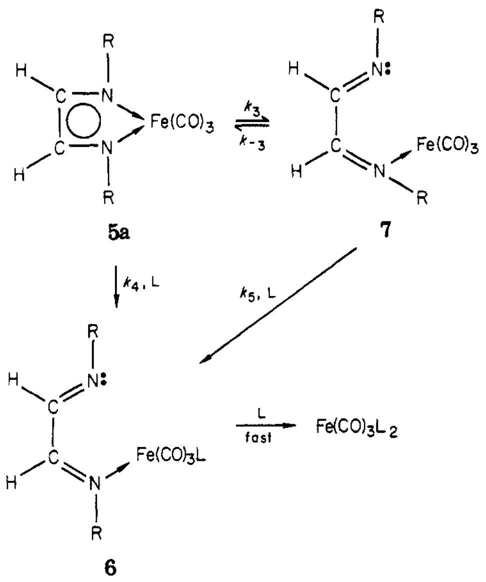
*Organometallics* **1982**, *1*, 1037–1040

Scheme II



unsaturated intermediate **7**, which rapidly adds L to yield **6**. Alternatively, direct nucleophilic attack on **5a** would lead to a pseudooctahedral transition state which is sterically crowded because of the bulky *tert*-butyl substituents. Dissociation of one end of the DAB ligand would reduce the steric strain and produce **6**. This intermediate can then react with another molecule of L, following dissociative loss of the monodentate DAB ligand, to give the observed product. With the assumption that the steady-state approximation holds for **7** and that $k_5[\mathrm{L}] \gg k_{-3}$, then $k_{\mathrm{obsd}}$ conforms to eq 9.

$$k_{\mathrm{obsd}} = k_3 + k_4[\mathrm{L}] \qquad (9)$$

Note (Table III) that the ligand-dependent term dominates only in the case of the small, strongly basic PMe$_3$ nucleophile. The dissociative pathway prevails for larger (P($n$-Bu)$_3$) or less basic (P(OMe)$_3$) ligands. Partial dissociation and subsequent loss of the DAB ligand seems to be a result of the steric bulk of the *tert*-butyl group. It is reasonable that a transition state of increased coordination should be susceptible to steric effects. Recall that the photochemical preparation of the monosubstituted *tert*-butyl derivatives **5b** and **5c** avoids the six-coordinate transition state.

These studies show that both steric and electronic factors may influence the thermal substitution chemistry of coordinately saturated Fe(CO)$_3$(DAB) complexes. Nucleophilic substitution occurs by an associative mechanism for this 18-electron system which may delocalize electron density onto the DAB ligand.[18] Consequently the rate of substitution increases with the ability of the metallacycle moiety to accept electron density. With bulky substituents in the 1,4 positions of the DAB ligand, steric interactions dominate and lead to DAB loss rather than CO substitution.

**Acknowledgment.** This work was supported in part by the National Science Foundation and by the Petroleum Research Fund, administered by the American Chemical Society. We thank Lanzhou University for a leave of absence given Q.-Z.S. and the Ministry of Education of the People's Republic of China for his support. We also thank the National Science Foundation for a Graduate Fellowship awarded to T.G.R.

**Registry No.** **1a**, 81847-60-1; **1b**, 81847-61-2; **1c**, 81847-62-3; **1d**, 81847-63-4; **1e**, 81847-64-5; **2a**, 15651-58-8; **2b**, 81847-65-6; **3a**, 65016-01-5; **3b**, 81847-66-7; **4a**, 54446-63-8; **4b**, 81856-96-4; **4c**, 81875-57-2; **5a**, 65036-35-3; **5b**, 81847-67-8; **5c**, 81847-68-9; PMe$_3$, 594-09-2; P(OMe)$_3$, 121-45-9; P($n$-Bu)$_3$, 998-40-3; iron tricarbonyl benzylideneacetone, 53861-80-6.

**Supplementary Material Available:** Tables of observed rate constants for CO substitution according to eq 1 and for DAB replacement in the *tert*-butyl complex **5a** (2 pages). Ordering information is given on any current masthead page.

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# Synthesis of β-Keto Sulfides and Thioesters from the Reaction of α-Thiocarbanions with Iron Pentacarbonyl

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*Received February 16, 1982*

α-Thiocarbanions, generated from the reaction of sulfides with organolithium reagents or lithium diisopropylamide, react with iron pentacarbonyl and then with methyl iodide, to give β-keto sulfides. Disulfides were obtained as byproducts of these reactions and as the only product when iodine was used as the electrophile. The utilization of acid halides as the electrophilic reagent afforded thioesters in fine yields.

There have been extensive investigations of the reactions of organolithium compounds[2] and Grignard reagents[2-4] with iron pentacarbonyl. The products of these reactions are acyltetracarbonylferrates (1) which are useful reagents in their own right being able, for example, to convert halides to ketones (2),[2,3] imidoyl chlorides to mesoionic 1,3-oxazol-5-ones (3),[5] and epoxides to α,β-unsaturated ketones (4).[6]

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[1] E. W. R. Steacie Fellow, 1980–1982.

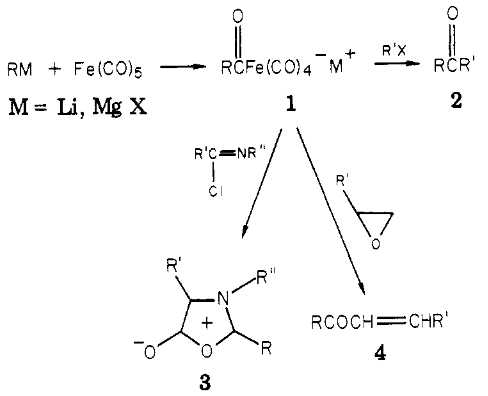
[2] Alper, H. In "Organic Syntheses via Metal Carbonyls"; Wender, I., Pino, P., Eds.; Wiley: New York, 1977; Vol. II, pp 545–593, and references cited therein.

[3] Yamashita, M.; Suemitsu, T. *Tetrahedron Lett.* **1978**, 761.

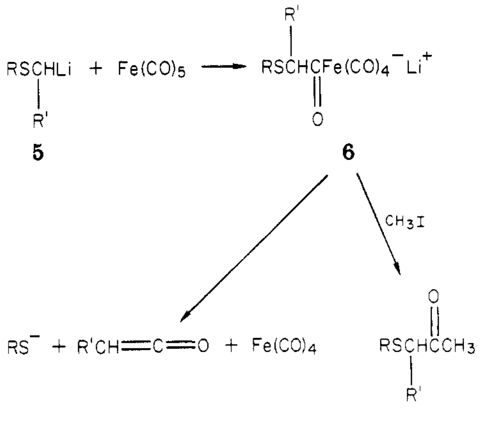
[4] Yamashita, M.; Suemitsu, T. *Tetrahedron Lett.* **1978**, 1477.

[5] Alper, H.; Tanaka, M. *J. Am. Chem. Soc.* **1979**, *101*, 4245.

[6] Yamashita, M.; Yamamura, S.; Kurimoto, M.; Suemitsu, R. *Chem. Lett.* **1979**, 1067.

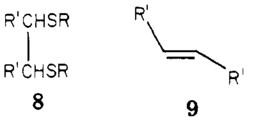


It seemed of interest to apply the above process to $\alpha$-thiocarbanions (**5**).[7] It was anticipated that reaction of **5** with iron pentacarbonyl would give the acyltetracarbonylferrate anion **6** which upon treatment with a halide (e.g., methyl iodide) would form the $\beta$-keto sulfide **7**, an important class of organic compounds.[7] Alternatively, complex **6** may experience decomplexation and elimination of $RS^-$, a reasonably good leaving group, the byproducts being ketenes and iron tetracarbonyl.



## Results and Discussion

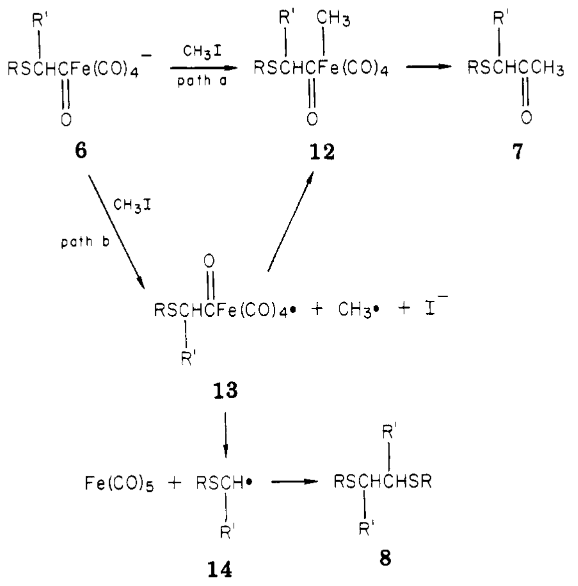
Treatment of benzyl phenyl sulfide with *n*-butyllithium in anhydrous tetrahydrofuran at −78 °C gave **5**, R = R′ = Ph. When the latter was reacted with an equivalent amount of iron pentacarbonyl at −78 °C and the solution warmed to room temperature (2 h) and then treated with methyl iodide, the $\beta$-keto sulfide **7**, R = R′ = Ph, was formed in 25% yield together with the coupled disulfide **8**, R = R′ = Ph (15%), and stilbene (**9**, R = R′ = Ph; 10% yield). A shorter reaction time for **5**, R = R′ = Ph, with $Fe(CO)_5$ resulted in lower product yields. The presence of 0.1 equiv of diisopropylamine in these reactions had small effects on the product distribution. However, if the amount of diisopropylamine is increased to 2 equiv and the complete reaction sequence is carried out at −78 °C, the $\beta$-keto sulfides (**7**) were obtained in good yields [44–60% (Table I)].



**8** **9**

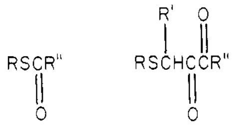
The use of *tert*-butyllithium instead of the *n*-butyl isomer in the reaction sequence resulted in minor changes in the proportions of **7** and **8** but not **9** (R = R′ = Ph). It is of interest to note that the disulfide (**8**) was obtained in good yield when iodine (in diisopropylamine) functioned as the electrophile. However, neither the $\beta$-keto sulfide (**7**) or olefin (**9**) was detected in this reaction.

### Scheme I



Acceptable yields of $\beta$-keto sulfides (**7**) were realized by the use of lithium diisopropylamide (LDA), rather than *n*- or *tert*-butyllithium, to generate the carbanion **5**. It is also worth noting that reactant sulfide was recovered when **5**, R = R′ = Ph (generated by using LDA), was treated with $Fe(CO)_5$ (first at −78 °C and then either at room temperature or in refluxing THF) and then with acid.

The use of an acid chloride [R″COCl] as the electrophile in these reactions resulted in the formation of thioesters (**10**) in 50–78% yields. In this reaction, the acid chloride was added at room temperature. The yields become almost quantitative when the electrophile is added at −78 °C, indicating that some decomposition of the intermediate, or alternate reaction, occurs on warming the solution to room temperature. In addition, the reaction is exceedingly facile at −78 °C, suggestive of the presence of a good leaving group. Thioesters were formed by using aliphatic, aromatic, heterocyclic, and $\alpha,\beta$-unsaturated acid chlorides or benzoic anhydride. In no case was the $\alpha$-diketone (**11**) detected in these reactions.



**10** **11**

The above results can be rationalized on the basis of the pathways outlined in Schemes I and II. The $\beta$-keto sulfide (**7**) probably arises from reaction of the anion **6** with methyl iodide to give **12**, followed by reductive elimination (path a Scheme I). The formation of significant amounts of disulfide **8** is indicative of the simultaneous occurrence of an electron-transfer pathway in the reaction of **6** with methyl iodide. The iron carbonyl radical **13** so formed may collapse to **14**, regenerating iron pentacarbonyl. Dimerization of **14** would then afford **8**. It is also conceivable that **13** can couple with the formed methyl radical to give **12** (and then **7**).

As previously noted, the best yields of **7** were achieved when the reaction (sulfide, $n$-$C_4H_9Li$, $Fe(CO)_5$, $CH_3I$) was carried out in the presence of 2 equiv of diisopropylamine.

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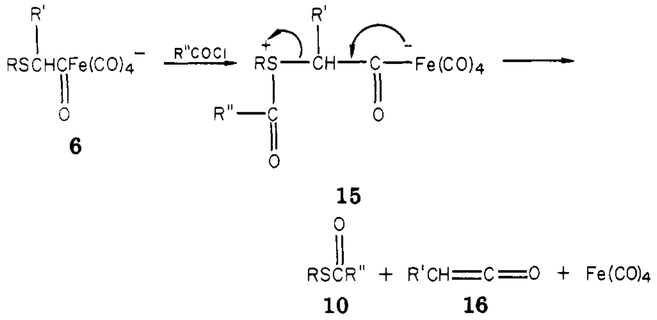
[7] Stowell, J. C. "Carbanions in Organic Synthesis"; Wiley: New York, 1979.

**Table I. Products Obtained from the Reaction of 5 with $Fe(CO)_5$**

| reactant | base[a] | electrophile | products | yield,[b] % |
|---|---|---|---|---|
| $PhSCH_2Ph$ | A | $CH_3I$ | 7, R = R′ = Ph | 25 |
| | | | 8, R = R′ = Ph | 15 |
| | | | 9, R′ = Ph | 10 |
| | A[c] | $CH_3I$ | 7, R = R′ = Ph | 10 |
| | | | 8, R = R′ = Ph | 15 |
| | | | 9, R′ = Ph | 5 |
| | B | $CH_3I$ | 7, R = R′ = Ph | 26 |
| | | | 8, R = R′ = Ph | 16 |
| | C | $CH_3I$ | 7, R = R′ = Ph | 44 |
| | | | 8, R = R′ = Ph | 21 |
| | D | $CH_3I$ | 7, R = R′ = Ph | 20 |
| | | | 8, R = R′ = Ph | 26 |
| | | | 9, R′ = Ph | 10 |
| | E | $CH_3I$ | 7, R = R′ = Ph | 45 |
| | | | 8, R = R′ = Ph | 10 |
| | A[d] | $I_2$/*i*-$Pr_2NH$ | 8, R = R′ = Ph | 55 |
| | E | $CH_3COCl$ | 10, R = Ph, R″ = $CH_3$ | 74 |
| | E | PhCOCl | 10, R = R″ = Ph | 69 |
| | E | PhCOCl | 10, R = R″ = Ph | 100[e] |
| | E | $(CH_3)_2CHCOCl$ | 10, R = Ph, R″ = $CH(CH_3)_2$ | 50 |
| | E | $CH_3CH{=}CHCOCl$ | 10, R = Ph, R″ = $CH_3CH{=}CH$ | 75 |
| | E | $CH_3CH{=}CHCOCl$ | 10, R = Ph, R″ = $CH_3CH{=}CH$ | 97[e] |
| | E | 2-furoyl chloride | 10, R = Ph, R″ = $C_4H_3O$ | 72 |
| | E | $(PhCO)_2O$ | 10, R = R″ = Ph | 52 |
| *p*-$CH_3C_6H_4SCH_2Ph$ | C | $CH_3I$ | 7, R = *p*-$CH_3C_6H_4$, R′ = Ph | 56 |
| | | | 8, R = *p*-$CH_3C_6H_4$, R′ = Ph | 22 |
| | E | $CH_3I$ | 7, R = *p*-$CH_3C_6H_4$, R′ = Ph | 29 |
| $PhSCH_2CH{=}CH_2$ | E | $CH_3I$ | 7, R = Ph, R′ = $C_2H_3$ | 18 |
| *p*-$CH_3OC_6H_4SCH_2Ph$ | C | $CH_3I$ | 7, R = *p*-$CH_3OC_6H_4$, R′ = Ph | 60 |
| | | | 8, R = *p*-$CH_3OC_6H_4$, R′ = Ph | 25 |
| | E | PhCOCl | 10, R = *p*-$CH_3OC_6H_4$, R′ = Ph | 78 |

[a] A = *n*-$C_4H_9Li$; B = *n*-$C_4H_9Li$ + 0.1 *i*-$Pr_2NH$; C = *n*-$C_4H_9Li$ + 2 *i*-$Pr_2NH$ (at −78 °C); D = *t*-$C_4H_9Li$; E = LDA. [b] Yields are of pure materials. Crude yields were much higher. [c] Reaction time for 5 and $Fe(CO)_5$ was 5 min instead of the usual 2 h. [d] 10% starting material was recovered. [e] Acid chloride was added at −78 °C.

Scheme II



One equivalent is required to generate LDA, and the second equivalent may participate in ligand substitution of iron pentacarbonyl, giving $Fe(CO)_4$(*i*-$Pr_2NH$). Ligand substitution of this type has been observed in the case of tertiary,[8] and secondary acyclic,[9] amines. The amine-substituted iron carbonyl may be more susceptible to attack by the α-thiocarbanion than iron pentacarbonyl itself. In olefin isomerization, an admittedly different reaction process, $Fe(CO)_4(R_3N)$ is a more active catalyst than $Fe(CO)_5$.[8]

The electrophilic acid chlorides, instead of effecting acylation of **6** at iron, may react at sulfur to give **15** (Scheme II). The latter dipolar species contains the thioester, an excellent leaving group, and thus collapse of **15** would generate **10**. The ketene (**16**) was not detected in any of these reactions, but that may be due to a possible subsequent reaction of **16** with the reactive species $Fe(CO)_4$. Ketenes apparently do not react thermally with $Fe(CO)_5$.[10]

Finally, it is not clear how alkenes (**9**) are produced as byproducts in several of the reactions.

In conclusion, β-keto sulfides are formed in moderate yields, and under very mild conditions, by treatment of α-thiocarbanions with $Fe(CO)_5$ and then methyl iodide. Thioesters were formed in good yields by using acid halides as electrophiles. The latter reaction is of less synthetic utility than the β-keto sulfide synthesis, since thioesters can be prepared from thiols and acid chlorides.[11] However, it is an intriguing carbon–sulfur bond cleavage process.

## Experimental Section

**General Data.** Infrared spectral determinations were made by using a Unicam SP-1100 spectrometer, equipped with a calibration standard. Mass spectra were recorded on a Varian MS902 spectrometer. Proton magnetic resonance spectral determinations were made by using a Varian T-60 or HA-100 spectrometer. Elemental analyses were carried out by Canadian Microanalytical Service, Vancouver, Canada. A Fisher-Johns apparatus was used for melting point determinations. Solvents were purified and dried by standard methods. All reactions were run under a dry nitrogen atmosphere.

The required sulfides were prepared by the phase-transfer-catalyzed reaction of thiophenols with halides.[12] Lithium diisopropylamide was prepared by adding, at below 0 °C, a stoichiometric amount of *n*-$C_4H_9Li$ (2.4 M in hexane) to a THF solution of diisopropylamine. Iron pentacarbonyl and *n*-butyl- or *tert*-butyllithium were commercial products and were used as received.

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[8] Birencwaig, F.; Shamai, H.; Shvo, Y. *Tetrahedron Lett.* **1979**, 2947.

[9] Miller, J. R.; Podd, B. D.; Sanchez, M. O. *J. Chem. Soc., Dalton Trans.* **1980**, 1461.

[10] Hong, P.; Sonogashira, K.; Hagihara, N. *Nippon Kagaku Zasshi* **1968**, *89*, 74.

[11] Satchell, P. *Q. Rev., Chem. Soc.* **1963**, *17*, 160.

[12] Herriott, A. W.; Picker, D. *Synthesis* **1975**, 447.

**General Procedure for the Reaction of $\alpha$-Thiocarbanions with Iron Pentacarbonyl.** To the sulfide (4.0 mmol) in anhydrous THF (30 mL) at −78 °C was added, drop-by-drop, 1 equiv of RLi or LDA. After the solution was stirred for 1 h (solution became yellow), iron pentacarbonyl (4.0 mmol) was added and the reaction mixture was stirred for 2 h either at −78 °C or while being warmed up to room temperature (see Table I). Then the electrophile (4.0 mmol in the case of RLi; 8.0 mmol for LDA) was added, and stirring was continued overnight. The reaction mixture was then concentrated by flash evaporation, and the resulting crude products were separated by first filtering through a short column of silica gel ($CH_2Cl_2$–ethyl acetate) and then by silica gel thin-layer chromatography (hexane–ethyl acetate).

**Products.** 7, R = R′ = Ph: IR $\nu$(CO) 1685 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 2.18 (s, 3 H, $CH_3$), 4.97 (s, 1 H, CH), 7.40 (s (br), 10 H, Ph); MS *m/e* 242 $[M]^+$, 199 ($[M - COCH_3]^+$; mp 64–65 °C (lit.[13] mp 64–66 °C). Anal. Calcd for $C_{15}H_{14}OS$: C, 74.36; H, 5.83; S, 13.20. Found: C, 74.18; H, 5.85; S, 12.81.

7, R = *p*-$CH_3C_6H_4$, R′ = Ph: IR $\nu$(CO) 1690 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 2.11, 2.25 (s each, 6 H, two methyl groups), 4.91 (s, 1 H, CH), 6.97 (d, 2 H, $J$ = 8 Hz, protons on carbon ortho to sulfur bearing carbon), 7.22 (d, 2 H, $J$ = 8 Hz, protons on carbon meta to sulfur bearing carbon), 7.27 (s, 5 H, Ph); MS *m/e* 256 $[M]^+$, 213 $[M - COCH_3]^+$; mp 71–73 °C. Anal. Calcd for $C_{16}H_{16}OS$: C, 74.96; H, 6.29; S, 12.51. Found: C, 74.60; H, 6.57; S, 12.93.

7, R = *p*-$CH_3OC_6H_4$, R′ = Ph: IR $\nu$(CO) 1685 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 2.16 (s, 3 H, $CH_3$), 3.72 (s, 3 H, $OCH_3$), 4.87 (s, 1 H, CH), 6.70–7.40 (m, 9 H, aromatic protons); MS *m/e* 270 $[M]^+$, 239 $[M - OCH_3]^+$, 227 $[M - COCH_3]^+$. Anal. Calcd for $C_{16}H_{16}O_2S$: C, 70.63; H, 5.92; S, 11.77. Found: C, 70.81; H, 6.11; S, 11.43.

Products 8–10 were identified by comparison of spectral data with those described in the literature and, in some cases, by comparison with authentic materials.

**Acknowledgment.** We are grateful to the Natural Sciences and Engineering Research Council for support of this research.

**Registry No.** 7 (R = R′ = Ph), 10371-49-0; 7 (R = *p*-$CH_3C_6H_4$, R′ = Ph), 81602-64-4; 7 (R = Ph, R′ = $C_2H_3$), 77119-58-5; 7 (R = *p*-$CH_3OC_6H_4$, R′ = Ph), 81602-65-5; 8 (R = R′ = Ph), 53104-99-7; 8 (R = *p*-$CH_3C_6H_4$, R′ = Ph), 76160-89-9; 8 (R = *p*-$CH_3OC_6H_4$, R′ = Ph), 81602-66-6; 9 (R′ = Ph), 588-59-0; 10 (R = Ph, R″ = $CH_3$), 934-87-2; 10 (R = R″ = Ph), 884-09-3; 10 (R = Ph, R″ = $CH(CH_3)_2$), 58443-71-3; 10 (R = Ph, R″ = $CH_3CH{=}CH$), 25542-72-7; 10 (R = Ph, R″ = $C_4H_3O$), 17357-38-9; 10 (R = *p*-$CH_3OC_6H_4$, R″ = Ph), 24197-73-7; $Fe(CO)_5$, 13463-40-6; $PhSCH_2Ph$, 831-91-4; *p*-$CH_3C_6H_4SCH_2Ph$, 5023-60-9; $PhSCH_2CH{=}CH_2$, 5296-64-0; *p*-$CH_3OC_6H_4SCH_2Ph$, 26905-24-8.

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[13] Newman, H.; Angier, R. B. *Tetrahedron* **1970**, *26*, 825.

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# Aspects of the Chemistry of Substituted Ruthenium Clusters Involving Bis(diphenylphosphino)- or Bis(diphenylarsino)methane as Bridging Ligands. Reactivity toward Hydrogen and Potential Applications in Catalysis. Crystal and Molecular Structure of $(\mu\text{-}H)_2Ru_3(CO)_6(\mu\text{-}P(C_6H_5)CH_2P(C_6H_5)_2)_2$ and $(\mu\text{-}H)_2Ru_3(CO)_6(\mu\text{-}As(C_6H_5)CH_2As(C_6H_5)_2)_2$

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*Received February 25, 1982*

Reaction of $Ru_3(CO)_8(dppm)_2$ (**1a**) (dppm = bis(diphenylphosphino)methane) with molecular hydrogen at 85 °C gives the trinuclear dihydrido cluster complex $(\mu\text{-}H)_2Ru_3(CO)_6(\mu\text{-}P(C_6H_5)CH_2P(C_6H_5)_2)_2$ (**3a**) in high yield and purity. Under the same experimental conditions, $Ru_3(CO)_8(dpam)_2$ (**1b**) (dpam = bis(diphenylarsino)methane) provides the intermediate monohydrido species $(\mu\text{-}H)Ru_3(CO)_7(\mu\text{-}As(C_6H_5)CH_2As(C_6H_5)_2)(dpam)$ (**2b**) which further reacts with $H_2$ at 120 °C, yielding the dihydrido cluster complex $(\mu\text{-}H)_2Ru_3(CO)_6(\mu\text{-}As(C_6H_5)CH_2As(C_6H_5)_2)_2$ (**3b**). The crystal and molecular structures of **3a** and **3b** are reported. Crystal data for **3a**: monoclinic, space group $C_2/c$; $a$ = 14.510 (2) Å, $b$ = 16.533 (1) Å, $c$ = 18.198 (2) Å, $\beta$ = 90.80 (1)°; current $R$ = 0.026, $R_w$ = 0.028 from 5151 reflections with $F_o > 3\sigma(F_o)$. Crystal data for **3b**: monoclinic, space group $P2_1/c$; $a$ = 14.726 (5) Å, $b$ = 16.931 (7) Å, $c$ = 18.097 (4) Å, $\beta$ = 92.40 (2)°; current $R$ = 0.041, $R_w$ = 0.039 from 3565 reflections. Both structures consist of a triangular array of Ru atoms (isosceles in **3a**) involving two equatorial CO ligands per metal atom; both cluster faces are capped in a similar way by identical ligand units $\mu\text{-}X(C_6H_5)CH_2X(C_6H_5)_2$ (X = P or As). In a typical ligand unit, the first P (or As) atom bridges a metal–metal edge, while the second one is coordinated to the third metal atom. The two hydrido ligands are found to bridge inequivalent metal–metal bonds. This feature is confirmed by $^1H$ NMR data, including variable-temperature experiments. Acidification of the reported complexes gives new cationic trihydrido cluster complexes which are characterized by $^1H$ NMR. Catalytic tests show that complex **3a** catalyzes the hydrogenation of cyclohexane to cyclohexanol (86% conversion after 18 h, using a 1/1000 catalyst/substrate ratio; $t$ = 90 °C; $P(H_2)$ = 100 bar).

## Introduction

Earlier work in this laboratory has led to the isolation of the new cluster complexes $Ru_3(CO)_8L_2$ (**1**) stabilized by bridging bis(diphenylphosphino)methane[1] or bis(diphenylarsino)methane ligands (**1a**, L = dppm, **1b**, L = dpam). In attempts to determine whether or not such species could be efficient catalyst precursors, we were prompted to investigate the nature of the complexes which could be generated under the conditions of a typical hydrogenation reaction. We were led to these studies through previous reports[2-11] dealing with some versatile effects of

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[1] Lavigne, G.; Bonnet, J.-J. *Inorg. Chem.* **1981**, *20*, 2713.

0276-7333/82/2301-1040$01.25/0