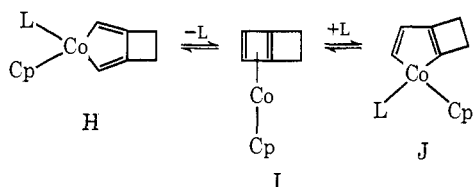
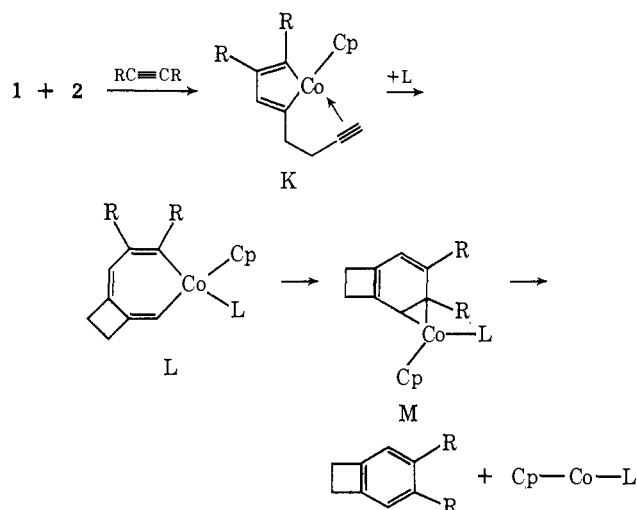


ing these reactions, some comment on other possible routes is warranted. We believe that the absence of 2,3-disubstituted benzocyclobutenes in the cooligomerizations reported here makes it unnecessary to invoke metalocycle rearrangement *via* a complexed cyclobutadiene intermediate<sup>4h</sup> (*i.e.*,  $H \rightleftharpoons I \rightleftharpoons J$ ).



However, it is conceivable that the first metalocycle formed in the cooligomerization is K, which arises



from interaction of two different acetylene molecules. Formation of product would then require direct insertion of the third acetylene group into the Co—C bond, leading to L, which could extrude the metal *via* "metalloncaradiene" M (insertion into the Co—C bond is, of course, also a possibility in E). Finally, it is quite possible that cluster complexes such as those formed<sup>8</sup> during the photochemistry of 1 are also produced thermally, and that these are involved in the acetylene dimerizations. Experiments are now under way aimed at distinguishing these alternatives.

**Acknowledgments.** We are grateful to Professors John E. Bercaw and Robert H. Grubbs for helpful discussions and to the National Science Foundation, the National Institutes of Health, and the Chevron Research Corporation for financial support.

(8) K. Peter C. Vollhardt, John E. Bercaw, and Robert G. Bergman, *J. Amer. Chem. Soc.*, **96**, 4998 (1974).

(9) Camille and Henry Dreyfus Teacher-Scholar, 1970-1975.

K. Peter C. Vollhardt, Robert G. Bergman\*<sup>9</sup>

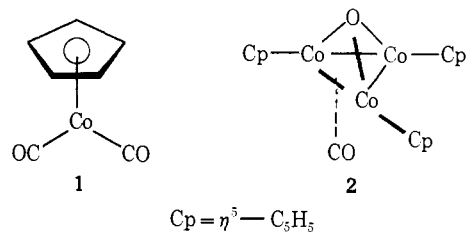
Contribution No. 4810, *Crellin Laboratory of Chemistry*  
California Institute of Technology  
Pasadena, California 91109

Received January 2, 1974

### Isolation of Unstable Bis( $\eta^5$ -cyclopentadienylcobalt) Tricarbonyl from the Irradiation of $\eta^5$ -Cyclopentadienylcobalt Dicarbonyl. Thermal Reactions of This Binuclear Complex Leading to Starting Material and Trinuclear and Tetranuclear Cobalt(I) Complexes

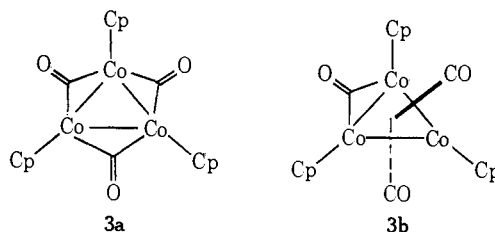
Sir:

Irradiation of  $\eta^5$ -cyclopentadienylcobalt dicarbonyl<sup>1</sup> ( $\eta^5$ - $C_5H_5Co(CO)_2$ ; 1) efficiently produces a new bi-



nuclear cobalt complex which reverts to starting material at room temperature in solution. Because (a) our observations significantly amplify earlier accounts<sup>2,3</sup> of the photochemistry of 1, (b) this reaction can be used as the starting point in the preparation of two additional polynuclear cobalt complexes, one of them a new compound, and (c) these substances are effective acetylene trimerization<sup>4</sup> catalysts,<sup>5</sup> we wish to report our preliminary results here.

Irradiation of 1 in *n*-hexane for long periods of time has been reported by King to yield black crystalline precipitates.<sup>2</sup> This material was separated<sup>2</sup> into two fractions, which were assumed to be two forms of a trinuclear complex possibly having structure 3a or 3b. Dahl isolated from a similar irradiation a small



amount of black crystals determined to have structure 2 by X-ray diffraction.<sup>3</sup>

We have studied the course of this irradiation more closely using nmr techniques. Under normal conditions extensive line-broadening occurs, rendering nmr observation difficult; this complication disappears, however, when oxygen and water are rigorously excluded and the irradiation is carried out in a sealed nmr tube. Employing this technique we find that 1-2 hr of irradiation of 1 in benzene-*d*<sub>6</sub>, cyclohexane, or

(1) (a) M. D. Rausch and R. A. Genetti, *J. Amer. Chem. Soc.*, **89**, 5502 (1967); (b) *J. Org. Chem.*, **35**, 3888 (1970); (c) Pressure Chemical Co., Pittsburgh, Pa.

(2) R. B. King, *Inorg. Chem.*, **5**, 2227 (1966).

(3) V. A. Uchtman and L. F. Dahl, *J. Amer. Chem. Soc.*, **91**, 3763 (1969).

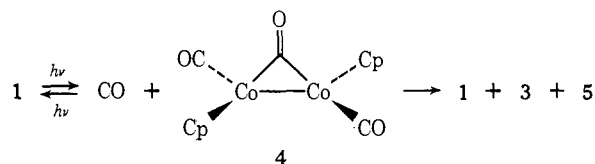
(4) For leading references, see (a) F. L. Bowden and A. B. P. Lever, *Organometal. Chem. Rev., Sect. A*, **3**, 227 (1968); (b) P. M. Maitlis, *Advan. Organometal. Chem.*, **4**, 95 (1966); (c) E. Ochiai, *Coord. Chem. Rev.*, **3**, 49 (1968); (d) G. Whitesides and W. J. Ehmann, *J. Amer. Chem. Soc.*, **91**, 3800 (1969); (e) J. Collman in "Transition Metal Chemistry," Vol. II, R. L. Carlin, Ed., Marcel Dekker, New York, N. Y., 1966, pp 89-100; (f) J. P. Collman, J. W. Kang, W. F. Little, and M. F. Sullivan, *Inorg. Chem.*, **7**, 1298 (1968).

(5) K. P. C. Vollhardt and R. G. Bergman, *J. Amer. Chem. Soc.*, **96**, 4996 (1974).

toluene- $d_6$  at  $5^\circ$  leads to a deep brown solution which contains an apparent photostationary mixture made up of *ca.* 50% **1** and 50% of a new substance (**4**). This new material shows a single resonance in the proton nmr at 4.82 ppm downfield from TMS (0.10 ppm upfield from that of **1**; *cf.* Figure 1) and is not the previously reported<sup>2</sup> trinuclear complex **3**. Upon standing at room temperature, **4** regenerates **1** (along with some **3** and a small amount of another unidentified compound) as is shown in Figure 1. On standing for longer periods of time, the peaks due to **3** and the unknown complex<sup>6</sup> also disappear with the formation of additional **1**.

When the irradiation is carried out on a preparative scale until about a 20% yield of CO is evolved (based on starting **1**), cooling the irradiated solution to  $-65^\circ$  yields violet crystals of **4**. After isolation these exhibit bands at 1965 and 1814  $\text{cm}^{-1}$  (Nujol mull) attributable to terminal and bridging carbonyl ligands, respectively.<sup>7</sup> This material also shows a parent peak in the mass spectrum at  $m/e$  332. On the basis of these data, elemental analysis, and the X-ray determined structure of an analogous rhodium compound,<sup>8</sup> we assign to **4** the dinuclear complex structure shown in Scheme I.<sup>9</sup>

Scheme I



The violet crystals of **4** are stable in the solid state but, surprisingly, still rapidly regenerate **1** when redissolved in *n*-octane or other solvents, even when no free carbon monoxide is present. However, under these conditions greater amounts of **3** are produced, and the solution begins to precipitate this material as dark green crystals. This complex can be obtained preparatively by alternately irradiating **1** on a vacuum line followed by stirring at room temperature with removal of CO.<sup>10</sup>

Compound **3** exhibits one resonance in the proton nmr (4.75 ppm downfield from TMS in cyclohexane). Its mass spectrum was previously reported<sup>2</sup> to exhibit a parent peak at  $m/e$  552; this was accounted for by postulating<sup>2</sup> the occurrence of a thermal reaction on the mass spectrometer inlet probe which led to an unknown tetranuclear complex having the composition  $(\text{C}_5\text{H}_5)_4\text{Co}_4(\text{CO})_2$ . This does in fact occur when the probe is heated; however, when the mass spectrum is run at  $75^\circ$ , a parent peak at  $m/e$  456 can be observed. Further-

(6) This material was not isolated; possibly its structure is that of coordinatively unsaturated  $[\text{CpCoCO}]_2$ .

(7) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 3rd ed, Interscience, New York, N. Y., 1972, Chapter 22.

(8) (a) O. S. Mills and J. P. Nice, *J. Organometal. Chem.* 10, 337 (1967); see also (b) O. S. Mills and E. F. Paulus, *Chem. Commun.*, 815 (1966); (c) *J. Organometal. Chem.*, 10, 331 (1967); (d) E. F. Paulus, E. O. Fischer, H. P. Fritz, and H. Schuster-Wolden, *ibid.*, 10, P3 (1967).

(9) Elemental analyses (including cobalt) consistent with the empirical formulas assigned have been obtained on complexes **3**, **4**, and **5**.

(10) A referee has requested brief details of this procedure. Compound **1** (3.6 g) in 30 ml degassed methylcyclohexane was irradiated in a closed system under vacuum at  $0^\circ$  for 2 hr. The CO evolved was pumped out and the dark brown mixture stirred at  $25^\circ$  for 12 hr. After repeating this cycle three times, CO evolution essentially ceased due to the formation of a light-absorbing polymer film on the surface of the flask. The solvent and remaining starting material were vacuum transferred out of the system (recovered **1**, 50%), and the residual green powder was recrystallized from toluene to give 0.51 g of analytically pure **3** (20% absolute yield, 40% based on recovered starting material).

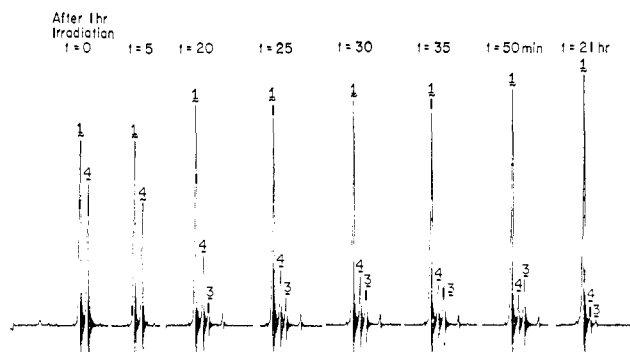
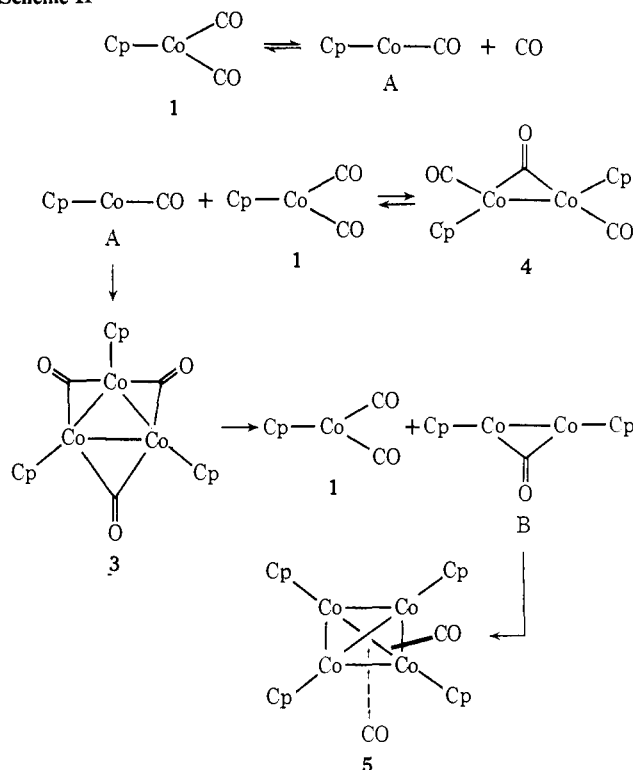


Figure 1. Changes in nmr spectrum observed at  $38^\circ$  following 1 hr of irradiation (sealed tube) of 0.5 M  $\eta^5$ -cyclopentadienylcobalt dicarbonyl (**1**) in cyclohexane.

more, we have found that the thermal reaction can be carried out on a preparative scale at  $130^\circ$  and low pressure; under these conditions **1** distills out leaving behind *black* crystals of tetranuclear complex **5**. This material shows a parent peak in the mass spectrum at  $m/e$  552, triply bridging carbonyl groups in the ir ( $\nu = 1665, 1680 \text{ cm}^{-1}$ ),<sup>11</sup> and two resonances (4.65 and 4.76 ppm downfield from TMS in toluene- $d_6$ ) in the proton nmr. On the basis of this data it is assigned the structure shown in Scheme II.

Scheme II



Our observations are well accounted for by the mechanism outlined in Scheme II. Irradiation of **1** causes photodissociation to  $\eta^5$ -cyclopentadienyl monocarbonyl (A), and this reacts with another molecule of **1** to give **4**. **4** is both thermally and photochemically unstable and can apparently redissociate to **1** and A. In the presence of CO, A returns mostly to **1**, but in the absence of CO it trimerizes<sup>12</sup> to **3**. At somewhat higher tem-

(11) This material does not seem to be identical with the compound obtained by King<sup>2</sup> in the pyrolysis of **3**, for which an ir band at  $1705 \text{ cm}^{-1}$  was reported.

(12) R. B. King, *Progr. Inorg. Chem.*, 15, 287 (1972).

peratures, **3** can also extrude **1**, leaving the coordinatively unsaturated dinuclear complex **B** which rapidly dimerizes to **5**. At no time do we observe any **2** in these reactions<sup>3</sup> and therefore suggest that it is formed by reaction of **1** or a derived photoproduct with trace amounts of atmospheric oxygen.

**Acknowledgments.** We are grateful to the National Science Foundation and the Chevron Research Corporation for partial support of this work.

(13) Camille and Henry Dreyfus Foundation Teacher-Scholar, 1970-1975.

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California Institute of Technology  
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Received January 2, 1974

### Convenient Synthesis of Silver Hyponitrite

Sir:

Silver hyponitrite is the starting material for the synthesis of alkyl hyponitrites, which are useful low-temperature sources of alkoxy radicals.<sup>1-5</sup> Numerous syntheses of sodium and silver hyponitrites have appeared in the literature.<sup>5-9</sup> Most are tedious, hazardous, poorly described, or require large quantities of mercury. In our hands, one procedure gave no product and the reaction mixture from another ignited during work-up.

The method described below is a modification of that of Weitz and Vollmer<sup>10</sup> which takes advantage of the known solubility of sodium in benzophenone solutions.<sup>11</sup> The yield is low (it might be improved by inverse addition), but the synthesis is shorter and more convenient than earlier procedures. The reaction of sodium in hexamethylphosphoramide<sup>12</sup> with nitric oxide proceeded exothermically, but the product was more difficult to isolate.

A 500-ml three-necked flask was equipped with a gas inlet, a magnetic stirrer, and an outlet connected to a bubbler. The inlet tube was connected by a T-joint so either N<sub>2</sub> or NO could be added. The flask was charged with 100 ml of 1,2-dimethoxyethane and 150 ml of toluene (each distilled from blue Na and benzophenone solutions). Benzophenone (26 g) was added and the solution was flushed with N<sub>2</sub>. Sodium (6.9 g) was then extruded as wire into the solution, and the flask was surrounded by an ice bath. After flushing with N<sub>2</sub>, stirring was begun, and nitric oxide was admitted at a rate such as to maintain a slight positive pressure. Shaking the flask greatly increased the rate of gas uptake. The re-

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(2) S. K. Ho and J. B. de Sousa, *J. Chem. Soc.*, 1788 (1961).

(3) H. Kiefer and T. G. Traylor, *Tetrahedron Lett.*, 6163 (1966), and references therein.

(4) D. Lindsay, J. A. Howard, E. C. Horswill, L. Iton, K. U. Ingold, T. Cobbley, and A. Ll, *Can. J. Chem.*, **51**, 870 (1973).

(5) R. C. Neuman and R. J. Bussey, *J. Amer. Chem. Soc.*, **92**, 2440 (1970).

(6) W. P. Neumann and H. Lind, *Chem. Ber.*, 2837 (1968).

(7) A. W. Scott, *J. Amer. Chem. Soc.*, **49**, 986 (1927).

(8) G. Brauer, "Handbook of Preparative Inorganic Chemistry," Vol. I, Academic Press, New York, N. Y., 1963, p 493 ff.

(9) P. Karrer and R. Schwyzer, *Recl. Trav. Chim. Pays-Bas*, **69**, 474 (1950).

(10) E. Weitz and W. Vollmer, *Ber.*, **57**, 1015 (1924).

(11) E. Backmann and T. Paul, *Justus Liebigs Ann. Chem.*, **266**, 1 (1891).

(12) G. Fraenkel, S. H. Ellis, and D. T. Dix, *J. Amer. Chem. Soc.*, **87**, 1406 (1965).

action was nearly complete within 20 min. After stirring 1 hr under NO, the solution was flushed with N<sub>2</sub>. Water (10 ml) was added dropwise with stirring (foaming), and the solution was extracted with additional water (70 ml) in three portions. Absolute ethanol (200 ml) was added to the combined extracts, and the solution was swirled with cooling if necessary to induce crystallization. The Na salt was filtered off and washed with absolute ethanol and ether. After drying in air, the cream solid weighed 3.5 g but contained bound ethanol and water.

A solution of silver nitrate (6.0 g) in water (600 ml) was added slowly with vigorous stirring to a 1% solution of the Na salt until the precipitate began to discolor.<sup>13</sup> About 420 ml was required. The product was filtered off, washed with water, and dried over P<sub>2</sub>O<sub>5</sub> at 25° and 0.5 Torr. The yellow solid contained 77.5% Ag (Volhard method<sup>14</sup>) and weighed 3.5 g (8% based on Na). With excess methyl bromide the product afforded methyl hyponitrite, a spontaneously explosive liquid that will be described elsewhere in detail.

**Acknowledgment.** This work was supported, in part, by Grant R 802288 from the Environmental Protection Agency.

(13) The product is black if silver is in excess.<sup>7</sup>

(14) H. H. Willard, N. H. Furman, and C. E. Bricker, "Elements of Quantitative Analysis," 4th ed, D. Van Nostrand Co., Princeton, N. J., 1956, p 129.

G. David Mendenhall

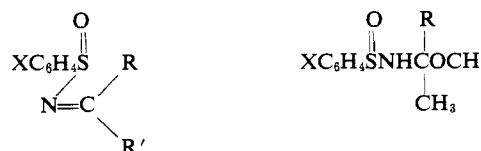
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Received April 1, 1974

### Chemistry of the Sulfur-Nitrogen Bond. VIII. *N*-Alkylidenesulfonamides<sup>1</sup>

Sir:

We wish to report the synthesis of a new class of reactive sulfur-nitrogen compounds,<sup>2</sup> *N*-alkylidenesulfonamides (*N*-(arylsulfonyl)imines), **1**. Compounds **1a-e** were prepared in good yield by dropwise addition of 1 equiv of *m*-chloroperbenzoic acid to a two-phase system containing the corresponding *N*-alkylidenesulfenamides<sup>3</sup> in chloroform and water-sodium bicarbonate. Although the C-N double bond in imines is known to be oxidized to oxaziridines<sup>4</sup> under these conditions, we were unable to detect any of these products.



**1a**, X = H; R = R' = CH<sub>3</sub>      **2a**, X = H; R = CH<sub>3</sub>  
**b**, X = H; R = H; R' = C<sub>6</sub>H<sub>5</sub>      **b**, X = 3-NO<sub>2</sub>; R = H  
**c**, X = 4-Cl; R = H; R' = C<sub>6</sub>H<sub>5</sub>  
**d**, X = 3-NO<sub>2</sub>; R = H; R' = CH<sub>3</sub>  
**e**, X = 3-NO<sub>2</sub>; R = H; R' = C<sub>6</sub>H<sub>5</sub>

(1) Part VII: F. A. Davis and E. B. Skibo, *J. Org. Chem.*, **39**, 807 (1974).

(2) For a recent review on the chemistry of the sulfur-nitrogen bond see F. A. Davis, *Int. J. Sulfur Chem.*, **8**, 71 (1973).

(3) F. A. Davis, W. A. R. Stegeir, S. Evans, A. Schwartz, D. L. Goff, and R. Palmer, *J. Org. Chem.*, **38**, 2809 (1973).

(4) W. D. Emmons, *J. Amer. Chem. Soc.*, **78**, 6208 (1956); **79**, 5739 (1957); L. Horner and L. B. Clapp, *ibid.*, **92**, 4902 (1970); Y. Ogata and Y. Sawaki, *ibid.*, **95**, 4692 (1973).