of bis(η^6-acylbenzene)chromium complexes affords mixtures of cis and trans products. The increase of the ligand to dimer ratio with increasing electron affinity of R, i.e., with decreasing arene–metal bond strength, suggests that the aromatic ketone remains attached to the metal during the deoxygenation step (alternative B). The generation of carbenes by deoxygenation of carbonyl groups has only rarely been reported[14] and, to our knowledge, is without precedent for aromatic ketones. In the case of the complexes **6–10** however, favorable disposition of the carbonyl groups and the "coupling agent", Cr(0), is likely to assist such a process.

Due to the high reactivity of carbenes, formation of ethene derivatives via dimerization is unlikely in solution and the products are usually explained by an attack of one carbene on the carbene precursor and by addition and insertion reactions. In the case of the π complexes **6–10**, however, neat material reacts in the condensed state below or at the melting point, and the relative disposition of the ligands, as governed by the crystal lattice, may be of prime importance in determining the nature of the products. Since 1,1′ derivatives of bis(benzene)chromium usually adopt an anti conformation with regard to the ring–metal–ring axis,[17] carbenes formed via deoxygenation from ligands of neighboring complex units may be juxtaposed more favorably for dimerization than species stemming from the same complex unit. This notion rationalizes the result of the **7**/**7**-d_{20} cross thermolysis. Indications for the intermediacy of arylcarbenes may also be found among the minor products of the thermolysis. In the case of **6** we obtained via GC/MS the following distribution (*m/e*, formula, %): 106, PhCHO, 13.6; 168, Ph_2CH_2, 1.6; 178, Ph_2C_2, 14.6; 180, *cis*-$Ph_2C_2H_2$, 30.5; 180, *trans*-$Ph_2C_2H_2$, 100.0; 194, Ph_2C_2O, 5.8; 258, $Ph_3C_2H_3$, 0.5; 268, Ph_3C_3H, 1.3, 3.2; 270, $Ph_3C_3H_3$, 0.2, 0.8; 272, $Ph_3C_3H_5$, 2.8; 284, Ph_3C_3HO, 3.1.

Whereas the mode of formation of tolan (*m/e* 178) is not clear at present, the species *m/e* 270 and 268 probably represent cyclopropane and cyclopropene derivatives formed by addition of phenylcarbene to stilbene and tolan. One of the most characteristic differences between thermolysis of neat **6** and of its solution is the abundance of benzil among the solution thermolysis products. The latter compound may arise via dimerization of benzoyl radicals generated from benzaldehyde and chromium oxides.[18] Therefore, in addition to the carbene path, radical mechanisms have to be taken into account, at least for the thermolysis of (η^6-acylbenzene)chromium complexes in solution.

A more detailed discussion will be given in conjunction with the results of an X-ray structure determination for **6**.

Acknowledgment is made to Deutsche Forschungsgemeinschaft and Fonds der Chemischen Industrie for support of this work. We also thank Metallgesellschaft A.G., Frankfurt/Main, for a gift of *n*-butyllithium.

Registry No. 1, 1271-69-8; **2**, 52445-45-1; **3**, 82555-98-4; **4**, 82571-34-4; **5**, 82555-99-5; **6**, 55140-34-6; **7**, 82556-00-1; **8**, 82571-35-5; **9**, 82556-01-2; **10**, 82556-02-3; Cr, 7440-47-3; benzophenone, 119-61-9.

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(14) Examples are the generation of carbenes from carbonyl compounds and carbon atoms[15] and the reaction of alicyclic ketones with magnesium atoms.[16]

(15) P. S. Skell and J. M. Plonka, *J. Am. Chem. Soc.*, **92**, 836 (1970).

(16) L. D. Wescott, Jr., C. Williford, F. Parks, M. Dowling, S. Sublett, and K. J. Klabunde, *J. Am. Chem. Soc.*, **98**, 7853 (1976).

(17) Examples include (Me-η^6-C_6H_5)$_2$CrI, O. V. Starovskii and Y. T. Struchkov, *Dokl. Chem.* (*Engl. Transl.*), **135**, 152 (1961); *J. Struct. Chem.* (*Engl. Transl.*) **2**, 152 (1961), and (Ph_2P-η^6-C_6H_5)$_2Cr^0$, B. Barnett, Ch. Elschenbroich, and F. Stohler, to be submitted for publication.

(18) The oxidation of aldehydes by metal complexes of Mn^{III}, Fe^{III}, and Co^{III} to yield acyl radicals is discussed in "Free Radicals", Vol. 1, J. K. Kochi, Ed., Wiley, New York, 1973, pp 656–660 and references therein.

Regio- and Stereoselective Addition of (Carbon disulfide)iron Complexes to α,β-Unsaturated Carbonyls in the Presence of Strong Acids

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Received May 17, 1982

Summary: The Fe(η^2-CS_2)(CO)$_2$(PR$_3$)$_2$ complexes add to α,β-unsaturated aldehydes, ketones, and esters in the presence of HPF_6 or HBF_4 to afford carbonyl derivatives having a bulky, cationic organometallic group at C-3. Cyclic substrates such as *l*-carvone and β-angelicalactone showed the stereoselectivity of the addition.

Electron transfer from a transition metal to an η^2-coordinated CS_2 molecule enhances the nucleophilicity of the uncoordinated sulfur atom and the dipolar character of the M–CS_2 moiety.[1] Such electronic changes might be expected to facilitate the incorporation of a metal–CS_2 fragment into an unsaturated substrate with potential implications for organic synthesis. Although electrophilic alkynes have been reported[2] to add smoothly to iron(0)–carbon disulfide complexes, cycloaddition was not observed with activated olefins. We now find that the readily available Fe(η^2-CS_2)(CO)$_2$(PR$_3$)$_2$[1] complexes can be incorporated into α,β-unsaturated carbonyls by regioselective addition, in the presence of a strong acid, to afford new cationic complexes having a bulky, sulfur-containing organometallic group linked to C-3 of the carbonyl substrate.

When 1.2 equiv of a strong acid such as $HPF_6 \cdot Et_2O$ was added at 0 °C to the orange, ethereal solution of 1 equiv of complex **1** and 1.1 equiv of the α,β-unsaturated carbonyl compound **3** [such as acrolein (**3a**), methyl vinyl ketone (**3b**), chalcone (**3c**), and methyl acrylate (**3d**)], a yellow compound precipitated which was isolated by filtration, crystallized from dichloromethane–hexane mixtures, and identified, respectively, as the salts **4a** (32%), **4b** (71%), **4c** (98%), and **4d** (59%).[3] This reaction appears general for the cationic complexes since **5c** (88%) and **6c** (85%)[3] were obtained similarly from complex **2** and chalcone **3c**

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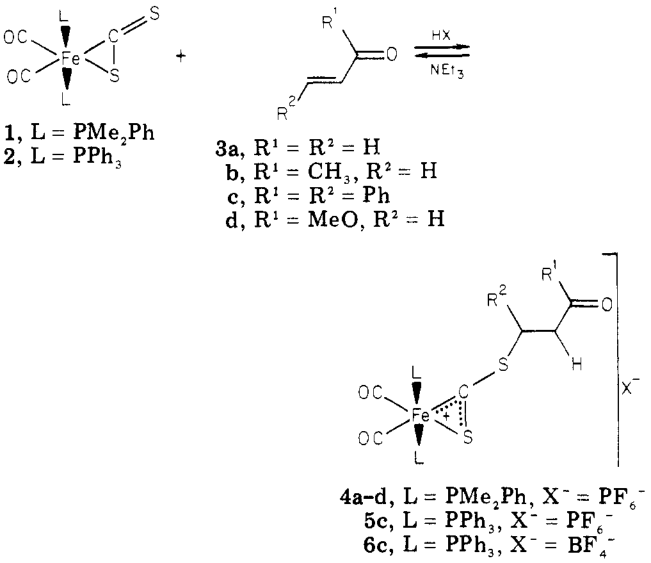
(1) Le Bozec, H.; Dixneuf, P. H.; Carty, A. J.; Taylor, N. J. *Inorg. Chem.* **1978**, *17*, 2568 and references cited therein.

(2) Le Bozec, H.; Gorgues, A.; Dixneuf, P. H. *Inorg. Chem.* **1981**, *20*, 2486.

(3) Melting points (°C): **4a**, 104–106; **4b**, 124–125; **4c**, 146–147; **4d**, 92–95; **5c**, 146–147; **6c**, 167–170. Anal. Calcd for **4a**: C, 39.66; H, 4.05; S, 9.63. Found: C, 39.82; H, 4.39; S, 9.96. Calcd for **4b**: C, 40.62; H, 4.26; S, 9.43. Found: C, 40.41; H, 4.21; S, 9.56. Calcd for **4c**: C, 49.88; H, 4.28. Found: C, 49.90; H, 4.30. Calcd for **4d**: C, 39.68; H, 4.26. Found: C, 39.61; H, 4.15. Calcd for **5c**: C, 60.82; H, 4.03. Found: C, 60.48; H, 4.28. Calcd for **6c**: C, 64.28; H, 4.27. Found: C, 64.34; H, 4.26. IR (Nujol; ν (cm^{-1})): **4a**, 2022, 1965, 1718; **4b**, 2020, 1972, 1715; **4c**, 2035, 1975, 1695; **4d**, 2027, 1985, 1732; **5c**, 2040, 1975, 1690; **6c**, 2035, 1970, 1682.

Scheme I



1, L = PMe$_2$Ph
2, L = PPh$_3$

3a, R^1 = R^2 = H
b, R^1 = CH$_3$, R^2 = H
c, R^1 = R^2 = Ph
d, R^1 = MeO, R^2 = H

4a–d, L = PMe$_2$Ph, X$^-$ = PF$_6^-$
5c, L = PPh$_3$, X$^-$ = PF$_6^-$
6c, L = PPh$_3$, X$^-$ = BF$_4^-$

in dichloromethane by addition, respectively, of HPF_6 and HBF_4 in ether (Scheme I).

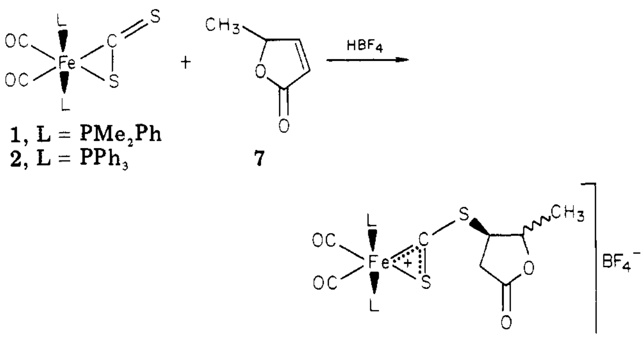
The compounds 4–6 showed in the infrared[3] (i) two strong carbonyl absorption bands at higher frequencies than those of the precursors 1 and 2 and (ii) one high-frequency acyl absorption which indicated the loss of conjugation of the carbonyl with the carbon–carbon double bond. In addition, the presence of an uncoordinated C–S bond (1120–1130 cm^{-1}) was observed.

The regioselective addition of the sulfur atom to the C-3 position of the α,β-unsaturated carbonyls 3 was clearly indicated by the ^{1}H NMR spectra which showed a $\ddot{S}CHCH_2C{=}O$ arrangement.[4] The methyl groups of the PMe_2Ph ligands in **4a**, **4b**, and **4d** show two apparent triplets in their ^{1}H NMR spectra,[5] as in that of 1, and the ^{31}P nuclei of **4b** show one line at $\delta(CDCl_3)$ 23.0. These data are consistent with (i) equivalent phosphorus groups, (ii) the trans position of the phosphines[1] as in 1, and (iii) the diastereotopy of the methyl groups of each phosphine ligand. In contrast, compound **4c** shows different behavior due to the presence of a chiral carbon atom linked to the uncoordinated sulfur atom; although the phosphorus nuclei appeared equivalent in the ^{31}P NMR spectrum [$\delta_P(CDCl_3)$ 22.95], the four methyl groups of the phosphines were differentiated as observed by ^{13}C NMR data.[6]

The cationic complexes 4–6 may result from the addition of the nucleophilic, uncoordinated sulfur atom to the protonated, activated olefin. They are stable in acidic or neutral media. In contrast, in the presence of a base, abstraction of the proton at the α-position of the carbonyl occurs and retroaddition takes place. Thus when **4c** or **6c** was treated in dichloromethane with triethylamine, the reaction occurred immediately and **1** or **2** and **3c** were recovered in 95–100% yield. The retroaddition is much slower when pyridine is used at room temperature. Therefore, such addition and retroaddition of a Fe(η^2-CS$_2$) complex should be useful to protect momentarily the C=C bond of an α,β-unsaturated carbonyl in acidic media. The addition of a Fe(η^2-CS$_2$) complex, which formally leads to the addition of a cationic organometallic group at C-3, contrasts with the regioselective, base-catalyzed addition of thiols to activated olefins[7] to afford a neutral adduct which is stable in basic media.

The addition of complexes **1** and **2** to two cyclic unsaturated carbonyls, the chiral β-angelicalactone (**7**) and *l*-carvone (**8**), has been investigated to study the stereochemistry of the reaction. The addition to **7** markedly depends on the nature of the phosphorus group, L (Scheme II). Compound **9**[8] was obtained by the addition of **1**, but the reversibility of the reaction, in neutral medium, did not allow the elucidation of the stereochemistry, whereas the addition of **2** led to the isolation of **10** (45%) which

Scheme II

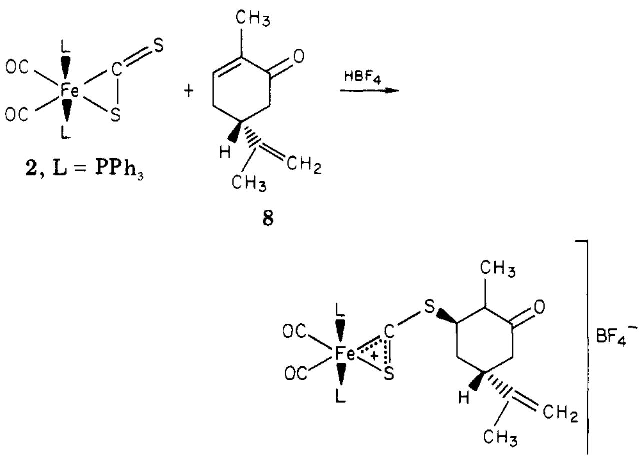


1, L = PMe$_2$Ph
2, L = PPh$_3$

7

9, L = PMe$_2$Ph
10, L = PPh$_3$

Scheme III

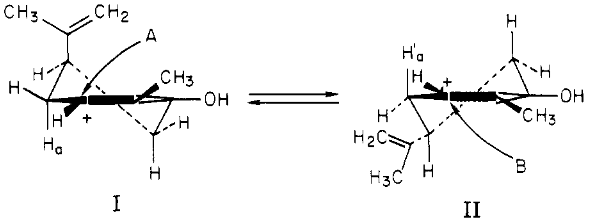


2, L = PPh$_3$

8

11, L = PPh$_3$

Scheme IV



I II

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(4) ^{1}H NMR (100 mHz, δ): **4a** (CDCl$_3$), 3.35 (t, CH$_2$S), 2.85 (t, CH$_2$CO, $^3J_{HH}$ = 6.0 Hz), 9.95 (s, CHO); **4b** (CDCl$_3$) 3.16 (t, CH$_2$S), 2.71 (t, CH$_2$CO, $^3J_{HH}$ = 5.7 Hz), 2.11 (s, COCH$_3$); **4c** (CDCl$_3$) 5.02 (dd, SCH, $^3J_{HH}$ = 7.5 Hz), 3.70 (m, CH$_2$CO); **4d** (CDCl$_3$) 3.20 (t, CH$_2$S), 2.45 (t, CH$_2$CO, $^3J_{HH}$ = 6.0 Hz), 3.64 (s, CO$_2$CH$_3$); **6c** (CD$_2$Cl$_2$) 4.46 (dd, SCH, $^3J_{HH}$ = 7.0 Hz), 2.9–3.5 (m, CH$_2$CO).

(5) ^{1}H NMR (100 mHz, δ, CDCl$_3$, ($|^2J_{PH} + {}^4J_{PH}|$): **4a**, 1.80 and 1.77 (12.0 Hz); **4b**, 1.63 and 1.68 (8.0 and 7.5 Hz); **4d**, 1.71 and 1.67; 1, 1.67 and 1.65 (8.5 Hz[1]).

(6) ^{13}C NMR of **4c** (CDCl$_3$, 20.115 mHz, δ): 283.0 (t, CS$_2$, $^2J_{PC}$ = 16.5 Hz), 213.0 (t, CO, $^2J_{PC}$ = 26.4 Hz), 212.3 (t, CO, $^2J_{PC}$ = 23.1 Hz), 196.2 (s, C=O), 60.9 (SCH), 42.9 (*CH*$_2$CO), 14.4 (t), 14.2 (t), 13.9 (t), 13.5 (t) (PCH$_3$, $|^1J_{PC} + {}^3J_{PC}|$ = 13.2 Hz).

(7) (a) Hiemstra, H.; Wynberg, H. *J. Am. Chem. Soc.* **1981**, *103*, 417. (b) Gawronski, J.; Gawronska, K.; Wynberg, H. *J. Chem. Soc., Chem. Commun.* **1981**, 307. (c) Abramovitch, R. A.; Singer, S. S. *J. Org. Chem.* **1976**, *10*, 1712.

(8) IR (Nujol) of **9**: 2040, 1975, and 1805 cm^{-1}.

which contained actually, as shown by NMR[9], spectroscopy, both cis/trans isomers stable in neutral medium.

The addition of **2** to **8** in the presence of $HBF_4{\cdot}Et_2O$ in CH_2Cl_2 led to the formation of **11** (61%; Scheme III). The ^1H NMR spectrum of **11** indicated[11] the selectivity of the addition to the intracyclic C=C bond and the presence of only one diastereoisomer.

The proposed relative configuration of **11** is based on the following rationale pertaining to the addition of a bulky nucleophile to forms I and II of the protonated *l*-carvone (Scheme IV): (i) forms I and II are expected to be in equilibrium at room temperature,[12] (ii) it has been established[7,13] for a six-membered ring that nucleophilic addition occurs antiparallel to the axial hydrogen atom H_a or H'_a at the adjacent carbon atom, and therefore nucleophilic addition to C-3 in forms I and II should occur as shown by A and B, respectively, in Scheme IV, (iii) the antiparallel addition of a bulky $Fe(\eta^2\text{-}CS_2)$ complex to form I is obviously disfavored with respect to the antiparallel addition to form II due to the axial position of the bulky 1-methylethenyl group in I. Therefore **11** should result from the addition to form II in the sense indicated by B.

The present study shows that the addition of a nucleophilic $Fe(\eta^2\text{-}CS_2)$ complex, in acidic medium, to α,β-unsaturated substrates is regiospecific and reaches a high stereoselectivity when the bulky nucleophile **2** is used. We are currently investigating ways to remove the metallic moiety from the sulfur-containing organic part of the cationic adducts.

Registry No. **1**, 64424-57-3; **2**, 64424-68-6; **3a**, 107-02-8; **3b**, 78-94-4; **3c**, 94-41-7; **3d**, 96-33-3; **4a**, 82665-43-8; **4b**, 82665-45-0; **4c**, 82665-47-2; **4d**, 82665-49-4; **5c**, 82665-51-8; **6c**, 82665-52-9; **7**, 591-11-7; **8**, 2244-16-8; *cis*-**9**, 82665-54-1; *trans*-**9**, 82729-18-8; *cis*-**10**, 82665-56-3; *trans*-**10**, 82729-20-2; **11**, 82665-58-5.

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(9) Data for complex **10**: mp 154–155 °C. Anal. Calcd: C, 58.80; H, 4.12; Fe, 6.24; P, 6.79. Found: C, 58.49; H, 4.19; Fe, 6.12; P, 6.66. IR (Nujol) 2042, 1985, 1790 cm^{-1}. NMR (δ, CD_2Cl_2): *cis*-**10**, ^1H (100 MHz) 1.38 (d, $CHCH_3$, $^3J_{HH}$ = 6.5 Hz), ^{13}C (20.115 MHz) 287.6 (t, CS_2), 172.7 (C=O), 79.6 ($CHCH_3$), 59.1 (CHS), 33.2 (CH_2), 20.6 (CH_3); *trans*-**10**, ^1H 1.22 (d, $CHCH_3$, $^3J_{HH}$ = 6 Hz), ^{13}C 288.3 (t, CS_2), 172.7 (C=O), 80.1 ($CHCH_3$), 59.1 (CHS), 33.2 (CH_2), 18.9 (CH_3). The *trans* configuration has been assigned to the major isomer in agreement with the nature of the major adduct[10] of thiols with **7**.

(10) Ducher, S.; Michet, A. *Bull. Soc. Chim. Fr.* **1973**, 1037.

(11) Data for complex **11**: mp 118–121 °C. IR (Nujol) 2038, 1970, 1715 cm^{-1}; ^1H NMR (CD_2Cl_2, 100 mHz) δ 4.58 ($C{=}CH_2$), 4.28 (SCH), 1.52 (s, $CH_3C{=}C$), 0.62 (d, CH_3CH, $^3J_{HH}$ = 5.8 Hz). Anal. Calcd: C, 61.89; H, 4.74; Fe, 5.89; P, 6.53. Found: C, 61.35; H, 4.73; Fe, 5.39; P, 6.03.

(12) Barieux, J. J.; Gore, J.; Richer, J. C. *Bull. Soc. Chim. Fr.* **1974**, 1020.

(13) (a) Chamberlain, P.; Whitman, G. H. *J. Chem. Soc., Perkin Trans. 2* **1972**, 130. (b) Allinger, N. L.; Riew, C. K. *Tetrahedron Lett.* **1966**, 1269.

Reinvestigations of Some Reactions of Metal Carbonyl Anions with Cyclopropenium Cations. Conversion of η^3-Cyclopropenyl to η^3-Oxocyclobutenyl Ligands

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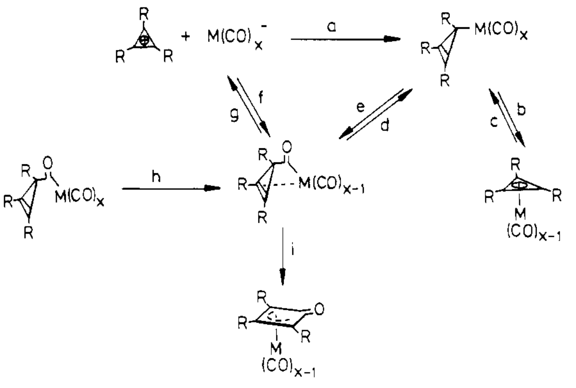
Summary: Contrary to some previous reports, cyclopropenium cations react with metal carbonyl anions to give both η^3-cyclopropenyl and η^3-oxocyclobutenyl complexes. External ligand induced conversions of η^3-cyclopropenyl to η^3-oxocyclobutenyl skeletons are also reported.

Scheme I



Curiously, there are no reported examples of the reaction of a cyclopropenium cation with a metal carbonyl *anion* to yield a (η^3-cyclopropenyl)metal compound, although a number of such compounds have been prepared by oxidative addition pathways involving *neutral* metal precursors.[2-8] As shown in Scheme I reactions of cyclopropenium cations with metal carbonyl anions can evolve along a variety of paths which we and others are attempting to define. Path a has been characterized for a single system; reaction of $[C_3Ph_3]^+$ with $[Fe(CO)_2(\eta\text{-}C_5H_5)]^-$ affords crystallographically characterized $[Fe(CO)_2(3\text{-}\eta^1\text{-}C_3Ph_3)(\eta\text{-}C_5H_5)]$, but this compound is resistant to decarbonylation (path b) to yield the corresponding η^3-cyclopropenyl compound or to thermal ring expansion (path e, i) to afford an oxocyclobutenyl ligand.[9,10] We have previously reported that substituted (3-η^1-cyclopropenyl)pentacarbonylrhenium compounds could be prepared by a synthetic sequence involving paths h and d and that path d proceeded with an unprecedented allylic rearrangement of the migrating cyclopropenyl group; no evidence for reverse cyclopropenyl migration (path e) or decarbonylation (path b) was observed in this system.[11,12] Finally an extensive study of the reactions of $[Co(CO)_4]^-$ with cyclopropenium cations has provided evidence for a surprising reaction pathway involving an apparent direct

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(1) (a) Alfred P. Sloan Research Fellow, 1980–1984. (b) On leave from Colby College, Waterville, ME 04901.

(2) Gowling, E. W.; Kettle, S. F. A. *Inorg. Chem.* **1964**, *3*, 604–605.

(3) Olander, W. K.; Brown, T. L. *J. Am. Chem. Soc.* **1972**, *94*, 2139–2140.

(4) Rausch, M. D.; Tuggle, R. M.; Weaver, D. L. *J. Am. Chem. Soc.* **1970**, *92*, 4981–4982.

(5) Chiang, T.; Kerber, R. C.; Kimball, S. D.; Lauher, J. W. *Inorg. Chem.* **1979**, *18*, 1687–1691.

(6) Hayter, R. G. *J. Organomet. Chem.* **1968**, *13*, P1–P3.

(7) Drew, M. G. B.; Brisdon, B. J.; Day, A. *J. Chem. Soc., Dalton Trans.* **1981**, 1310–1316.

(8) Unsymmetrically η^2-bound cyclopropenyl ligands have also been reported. (a) McClure, M. D.; Weaver, D. L. *J. Organomet. Chem.* **1973**, *54*, C59–C61. (b) Mealli, C.; Midollini, S.; Moretti, S.; Sacconi, L. *Angew. Chem., Int. Ed. Engl.* **1980**, *11*, 931. (c) Mealli, C.; Midollini, S.; Moretti, S.; Sacconi, L.; Silvestre, J.; Albright, T. A. *J. Am. Chem. Soc.* **1982**, *104*, 95–107.

(9) Gompper, R.; Bartmann, E. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 456–457.

(10) Gompper, R.; Bartmann, E.; Noth, H. *Chem. Ber.* **1979**, *112*, 218–233.

(11) Desrosiers, P. J.; Hughes, R. P. *J. Am. Chem. Soc.* **1981**, *103*, 5593–5594.

(12) DeSimone, D. M.; Desrosiers, P. J.; Hughes, R. P. *J. Am. Chem. Soc.* **1982**, *104*, 4842.