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Designed Syntheses of Heterobimetallic Fulvalene Complexes

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Summary: Two synthetic strategies to the construction of heterobimetallic fulvalene (η^5:η^5-$C_{10}H_8$) complexes are reported. The first is based on the previously described monometallic ring-slippage products of (η^5:η^5-$C_{10}H_8$)$Mo_2(CO)_6$ and (η^5:η^5-$C_{10}H_8$)$Ru_2(CO)_4$ that undergo recomplexation with a variety of metal carbonyls. The second utilizes a potentially iterative synthetic organic strategy in which cyclopentadienyl anion is subjected to an alkanoylation–ring closure sequence that assembles a new attached cyclopentadiene unit.

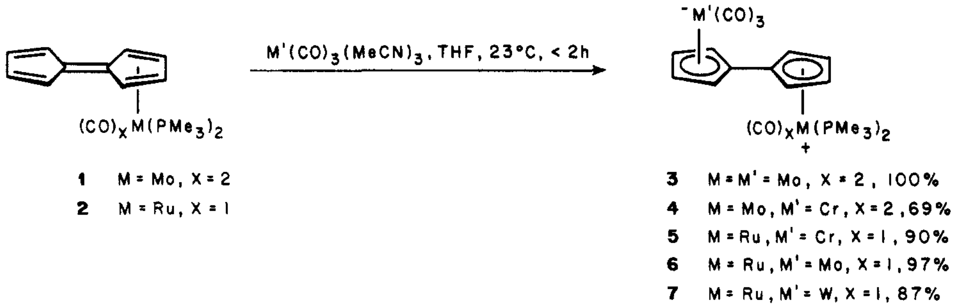
The chemistry of heterodinuclear organo-transition-metal complexes has been the focus of significant recent attention because it is believed that combining the different properties of two metals should give rise to unique reactivity features, especially compared to those found in homobimetallic systems.[1] There are few designed synthetic approaches to these compounds, and most employ heterodifunctional and relatively readily dissociated ligands.[1] We report the synthesis of such compounds anchored on the strongly bound fulvalene (η^5:η^5-$C_{10}H_8$, Fv) ligand[2] based on two strategies: a, the complexation of the monometallic fulvalene complexes **1**[3] and **2**;[4] b, the development of a potentially iterative sequence that constructs new Cp ligands attached to already present ones (all yields are unoptimized).[5]

Schemes I and II exemplify the first approach giving rise to a number of novel heterodinuclear organometallic zwitterions,[3] as well as **10** and **11**. Scheme III depicts the successful application of synthetic organic methodology[6] to the construction of **18** and **19** and the subsequent assembly of metal–metal bonded **20a–c** as well as **21**. Considering the importance of the CpM unit in organometallic chemistry, this scheme should prove useful to those investigators who are interested in extending already existing CpM systems to oligocyclopentadienylmetal chains.

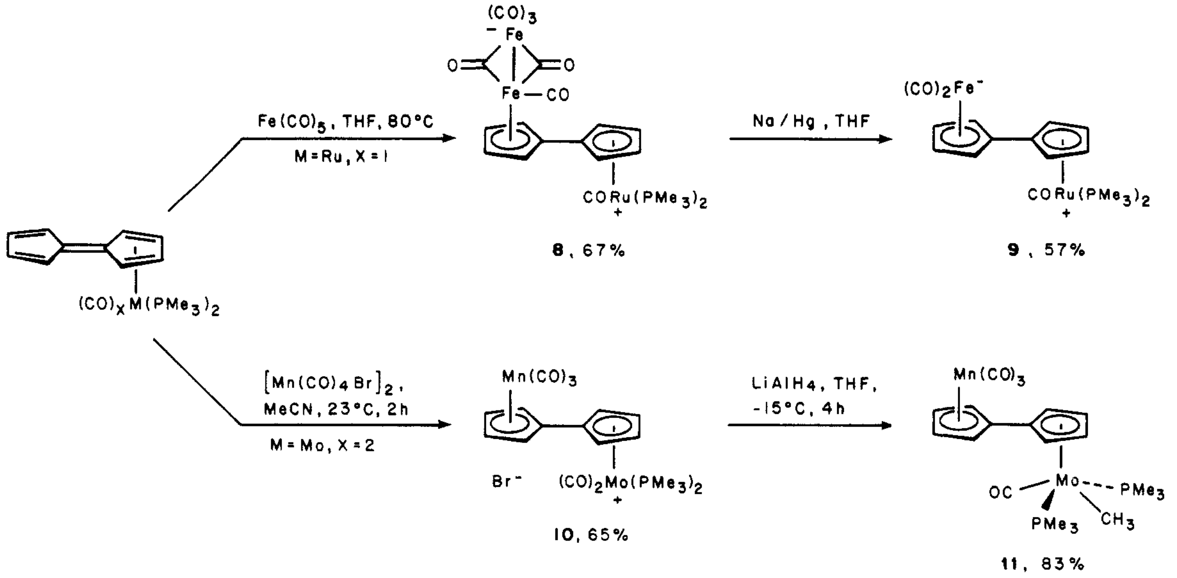
For example (Scheme I), $(MeCN)_3Mo(CO)_3$ (1.1 equiv) in THF (2 mL) was added in a glovebox to **2** (1 equiv) in THF (2 mL) without stirring. Within 5 min **6** precipitated as yellow needles which were collected, washed with successive portions of THF and Et_2O (2 × 2 mL), and dried under vacuum.

The synthetic methodology displayed in Scheme III was designed to provide a more flexible route to heterobimetallic fulvalene complexes and higher oligomers. It centers around the use of the 3-oxo-1-cyclopentenyl unit as a masked cyclopentadienyl fragment. The reaction of a fourfold excess of dimethyl succinate with a 0.5 M solution of NaCp·DME in THF led to the precipitation of **12** (plus 1 equiv of CH_3OH).[6a] Addition of a slurry of lithium dimethyl methylphosphonate to a slurry of **12** (5

Scheme I



Scheme II



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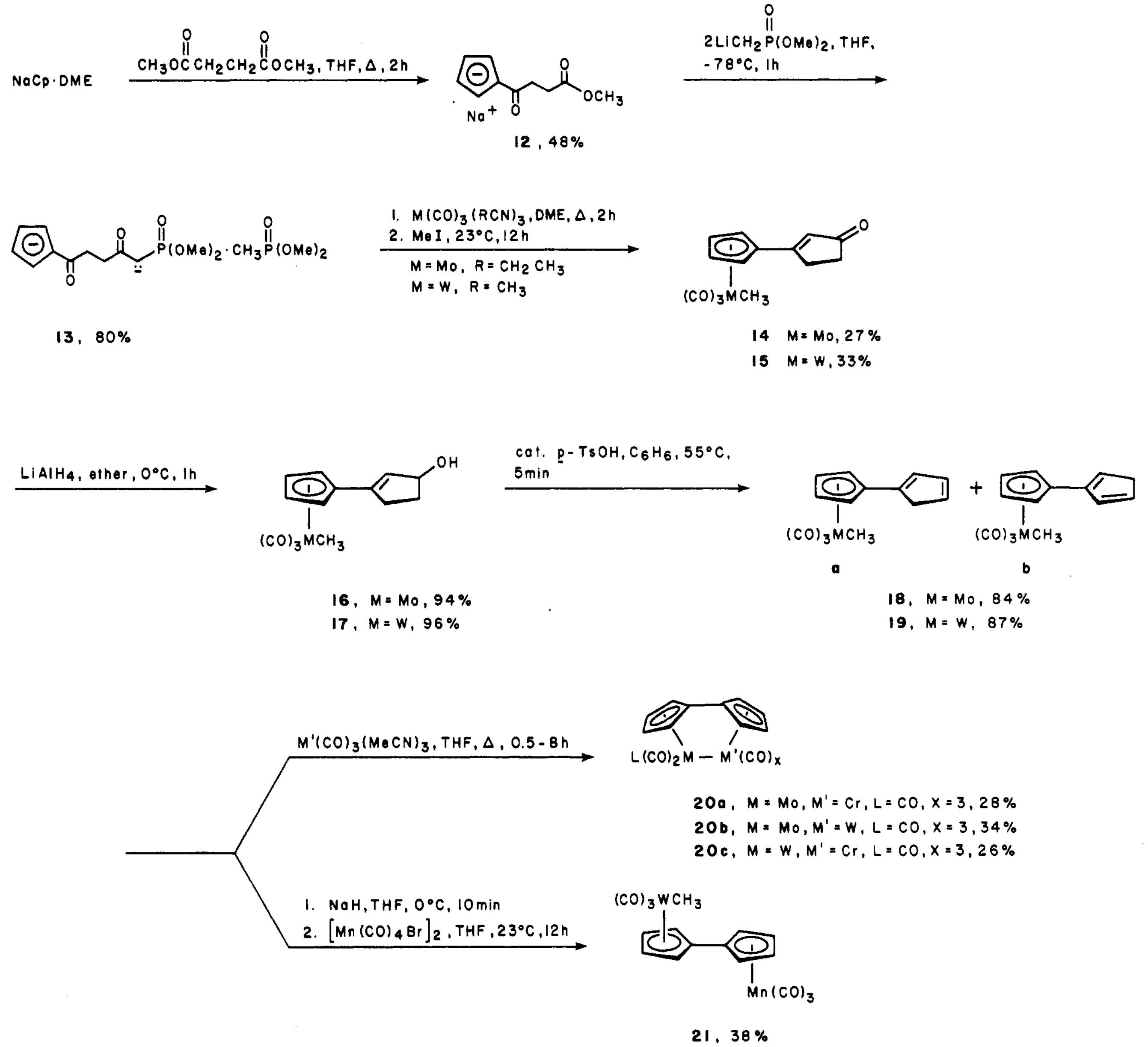
Scheme III



mmol in 10 mL of THF) yielded a solution of 13.[6b] Addition of hexane caused 13 to precipitate. Exposure of $M(CO)_3(RCN)_3$ to a 0.1 M solution of 13 followed by methylation permitted cyclization to occur, producing 14 and 15, which were reduced by $LiAlH_4$[6c] to 16 and 17. Treatment of a 0.05 M solution of 16 and 17 with 0.1 equiv of *p*-toluenesulfonic acid for short periods of time gave good yields of 18 and 19.[6d] When a 0.02 M solution of 18 was treated with a slight excess of $W(CO)_3(MeCN)_3$ for 1 h at 23 °C, a new compound formed. The ^1H NMR spectrum (THF-d_8) of this intermediate displayed a peak at δ −7.0, consistent with the presence of $(\eta^5{:}\eta^5\text{-}C_{10}H_8)[Mo(CO)_3Me][W(CO)_3H]$. When this solution was heated (66 °C, 0.5 h), the metal–metal bonded **20b** was formed, along with acetaldehyde.[6e]

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(2) (a) Drage, J. S.; Vollhardt, K. P. C. *Organometallics* **1986**, *5*, 280. (b) Vollhardt, K. P. C.; Weidman, T. W. *Ibid.* **1984**, *3*, 82.

(3) Tilset, M.; Vollhardt, K. P. C. *Organometallics* **1985**, *4*, 2230.

(4) Boese, R.; Tolman, W. B.; Vollhardt, K. P. C. *Organometallics* **1986**, *5*, 582.

(5) All new compounds gave satisfactory spectral and/or elemental analysis. These data are listed in the supplementary material.

(6) (a) Macomber, D. W.; Hart, W. P.; Rausch, M. D. *Adv. Organomet. Chem.* **1982**, *21*, 1. (b) Clark, R. D.; Kozar, L. G.; Heathcock, C. H. *Synth. Commun.* **1975**, *5*, 1. (c) Brown, H. C.; Hess, H. M. *J. Org. Chem.* **1969**, *34*, 2206. (d) Halterman, R. L.; Vollhardt, K. P. C. *Tetrahedron Lett.*, **1986**, *27*, 1461. (3) Jones, J. D.; Huggins, J. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 4415.

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Further manipulation of the resulting compounds gave rise to additional derivatives. For example, complexes **3** and **4** were converted to **20d**[3] (M = M′ = Mo, L = PMe_3, x = 3, 74% from **1**) and **20e** (M = Mo, M′ = Cr, L = PMe_3, x = 3, 57% from **1**), via reduction (Na/Hg, THF, 23 °C, 1 h), protonation (CF_3COOH, 0 °C, 5 min), and irradiation (300 nm, THF, 3–5 h), as described for **3** previously.[3] In the presence of $Ru_3(CO)_{12}$ (DME, Δ, 4 H), **1** furnished the known cluster $Ru_3(CO)_9[P(CH_3)_3]_3$,[7] as well as the two Ru–Mo bonded systems **20f**[2b] (M = Mo, M′ = Ru, L = CO, x = 2) and **20g** (M = Mo, M′ = Ru, L = PMe_3, x = 2) in approximately 1:1 ratio (70%, overall yield). Similarly, treatment of **1** with $Fe_2(CO)_9$ (THF, 23 °C, 1 h, then Δ, 12 h) led to the analogous mixed-metal complexes **20h** (M = Mo, M′ = Fe, L = CO, x = 2, 8%) and **20i** (M = Mo, M′ = Fe, L = PMe_3, x = 2, 29%). Alternatively, **20i** could be prepared by reduction of **1** with loss of one phosphine group, to the corresponding dianion **22** (Na/Hg, THF, 23 °C, 2 h, 100%), and subsequent treatment with $Fe(CO)_4Br_2$ (THF, −78 °C, 5 min, 29%).

The ready availability of most of these structures opens up a variety of synthetic and mechanistic avenues to the exploration of heterobimetallic reactivity in strongly bound metal–ligand systems.

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Supplementary Material Available: Melting point, analytical, and spectral data on 25 new compounds (7 pages). Ordering information is given on any current masthead page.

Book Reviews

Gmelin Handbook of Inorganic Chemistry. 8th Edition. Organocopper Compounds. Part 1. J. Faust, J. Füssel, and H. Somer, volume authors. J. Füssel, volume chief editor. Gmelin Institut für Anorganische Chemie der Max-Planck-Gesellschaft zur Förderung der Wissenschaften and Springer Verlag, Berlin. 1985. x + 470 pages. DM 1725

Part 2 of the organocopper volumes has already been published and has been reviewed in *Organometallics* (**1985**, *4*, 958). Part 1 deals with mononuclear organocopper species, more specifically with compounds with substituents bonded via one carbon atom. The authors are at a disadvantage in the subject they treat. Very few organocopper compounds have been isolated as pure materials. Even when this is possible, their investigation is not easy. For instance, pure CH_3Cu is prone to detonation when dry; C_6H_5Cu is associated to the point of insolubility in all solvents with which it does not react. Various other arylcopper compounds are more amenable to study. These have been found to be oligomeric, $(ArCu)_n$ (n = 4, 5, 8), and thus are classified as polynuclear species and, for this reason, are not treated in this volume. All other RCu species about which no definite structural information exists are included in the present volume, even if their properties strongly suggest that they too are oligomeric or polymeric. This quite naturally leads to some confusion.

Included in this volume also are the lithium and magnesium cuprates (273 pages worth!) and finally, complexes of RCu with copper, silver, gold, zinc, and tin compounds, with other metal compounds and ammonium salts, with boron compounds, with 1,4-dioxane; with dialkyl sulfides, with nitrogen donor compounds, and with phosphorus donor compounds (isolated compounds and reaction mixtures). And, in conclusion, there is a short section on products of ylides of phosphorus and sulfur with Cu(I) halides.

For those organocopper compounds which were isolated, all that is known about them is provided, but in the cases of the lithium and magnesium cuprates (presented as RCu·LiX and RCu·MgXY, respectively) and some of the $RCu{\cdot}PR'_3$, $RCu{\cdot}P(OR')_3$, and $RCu{\cdot}SR'_2$ species, it was merely a matter of mixing the reactants to make the organocopper reagent solution and then adding the desired electrophile. Such "reaction mixture" chemistry is brought in extensive tables (therefore the 273 pages on cuprates) which are organized, for each type of reagent (RCu·LiX, RCu·LiCN, RCu·LiOR′, RCu·LiSR′, etc.) according to the reaction it is used in: thermolysis, reaction with oxygen; reaction with I_2; reactions with inorganic compounds; reactions with organometallic compounds; addition reactions to unsaturated organic compounds (by far the biggest sections in view of the major application of cuprates in 1,4 addition to α,β-unsaturated systems); substitution reactions with organic electrophiles; cleavage of epoxides and azo compounds. Most of this information (table headings: electrophile, RCu, LiY, product) will be of interest and use to the organic chemist since useful applications of cuprates outside of organic synthesis are almost nonexistent. As in the case of Part 2, there is some question in your reviewer's mind if it is really useful and necessary to have all this information on the utilization in organic synthesis of reagents defined only in terms of reactant stoichiometry in a handbook of inorganic chemistry. There may be one benefit from doing so: perhaps some more physically and structurally oriented organometallic chemist will, on seeing all these wonderful brews in the various tables, be inspired to do some meaningful investigation of the constitution and solution and solid-state structures of such cuprate reagents. A beginning has been made with the structural characterization of $[Li(12\text{-crown-}4)_2][CuR_2]$ (R = CH_3, C_6H_5) and $(Li(12\text{-crown-}4)_2)[BrCuCH(SiMe_3)_2]{\cdot}C_6H_5CH_3$ by Power and his co-workers in a study so recent (*J. Am. Chem. Soc.* **1985**, *107*, 4337) that it is not included in the present volume (which has a literature cutoff date of December 31, 1983).

Neither the present volume nor Part 2 has an index. At least another volume covering polynuclear organocopper compounds and containing the index for all organocopper volumes may be expected.

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