorial sites. It has been suggested that steric factors also favor axial coordination.[18] In our systems however, this is clearly not the case, and consequently, to our knowledge, **5** and **8** represent the first examples of $\sigma$-donor, poor $\pi$-acceptor monodentate ligands equatorially coordinated to alkyne−dicobalt complexes.

**(D) Fluxional Behavior and Solution Structure of 4 and 5.** Cobalt complex **5** was submitted to a variable-temperature $^1$H NMR study in $CD_2Cl_2$ (Figure 3). Whereas at room temperature the four benzylic protons gave a sole broad resonance at $\delta$ 3.91, when the temperature was lowered (−10 °C) this signal split into two broad resonances ($\delta$ 4.21 and 3.69) in a 1:1 ratio. Upon further cooling the NMR probe, these resonances emerged as an AB system ($J$ = 13 Hz) at −30 °C. Eventually, before a well-defined doublet forms, the resonance at $\delta$ 4.21 smears and at −80 °C separates into three signals, a doublet ($J$ = 13 Hz) and two broad singlets. At the same time, approximately at −60 °C, the Bu$^t$ resonance has split into two different singlets at $\delta$ 1.49 and 1.39 in an aproximate 1:1 ratio.

The dynamic behavior visible on $^1$H NMR for **5** is consistent with two different processes: (1) slow exchange between two enantiomeric complexes showing the nonequivalence of the diastereotopic benzylic pro-

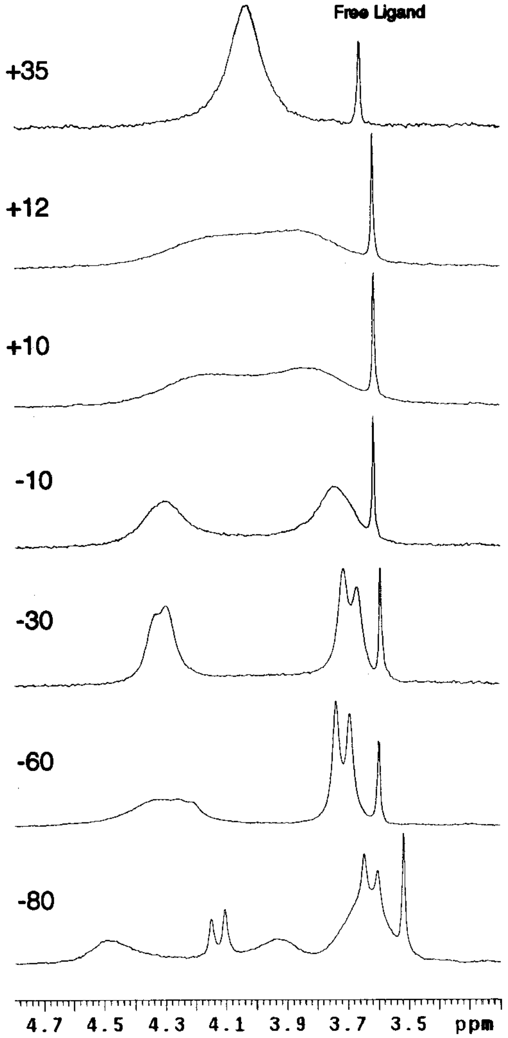

**Figure 3.** Variable-temperature $^1$H NMR spectrum of the benzyl region of **5** in $CD_2Cl_2$. Temperatures are given in °C.

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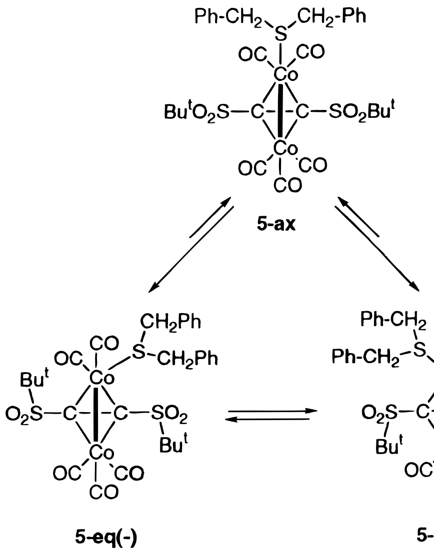
(18) Simpson and co-workers have found that in complex $Co_2(CF_3)_2C_2(CO)_5(CH_3CN)$ the acetonitrile replaces an equatorial CO. To explain this, they have argued that it is due to the small size of $CH_3CN$, which is isolobal to CO. Arewgoda, M.; Robinson, B. H.; Simpson, J. *J. Am. Chem. Soc.* **1983**, *105*, 1893−1903.

**Scheme 3. Postulated Equilibrium Involved in the Fluxional Process of 5**[a]



[a] Rotation signs are given arbitrarily.

tons and (2) hindered rotation around the Co−S axis. The coordination of $Bn_2S$ to one of the cobalt centers can lead to two different isomers: one in which $Bn_2S$ is axially coordinated and one equatorially coordinated complex. There is, however, a degenerate process interconverting two enantiomeric equatorially coordinated species. The observed splitting of the methylene protons of the benzyl groups into an AB system at −30 °C (Figure 3) is in agreement with a slow interchange between the two enantiomeric complexes **5-eq(+)** and **5-qe(−)** (Scheme 3). In such a situation, the benzylic protons $-CH_AH_B-$ in the ligand are no longer magnetically equivalent and the corresponding AB system shows up in the spectrum. The coalescence temperature of +13 °C was used to calculate the activation free energy for the this equilibrium: $\Delta G^{\ddagger} = 14.4 \pm 0.2$ kcal mol$^{-1}$. This value falls in the same range as the one found by Vollhardt for a similar equilibrium in an (alkyne)$Mo_2(CO)_4$(fulvalene) complex.[19,20] The appearance of two singlets for the Bu$^t$ groups at low temperatures can also be explained by this model. In **5-eq(+)** and **5-eq(−)** the sulfide ligand is always closer to one of the two *tert*-butyl groups, providing different chemical environments, which finally results in two separate chemical shifts. No other signals are observed in the benzyl region, suggesting that abundance of the axial coordinated complexes **5-ax** in solution is less than 10%.

Changes in the $^1$H NMR spectra of **5** from −30 to −80 °C can be attributed to hindered rotation around the S−Co bond. While at −80 °C the AB doublet at $\delta$ 4.21 has separated into three signals, consistent with the formation of three rotamers, the other AB doublet ($\delta$ 3.69) is just starting to broaden, suggesting this process is still rapid at − 80 °C. Although hindered rotations around sulfide−metal bonds have not been reported, this behavior is well documented for M−P bonds possessing bulky phosphine ligands.[21] In the present case the highly crowded environment around the Co core is presumably responsible for the observation of this phenomenon at relatively high temperatures.

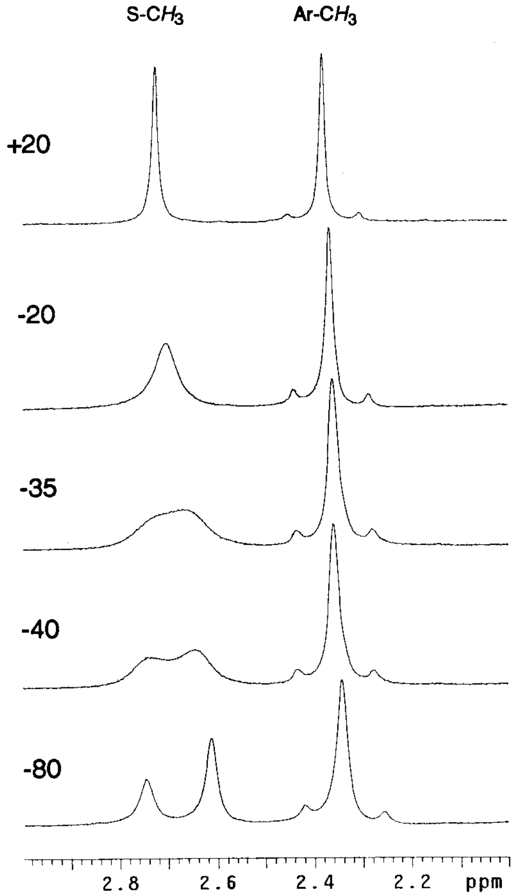


**Figure 4.** Variable-temperature $^1$H NMR spectrum of **4** in $CD_2Cl_2$. Temperatures are given in °C.

In an effort to further clarify the existence of axially coordinated complexes vs equatorial ones we also studied the dynamic behavior of the cobalt complex **4**. The methyl *p*-tolyl sulfide ligand in **4** has no $-CH_AH_B-$ groups, and therefore the exchange process between equivalent equatorial complexes should be invisible on $^1$H NMR. According to our expectations, on cooling a solution of **4** in $CD_2Cl_2$, no splitting was observed around 10 °C. However, the $-SCH_3$ resonance started broadening at −20 °C and split around −35 °C into two singlets (Figure 4). At −80 °C two singlets at $\delta$ 2.74 and 2.61 with a 1:1.5 ratio could be observed.

Unlike the precedent example, the presence of two signals with different intensity for $-SCH_3$ protons indicated that an equilibrium between unequally populated species (with different energies) was taking place. We thought, at first, that such behavior could be characteristic of an equilibrium between the axial sulfide and the equatorial ones, since the corresponding species should have different energies. Still, the much lower coalescence temperature ($T_c = -35$ °C) than the one observed for ligand pseudorotation in **5** pointed to

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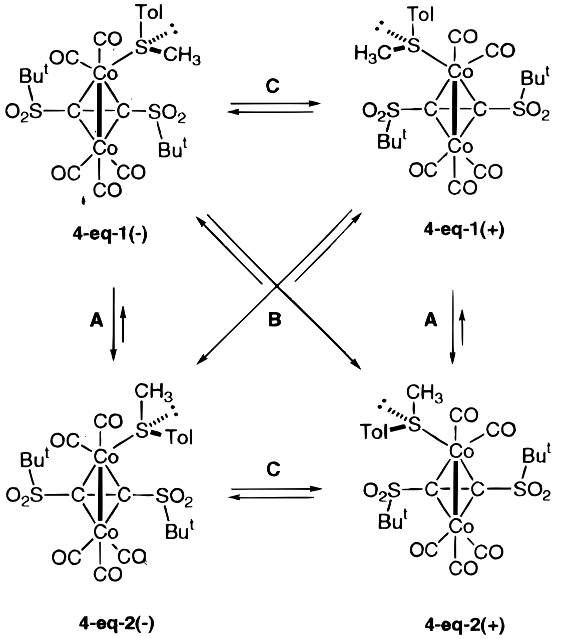
(19) Drage, J. S.; Vollhardt, K. P. C. *Organometallics* **1986**, *5*, 280−297.

(20) (a) Bailey, W. I.; Chisholm, M. H.; Cotton, F. A.; Renkel, L. A. *J. Am. Chem. Soc.* **1978**, *100*, 5764−5773. (b) Amouri, H. E.; Gruselle, M. *Chem. Rev.* **1996**, *96*, 1077−1103. (c) Griffith, D. L.; Roberts, J. D. *J. Am. Chem. Soc.* **1965**, *87*, 4089−4091.

(21) (a) Bushweller, C. H.; Rithner, C. D.; Butcher, D. J. *Inorg. Chem.* **1986**, *25*, 1610−1616. (b) Mann, B. E.; Masters, C.; Shaw, B. L.; Stainbank, R. E. *J. Chem. Soc., Chem. Commun.* **1971**, 1103−1104. (c) Widenhoefer, R. A.; Zhong, A.; Buchwald, S. L. *Organometallics* **1996**, *15*, 2745−2754.

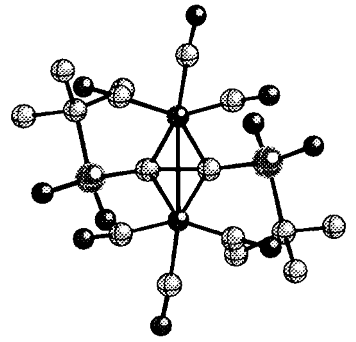
**Scheme 4. Postulated Equilibrium Involved in the Fluxional Process of 4**[a]



[a] Rotation signs are given arbitrarily.

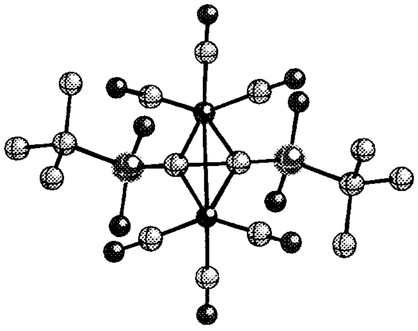
a different kind of process. A possible explanation for this observations comes from the ability of the sulfide ligand to coordinate through one of the two electron lone pairs (Scheme 4). Bearing two different substituents (R = Me, R′ = Tol), upon coordination, the sulfur atom becomes stereogenic. Thus, when the ligand is coordinated equatorially, we can expect the formation of as much as four isomers, i.e., the diastereomeric pairs of enantiomers **4-eq-1(+)**, **4-eq-1(−)**, and **4-eq-2(+)**, **4-eq-2(−)** (Scheme 4). There are two possible single equilibrium processes between all four complexes: inversion at the sulfur center (A type equilibrum), and ligand pseudorotation followed by a conformational change of the *tert*-butyl groups (B type equilibrium). Transformation of one complex to its corresponding enantiomer (C type equilibrium) would involve inversion at sulfur, pseudorotation on cobalt, and conformational change of the *tert*-butyl groups (A and B). In view of this, having in mind that pseudorotation is a higher energy process as we have shown for **5**, the exchange from one set of diastereomers to the other through an A type of equilibrium would account for the observed spectra of **4** in the low-exchange region (−80 °C). Finally, the 1:1.5 ratio observed for the MeS− resonance at −80 °C is in accordance with one pair of enantiomers being energetically more stable than the other.

**(E) Molecular Orbital Calculations of Cobalt Complexes.** To shed light on the main features of the crystal structures of **5** and **8** described above and to explain the solution behavior of this family of compounds, we decided to perform a conformational study of complexes **3** and **5** by computational means. It is worth mentioning that this semiempirical procedure has already been shown to be suitable for the description of related alkyne dicobalt carbonyl complexes.[5c] The geometries of all conformers were fully optimized using the semiempirical procedure PM3(tm) as implemented in the MacSpartan Plus package of programs.[22]



**3g**

$E_{rel}$ = 3.4 kcal mol$^{-1}$ [a]
$E_{rel}$ = 2.0 kcal mol$^{-1}$ [b]



**3a**

$E_{rel}$ = 0.0 kcal mol$^{-1}$ [a]
$E_{rel}$ = 0.0 kcal mol$^{-1}$ [b]

**Figure 5.** Optimized structures of the most relevant conformers of compound **3** at the PM3(tm) level. H atoms have been omitted for clarity. [a] Relative Energy without geometrical restrictions. [b] Relative energy with the C−C bond of the cluster fixed at 1.35 Å.

A systematic exploration of the conformational energy hypersurface of **3** led to the characterization of several minima. In the lowest energy conformer (**3a**) both *tert*-butyl groups were antiperiplanar to the C−C bond of the cluster, the value of the dihedral angles C−C−S−C(Bu$^t$) being 160°. This structure has $C_2$ symmetry, probably to minimize the repulsion between the *tert*-butyl groups and the equatorial carbonyls of the complex (Figure 5). Interestingly, conformer **3g**, with both *tert*-butyl groups synclinal to the C−C bond of the cluster and consequently with a disposition analogous to the one present in the crystal structure of **5**, was located 3.4 kcal mol$^{-1}$ higher in energy (Figure 3). It is worth noting that the calculated C−C−S−C(Bu$^t$) dihedral angle (87°) in this conformer (**3g**) is very close to the observed dihedral angles in the crystal. With respect to the $C_2Co_2$ cluster, both the Co−Co (2.531 Å) and the C−Co (1.974 Å) distances were accurately reproduced, while the C−C bond (1.516 Å) was somewhat overestimated.

A conformational study of the cobalt complex $Co_2(\mu\text{-}Bu^tSO_2C)_2(CO)_4(SCH_3)_2$ **(10)**, in which dimethyl sulfide replaces a carbon monoxide ligand, was next performed in order to evaluate the structural and energetic influ-

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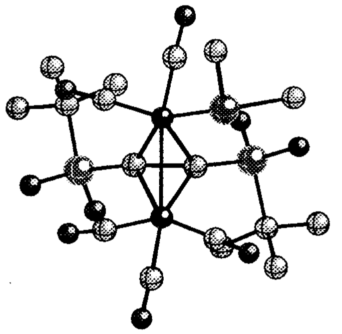
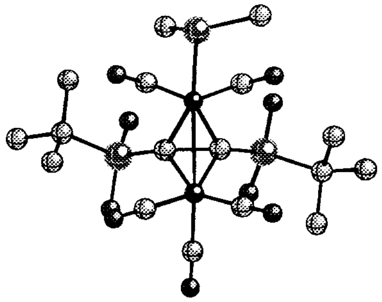
[22] *MacSpartan Plus*, version 1.0; Wavefunction, Inc.: 18401 Von Karman Ave., Suite 370, Irvine, CA, 92612.



**10g-eq**

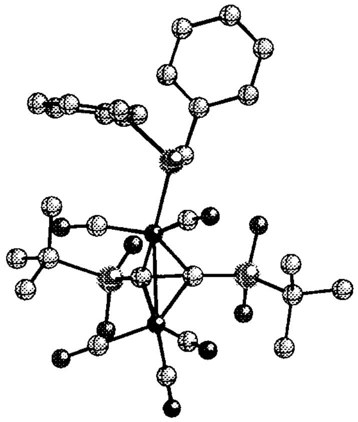
$E_{\mathrm{rel}} = 3.1$ kcal mol$^{-1\ a}$
$E_{\mathrm{rel}} = 0.9$ kcal mol$^{-1\ b}$



**10a-ax**

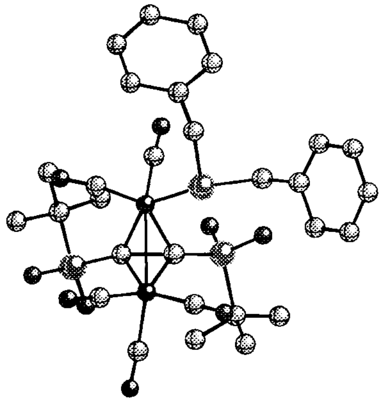
$E_{\mathrm{rel}} = 0.0$ kcal mol$^{-1\ a}$
$E_{\mathrm{rel}} = 0.0$ kcal mol$^{-1\ b}$

**Figure 6.** Optimized structures of the most relevant conformers of compound **10** at the PM3(tm) level. H-atoms have been omitted for clarity. [a]Relative energy without geometrical restrictions. [b]Relative energy with the C−C bond of the cluster fixed at 1.35 Å.



**5a-ax**

$E_{\mathrm{rel}} = 2.2$ kcal mol$^{-1\ a}$
$E_{\mathrm{rel}} = 3.9$ kcal mol$^{-1\ b}$



**5g-eq**

$E^{a}_{\mathrm{rel}} = 0.0$ kcal mol$^{-1\ a}$
$E^{b}_{\mathrm{rel}} = 0.0$ kcal mol$^{-1\ b}$

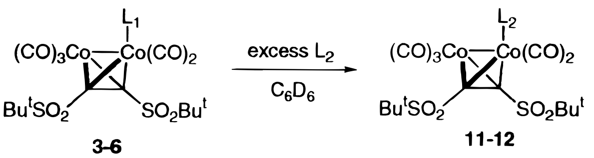
**Figure 7.** Optimized structures of the most relevant conformers of compound **5** at the PM3(tm) level. H atoms have been omitted for clarity. [a]Relative energy without geometrical restrictions. [b]Relative energy with the C−C bond of the cluster fixed at 1.35 Å.

ence of a non sterically demanding sulfide. Conformers with dimethyl sulfide in pseudoequatorial or pseudoaxial sites were considered. Among the species where both *tert*-butyl groups are antiperiplanar to the C−C bond of the cluster (**10a**), the most stable complex was the axially substituted complex **10a-ax**, which was 4.6 kcal mol$^{-1}$ more stable than the corresponding equatorial one, **10a-eq**. On the other hand, among the conformers with both *tert*-butyl groups gauche to the C−C cluster bond (**10g**) the equatorially substituted complex was 7.0 kcal mol$^{-1}$ more stable than the corresponding axial one. Significantly, the most stable axial complex **10a-ax** was 3.1 kcal mol$^{-1}$ more stable than the lowest energy equatorial one, **10g-eq** (Figure 6).

These results are in good agreement with what is observed in complex **1** and in most phosphine-substituted cobalt complexes. However, the most important features present in the X-ray structure of **5** were not reproduced in the conformational preferences of complexes **10** with dimethyl sulfide as a ligand. We reasoned that steric interactions provoked by large benzylic groups could be responsible for this different conformational bias. Consequently, the conformational hypersurface of the benzyl sulfide complex **5** was screened. In this case, the relative energetic order was completely reversed with respect to **10**. The lowest energy conformer was **5g-eq** (equatorially substituted with both *tert*-butyl groups in gauche position), in complete agreement with the crystal structure of this compound. This conformer was 6.0 kcal mol$^{-1}$ more stable than the corresponding axial one, **5g-ax**, and 2.2 kcal mol$^{-1}$ more stable than the lowest axially substituted complex, **5a-ax** (Figure 7). Since the cluster C−C bond distance is overestimated by the PM3(tm) calculations, all minima were reoptimized with this bond distance fixed to the crystallographic value of 1.35 Å. In doing so, all conformers with the *tert*-butyl groups antiperiplanar to the C−C cluster bond were destabilized with respect to the synclinal ones, thus indicating that the steric interactions between *tert*-butyl sulfonyl groups and the metal cluster can be alleviated in the synclinal conformers (Table 4). In the case of complex **5**, the energetic difference between **5a-ax** and **5g-eq** increased to 3.9 kcal mol$^{-1}$.

Thus, the present calculations clearly show that the most important features found in the crystal structure of **5** are mainly due to the steric interactions originated by the benzyl groups, since these structural characteristics are not present in the dimethyl sulfide complex **10**. Whereas in complexes **3** and **10**, the minimal energy

**Table 4. Sulfide−Phosphine Ligand Exchange at 20 °C**



| entry | s. mat. | $L_1$ | prod. | $L_2$ | time | conv. |
|---|---|---|---|---|---|---|
| 1 | **3** | CO | **11** | $P(OCH_3)_3$ | 1 day | 3% |
| 2 | **6** | $SEt_2$ | **11** | $P(OCH_3)_3$ | 2 h | 22% |
| 3 | **6** | $SEt_2$ | **12** | $PPh_3$ | 2 h | 22% |
| 4 | **5** | $S(CH_2Ph)_2$ | **12** | $PPh_3$ | 2 h | 56% |
| 5 | **4** | MeS*p*-tolyl | **12** | $PPh_3$ | 2 h | 93% |
| 6 | **4** | MeS*p*-tolyl | **11** | $P(OCH_3)_3$ | 2 h | 97% |

conformer has both *tert*-butyl groups in an antiperiplanar arrangement with respect to the C−C bond of the cluster, in complex **5** the presence of a large sulfide ligand forces a conformation in which both *tert*-butyl groups adopt a synclinal arrangement that permits the accommodation of the large ligand in one of the equatorial sites. Moreover the higher energy of the axial conformers relative to the equatorial ones in compound **5** is also in complete agreement with the observations made in the low-temperature $^1$H NMR studies of **4** and **5**.

**(F) Ligand Exchange Experiments.** The sulfide complexes sythesized in this study were not good Pauson−Khand substrates, as could be anticipated from an inspection of the bulky disubstituted alkyne complex. Thus, reaction of **4** with norbornadiene, one of the most reactive alkenes, even at high temperatures did not yield any cyclopentenone product. However, these complexes constitute an excellent probe for testing the lability of the sulfide ligand compared to a carbonyl in connection with the mechanism of the Pauson−Khand reaction. The generation of a vacant cordination site at cobalt as a preliminary step to the coordination of the incoming olefin has been postulated to be the rate-determining step in the Pauson−Khand reaction. As has been already mentioned, we have developed a sulfur chelating auxiliary with rate-enhancing properties[5] (Scheme 1), and we have proposed[5c] that this effect was due to a decreased strength of the sulfide−cobalt bond vs the original carbonyl−cobalt bond. The lability of the sulfide ligand would facilitate the coordination of the olefin to the open site left by the sulfide. To further verify this hypothesis, we decided to study the reaction between cobalt complexes **3**−**6** and phosphorus derivatives. In this way we would be able to easily monitor the interchange between the carbonyl or sulfide ligands and a phosphorus ligand. The results of this study are depicted in Table 4.

First, hexacarbonyl complex **3** was treated with trimethyl phosphite in $C_6D_6$ at 20 °C, and the formation of complex $Co_2(\mu\text{-}Bu^tSO_2C)_2(CO)_4P(OCH_3)_3$ (**11**) was monitored by NMR. After 1 day, only 3% conversion was observed, clearly indicating the difficulty of the substitution of a carbonyl ligand at this temperature (Table 4, entry 1). Conversely, the reaction of triphenyl phosphite or triphenylphosphine with complex **6** ($L_1 = Et_2S$) at room temperature produced 22% of the corresponding complexes **11** ($L_2 = P(OCH_3)_3$) and **12** ($L_2 = PPh_3$) after 2 h (Table 4, entries 2 and 3). Conversion numbers increased when complexes with bulkier sulfide ligands where tested. Thus, with complex **5** the conversion went to 56% in 2 h using triphenyl phosphine as an incoming ligand (Table 4, entry 4). Methyl *p*-tolyl sulfide was the most labile ligand tested, since the treatment of **4** with $PPh_3$ and $P(OCH_3)_3$ led to almost complete conversion (93% and 97%) after only 2 h (Table 4, entries 5 and 6). Along with steric effects, the decreased basicity of sulfur through conjugation with the aromatic ring in the methyl *p*-tolyl sulfide might be reponsible for this fact. The similar conversion numbers obtained when using $PPh_3$ and $P(OCH_3)_3$ indicate that the reaction rate depends solely on the nature of the departing ligand. Such behavior agrees with a two-step mechanism in which the first event, sulfide dissociation, is the rate-determining step, as it has been described for several metal carbonyl substitution reactions,[23] and explains the high reactivity in Pauson−Khand reactions of the cobalt complexes of alkynes bearing sulfide ligands coordinated to the cobalt atom.

## Conclusions

Thermal reaction of the hexacarbonyl cobalt complex of bis(*tert*-butylsulfonylethyne) ($Co_2(\mu\text{-}Bu^tSO_2C)_2(CO)_6$, **3**) with a variety of simple organic thioethers in toluene yields the corresponding sulfide-substituted complexes in good yield. These cobalt complexes are stable compounds most likely due to the shielding and electron-withdrawing effect that the two *tert*-butylsulfonyl groups exert. Whereas large sulfide ligands give rise to monosubstituted complexes, small nucleophilic ones, (i.e., tetrahydrothiophene) lead to the substitution of two carbonyl units. X-ray analysis of complexes derived from dibenzyl sulfide and oxathiane **9** showed the preference of the sulfide ligand for an equatorial coordination site rather than the axial one. To accommodate the incoming ligand, the two $Bu^tSO_2-$ groups adopt a synclinal arrangement with respect to the C−C bond of the cluster. Variable-temperature $^1$H NMR indicated that large sulfide ligands present a dynamic process in which the ligand switches between both adjacent equatorial sites and that axially coordinated complexes are not major species in solution. In further agreement with solid-state and solution studies, molecular orbital calculations showed that small sulfides prefer axial coordination and that larger ligands (i.e., dibenzyl sulfide) in the present system prefer equatorial sites. This represents the first example of a poor $\pi$-acceptor ligand coordinated equatorially in such type of compounds and demonstrates that steric effects may overcome electronic ones. Finally, in a series of ligand exchange experiments, we have demonstrated that alkyne dicobalt carbonyl complexes containing a sulfide ligand exhibit a greatly facilitated dissociation. This provides an explanation for the high reactivity in Pauson−Khand reaction of intramolecularly chelated complexes of alkynes with an adequately positioned thioether function. We are currently investigating the application of sulfide ligands not bonded to the alkyne as readily

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removable chiral auxiliaries in the asymmetric Pauson–Khand reaction.

## Experimental Section

**General.** All reactions were conducted under nitrogen or argon atmosphere using standard Schlenk techniques. Nuclear magnetic resonance (NMR) spectra were recorded on a Varian Unity-300 spectrometer. $^{1}$H and $^{13}$C NMR spectra were referenced relative to residual solvent peaks. In most akyne dicobalt complexes the signals corresponding to the cluster carbons do not appear in the $^{13}$C NMR spectrum and the CO signals have been omitted. Infrared (IR) spectra were recorded on a Nicolet 510 FT spectrometer. Melting points of cobalt complexes were determined by differential scanning calorimetry (DSC) on a Mettler DSC-30 under nitrogen. Elemental analyses were performed at "Serveis científico tècnics de la Universitat de Barcelona". High-resolution mass spectra (HRMS) were conducted at "Laboratori d'espectrometria de masses del CSIC de Barcelona". Dichloromethane was distilled from $CaH_2$. Toluene and ether were distilled from sodium benzophenone ketyl. Hexane was dried with Na wire and degassed by bubbling argon. Commercially available sulfides (methyl *p*-tolyl sulfide, dibenzyl sulfide, diethyl sulfide, tetrahydrothiophene, di(*tert*-butyl) sulfide, and diphenyl sulfide) were purchased from Aldrich and were used as received. Bis(*tert*-butylsulfonyl)ethyne[10a] and (+)-(2*R*)-10-mercaptoisoborneol[24] were prepared according to published literature procedures.

**$Co_2(\mu\text{-}Bu^tSO_2C)_2(CO)_6$, 3.** To a slurry of freshly recrystallyzed (AcOEt) bis(*tert*-butylsulfonyl)ethyne (260 mg, 1.0 mmol) in ether (30 mL) was added solid dicobaltoctacarbonyl (375 mg, 1.1 mmol). The reaction mixture was stirred at room temperature until CO evolution had ceased (1 h). Solvent removal in vacuo and filtration through a pad of silica (hexane/AcOEt, 20%) afforded 525 mg (97%) of **3** as a red crystalline solid.

Mp: 172 °C (DSC). IR (KBr): $\nu_{max} = 2045, 2055, 2062, 2083, 2118$ cm$^{-1}$. $^{1}$H NMR (300 MHz, $CDCl_3$): $\delta$ 1.59 (s, 18H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 24.4 (C($C$H$_3$)$_3$), 62.6 ($C$(CH$_3$)$_3$), 88.7 (C-cluster), 195.5 (CO) ppm. MS (DIP–CI–NH$_3$): *m*/*e* = 569 (M$^+$ + 18, 100), 558 (M$^+$ − CO + 35, 32), 530 (M$^+$ − 2CO + 35, 11). Anal. Calcd for $C_{16}H_{18}Co_2O_{10}S_2$: C, 34.79; H, 3.28; S, 11.61. Found: C, 35.03; H, 3.18; S, 11.75.

**$Co_2(\mu\text{-}Bu^tSO_2C)_2(CO)_5S(p\text{-}C_6H_4CH_3)(CH_3)$, 4. (A) *N*-Oxide-Promoted Reaction.** Complex **3** (150 mg, 0.27 mmol), methyl *p*-tolylsulfide (44 mg, 0.32 mmol), and $CH_2Cl_2$ (5 mL) were charged in a Schlenk flask under nitrogen. To this mixture, at room temperature, a solution of trimethylamine *N*-oxide (TMANO) (22 mg, 0.29 mmol) in $CH_2Cl_2$ (2 mL) was added dropwise via cannula. This resulted in a rapid color change of the reaction mixture from bright red to dark brown. After stirring the reaction for 1 h at room temperature another equivalent of TMANO was added (20 mg, 0.27 mmol, 2 mL of $CH_2Cl_2$) via cannula. Upon further stirring the reaction mixture at room temperature for 30 min, the solvent was removed in vacuo. The remaining solid residue was extracted with hexane, filtered through Celite under nitrogen, and crystallyzed at −20 °C overnight. This afforded 43 mg (24%) of **4** as a dark brown microcrystalline solid.

**(B) Thermal Reaction. General Procedure for the Preparation of Complexes $Co_2(\mu\text{-}Bu^tSO_2C)_2(CO)_5SR_2$.** Complex **3** (50 mg, 0.09 mmol), methyl *p*-tolyl sulfide (50 mg, 0.36 mmol), and toluene (1 mL) were charged in a Schlenk flask under nitrogen. The reaction mixture was heated at 65 °C for 36 h, removing periodically the CO with vacuum and refilling with nitrogen. Upon reaction completion the color had changed from bright red to brown. The solvent was removed in vacuo. The residue was solved in hexane, filtered, and crystallized at −20 °C, yielding 35 mg (59%) of **4** as a dark brown microcrystalline solid.

Mp: 110 °C (DSC). IR (KBr): $\nu_{max} = 2010, 2031, 2044, 2049, 2095$ cm$^{-1}$. $^{1}$H NMR (300 MHz, $C_6D_6$): $\delta$ 1.52 (s, 18H), 1.90 (s, 3H), 2.39 (s, 3H), 6.75 (d, *J* = 8 Hz, 2H), 7.10 (d, *J* = 8 Hz, 2H) ppm. $^{13}$C NMR (75 MHz, $C_6D_6$): $\delta$ 20.9, 24.6, 26.0, 62.3, 129.1, 130.5, 134.0, 139.5 ppm. MS (FAB$^+$, NBA): *m*/*e* = 663 (M$^+$ + 1, 54), 635 (M$^+$ − CO, 46), 550 (M$^+$ − 4CO, 100), 522 (M$^+$ − 5CO, 62). Anal. Calcd for $C_{23}H_{28}Co_2O_9S_3$: C, 41.69; H, 4.26; S, 14.52. Found: C, 41.68; H, 4.20; S, 14.83.

**$Co_2(\mu\text{-}Bu^tSO_2C)_2(CO)_5S(CH_2Ph)_2$, 5.** According to the general procedure described above, dicobalt complex **3** (100 mg, 0.18 mmol), dibenzyl sulfide (77 mg, 0.36 mmol), and toluene (1 mL) were used. The reaction mixture was heated at 70 °C for 20 h. Crystallization from hexane afforded 87 mg (65%) of **5** as red needles. Dark red crystals suitable for X-ray diffraction were obtained when **5** was recrystallized from hot hexane.

Mp: 125.9 °C (red needles), 129.5 °C (dark red cryst.) (DSC). IR (KBr): $\nu_{max} = 2012, 2029, 2037, 2054, 2091$ (red needles); 2004, 2035, 2041, 2053, 2093 (dark red cryst.) cm$^{-1}$. $^{1}$H NMR (300 MHz, $C_6D_6$): $\delta$ 1.49 (s, 18H), 2.90–4.50 (coalescing s, 4H), 6.95–7.10 (m, 6H), 7.12–7.21 (m, 4H) ppm. $^{13}$C NMR (75 MHz, $C_6D_6$): $\delta$ 24.5, 44.7, 62.0, 127.9, 128.8, 129.8, 135.1 ppm. MS (FAB$^+$, NBA): *m*/*e* = 739 (M$^+$ + 1, 30), 598 (M$^+$ − 5CO, 100). Anal. Calcd for $C_{29}H_{32}Co_2O_9S_3$: C, 47.15; H, 4.36; S, 13.02. Found: C, 47.19; H, 4.41; S, 13.14.

**$Co_2(\mu\text{-}Bu^tSO_2C)_2(CO)_5S(C_2H_5)_2$, 6.** According to the general procedure described above, dicobalt complex **3** (100 mg, 0.18 mmol), diethyl sulfide (97 $\mu$L, 0.9 mmol), and toluene (1 mL) were used. The reaction mixture was heated at 60 °C for 24 h. This yielded a brownish solution. Removal of solvent and the excess sulfide was effected under vacuum. The residue was washed with hexane and dried under vacuum. This afforded 70 mg (63%) of **6** as an air-stable brown solid.

Mp: 120 °C (DSC). IR (KBr): $\nu_{max} = 2010, 2027, 2037, 2052$ (sh), 2089 cm$^{-1}$. $^{1}$H NMR (300 MHz, $C_6D_6$): $\delta$ 0.78 (t, *J* = 7 Hz, 6H), 1.50 (s, 18H), 2.21 (broad s, 4H) ppm. $^{13}$C NMR (75 MHz, $C_6D_6$): $\delta$ 12.7, 24.6, 31.8, 62.2 ppm. MS (FAB$^+$, NBA): *m*/*e* = 615 (M$^+$ + 1, 60), 587 (M$^+$ − CO, 75%), 474 (M$^+$ − 5CO, 100). HRMS (FAB$^+$): calcd for $C_{19}H_{29}Co_2O_9S_3$ 614.9637, found 614.9647.

**$Co_2(\mu\text{-}Bu^tSO_2C)_2(CO)_4(SC_4H_8)_2$, 7.** According to the general procedure described above, dicobalt complex **3** (100 mg, 0.18 mmol), tetrahydrothiophene (80 $\mu$L, 0.9 mmol), and toluene (1 mL) were used. The reaction mixture was heated at 70 °C for 5 h. The original bright red solution turned brown and finally changed to a green color. Removal of the solvent and the excess of sulfide under vacuum afforded a solid, which was washed with hexane and dried under vacuum, yielding 89 mg (74%) of **7** as an air-stable green solid.

Mp: 153 °C (DSC). IR (KBr): $\nu_{max} = 1991, 2020, 2054$ cm$^{-1}$. $^{1}$H NMR (300 MHz, $C_6D_6$): $\delta$ 1.16 (broad s, 8H), 1.70 (s, 18H), 2.59 (broad s, 8H) ppm. $^{13}$C NMR (75 MHz, $C_6D_6$): $\delta$ 24.8, 29.8, 41.9, 62.0 ppm. MS (FAB$^+$, NBA): *m*/*e* = 673 (M$^+$ + 1, 30), 472 (M$^+$ − 5CO − $C_4H_8S$, 100). HRMS (FAB$^+$): calcd for $C_{22}H_{35}Co_2O_8S_4$ 672.9878, found 672.9875.

**(1*S*,4*R*,6*R*,8*R*)-4-(Chlorophenyl)-11,11-dimethyl-5-oxa-3-thiatricyclo[6.2.1.0$^{1,6}$]undecane, 9.** To a cooled solution (ice bath) of (+)-10-mercaptoisoborneol (1.0 g, 5.3 mmol) and *p*-chlorobenzaldehyde (0.83 g, 5.9 mmol) in $CH_2Cl_2$ (10 mL) under nitrogen was added $BF_3$–$OEt_2$ (0.73 mL, 5.9 mmol). The reaction mixture was stirred at 0 °C for 0.5 h, and the crude was filtered through a pad of silica eluting with hexane/AcOEt (90:10). Solvent removal under vacuum and recrystalization from hexane afforded 1.18 g (71%) of **9** as colorless needles.

Mp: 134 °C. $[\alpha]_D = -86.4$ (*c* 1.0, $CHCl_3$). IR (KBr): $\nu_{max} = 740, 1060, 1485, 2950$ cm$^{-1}$. $^{1}$H NMR (300 MHz, $CDCl_3$): $\delta$ 0.95 (s, 3H), 0.91–1.13 (m, 2H), 1.45 (s, 3H), 1.49–1.59 (m, 1H), 1.67–1.80 (m, 3H), 1.96–2.07 (m, 1H), 2.77–3.29 (AB, *J*

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= 14 Hz, 2H), 3.73−3.77 (dd, $J$ = 3 and 8 Hz, 1H), 5.65 (s, 1H), 7.28−7.40 (m, 4H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): 20.4, 23.3, 27.2, 29.8, 34.4, 37.9, 41.8, 45.5, 46.7, 82.2, 85.7, 127.7, 128.4, 133.9, 137.9 ppm. MS (DIP−CI−$NH_3$): $m/e$ = 309 ($M^+$ + 1, 100), 326 ($M^+$ + 18, 16). Anal. Calcd for $C_{17}H_{21}ClOS$: C, 66.11; H, 6.85; S, 10.38. Found: C, 66.02; H, 6.85; S, 9.94.

**$Co_2(\mu\text{-}Bu^tSO_2C)_2(CO)_5(SC_{17}H_{21}ClO)$, 8.** According to the general procedure described above, dicobalt complex **3** (100 mg, 0.18 mmol), oxathiane **9** (61 mg, 0.2 mmol), and toluene (1 mL) were used. The reaction mixture was heated at 65 °C for 36 h. Solvent removal under vacuum and crystallization from hexane afforded 88 mg (58%) of **8** as air-stable red crystals.

Mp: 160 and 177 °C (DSC). $[\alpha]_D = -138°$ ($c$ 0.02, $CH_2Cl_2$). IR (KBr): $\nu_{max}$ = 2004, 2033, 2049, 2059, 2095 cm$^{-1}$. $^1$H NMR (300 MHz, $C_6D_6$): $\delta$ 0.50−0.59 (m, 1H), 0.67−0.75 (m, 1H), 1.01 (s, 3H), 1.14−1.28 (m, 1H), 1.40−1.50 (m, 3H), 1.42 (s, 9H), 1.51 (s, 9H), 1.58 (s, 3H), 1.80−1.90 (m, 1H), 2.92, 3.97 (AB, $J$ = 14 Hz, 2H), 3.32−3.36 (dd, $J$ = 3 and 8 Hz, 1H), 4.92 (s, 1H), 7.15−7.25 (m, 4H) ppm. $^{13}$C NMR (75 MHz, $C_6D_6$): $\delta$ 20.1, 23.1, 24.5, 27.1, 33.6, 37.9, 40.7, 44.9, 45.8, 47.1, 61.9, 62.5, 86.5, 90.1, 129.3, 130.1, 134.7, 136.5 ppm. MS (FAB$^+$, NBA): $m/e$ = 833, 835 ($M^+$, 7), 692, 694 ($M^+$ − 5CO, 100). Anal. Calcd for $C_{32}H_{40}ClCo_2O_{10}S_3$: C, 46.07; H, 4.83; S, 11.53. Found: C, 45.99; H, 4.79; S, 11.52.

**$Co_2(\mu\text{-}Bu^tSO_2C)_2(CO)_5P(C_6H_5)_3$,12.** According to the general procedure described for the preparation of sulfide complexes, dicobalt complex **3** (95 mg, 0.17 mmol), triphenylphosphine (49 mg, 0.18 mmol), and toluene (1 mL) were used. The reaction mixture was heated at 60 °C for 7 h. Solvent removal was effected under vacuum. The resulting solid was washed with hexane and dried under vacuum. This afforded 108 mg (80%) of the target complex as an air-stable dark pink solid.

Mp: Amorphous solid, no sharp fusion peak was detected by DSC. IR (KBr): $\nu_{max}$ = 2004, 2035, 2051, 2093 cm$^{-1}$. $^1$H NMR (300 MHz, $C_6D_6$): $\delta$ 1.52 (s, 18H), 6.94−7.10 (m, 9H), 7.64−7.73 (m, 6H) ppm. $^{13}$C NMR (75 MHz, $C_6D_6$): $\delta$ 24.8, 62.8, 128.7 ($J_P$ = 10 Hz), 130.6, 134.2 ($J_P$ = 11 Hz), 134.7 ppm. HRMS (FAB$^+$): calcd for $C_{33}H_{33}Co_2O_9PS_2Na$ 808.9865, found 808.9874.

**Conversion Determination for Ligand Exchange Reactions.** Complexes **3**−**6** (0.015 mmol) were dissolved in an NMR tube in $C_6D_6$ (0.7 mL). To this solution a 3-fold excess of $PPh_3$ or $P(OMe)_3$ was added. The tube was shaken, and its contents were analyzed by $^1$H NMR at 20 °C. Exchange conversions were calculated from the integration of the coordinated vs free ligand resonances. In the reaction of the parent hexacarbonyl complex **3** the areas of the $Bu^t$ resonances of **3** ($\delta$ 1.35) and the product phosphite complex **11** ($\delta$ 1.53) were taken. When using $PPh_3$, upon complete conversion the reaction mixture showed a $^1$H NMR spectrum consistent with formation of $Co_2(Bu^tSO_2C)_2(CO)_5P(C_6H_5)_3$, **12**, as verified by the independent synthesis described above. The following signals were used in the other cases: for **4** the protons corresponding to $CH_3$−S and Ar−$CH_3$ ($\delta$ 2.39 and 1.40 coord., $\delta$ 2.04 and 2.02 free); for **5** the benzyl protons ($\delta$ 2.40−4.50 −broad− coord., $\delta$ 3.34 free); and for **6** the methyl protons of $Et_2S$ ($\delta$ 0.79 coord., $\delta$ 1.05 free).

**Crystal Structure Determination of 5 and 8.** Suitable crystals of **5** and **8** were grown from warm hexane. Relevant crystal data and structure refinement information are displayed in Tables 2 and 3. Cell constants were obtained by least-squares refinement on diffractometer angles for 25 automatically centered reflections. Data measured on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo K$\alpha$ radiation ($\lambda$ = 0.71069 Å) and a $\omega-2\theta$ scan. $Lp$ and empirical absorption corrections[25] were applied. The structure was solved by direct methods (SHELXS-86)[26] and refined by full-matrix least-squares procedures on $F^2$ for all reflections (SHELX-97).[27] All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were placed in calculated positions with isotropic temperature factors 1.5 (methyl hydrogens) or 1.2 (the rest) times the $U_{eq}$ values of the corresponding carbons. Full details of the structure determination for **5** and **8** are available as Supporting Information.

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**Supporting Information Available:** Tables of complete X-ray crystal data, ORTEP drawings, refinement parameters, atomic coordinates, and bond distances and angles for **5** and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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