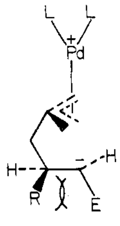
a Z acceptor as a criterion of concertedness—a conclusion not in accordance with many of our other observations. On the other hand, the suggested source of this rate discrimination may indeed apply. For minimization of charge separation, a rigid cisoid (e.g., **15** or **16**) rather than a transoid geometry would likely prevail and thereby approach the geometrical constraints of a lopsided concerted process. Thus, rehybridization of the β-carbon would increase the nonbonded interactions with a Z acceptor as in **15** compared to an E acceptor.[8] A broadening of the interpretation of the E/Z rate factor to include nonconcerted reactions whose transition-state geometry approaches that of a concerted process may be necessitated.



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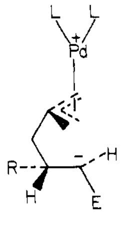

16

Acknowledgment. We thank the National Science Foundation for their generous support of our programs. We thank Johnson Matthey Ltd. and Englehardt Industries for generous supplies of palladium salts.

Registry No. 1, 72047-94-0; **2**, 82823-81-2; **3**, 82823-82-3; **6**, 82823-83-4; **7**, 82823-84-5; **8**, 82863-89-6; **9**, 82823-85-6; **10**, 82863-90-9; **11**, 82863-91-0; dimethyl (E,E)-muconate, 1119-43-3; dimethyl (E,-E)-muconate, 692-92-2; $(Ph_3P)_4Pd$, 14221-01-3; $[i\text{-}C_3H_7O)_3P]_4Pd$, 82838-61-7.

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[8] In a typical experiment, a solution of 1.4 equiv of dimethyl (E,E-muconate, 1.2 equiv of **1**, 7.1 mol % of $(Ph_3P)_4Pd$, and 1.5 mol % of dppe in dioxane (0.2–0.25 M in substrate) was refluxed for 8 h. After the solution was cooled, the solvent was evaporated and the residue directly chromatographed to give pure products.

Thermal Extrusion of Sulfur Dioxide from (η^5-Cyclopentadienyl)cobalt η^4-Thiophene 1,1-Dioxides: A New Organometallic Reaction

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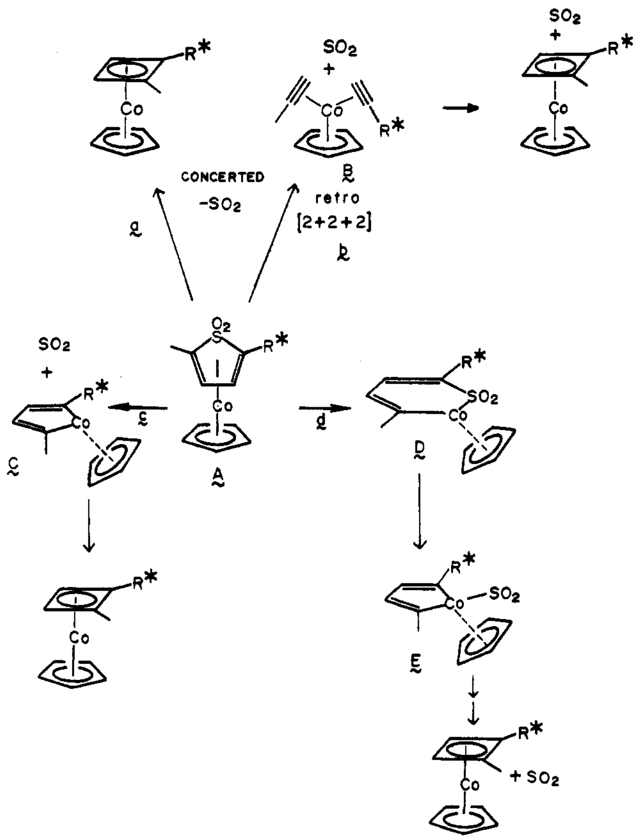
Summary: Flash vacuum pyrolysis of several (η^5-cyclopentadienyl)cobalt η^4-thiophene 1,1-dioxides leads to extrusion of SO_2 and the formation of (η^5-cyclopentadienyl)cobalt η^4-cyclobutadiene complexes. Stereochemical labeling experiments have been employed to pinpoint a likely pathway for this new transformation.

The prospect of increasing utilization of coal and coal-derived liquids as a source of fuel and chemical feed stocks has renewed interest in the development of chemical means by which sulfur may be removed from coal.[1] A large proportion of the organically bound sulfur in coal occurs in the form of thiophene and its derivatives. A potential way of eliminating its presence from such structures would be by an oxidation thermal desulfonation sequence. Thus, flash vacuum pyrolysis (FVP) of thiophene 1,1-dioxides derived from oxidation of the corresponding thiophenes leads to the predominant formation of furans by presumed loss of "SO".[2]

Scheme I



We have been interested in effecting transition-metal-mediated SO_2 extrusions from such systems in an effort to ultimately find catalytic organometallic pathways by which thiophene units may be converted into desulfurized chemicals. A previous thermal reactivity study[2a] of an iron tricarbonyl complexed thiophene dioxide was rendered inconclusive due to extensive decomposition and metal deposition, most likely a result of the relatively weak Fe–CO bond. We have previously established the utility of the remarkable thermal stability[3] of the CpCo unit (Cp = η^5-C_5H_5) in studies aimed at discovering novel ligand reorganizations.[4] It therefore appeared promising to extend this work to the thermal chemistry of (η^5-cyclopentadienyl)cobalt thiophene dioxides. This report details the first observation of the elusive[2a] SO_2 extrusion from such complexes and describes experiments, the outcome of which has considerably narrowed the number of alternatives by which this transformation occurs.

(η^5-Cyclopentadienyl)cobalt η^4-2,5-dimethylthiophene 1,1-dioxide (**1**) was prepared from $CpCo(CO)_2$ and the free heterocycle[5] by irradiation in boiling benzene (84%).[6] In

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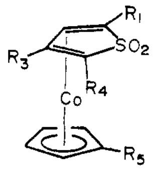
[1] R. A. Meyers, "Coal Desulfurization", Marcel Dekker, New York, 1977.

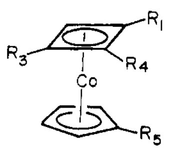
[2] (a) W. J. M. van Tilborg and R. Plomp, *Recl. Trav. Chim. Pays-Bas*, **96**, 282 (1977); (b) E. K. Fields and S. Meyerson, *J. Am. Chem. Soc.*, **88**, 2836 (1966); T. G. Squires, C. G. Venier, B. A. Hodgson, L. W. Chang, F. A. Davis, and T. W. Panunto, *J. Org. Chem.*, **46**, 2373 (1981).

[3] J. A. Connor, *Top. Curr. Chem.*, **71**, 71 (1976).

[4] (a) J. R. Fritch and K. P. C. Vollhardt, *Organometallics*, **1**, 590 (1982); (b) G. Ville, K. P. C. Vollhardt, and M. J. Winter, *J. Am. Chem. Soc.*, **103**, 5267 (1981); (c) J. R. Fritch and K. P. C. Vollhardt, *ibid.*, **100**, 3643 (1978); (d) *Angew. Chem.*, **91**, 439 (1979); *Angew. Chem., Int. Ed. Engl.* **18**, 409 (1979).



1, $R_1 = R_4 = CH_3$, $R_3 = R_5 = H$
4, $R_1 = R_3 = CH_3$, $R_4 = R_5 = H$
5, $R_1 = R_4 = R_5 = CH_3$, $R_3 = H$
6, $R_1 = CH_3CH_2$, $R_4 = CH_3$, $R_3 = R_5 = H$
9, $R_1 = CH_3CH_2CH(CH_3)$, $R_4 = CH_3$, $R_3 = R_5 = H$



2, $R_1 = R_4 = CH_3$, $R_3 = R_5 = H$
3, $R_1 = R_3 = CH_3$, $R_4 = R_5 = H$
7, $R_1 = R_4 = R_5 = CH_3$, $R_3 = H$
8, $R_1 = CH_3CH_2$, $R_4 = CH_3$, $R_3 = R_5 = H$
10, $R_1 = CH_3CH_2CH(CH_3)$, $R_4 = CH_3$, $R_3 = R_5 = H$

solution the compound is stable to light (medium-pressure Hg lamp) but unstable when heated beyond 200 °C to give intractable tars. In contrast, under flash vacuum pyrolytic conditions[4] (575 °C (10^{-4} torr)), **1** is converted to the cyclobutadiene complex **2**[6] as the only isolable product (50% isolated yield). Some decomposition is responsible for the formation of a cobalt mirror in the hot zone of the pyrolysis tube. In addition, a small amount (4%) of starting material is recovered. The mass spectral fragmentation pattern[7] of **2**, and particularly the negligible coupling (<1 Hz) between the cyclobutadiene protons[4a,8] (measured in the ^{13}C satellite ^1H NMR spectrum), clearly showed the presence of the 1,2-disubstitution pattern in the four-ring, indicating the occurrence of SO_2 extrusion and ligand bond formation *without concomitant rearrangement*. However, **2** could be equilibrated with its 1,3-dimethylcyclobutadiene isomer **3** ($J_{H_2H_4}$ = 9 Hz)[6] at temperatures *above* 620 °C. Compound **3** was independently prepared by SO_2 extrusion from complex **4** (51%),[6] in turn synthesized in the same way as **1** (97%). We have shown that such isomerizations (e.g., **2** $\rightleftarrows$ **3**) proceed through retrocyclization of the four-ring to bis(alkyne) complexes capable of rotation and ring closure,[4b,d] and it is significant that the SO_2 extrusion reaction from **1** or **4** does not enter that manifold at the (lower) temperatures employed.

That the two ligands stay attached to the metal during SO_2 elimination was ascertained through a crossover experiment involving a 1:1 mixture of the (η^5-$CH_3C_5H_4$)Co and η^4-2-ethyl-5-methylthiophene 1,1-dioxide[9] analogues of **1**, complexes **5** and **6**.[6] FVP (579 °C (10^{-4} torr)) gave equimolar amounts of the cyclobutadienes **7** and **8** (40%), in addition to starting materials (15%), but *no sign of ligand crossover* in any of the recovered complexes (*m/e*; ^1H NMR).

Table I. Results of the FVP of 9a and 9b

starting material	pyrolysis temp, °C	**9a**:**9b** (% yield)	**10a**:**10b** (% yield)
9a	507	87:13 (72)	50:50 (18)
	541	79:21 (37)	50:50 (36)
	575	75:25 (4)	50:50 (49)
9b	510	15:85 (70)	50:50 (18)
	540	20:80 (36)	50:50 (34)
	577	25:75 (5)	50:50 (52)

Among the variety of mechanisms which may be envisaged to describe the loss of SO_2 from complexes **1** and **4–6**, the four most reasonable are pictured on Scheme I. Pathway a constitutes a concerted loss of SO_2 from A, an "organometallic" cheletropic extrusion reminiscent of that observed in its organic equivalent, the loss of SO_2 from 2,5-dihydrothiophene 1,1-dioxides,[10] but involving simultaneous C–C bond formation. In contrast, b proposes a concerted retrocyclization of A to SO_2 and a bis(alkyne) complex B which would readily close[4b] to product, most likely through the intermediacy of a metallacyclopentadiene of the type C.[11] The latter might also be directly accessible via c, this route possibly involving SO_2 expulsion from a valence tautomer of A in which the metal is bound in an η^2 manner to the ligand at C-2 and C-5. Finally, pathway d suggests an insertion into the C–SO_2 bond to give D, followed by SO_2 loss, most likely involving complex E and then C. The last sequence is superficially related to the extensively investigated SO_2 insertion–deinsertion reactions into metal alkyls.[12]

Information with respect to the relative likelihood with which each of these mechanisms (or their topological equivalents) might occur may be obtained by a stereochemical labeling experiment. Thus, introduction of two different substituents at C-2 and C-5, one of which is chiral (as indicated in A, Scheme I), gives rise to diastereomers, the stereochemical (non)integrity of which during FVP would be of interest. With this thought in mind the two isomers of (η^5-cyclopentadienyl)cobalt 2-methyl-5-*sec*-butylthiophene 1,1-dioxide (**9a,b**) were prepared[13] (1:1 mixture) and separated by HPLC (silica gel, $CHCl_3$).[6]

The results of the pyrolyses of each isomer are shown in Table I. It is evident that the product cyclobutadienes **10a,b**[6] are *completely diastereoisomerized*, while the starting material is recovered only partially diastereoi-

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(5) W. J. M. van Tilborg, *Synth. Commun.* **6**, 583 (1976).

(6) All new compounds isolated gave satisfactory analytical and/or spectral data. The following compounds are representative. **1**: orange crystals; mp 188–190 °C; mass spectrum, *m/e* (relative intensity) 268 (M^+, 46), 204 (21), 189 (18), 124 (100); NMR (90 MHz, $CDCl_3$) δ 5.00 (s, 2 H), 4.90 (s, 5 H), 1.70 (s, 6 H). **2**: yellow oil; mass spectrum, *m/e* (relative intensity) 204.0355 (calcd 204.0349, M^+, 62.7), 189 (19.5), 178 (5.9), 124 (100); NMR (90 MHz, $CDCl_3$) δ 4.65 (s, 5 H), 3.62 (s, 2 H), 1.60 (s, 6 H). **3**: yellow oil; mass spectrum, *m/e* (relative intensity) 204.0341 (calcd 204.0349, M^+, 56.4), 164 (25.7), 124 (100); NMR (200 MHz, $CDCl_3$) δ 4.74 (s, 5 H), 3.82 (s, 2 H), 1.51 (s, 6 H). **4**: orange oil; mass spectrum, *m/e* (relative intensity) 267.9963 (calcd 267.9968, M^+, 25), 204 (11.8), 124 (100). **9a**: orange oil; mass spectrum, *m/e* (relative intensity) 310.0439 (calcd 310.0437, M^+, 53.6), 246 (5.5), 124 (100); NMR (250 MHz, $CDCl_3$) δ 5.02 (d, *J* = 3.8 Hz, 1 H), 4.99 (d, *J* = 3.8 Hz, 1 H), 4.92 (s, 5 H), 2.37 (m, 1 H), 1.88 (m, 1 H), 1.60 (s, 3 H), 1.52 (m, 1 H), 1.06 (d, *J* = 7.0 Hz, 3 H), 0.90 (t, *J* = 7.4 Hz, 3 H). **9b**: orange oil; mass spectrum, *m/e* (relative intensity) 310.0437 (calcd 310.0437, M^+, 56.6), 246 (5.2), 124 (100); NMR (250 MHz, $CDCl_3$) δ 5.00 (s, 2 H), 4.94 (s, 5 H), 2.02 (m, 1 H), 1.75 (m, 1 H), 1.59 (s, 3 H), 1.37 (m, 1 H), 1.35 (d, *J* = 7.0 Hz, 3 H), 0.95 (t, *J* = 7.4 Hz, 3 H). **10a + 10b** (inseparable): yellow oil; mass spectrum, *m/e* (relative intensity) 246.0817 (calcd 246.0818, M^+, 74.3), 124 (100); NMR (250 MHz, $CDCl_3$) δ 4.78 (s, 5 H), 4.77 (s, 5 H), 3.74 (s, 1 H), 3.72 (s, 1 H), 3.61 (s, 1 H), 3.60 (s, 1 H), 2.04–1.83 (m, 2 H), 1.58 (s, 3 H), 1.56 (s, 3 H), 1.43–1.15 (m, 4 H), 1.02 (d, *J* = 5.0 Hz, 3 H), 1.00 (d, *J* = 5.0 Hz, 3 H), 0.87 (t, *J* = 7.6 Hz, 3 H), 0.83 (t, *J* = 7.6 Hz, 3 H).

(7) M. D. Rausch, I. Bernal, B. R. Davies, A. Siegel, F. A. Higbie, and G. F. Westover, *J. Coord. Chem.*, **3**, 149 (1973).

(8) H. A. Brune, H. P. Wolff, and H. Hüther, *Z. Naturforsch., B: Anorg. Chem., Org. Chem., Biochem., Biophys. Biol.*, **23B**, 1184 (1968).

(9) Prepared[6] as follows from 2-methyltiophene: (a) CH_3COCl, $SnCl_4$ (64%); (b) $H_2NNH_2 \cdot H_2O$, KOH, Δ (36%); (c) MCPBA–CH_2Cl_2 (44%); (d) $CpCo(CO)_2$, C_6H_6, Δ, *hν* (86.5%).

(10) W. L. Mock, *J. Am. Chem. Soc.*, **97**, 3666, 3673 (1975).

(11) H. Yamazaki and N. J. Hagihara, *J. Organomet. Chem.*, **21**, 431 (1970); R. G. Gastinger, D. A. Sullivan, and G. J. Palenik, *J. Am. Chem. Soc.*, **98**, 719 (1976); L. P. McDonnell-Bushnell, E. R. Evitt, and R. G. Bergman, *J. Organomet. Chem.*, **157**, 445 (1978); see also D. L. Thorn and R. Hoffmann, *Nouv. J. Chim.*, **3**, 39 (1979).

(12) A. Wojcicki, *Acc. Chem. Res.*, **4**, 344 (1971); *Adv. Organomet. Chem.*, **12**, 32 (1974).

(13) From 2-methylthiophene as follows: (a) CH_3COCl, $SnCl_4$ (64%); (b) CH_3CH_2MgBr, ether (78%); (c) $NaCNBH_3$, HCl, CH_3OH (95%) see J. S. Drage, R. E. Earl, and K. P. C. Vollhardt, *J. Heterocycl. Chem.*, **19**, 701 (1982); (d) MCPBA–CH_2Cl_2 (25%); (e) $CpCo(CO)_2$, C_6H_6, Δ, *hν* (95%).

somerized. This finding in conjunction with the absence of positional isomerization in product as well as starting materials narrows any available mechanistic options. Path a should have generated only one product isomer; bath **b** would have necessitated positional isomerization. Path c requires configurational nonintegrity around the metal in C, a possibility made unlikely by earlier results.[4b] Thus, although by no means proven to be correct, d is left as the currently most appealing mechanistic candidate, involving the postulate of the reversible generation of a configurationally unstable (and rapidly disastereoisomerizing) initial intermediate D, providing the rationale for both stereochemical observations. The reason for the contrasting barriers to inversion at cobalt in C vs. D might be attributed to the presumed "antiaromatic" transition state involved when isomerizing the former. Further mechanistic and theoretical work is in order to clarify these points.

Nevertheless, and in summary, we have uncovered a new organometallic reaction which is likely to proceed through novel organometallic intermediates. These findings might be of some stimulus to mechanistic and synthetic chemists in general and those interested in particular in sulfur removal from thiophenic contaminants of industrial liquids.

Acknowledgment. This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098. K.P.C.V. is a Camille and Henry Dreyfus Teacher-Scholar (1978–1983).

Registry No. **1**, 83152-10-7; **2**, 83152-11-8; **3**, 83152-12-9; **4**, 83152-13-0; **5**, 83152-14-1; **6**, 83152-15-2; **7**, 83152-16-3; **8**, 83152-17-4; **9a**, 83152-18-5; **9b**, 83198-81-6; **10a**, 83152-19-6; **10b**, 83198-82-7.

Group 6B Complexes Containing Arsenic–Arsenic Double Bonds. Synthesis and Crystallographic Characterization of $[\eta^5\text{-}C_5H_5M(CO)_2]_2(\mu\text{-}\eta^2\text{-}As_2)$ (M = Mo or W)

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Received July 15, 1982

Summary: Hexaphenylcyclohexaarsine when heated with $[CpMo(CO)_3]_2$ or $CpW(CO)_3H$ forms the new cluster compounds $[CpM(CO)_2]_2(\mu\text{-}\eta^2\text{-}As_2)$ (M = Mo (**1**) or W (**2**)). Both **1** and **2** have been characterized by X-ray crystallographic methods; they are isomorphous and belong to the monoclinic space group *P*2/*n*. For **1**: a = 13.594 (6) Å, b = 7.559 (2) Å, c = 15.862 (8) Å, β = 95.94 (4)°, V = 1621.2 (12) Å^3, Z = 4, and R = 6.17%. For **2**: a = 13.505 (3) Å, b = 7.543 (1) Å, c = 15.845 (4) Å, β = 95.57 (2)°, V = 1606.6 (6) Å^3, Z = 4, and R = 6.91%. Two independent, but not significantly different, half molecules form the asymmetric unit. The heavy atoms form distorted tetrahedral frames characterized by very short As–As bond distances ⟨average⟩ = 2.312 (3) Å (**1**) and ⟨average⟩ = 2.323 (5) Å (**2**) (approximate bond order = 2) and normal, single M–M bond distances ⟨average⟩ = 3.039 (2) Å (**1**) and ⟨average⟩ = 3.020 (2) Å (**2**).

Table I. Data Collection and Refinement Parameters for $[CpMo(CO)_2]_2As_2$ and $[CpW(CO)_2]_2As_2$

	$[CpMo(CO)_2]_2As_2$ (1)	$[CpW(CO)_2]As_2$ (2)
mol formula	$C_{14}H_{10}As_2Mo_2O_4$	$C_{14}H_{10}As_2O_4W_2$
fw	583.94	759.76
crystl system	monoclinic	
space group	*P*2/*n*	
a, Å	13.594 (6)	13.505 (3)
b, Å	7.559 (2)	7.543 (1)
c, Å	15.862 (8)	15.845 (4)
β, deg	95.94 (4)	95.57 (2)
V, Å^3	1621.2 (12)	1606.6 (6)
Z	4	
d_{calcd}, g cm^{-3}	2.17	2.86
μ, cm^{-1} (Mo Kα)	55.68	187.16
crystal size (mm), color	0.21 × 0.23 × 0.40, red-orange	0.16 × 0.29 × 0.37, red
reflns measured	$\pm h,k,l$	
scan type	$\theta-2\theta$	
scan range	3–45°	3–50°
scan speed, deg/min	variable 3–15	
std reflns	3/141	
unique data	2124	2832
unique data ($F_o \geqslant 3\sigma(F_o)$)	1574	2147
R_F, %	6.17	6.91
R_{wF}, %	5.30	6.56

In comparison to the extensive attention given in the last decade to metal clusters containing multiple metal–metal bonds,[1] little effort has been devoted to the preparation of metal clusters containing bridges with multiple nonmetal–nonmetal bonds. Nonetheless, sufficient knowledge exists to demonstrate unquestionably that such bonds should provide new reaction pathways in metal cluster chemistry and provide a basis for the design of new structural classes of compounds. The E–E single bond in $Fe_2(CO)_6(\mu\text{-}E_2)$, E = S[2] or Se or Te,[3] undergoes a diverse range of bond cleavage reactions. Many different modes and bond orders of S–S bridging have been observed and the subject recently surveyed.[4] In comparison, far less is known about P–P, As–As, and Sb–Sb bridging. Prior to the present study, the only confirmed structures were derivatives of $[Co(CO)_3]_2E_2$ (E = P or As) formed via carbonyl group replacement[5] and $[W(CO)_5]_3E_2$, E = As[6] or Sb.[7] These compounds are characterized by a very short $\mu\text{-}\eta^2$ or $\mu_3\text{-}\eta^2$ (E_2) bond leading to the conclusion that they may be treated as complexes of "E≡E". As a part of our continuing survey of the reactions of cyclopolyarsines with cyclopentadienylmetal carbonyls, we have investigated the thermal reactions of hexaphenylcyclohexaarsine, $(AsC_6H_5)_6$, with $[CpMo(CO)_3]_2$ and $CpW(CO)_3H$. In both cases, the compound $[CpM(CO)_2]_2(\mu\text{-}\eta^2\text{-}As_2)$ (M = Mo (1) or W (2)) is formed.

All manipulations were carried out in a glovebox or carried out by using Schlenk techniques. Compound 1 was prepared by combining cyclopentadienylmolybdenum

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(1) Chisholm, M. H.; Cotton, F. A. *Acc. Chem. Res.* **1978**, *11*, 356. Chisholm, M. H.; Rothwell, I. P. *Prog. Inorg. Chem.* **1982**, *29*, 1.

(2) Seyferth, D.; Henderson, R. S.; Song L.-C. *Organometallics* **1982**, *1*, 125.

(3) (a) Lesch, D. A.; Rauchfuss, T. B. *Organometallics* **1982**, *1*, 499. (b) *Inorg. Chem.* **1981**, *20*, 3583.

(4) Bolinger, C. M.; Rauchfuss, T. B.; Rheingold, A. L. *Organometallics* in press.

(5) (a) Foust, A. S.; Foster, M. S.; Dahl, L. F. *J. Am. Chem. Soc.* **1969**, *91*, 5633. (b) Foust, A. S.; Campana, C. F.; Sinclair, J. D.; Dahl, L. F. *Inorg. Chem.* **1979**, *18*, 3047.

(6) Sigwarth, B.; Zsolnai, L.; Berke, H.; Huttner, G. *J. Organomet. Chem.*, **1982**, *226*, C5.

(7) Huttner, G.; Weber, U.; Sigwarth, B.; Scheidsteger, O. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 215.

(8) IR (KBr, carbonyl, cm^{-1}; 1985 (sh), 1960 (m), and 1910 (s).

0276-7333/82/2301-1547$01.25/0