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**Novel Bimetallic Dispersed Catalysts for
Temperature-Programmed Coal Liquefaction**

**Technical Progress Report
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Derrick S. Parfitt, Chunshan Song, and Harold H. Schobert

**Fuel Science Program
Department of Materials Science and Engineering,
209 Academic Projects Bldg., The Pennsylvania State University
University Park, Pennsylvania, PA 16802**

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ABSTRACT

Development of new catalysts is a promising approach to more efficient coal liquefaction. It has been recognized that dispersed catalysts are superior to supported catalysts for primary liquefaction of coals, because the control of initial coal dissolution or depolymerization requires intimate contact between the catalyst and coal. This research is a fundamental and exploratory study on catalytic coal liquefaction, with the emphasis on the development of novel bimetallic dispersed catalysts for temperature-programmed liquefaction.

The ultimate goal of the present research is to develop novel catalytic hydroliquefaction process using highly active dispersed catalysts. The primary objective of this research is to develop novel bimetallic dispersed catalysts from organometallic molecular precursors, that can be used in low concentrations (<1%) but exhibit high activity for efficient hydroliquefaction of coals under temperature-programmed conditions. In this quarter, we have synthesised several bimetallic complexes that contain Mo, Co, and S in a single molecule. Three of them are bimetallic thiocubanes: $\text{Mo}_2\text{Co}_2\text{S}_4(\text{S}_2\text{CNEt}_2)_2(\text{CH}_3\text{CN})_2(\text{CO})_2$ [designated as MoCo-TC1], $\text{Mo}_2\text{Co}_2\text{S}_4\text{Cp}_2(\text{CO})_2$ [MoCo-TC2], and $\text{Mo}_2\text{Co}_2\text{S}_4(\text{Cp}')_2(\text{CO})_2$ [MoCo-TC3], in which Et, Cp and Cp' represent ethyl, cyclopentadiene, and pentamethylcyclopentadiene, respectively. These thiocubanes were synthesized in our laboratory based on the procedures reported in literature. For comparative examination, the trianionic bimetallic complex, $(\text{PPh}_4)_3\text{Co}(\text{MoS}_4)_2$, was also synthesized. This bimetallic sulfide complex contains cobalt bis-tetrathiomolybdate trianion, $\text{Co}(\text{MoS}_4)_2^{3-}$, and is designated as MoCo-S.

INTRODUCTION

Direct coal liquefaction is the process for producing liquid fuel from coal and involves the reactions of coal with reducing gas (H_2) in a solvent vehicle at high temperature and high pressure. On the microscopic level, the coal conversion into liquids is an extremely complex process and involves both chemical and physical transformations. Despite enormous strides in coal liquefaction research, and great effort at Wilsonville Advanced Two-Stage Liquefaction Facility to reduce the cost of coal-derived distillates, coal-derived liquids are still not competitive with petroleum crudes. Further improvements are required and the most promising approach would be the development of improved catalytic process. It is known that direct coal liquefaction proceeds through two loosely defined stages, coal dissolution into solvent-soluble materials, followed by upgrading of the solubilized products. The distribution and quality of primary liquefaction (coal dissolution) products depend on the coal, catalyst, solvent and process conditions used in the first stage. The upgrading of primary liquefaction products into transportation fuels requires two conversion steps: an overall upgrading of heavy materials to distillate materials, followed by the upgrading of different distillate fractions to liquid products with the necessary properties for use as transportation fuels including gasoline, jet fuels, and diesel fuels.

Numerous studies have been conducted of the application or improvement of conventional catalysts and of the development of new catalysts for hydroliquefaction of coals. As indicated recently by Derbyshire (1988, 1990), research on catalytic liquefaction has been retarded by the persistent and misguided belief that catalysts cannot influence the reactions whereby the solid coal feed is converted to soluble products. It is relatively easy for conventional supported catalysts to promote the reactions after the primary liquids are formed. However, by this time the most critical reactions may have taken place and distributions of products may have already been determined (DOE COLIRN Panel, 1989). In this respect, dispersed catalysts are superior because they may be able to affect the coal dissolution due to their more intimate contact with coal. Monitoring the change of system pressure for catalytic reactions has clearly demonstrated that some dispersed Ni and Mo catalysts can promote the hydrogenation reactions of coals at fairly low temperatures, as revealed by the considerable H_2 uptake at 300-350 °C (Bockrath et al., 1990; Song et al., 1991a). Some novel Lewis acidic Ni and Mo catalysts also enhance the coal pyrolysis at temperatures as low as 300°C, even under N_2 atmosphere (Song et al., 1986a, 1987a, 1991a).

Extensive research at Pittsburgh Energy Technology Center, PETC (Bockrath et al., 1984, 1986, 1991; Utz et al., 1989; Cugini et al., 1991a, 1991b) and Penn State (Davis et al., 1986, 1989; Derbyshire et al., 1986a, 1986b, 1989; Stansberry et al., 1987; Burgess and Schobert, 1990; Burgess et al., 1991; Artok et al., 1991) has demonstrated the potential of using dispersed molybdenum or iron catalyst. The work at Penn State has demonstrated that the combination of low-temperature catalytic reaction followed by the high temperature catalytic reaction using dispersed molybdenum significantly enhanced coal conversion and oil production. More recent work in this laboratory has shown that temperature-programmed liquefaction is more effective for converting low rank coals (Song et al., 1991b; Song and Schobert, 1992b; Huang et al., 1992). We have found that low-temperature catalytic reactions using dispersed Mo catalyst lead to some desirable changes in coal structure, and the temperature-programmed catalytic liquefaction affords considerably higher conversion than the conventional non-programmed or the temperature-staged liquefaction (Song et al., 1992b; Huang et al., 1992). All these results point to the beneficial effects of dispersed catalysts for lower-severity liquefaction, and clearly indicate that dispersed catalysts could significantly affect the chemistry of initial coal dissolution (primary liquefaction) and reduce undesirable reactions. It should be noted that almost all of the previous work used precursors of single transition metal sulfides, and little has been reported about bimetallic dispersed catalysts.

Development of new catalysts is a promising approach to more efficient coal liquefaction. Coal conversion catalysis is a comparatively immature field. Perhaps the most promising approach to the development of novel catalysts lies in research into multi-component systems, which, compared to the work with single metal catalysts, are essentially unexplored (Derbyshire, 1990). Several reports have demonstrated on the synergistic effects for multi-component Lewis acidic Zn-, Ni-, and Mo-based catalysts for coal liquefaction or model reactions (Mobley and Bell, 1980; Song et al., 1986a, 1988a, 1991a). Synergism has been reported for Fe-Mo catalysts by Garg and Givens (1984). Even under high-severity conditions (440°C, 2000 psi H₂), significant benefits were observed by using Fe and Mo together; simultaneous impregnation of coal with Fe and Mo significantly increased coal, preasphaltene and asphaltene conversion as compared to individual metals for liquefaction of a Kentucky bituminous coal in the presence of SRC-II heavy distillate. There are clear evidences of the synergism for two or multi-component supported catalysts in the field of heterogeneous catalysis, especially hydrotreating catalysts such as Co-Mo and Ni-Mo. We can anticipate that synergistic effects of multicomponent dispersed catalysts could lead to significantly improved catalytic processes for direct conversion of coal to transportation fuels.

Emphasis for developing novel catalytic process should be directed at promoting the direct transformation of coal to distillates that have low aromaticity and low heteroatom content . This is primarily because the 1990 Clean Air Act Amendments and the increased worldwide concern about global warming will require the production of liquid transportation fuels from coals be based on new strategy away from the formation of aromatic products and more toward formation of hydrogen-rich aliphatic hydrocarbons. Equally important, novel catalysts should promote coal conversion into low-molecular-weight products and their hydrogenation at lower-severity conditions. The present research is a fundamental and exploratory study on catalytic coal liquefaction, with the emphasis on the development of novel bimetallic dispersed catalysts for temperature-programmed liquefaction.

TECHNICAL PROGRESS

Methodology for Synthetic Preparation of Catalyst Precursors

The main objective of this Task is to synthesize the organometallic compounds that contain two different transition metals and sulfur in a single cluster. The candidates are Co-Mo, Ni-Mo, and Fe-Mo bimetallic complexes. In general, the synthesis will be carried out using the published procedures, and the preferable procedures will be selected based on the metal species of interest, simplicity, and ease to scale up in the future. Two to three different complexes for each of the Fe-Mo, Co-Mo, and Ni-Mo combinations will be prepared. The information feedback from liquefaction (Task 4) and model reactions (Task 3) will be used to guide further work on the preparation of novel catalysts.

There are several types of complexes containing the same metal species (for example, Co-Mo). The first method to be used is the procedure for synthesis of thiocubane cluster, which was originally developed by Brunner and Watcher (1982). The reaction for preparing Mo-Co thiocubane, $(C_5H_5)_2Mo_2Co_2S_4(CO)_2$ (*II*), is shown in equation 1. Compound *II* can be prepared by adding *IB* to the brown solution of *IA* in toluene.

There are several other methods for synthesizing bimetallic complexes (Muller et al., 1971, Brunner et al., 1983; Halbert et al., 1985; Dias et al., 1985). Another general method is the procedure developed by Muller et al. (1971). Bimetallic transition metal thioanions with d^0 -configuration of the central atom form complexes with ions of first transition series. As shown in equation 2, MoS_4^{2-} ion (*IIIA*) forms complexes with transition metals (*IIIB*), which can be isolated in the form of the tetraphenylphosphonium salts (*IV*). The synthesis shown in equation 2 is simple and can be applied for preparing Fe-Mo, Co-Mo, Ni-Mo, and Zn-Mo bimetallic complexes. Bimetallic complexes of Ni-Mo and Zn-Mo are stable as the $[\text{M}(\text{MoS}_4)_2]^{2-}$ dianions. However, bimetallic complexes of Co-Mo and Fe-Mo are only stable as the $[\text{M}(\text{MoS}_4)_2]^{3-}$ trianions. They should be prepared according to equation 2B), whose details can be seen from Scheme VI.

Several methods will be used in the early periods for preparation of bimetallic complexes. Appropriate methods will be finally selected based on the initial screening tests to be performed in Tasks 3 and 4.

Bimetallic Catalyst Precursors Prepared in This Quarter

Scheme I gives a list of the bimetallic compounds prepared. All the bimetallic compounds were synthesized under a N_2 atmosphere using reagent-grade chemicals of the highest purity. Three bimetallic thiocubanes were used as catalytic precursors: $\text{Mo}_2\text{Co}_2\text{S}_4(\text{S}_2\text{CNEt}_2)_2(\text{CH}_3\text{CN})_2(\text{CO})_2$ [designated as MoCo-TC1], $\text{Mo}_2\text{Co}_2\text{S}_4\text{Cp}_2(\text{CO})_2$ [MoCo-TC2], and $\text{Mo}_2\text{Co}_2\text{S}_4(\text{Cp}')_2(\text{CO})_2$ [MoCo-TC3], in which Et, Cp and Cp' represent

ethyl, cyclopentadiene, and pentamethylcyclopentadiene, respectively. These thiocubanes were synthesized in our laboratory based on the procedures of Brunner and Watcher [1982] and Halbert et al. [1985]. For comparative examination, the trianionic bimetallic complex, $(\text{PPh}_4)_3\text{Co}(\text{MoS}_4)_2$, was also synthesized based on the procedure of Pan et al. [1985]. This bimetallic sulfide complex contains cobalt bis-tetrathiomolybdate trianion, $\text{Co}(\text{MoS}_4)_2^{3-}$, and is designated as MoCo-S.

The Synthesis of $\text{Mo}_2\text{Co}_2\text{S}_4(\text{S}_2\text{CNEt}_2)_2(\text{CH}_3\text{CN})_2(\text{CO})_2$, MoCo-TC1

Experimental

All reactions were carried out in a N_2 atmosphere. Triphenylphosphine, $\text{Co}_2(\text{CO})_8$ (Strem), sublimed sulfur, acetonitrile (Baker), $(\text{NH}_4)_2\text{MoS}_4$, dimethylformamide, tetraethylammonium bromide, diethyldithiocarbamic acid sodium salt trihydrate (Aldrich), and toluene, methylene chloride (Fisher) were used as purchased from the respective suppliers. Scheme II gives the procedure for synthesis of MoCo-TC1, and Scheme III shows its structure.

ATTM (3.022 g, 11.6 mmole), sulfur (3.018 g, 15.7 moles), and DMF (50 ml) were placed in a 250 ml three-neck flask equipped with a condenser, stirbar, thermometer, and a N_2 inlet and outlet. A heating mantle was used to heat the solution to 95°C . The solution was allowed to stir for 3.5 hours before NEt_4Br was added. After 40 minutes the volatile components were removed by rotary evaporation. The resulting solid was dissolved in acetonitrile and filtered through a Buchner funnel. The volatile components in the filtrate were removed by rotary evaporation to yield a brick-red solid, $[\text{NEt}_4]_2[\text{Mo}_2\text{S}_{12}]$ (7.23 mmole).

$[\text{NEt}_4]_2[\text{Mo}_2\text{S}_{12}]$ (7.23 mmole), diethyldithiocarbamic acid sodium salt trihydrate (4.8903 g, 21.7 mmole), triphenylphosphine (11.383 g, 23.1 mmole), NH_4PF_6 (7.072 g, 23.1 mmole), and acetonitrile (100 ml) were placed in a three-neck 250 ml round-bottom flask equipped with a stirbar, condenser, N_2 inlet and outlet and heated for 50 minutes at 75°C before allowing the solution to cool to room temperature. The solution is dark orange-red while the large amounts of white insoluble solids give the stirred solution a cloudy orange tinted brown color. The contents were transferred to a 250 ml flask and the volatile components were removed by rotary evaporation. The primary product, $\text{Mo}_2\text{S}_4(\text{S}_2\text{CNEt}_2)_2$, was purified by TLC by eluting with CH_3CN .

$\text{Mo}_2\text{S}_4(\text{S}_2\text{CNEt}_2)_2$ and $\text{Co}_2(\text{CO})_8$ (2.51 g, 7.34 mmol) were added to 30 ml CH_3CN in a three-neck 250 ml flask equipped with a stirbar, and a N_2 inlet and outlet. The solution was allowed to stir for five hours at room temperature before the solution was filtered. The acetonitrile-soluble portion had the solvent removed by rotary evaporation. The product was dissolved in methylene chloride before being applied onto the TLC plate; the eluting solvent, acetonitrile, gave an olive-green product. Yield of $\text{Mo}_2\text{Co}_2\text{S}_4(\text{S}_2\text{CNEt}_2)_2(\text{CH}_3\text{CN})_2(\text{CO})_2$, 1.430 g, 1.627 mmol, 14% (literature yield: 20%).

Synthesis of $\text{Mo}_2\text{Co}_2\text{S}_4\text{Cp}_2(\text{CO})_2$, MoCo-TC2

Experimental

All reactions were carried out under a N_2 atmosphere. $\text{Mo}(\text{CO})_6$ and $\text{Co}_2(\text{CO})_8$ (Strem), dicyclopentadiene and n-decane (Aldrich), HPLC-grade toluene (Fisher), and sublimed sulfur (Baker) were used as purchased from the respective suppliers. Scheme IV gives the procedure for synthesis of MoCo-TC2, and Scheme V shows its structure.

$\text{Mo}(\text{CO})_6$ (4.038 g, 15.3 mmol), dicyclopentadiene (1.2 ml, 1.183 g, 8.95 mmol), and 50 ml n-decane were placed in a 250 ml three-neck round bottom flask equipped with a condenser, stirbar, N_2 inlet and outlet, and a thermometer. An oil bath was used to bring the solution to reflux ($\sim 175^\circ\text{C}$). The solution started out as colorless with $\text{Mo}(\text{CO})_6$ being only slightly soluble in the n-decane at room temperature, but as the temperature increased $\text{Mo}(\text{CO})_6$ became completely soluble. The solution started to turn yellowish at around 90°C and brownish at around 130°C ; sublimation of $\text{Mo}(\text{CO})_6$ as white crystals on the sides of the flask started around 110°C . It took around 45 minutes for refluxing to occur (by this time the solution was an opaque dark brown with a substantial amount of white gas throughout the flask). Reflux was allowed to continue for about five hours longer during which the white crystals of $\text{Mo}(\text{CO})_6$ were periodically washed with n-decane and scraped with a spatula from the sides of the flask throughout the reaction. The solution was filtered with n-decane into a 500 ml round bottom flask leaving a blackish residue and a very dark red filtrate. The residue was discarded and the filtrate had the volatile components removed by rotary evaporation to yield a brick-red solid, $\text{Mo}_2\text{Cp}_2(\text{CO})_4$ with some $\text{Mo}_2\text{Cp}_2(\text{CO})_6$ as a by-product.

The brick-red solid, $\text{Mo}_2\text{Cp}_2(\text{CO})_4$, was dissolved in toluene and filtered again giving a residue and a red filtrate. The red filtrate was placed in a 250 ml two-neck round bottom flask

with S₈ (0.555 g, 2.16 mmoles) and 50 ml toluene. The round bottom flask was equipped with a condenser, stirbar, and a N₂ inlet and outlet. The oil bath that heated the flask was monitored with a thermometer. The mixture was allowed to stir overnight (16-20 h) at 50°C whereby the solution was filtered with toluene into another flask giving a grayish-green residue and a brownish-red filtrate, Mo₂Cp₂S₄.

The brownish-red filtrate, Mo₂Cp₂S₄, was dried to a solid by rotary evaporation to find the mass and was subsequently placed in a 250 ml two-neck flask equipped with a stirbar and a N₂ inlet and outlet. Toluene (50 ml) was added and the dark brownish-red solution was stirred for ten minutes before Co₂(CO)₈ (0.940g, 2.75 mmoles) was slowly added. Small bubbles formed almost immediately upon the introduction of Co₂(CO)₈ due to the release of free CO from Co₂(CO)₈. The reaction was allowed to stir for thirty minutes more whereby the solution was observed to have a increasingly purplish cast. The solution was filtered with toluene giving a dark residue and a violet filtrate. A dark violet solid was obtained after rotary evaporation of the filtrate.

The dark violet solid was dissolved in methylene chloride and applied to a thin-layer chromatography silica gel plate (Whatman PK6F, silica gel 20 cm x 20 cm plates, 1 mm thick, 60 Å particles). The eluting solvent was toluene. The only band to appear was a purple band with reddish-purple trailings which came off quite easily using only toluene. The purple band was extracted from the thin-layer chromatography plate with methylene chloride through a water-aspirated fritted filter giving a dark violet solution. The dark violet solution was transferred to a round bottom flask where the solvent was removed by rotary evaporation. The violet solid was vacuum dried at 45°C for two hours to remove any trace of solvent. The product, Mo₂Co₂S₄Cp₂(CO)₂, was stored under a N₂ atmosphere in a vial and placed in the freezer. A typical yield of Mo₂Co₂S₄Cp₂(CO)₂ is 16% based on molybdenum in Mo(CO)₆ (literature yield 18%).

Observations

One observation is that the first step is very touchy; there was a large variation in the product even when the experimental procedure was followed closely. If the conditions aren't harsh enough a reaction to the desired product, Mo₂Cp₂(CO)₄, doesn't occur and if the conditions are too harsh the reactants decompose into molybdenum metal and organic polymeric sludge.

There is an equilibrium in the reaction of $\text{Mo}(\text{CO})_6$ and dicyclopentadiene between the desired product, $\text{Mo}_2\text{Cp}_2(\text{CO})_4$, which has a highly reactive triple bond between the two molybdenum centers, and $\text{Mo}_2\text{Cp}_2(\text{CO})_6$, which has a single bond between the two molybdenum centers. The equilibrium favors $\text{Mo}_2\text{Cp}_2(\text{CO})_4$ at higher temperatures thus necessitating a high boiling point solvent such as decane (bp 175°C). $\text{Mo}_2\text{Cp}_2(\text{CO})_6$ would be the major product if the reaction was carried out in refluxing toluene (bp 110°C). Decane was found to be a better solvent for the reaction of $\text{Mo}(\text{CO})_6$ and dicyclopentadiene than p-cymene (bp 175°C), possibly due to the greater polarity of p-cymene. Sometimes an insoluble polymeric sludge was formed during the first step when p-cymene was used.

During the reaction between $\text{Mo}_2\text{Cp}_2\text{S}_4$ and $\text{Co}_2(\text{CO})_8$, sometimes a small amount of $\text{Co}_2(\text{CO})_8$ (around 0.2 g, 0.4 mmoles) was added to the reaction mixture after thirty minutes to see if the reaction was complete. The reaction was determined complete if there weren't any bubbles observed when the extra $\text{Co}_2(\text{CO})_8$ was added to the solution.

Methylene chloride was determined to be a better solvent than toluene to dissolve the product in before being applied to the thin-layer chromatography silica gel plate and when the product was extracted from the silica gel. The product was always found to be "wet" when toluene was used; this could be due to the lower vapor pressure of toluene compared to that of methylene chloride at the relatively low temperatures ($40\text{--}50^\circ\text{C}$) during the vacuum-drying stage of the final product.

Synthesis of $\text{Mo}_2\text{Co}_2\text{S}_4\text{Cp}'_2(\text{CO})_2$, MoCo-TC3

The procedure is the same as for MoCo-TC2, except that Cp'_2 [$(\text{C}_5\text{Me}_5)_2$, pentamethylcyclopentadiene] is substituted for Cp_2 [$(\text{C}_5\text{H}_6)_2$, cyclopentadiene] in the first step. The structure of MoCo-TC3 is also shown in Scheme V.

Synthesis of $(PPh_4)_3[Co(MoS_4)_2]$, MoCo-S

Experimental

$CoCl_2 \cdot 6H_2O$ (Strem), triethylamine, thiophenol, ammonium tetrathiomolybdenum, tetraphenylphosphonium bromide (Aldrich), and acetonitrile (Baker) were used as received from the various suppliers. All reactions were carried out under a N_2 atmosphere except for the filtrations. Scheme VI gives the procedure for synthesis of bimetallic sulfide complexes including MoCo-S, and Scheme VII shows its structure.

$CoCl_2 \cdot 6H_2O$ (1.190 g, 5.00 mmol) was placed in a flask with 10 ml acetonitrile. The red-purple compound turned a brilliant blue in the acetonitrile solution. In a second flask, triethylamine (1.307 g, 12.9 mmol) and thiophenol (1.395 g, 12.7 mmol) were mixed together and then added to the $CoCl_2$ /acetonitrile solution. The resulting solution immediately became an olive-green and was then added to a mixture of ammonium tetrathiomolybdenum (2.619 g, 10.06 mmol) and 100 ml acetonitrile and allowed to stir for thirty minutes. The solution was filtered leaving a black residue and a very dark olive filtrate. Tetraphenylphosphonium bromide (5.423 g, 12.9 mmol) was added to the filtrate and allowed to stir for thirty minutes. The resulting precipitate was collected by repeated filtrations to give a very dark olive solid that is air sensitive. Yield: 2.501 g, 38.1 % (literature yield: variable, up to 70 %).

Observations

MoCo-S is very air sensitive and is known to decompose in an aerobic solution in fifteen minutes. It must be dissolved in one of the few solvents (see below) that it is soluble in and then filtered to remove any decomposed material before any liquefaction work is done with it.

It is soluble in chloroform and methylene chloride but not in any of the common organic solvents (toluene, THF, etc) that are used in dispersing catalyst onto coal before liquefaction.

The performance of these bimetallic compounds as precursors to in-situ generated Mo-Co sulfide catalysts will be reported in the next quarter.

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Scheme I

Organometallic Catalyst Precursors

Code	Molecular Formula	Structure
MoCo-TC1:	$\text{Mo}_2\text{Co}_2\text{S}_4(\text{S}_2\text{CNEt}_2)_2(\text{CH}_3\text{CN})_2(\text{CO})_2$	Thiocubane ^a
MoCo-TC3:	$\text{Mo}_2\text{Co}_2\text{S}_4(\text{Cp}')_2(\text{CO})_2$	Thiocubane ^b
MoCo-TC2:	$\text{Mo}_2\text{Co}_2\text{S}_4\text{Cp}_2(\text{CO})_2$	Thiocubane
MoCo-S	$(\text{PPh}_4)_3\text{Co}(\text{MoS}_4)_2$	Sulfide complex ^c
$\text{Mo}(\text{CO})_6$	$\text{Mo}(\text{CO})_6$	Metal Carbonyl
$\text{Co}_2(\text{CO})_8$	$\text{Co}_2(\text{CO})_8$	Metal Carbonyl

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Scheme II

SYNTHESIS OF BIMETALLIC THIOCUBANE
COMPOUNDS

Scheme III

STRUCTURE OF THE BIMETALLIC THIOCUBANE MoCo-Tc1

Scheme IV

SYNTHESES OF BIMETALLIC THIOCUBANE
COMPOUNDS

Scheme V

STRUCTURE OF BIMETALLIC THIOCUBANES MoCo-TC2 and MoCo-TC3

MoCo-TC2, R = C₅H₅-
MoCo-TC3, R = C₅Me₅-

Scheme VI

SYNTHESES OF BIMETALLIC SULFIDES

1) Dianionic compounds, $[M(M'S_4)_2]^{2-}$
 $(M' = Mo, M = Ni; M' = W, M = Ni, Co, Fe)$

2) Trianionic compounds, $[M(MoS_4)_2]^{3-}$
 $M = Co, Fe$

Scheme VII

STRUCTURE OF BIMETALLIC INORGANIC
SULFIDE

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